ALD Applications
Room 116-118 - Session AA1-MoA
Memory Device & Materials I

Moderators: Steven M. George, University of Colorado at Boulder, Christophe Vallee, LTM - MINATEC - CEA/LETI, France

1:30pm **AA1-MoA-1 Atomic Layer Deposition as a Key Technology for Manufacturing 3D V-NAND Flash Memory***, **Jaeyoung Ahn**,* Samsung Electronics, South Korea*; J Jee, P Nam, B Kim, J Yang, D Kim, H Choi,* Samsung Electronics **INVITED**

The introduction of 3D V-NAND enables the high capacity, fast processing storage solutions to implement the emerging technologies such as cloud computing, big data, internet of things and mobile devices. Since the memory array size of 3D V-NAND has been increasing over the years, it is inevitable to stack more cells vertically, which builds stumbling blocks in deposition of various materials on the cell structures. ALD has been successfully adopted in the process integration as the key technology for CTF dielectric layers, gap-filling dielectrics, and word-line metals due to its superior step coverage and uniformity. However, since the surface area of the structures is expanding rapidly, it is very challenging to maintain good step coverage and uniformity for future generations of 3D V-NAND. During the process flow of 64-stacked V-NAND Flash devices, patterned wafers frequently show over 30 times larger surface area compared to blanket wafers and very high vertical and lateral aspect ratios. Consequently, we need advanced technologies employing new hardware platforms, more efficient precursors, and optimized process conditions. At the same time, we also need selection criteria to identify the right solution for each ALD step in the process flow. For these purposes, we propose numerical simulation of mass transfer using computational fluid dynamics approach as a tool for developing advanced ALD hardware and materials as well as optimizing existing processes.

2:00pm **AA1-MoA-3 Room-temperature Resonant Tunneling by Band-offset Engineering of Nanolaminated High-k Oxides Deposited by Atomic-layer Deposition***, **Hector Uribe-Vargas**, J Molina-Reyes,* National Institute of Astrophysics, Optics and Electronics

Due to the continuous scaling of advanced CMOS technology, high-k oxides became very important due to a low leakage current and high dielectric constant (k>8). These oxides are often deposited by atomic-layer deposition (ALD), which has a high reproducibility, conformality, outstanding control (to atomic level) on the thickness and stoichiometry and a low deposition temperature (T≤250°C). Because of these characteristics and taking advantage of the band offsets between silicon and different high-k oxides, a double barrier resonant tunneling (RT) diode could be formed. In this regard, RT devices have shown promise at achieving very high speed in wide-band devices and circuits that are beyond conventional transistor technology, nevertheless, this effect is often seen in highly complex crystalline heterostructures (usually fabricated by epitaxial growth), and only at very low temperatures (T<77 K).

In this work, 2 sets of 2 samples of metal-insulator-insulator-insulator-semiconductor (MIIIS) devices were fabricated. The first set of 2 samples is a stack of ultra-thin Al_2O_3, HfO_2 and Al_2O_3 (AHA stack with 2nm, 1nm and 2nm in thickness) deposited by ALD. After gate deposition, one sample was subjected to post metallization annealing (PMA) at 450°C for 30 minutes in an H_2/N_2 ambient. For the second set of 2 samples, a stack of ultra-thin Al_2O_3, TiO_2 and Al_2O_3 (ATA stack with 2nm, 1nm and 2nm in thickness) was also deposited by ALD and similarly, one sample was also subjected to PMA. These devices were designed in order to promote quantum-well (QW) formation at the intermediate oxide layer, having QW of 1.3 eV and 3.1 eV respectively and promoting RT conduction during substrate injection of electrons.

After Ig-Vg measurements at room temperature, experimental proof of RT via negative differential resistance (NDR) was demonstrated in MIIIS structures fabricated using ALD, putting this deposition technique as a powerful tool to obtain this phenomena after atomic control of all high-k layers. Due to the difference in the band gaps of different high-k materials, it is possible to promote quantization of discrete energy levels in intermediate layers of stacked ultra-thin high-k oxides. For the case of the AHA ($Al_2O_3/HfO_2/Al_2O_3$) structure, 3 distinctive NDR zones are observed after substrate injection. For the case of the ATA ($Al_2O_3/TiO_2/Al_2O_3$) structure, even though no evident NDR is present, RT is a strong possibility due to a high non-linearity (~20), high asymmetry and low dynamic resistance. When PMA is performed, no sign of RT/NDR is obtained in both AHA and ATA structures, due to an inner diffusion of atomic elements within the stacked oxides.

2:15pm **AA1-MoA-4 Atomic Layer Deposition of HfO_2 Thin Films using $Hf(BH_4)_4$ and H_2O***, **Devika Choudhury**, A Mane, R Langesley, M Delferro, J Elam,* Argonne National Laboratory

High dielectric constant (high-k) metal oxides and their silicates have been extensively studied as alternatives to SiO_2 for electronic and optoelectronic applications [1]. Excellent dielectric properties coupled with high thermal stability has made HfO_2 one of the most popular replacements for SiO_2 in CMOS and DRAM devices. HfO_2 thin films have been deposited using various methods including CVD, ALD, sputtering, and sol-gel techniques [2]. However, with the decreasing size of devices and increasing demand for ultrathin conformal films with precise thickness and composition control, ALD has emerged as the preferred method.

ALD of HfO_2 has so far been successfully implemented using different precursors. $HfCl_4$ and HfI_2 are two of the most commonly used Hf sources, which however require high deposition temperatures (>300°C) and generate corrosive byproducts (HCl and HI). Although alternative precursors like metalorganics or amides have also been used, the possibility of carbon contamination has restricted their use in electronic applications [3].

In this work, we demonstrate the relatively low temperature ALD of HfO_2 thin films using a carbon free precursor, tetrakis(tetrahydroborato)hafnium [$Hf(BH_4)_4$], and H_2O. As both precursors have substantial vapor pressure at room temperature, low temperature deposition growth is possible. Self-limiting, linear growth of HfO_2 is obtained at 200°C, and experiments on the feasibility of lower temperatures deposition are underway. The refractive index of the as-grown films measured at 632 nm is found to be 1.91, which indicates the formation of HfO_2. Stronger confirmation for HfO_2 is obtained by elemental analysis using X-ray photoelectron spectroscopy (XPS). The doublet of the Hf 4f orbital electrons obtained at binding energies of 18.4 and 20.1eV can be assigned to the Hf $4_{7/2}$ and Hf $4_{5/2}$ electronic states of Hf in Hf-O bonds respectively. Moreover, the O1s peak obtained observed at 531.9eV also corresponds to formation of Hf-O bonds in the as-deposited film. XRD analysis showed the films deposited at 200°C to be amorphous, but rapid thermal annealing at 750°C for 60s yields crystalline, monoclinic HfO_2 films.

References:

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2:30pm **AA1-MoA-5 TaN Based Multi-Vth Devices for 7nm and Beyond Technology***, **Donghun Kang**, T Abrams, V Chhabra, S Han, H Parvaneh, B Kannan, G Xu, R Lu, M Ozbek, S Krishnamurthy, P Mennell, H Wang, J Liu,* GLOBALFOUNDRIES U.S. Inc.

Multiple Vth (Multi-Vth) have been one of key components in RMG to meet different industry demands. To extend it to future technologies, several issues need to be resolved; lowering nFET Vth, developing etching process and mitigating TaN loading at different macros. In this study, we demonstrated TaN based multiple Vth devices with 12% better Toxgl adopting higher Al contained nFET work function, selective TiN etching and improved TaN micro-loading.

Fig.1 illustrated simplified process flow in RMG area. Etch of TiN/TaN stack were carried out by using different chemistries (Fig2). Chemistry A removes completely both TiN and 99% of TaN, which is good one for none-selective etching. On the other hand, other chemistries show reasonable selectivity with TaN, which could be a potential selective TiN removal process. Among them, chemistry D is chosen for the selective removal, considering RIE effect on TaN etching rate in Fig.3

Micro-loading was evaluated at three locations, flat, short channel and long channel regions. Each location has its own unique physical structure and surrounds, which could influence source population. Fig.4 compares deposited TaN thickness with different TaN deposition conditions. Significant loading (short/long channel thickness, >50%) was observed from control process. To compensate geometry effect, precursor flow, pule and purge time have increased, expecting better delivery to FIN in trench. With this approaches, loading short to long channel dramatically reduces to 15% in Fig. 4.

Fig.5 and Fig 6 summarize key device results. In Fig 5, both high Al conditions can lower nFET Vth than that of baseline process, demonstrating the ability to push nVTh down further. Fig. 6 shows the benefit of Toxgl for different Al content devices. High Al conditions achieves around 12% better Toxgl than control due to high K protection by TaN during patterning process. TaN based multi-Vth has successfully demonstrated with resolving, 1) nFET Vth lowering by higher Al content in NWF, 2) development/optimization of selective and none-selective etch, and 3) improvement in TaN micro-loading associated with physical shapes of macros. Higher Al nWF process is very effective to lower nFET Vth with matching device parameters. Improved source delivery is a key factor to reduce micro-loading up to 15%. Toxgl benefit of 12% has confirmed by better HfOx protection from patterning process.

2:45pm **AA1-MoA-6 Atomic Layer Deposition: A Few Prospective Applications Aiming Mass-production after Current Si-based Semiconductor Process***, **Tae Joo Park,*** Hanyang University, Republic of Korea **INVITED**

ALD (atomic layer deposition) is one of the most advanced thin film coating or deposition technique in the current vacuum science or electronic device fabrication processes. Recently, the matured ALD technique begins to look for new applications with its strong advantages such as the superior step coverage (conformality) on complicated 3D structures and extremely-precise film thickness controllability. Up to now, there have been a few feasible applications of ALD technique aiming at mass production; electrical and chemical passivation of the assorted solar cells and organic/inorganic flat panel displays, of which fabrication process and physics are familiar with those of semiconductor devices.

This presentation starts with the introduction of modified/advanced ALD process for current Si based industry; discrete feeding method (DFM) and electric field-assisted ALD (EA-ALD) technique for efficient metal film growth to achieve ultrathin and continuous thin film. Next, new-type 2-dimensional electron gas (2DEG) field-effect transistor comprised of only two ALD binary oxide films and wafer-scale uniform ALD growth of 2D chalcogenides will be introduced as part of post-CMOS technology. ALD applications for energy system are also briefly discussed such as Li-based composite thin films for secondary batteries and catalytic/protective layer for photoelectrochemical cells. Another important application of ALD technique could be the design of core-shell structured nano/micro particles for multifunctional applications. A specially designed ALD reactor enables the successful fabrication of core-shell structured nano/micro particles irrespective of the chemical reaction conditions (pH, temperature etc). This technique is also applicable to passivation of various quantum dots and microparts.

3:15pm **AA1-MoA-8 Atomic Layer Deposition of NbO$_x$ Films with Tunable Stoichiometry Using Hydrogen Plasma Reduction***, **Alexander Kozen**, T Larrabee, M Twigg, H Cho, S Prokes,* U.S. Naval Research Laboratory

The Niobium oxide system has seen recent interest, particularly due to its potential use as both a non-volatile, in the case of Nb_2O_5, or volatile, in the case of NbO_2, memristor material. Nb_2O_5 is a high k dielectric (k~41) with a high refractive index (n~2.2) and a wide bandgap (3.6 eV), while NbO_2 is a thermochromic material that undergoes a first order crystalline phase transition at a critical temperature (T_c) of 800˚C. Both of these phases, along with their intermediate sub-oxides, can serve as material components of memristors to facilitate low-power neural computing hardware.

Using the same metalorganic precursor, $^tBuN=Nb(NEt_2)_3$, we demonstrate deposition of NbOx films containing tunable ratios of Nb^{4+} and Nb^{5+} by incorporating additional H_2 plasma steps into the ALD process to selectively reduce Nb^{5+} atoms to a lower oxidation state. The ability to produce NbOx thin films with specific metal to oxygen ratios is critical to understanding the memristive switching behavior of the NbOx materials system, while use of one chemical precursor to deposit a spectrum of varying material stoichiometry and phase can greatly simplify fabrication and design of neuromorphic circuits.

We will examine the impact of plasma chemistry, number, and duration of both single and multiple H_2 plasma steps in the Nb_2O_5 ALD process on film growth, chemistry, and morphology, and will discuss how these additional steps can be used to reduce the resulting film from pure phase amorphous Nb_2O_5 to a NbO_2-rich amorphous film. Additionally, we elucidate the relationship between overall film stoichiometry and electrical properties, with a focus on memristive switching behavior of these materials.

ALD Applications
Room 116-118 - Session AA2-MoA

Memory Device & Materials II

Moderator: Ji-Hoon Ahn, Korea Maritime and Ocean University

4:00pm **AA2-MoA-11 Effects of Fluorine in ALD W on Dielectric Properties***, **Hyung Chul Kim**, S Lee, H Cho, S Jin,* SK Hynix, Republic of Korea **INVITED**

Recently, it has been recognized that both achieving low resistivity at the gate electrode and suppressing poly-Si gate depletion are key factors for developing deep submicron metal–oxide–semiconductor field effect transistors (MOSFETs). The tungsten (W) metal gate electrode is a good candidate for solving simultaneously the problems mentioned above. However, it has been known that pure tungsten gate is unstable when it is deposited on the SiO_2 and that fluorine (F) diffusion into SiO_2 during the deposition and annealing process causes many undesirable effects . Little is known about the effect of the impurity present in the metal on the properties of the oxide . In this paper, we show the changes of the capacitance equivalent thickness (CET) by the F in atomic layer deposition (ALD) W on the oxide in the W / barrier metal / oxide / Si metal oxide semiconductor capacitor (MOSCAP) . The CET increased by 4 ~ 5 Å in ALD W compared to PVD W, and the change of oxide by F was confirmed. As the barrier metal thickness increases, the CET decreases. Also when the RTA proceeds after the W deposition, the CET increases . F reacts with SiO_2 in Al_2O_3/SiO_2 stack to increase CET. The SiO_2 reacted with F makes a defect source inside SiO_2, leading to the increase of the frequency dispersion and the leakage current. The results of this study can be usefully used as the basic data for metal development and oxide reliability in DRAM and Flash devices.

4:30pm **AA2-MoA-13 Low Temperature Atomic Layer Deposition of Ru for Copper Metallization***, A Mane, **Yan Zhang**,* Argonne National Laboratory*; A Kumar, J Allgair,* BRIDG*; J Hryn, J Elam,* Argonne National Laboratory

Contact metallization in large-scale semiconductor devices such as logic, memory, MEMS, and SoC using 2.5D and 3D interposers requires a high quality and conductivity metal barrier/seed layer for subsequent metal electroplating. Ruthenium metal has a bulk resistivity of 7.1 µΩ cm, a work function of 4.7 eV, and a low solid solubility with strong adhesion to Cu, making Ru an attractive contact metal barrier metal or seed layer for Cu electroplating. There have been numerous reports of Ru ALD using a variety of precursors. However, technical challenges remain including the need for high growth temperature, very long nucleation delay, and the use of plasma that limits Ru conformality in high aspect ratio features. Currently, there is a strong desire and demand for 3D-devices where high quality, uniform, and conformal metal growth on high aspect ratio structures for ultra largescale integration (ULSI) process flow including for 2.5D and 3D interposer substrates creation.

Here we have developed a low temperature (200^{o}C) Ru atomic layer deposition process using $Ru(DMBD)(CO)_3$ and O_2 precursors. To enhance the Ru nucleation and growth, especially at low temperature, we performed low temperature Pt ALD using $Pt(MeCp)Me_3$ and O_2 to deposit a sub-monolayer Pt seed layer that greatly accelerates the subsequent Ru nucleation. High quality Ru films were deposited on a variety of substrates including Si(100), fused silica, Al_2O_3 and TiN. The ALD Ru films were uniform across the 18” deposition zone of our tubular ALD reactor. Thin Ru films were characterized by XPS, SEM, TEM, four point IV measurements, XRD and XRF. We have also performed Cu electroplating on the ALD Ru layers and found that the Ru films deposited using the Pt seed layer exhibited excellent Cu electroplating. Here we will present details of the Ru ALD and Cu electroplating.

4:45pm **AA2-MoA-14 Conformal Growth of Low-resistivity Ru by Oxygen-free Thermal Atomic Layer Deposition***, **Guo Liu**, J Woodruff, D Moser,* EMD Performance Materials

Ru has been widely investigated as an alternative material for metallization applications in semiconductor devices to replace the Co adhesion layer or as a filling material to replace Cu without the need for a barrier layer. ALD deposition of low resistivity Ru is typically achieved using O_2 as the co-reactant or by plasma enhanced ALD using N_2/H_2 or NH_3 in an oxygen-free process. However, for certain semiconductor applications, the strongly oxidizing O_2 co-reactant can cause damages to other layers especially metal films, while a PEALD process has limited capability for step coverage. An oxygen-free thermal ALD process for Ru would be desirable. Current oxygen-free thermal ALD processes for Ru generally suffer from low growth rate and high resistivity problems due to high impurity levels and/or low film density because of limited reactivity of common O_2-free co-reactants with most Ru precursors below their thermal decomposition temperatures.

In this work, we present an oxygen-free thermal ALD process that can deposit low-resistivity Ru thin films down to a few nm thick with a short nucleation delay of less than 30 cycles as shown in Fig. 1. The methods include ALD growth of a ruthenium film at lower temperatures using an oxygen-free co-reactant and post-deposition annealing at higher temperatures. The deposition step was carried out in the temperature range of 150-250°C using a thermally stable high vapor pressure precursor, dimethylbutadiene ruthenium tricarbonyl or $(DMBD)Ru(CO)_3$. The annealing step was performed at 300°C or higher in an oxygen-free atmosphere. The deposition and annealing conditions have been optimized for high growth rate and low resistivity. Under optimal deposition and annealing conditions, low resistivity of about 20 μΩ-cm comparable with the O_2 ALD process of the same precursor (1) has been achieved. Conformal step coverage has also been demonstrated as shown in Fig. 2.

References:

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5:00pm **AA2-MoA-15 Plasma Enhanced Atomic Layer Deposition of Nickel and Nickel-based Alloy Thin Films for High-quality and Thermally Stable Nickel Silicide***, S Kim, **Shunichi Nabeya,*** Yeungnam University, Republic of Korea

Metal silicides are silicon compounds with metals, and they have low resistivity like metals as well as good compatibility with Si and metals. So, metal silicides, which have been formed by metal deposition on Si followed by post silicidation annealing, have been used for contact materials in Si devices. $TiSi_2$ have been widely used for contacts, however NiSi and $CoSi_2$ are applied to sub-100 nm Si devices since $TiSi_2$ shows narrow line width effect that is increase in $TiSi_2$ resistivity with decreasing linewidth. In order to overcome limitations of current Si devices in downscaling, emerging nanodevices have been intensively studied, and their structures are moved from 2D planar to 3D structure. So, the schemes of contact fabrication used for 2D devices are changed in 3D emerging nanodevices, and conformality of metal thin films is the most important requirement to be achieved. In view of this, ALD is a good alternative to conventional PVD techniques for fabricating the silicide contact. Earlier, there are few reports on nickel deposition by thermal ALD process due to the lack of suitable Ni precursors for it [1, 2]. Though ALD of nickel oxide processes are relatively easy to develop, a rather complex step is needed to obtain nickel silicides from this oxide. In our previous research, we successfully obtained metallic Ni film by using thermal ALD process using a Ni metalorgarnic precursor and H_2 or NH_3 molecules as reactants. One drawback of thermal ALD Ni process is that much amount of impurities of O and C are included in as-deposited film, leading to a relatively high resistivity of ~1700 μΩ-cm and a post annealing process at 480˚C was needed to obtain high-quality Ni film. In order to obtain NiSi with a simpler process, it is necessary to realize a high-purity Ni film by ALD. Generally, plasma enhanced ALD (PEALD) is a better method for obtaining high-quality metal thin films as compared to the thermal ALD. In this study, PEALD Ni processes are developed by using various reactants including N_2, H_2 or NH_3 plasma. The properties of PEALD-Ni films depending on the reactants used are compared using various analysis such as XRD, XPS, 4-point probe, TEM etc. We also evaluate the silicidation behavior of PEALD-Ni films deposited with optimized condition. Finally, Ni-based alloy films where a noble metal is incorporated in them are also prepared using PEALD for improving the thermal stability of the nickel silicide film.

Acknowledgement

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References

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5:15pm **AA2-MoA-16 Ternary Thin Film Alloys of Ti-Si-N as Low Resistance Diffusion Barrier for Memory Applications***, **Somilkumar Rathi,** J Mack, Z Karim, N Mukherjee,* Eugenus, Inc.

The rapid advances in memory technology, coupled with decreasing feature sizes and increasing aspect ratios, have imposed stringent requirements on the physical and electrical properties of metal-to-semiconductor interfaces. This has resulted in several integration and material challenges for low-resistance contacts and diffusion-barrier films. Reactively-sputtered titanium nitride (TiN) is widely used as diffusion-barrier layer due its high thermal and chemical stability, low electrical resistivity, and process maturity. However, the columnar and polycrystalline grain structure provides a pathway for diffusion during higher-temperature anneal steps. This undesirable effect, which leads to device degradation and failure, has led to the search for alternative films. In this work, we report recent advancements on the amorphous ternary alloy films composed of titanium, silicon and nitrogen (TSN), an excellent alternative to TiN films. These TSN films were grown using Atomic Layer Deposition (ALD) technique on the Eugenus 300mm QXP commercial reactor. In order to understand the feasibility and tunability for a variety of applications, the films were grown over a wide temperature window of 400-620°C and using several different chlorine-based Si precursors. Film thickness and silicon content were varied and corresponding electrical characterization was performed. X-ray photoelectron spectroscopy and Rutherford Back Scattering techniques were utilized for compositional analysis. The results indicate that ALD-based TSN films are not only high volume manufacturing compatible, but have excellent mechanical, thermal and electrical properties and are scalable to the next technology nodes.

5:30pm **AA2-MoA-17 Atomic Layer Deposition of Mixed Phase TiN_xC_y using Highly Reactive Substituted Hydrazines and Tetrakis(dimethylamido)Titanium***, **Jaime DuMont**, M Knez,* CIC nanoGUNE, Spain

Tribology, in spite of being one of the most traditional industrial sectors, is in great demand of innovation. At over 6% of the worlds GDP, corrosion and wear represent significant expenses in the global economy and yet they seldom receive the attention they require. The development of protective coatings that can suppress both factors at the same time is therefore of great economic interest. Among the materials which have demonstrated superior hardness, strength and chemical stability are titanium nitride (TiN) and titanium carbide (TiC). The protective capability of these materials is not, however, without limitation. When exposed to high temperature applications or high-speed machining these coatings can become brittle and easily fracture because of poor resistance to high temperature oxidation. Inclusion of carbon atoms in the TiN lattice has been shown to substantially increase the hardness and lower the friction coefficient. These beneficial properties are a result of the TiN_xC_y composition and can be adjusted by controlling the material's C-N ratio to a precise level. When tuned correctly, TiCN films can display anti-wear capabilities and higher hardness that far surpass those of TiN and TiC alone.

Next generation TiN_xC_y coatings will require a deposition strategy that 1) functions at temperatures low enough to keep critical tool dimensions within tolerance 2) circumvents corrosive hydrogen halide by-products 3) maintains a strong chemical binding of the coating to the substrate and 4) can be easily scaled for large-area applications. Atomic layer deposition is a technique primed to meet these requirements. In this work we develop a new low-temperature, halide-free, mixed phase TiN_xC_y thermal atomic layer deposition (ALD) process. We exploit the high reactivity of substituted hydrazines, including tertiary butyl hydrazine (TBH) and monomethylhydrazine (MHH), together with the amide based precursor, TDMATi. These superior precursor combinations circumvent the corrosive hydrogen halide by-products of conventional metal nitride ALD processes, provide the required C and N atoms and further lower the deposition temperature through transamination-like exchange reactions. We will discuss process parameters (substrate temperature and precursor exposure times) as well as ex situ characterization studies (X-ray diffraction (XRD) and reflectivity (XRR) and scanning electron microscopy (SEM)) of the TiN_xC_y materials deposited as well as their effectiveness as next generation protective coatings.

ALD Applications
Room Premier Ballroom - Session AA-MoP
ALD Applications Poster Session

AA-MoP-1 Highly Visible Light Photocatalytical Activity of Ozone-Assisted Atomic Layer Deposited Fe_2O_3 Coated TiO_2 Powders*, X Zhao,* Nanjing Unviersity, China*; **Yan-Qiang Cao**, A Li,* Nanjing University, China

With the rapid development of modern industry, environmental pollution has become a serious issue. TiO_2, as an efficient and safe photocatalyst, can only absorb ultraviolet light. In order to make full use of visible light, the doping and modification of TiO_2 powders have drawn great attention. Herein, Fe_2O_3 coated TiO_2 powders was prepared by ozone-assisted atomic layer deposition (ALD) strategy, taking advantage of its 3D conformality, precise control of film thickness and flexible surface modification. Fe_2O_3 coating with various ALD cycles of 200-800 was derived using $Fe(Cp)_2$ and O_3 as precursors of iron and oxygen at 250°C, respectively. 400-cycle Fe_2O_3 coated TiO_2 sample exhibits optimal photocatalytic activity with ~72% degradation of methyl orange in half an hour under illumination of visible light, much higher than pure TiO_2 of less than 2%. X-ray diffraction results indicate that there is no significant change in the particle size and anatase structure of TiO_2 powder coated with 400 Fe_2O_3. Instead, ultrathin Fe_2O_3 amorphous layer is formed on the surface of TiO_2 with reduced bandgap from 3.2 eV to 2.9 eV and improved visible light adsorption. Mott-Schottky curves confirm the formation of Fe_2O_3/TiO_2 p-n junction could suppress the electron-hole recombination. Above all, compared to plasma-enhanced ALD, ozone-assisted ALD shows better depostion efficiency in powder samples and is more suitable for the surface modification of TiO_2 powders.

Keywords: Ozone-assisted atomic layer deposition; TiO_2 powders; Fe_2O_3 coating; Photocatalytic activity; p-n heterojunction

AA-MoP-2 Synaptic Behaviors of Pt/HfO_2/HfO_x/TiN Bilayer-structure Memristors by Atomic Layer Deposition*, **Chang Liu**, Y Cao, A Li,* Nanjing University, China

HfO_x-based resistive random access memory shows remarkable potential for next-generation non-volatile memories, however it is not optimized as synaptic devices for neuromorphic system applications. Herein, we focused on the fabrication and synaptic behaviors of HfO_2/HfO_x bilayer-structure memristive devices. 4-nm nonstoichiometric HfO_x films on TiN-coated Si substrates were prepared using $Hf[N(C_2H_5)CH_3]_4$ (TEMAH) and hydrogen plasma by plasma-enhanced atomic layer deposition (PEALD), while 2-nm stoichiometric HfO_2 films were deposited using TEMAH and H_2O precursors via thermal ALD. X-ray photoelectron spectroscopy analyses shows that the atomic ratio of Hf: O in HfO_2 and HfO_x active layers is 1: 2.00-2.05 and 1: 1.60-1.74, respectively, indicating HfO_2/HfO_x bilayer-structure memristors have been obtained.. The Pt/HfO_2/HfO_x/TiN memistive cells exhibit bipolar resistive switching features with 20 intermediate resistance states by applying 1 V to 3 V reset voltages with 0.1 V interval, based on the migration/diffusion of oxygen vacancies. Several essential synaptic functions are simultaneously achieved in such a bilayer-structure device, such as nonlinear transmission characteristics, spike-timing-dependent plasticity, and long-term/short-term plasticity.

Keywords: memristor, bilayer-structure, atomic layer deposition, oxygen vacancy, synaptic behaviors

AA-MoP-3 Wafer-scale Single-domain-like Graphene with Enhanced Electronic Transport Properties by Defect-selective Atomic Layer Deposition of Hexagonal ZnO*, M Sung, **JinWon Jung**,* Hanyang University, Republic of Korea

Large-area graphene films produced by means of chemical vapor deposition (CVD) are polycrystalline and thus contain numerous grain boundaries that can greatly degrade their performance and produce inhomogeneous properties. A better grain boundary engineering in CVD graphene is essential to realize the full potential of graphene in large-scale applications. Here, we used atomic layer deposition (ALD) technique to deposit ZnO selectively on grain boundaries of the CVD graphene so as to depress the highly resistive effect of the grain boundaries. The ZnO ALD / Graphene film showed the electrical properties—a sheet resistance of 68 Ω/□, a field effect mobility of 7,460 and 2,610 $cm^2 \cdot V^{-1} \cdot s^{-1}$ for hole and for electron, respectively. A defect-selective atomic layer deposition (ALD) for stitching grain boundaries of CVD graphene with conductive ZnO so as to increase the connectivity between grains. In the present ALD process, ZnO with a hexagonal wurtzite structure was selectively grown mainly on the defect-rich grain boundaries to produce ZnO-stitched CVD graphene with well-connected grains. For the CVD graphene film after ZnO stitching, the inter-grain mobility is notably improved with only a little change in the free carrier density. We also demonstrate how ZnO-stitched CVD graphene can be successfully integrated into wafer-scale arrays of top-gated field-effect transistors on 4-inch Si and polymer substrates, revealing remarkable device-to-device uniformity.

AA-MoP-4 Atomic Layer Deposition Under in situ Ultraviolet Radiation for Highly Conductive Air Stable ZnO Thin Film Fabrication*, **Hong-rho Yoon**, M Sung,* Hanyang University, Republic of Korea

Compounds of ZnO is very attractive compound semiconductors due to their wide band gap (~3.3eV) characteristics and large exciton binding energy (60meV). However, ZnO preparing by low temperature atomic layer deposition (ALD) has low conductivity. Here, we report the highly transparent, and highly conductive air-stable thin film of ZnO using ALD at low temperature under in situ UV irradiation of the growing film. X-ray photoelectron spectroscopy (XPS) was used to reveal that the UV irradiation generates oxygen vacancies, partially removes O–H bonds, and thereby improves the electrical conductivity. Thus, the in situ UV irradiated ZnO film shows an electrical resistivity of 5.5 × 10-4 Ω cm, compairing to 0.25 Ω cm resistivity of the pristine ZnO film, and an optical transparency of nearly 90%. In addition, even on prolonged exposure of the film to air, it maintains high stability and conductivity against the degradation of the electrical conductivity.

AA-MoP-5 Annealing Temperature Modulated Interfacial and Electrical Properties of PEALD-derived HfLaO/Si Stack*, **Duo Cao**, F Liu, H Shi, W Shi,* Shanghai Normal University, China*; X Cheng, L Zheng, L Shen, Y Yu,* SIMIT, Chinese Academy of Sciences, China*; J Wang,* University of California Los Angeles

HfLaO dielectric films have been shown to lead to significantly superior performance as the gate dielectric layer. Recent research on HfLaO has shown this material demonstrates a high crystallization temperature and a low leakage current while preserving a low equivalent oxide thickness (EOT) value. In this work, we investigated the effects of rapid thermal annealing on the interfacial and electrical properties of HfLaO films deposited on Si substrate. Films with different thicknesses were grown by plasma enhanced atomic layer deposition (PEALD) at 200°C with in situ pre-O_2, pre-NH_3 and post-O_2 plasma treatments. Films were treated with rapid thermal annealing (RTA) at a series of temperatures. The HfLaO films retain its insulating characteristics and are thermally stable even after annealing at 800 °C. X-ray photoelectron spectroscopy (XPS) spectra indicates that the main component of the interfacial layer is silicate without any silicide. Leakage current-voltage and capacitance-voltage characteristics of the MIS capacitors were obtained. Heat treatment can effectively improve the dielectric performance, such as increase of effective permittivity, reduction in ΔV_{fb} and no obvious frequency dispersion. However, the increase of annealing temperature leads to the increase of leakage current density, which is due to the decrease of the conduction band offset (ΔE_c) and further crystallization of the samples. These investigation results might provide the guidance for the performance optimization of high k gated dielectrics to meet the requirements of future complementary-metal-oxide-semiconductor (CMOS) devices.

AA-MoP-6 Atomic Layer Deposition of Yttrium Oxide using Heteroleptic Y Precursors*, **Daehyeon Kim**, J Lee,* Air Liquide Laboratories Korea, Republic of Korea

Rare earth based oxides are of interest for their potential application in future logic and memory technologies, and Yttrium oxide (Y_2O_3) is well-known as high-k material for metal gate transistor and a dopant for high-k materials. Not only semiconductor applications, usage for non-semiconductor applications (such as coating material) has been also considered. In past studies, heteroleptic precursors which have alkylcyclopentadiene and amidine ligands, $Y(RCp)_2(R'\text{-amd})$, have been developed to aim to be liquid and to enhance its volatility and thermal stability. In this work, two heteroleptic precursors, $Y(EtCp)_2(iPr\text{-amd})$ and $Y(iPrCp)_2(iPr\text{-amd})$, and one homoleptic precursor, $Y(EtCp)_3$, were evaluated and their physical properties and ALD results were compared. Both $Y(EtCp)_2(iPr\text{-amd})$ and $Y(iPrCp)_2(iPr\text{-amd})$ showed high thermal stability and clean TG evaporation. $Y(EtCp)_2(iPr\text{-amd})$ is liquid and showed the highest vapor pressure (1Torr at 150°C) among three precursors. Atomic layer deposition (ALD) of Y_2O_3 films was performed using these precursors with various oxidant such as ozone, oxygen, and water. $Y(EtCp)_2(iPr\text{-amd})$ gave flat ALD window up to 450°C with a growth rate of 0.8~1.0Å/ cycle. X-ray photoelectron spectroscopy (XPS) showed that obtained thin film was pure and carbon and nitrogen impurities were below the detection limits. Step coverage of the film was also good (~100%, AR= 1:20) at 350, 400°C.

AA-MoP-7 Atomic Layer Deposition Y_2O_3 on GeSn/III-V for Application to MOSFET Common Gate Process*, C Chu,* ***Guang-Li Luo****, S Chen, W Wu, W Yeh,* National Nano Device Laboratories, Republic of China

Integration technology between GeSn and GaAs is attractive due to high GeSn hole mobility (>1500 cm^2/Vs) and high III-V electron mobility (8500 cm^2/Vs, GaAs) as well as the CMOS compactness (GeSn p-channel and III-V n-channel MOSFETs [1, 2]. Sub-nm equivalent oxide thickness (EOT) gate stacks are required to keep the intrinsically high performance of GeSn and III-V. The focus here is on finding suitable high permittivity (k) dielectric (k>20) to form a gate stack with low interface state density and EOT. The most perilous issue is engineering a high-quality interface between GeSn /III-V and the high-k dielectric, that is, passivation of the GeSn /III-V surface. An interfacial layer (IL) either intentionally or unintentionally formed during the high-k dielectrics deposition process is usually necessary for achieving high electrical performance of Ge and III-V based MOS devices, but its presence could increase EOT, and is not beneficial to device performance. Therefore, the IL has to be as thin as possible, and permittivity for dielectric has to be as high as possible. Atomic layer deposition (ALD) is an important tool to fabricate these proposed IL because it offers precise, monolayer-level thickness control. In order to further improve on interface properties of Y_2O_3/ GeSn and III-V interface, it is quite important to clarify the dominant factor determining the interface properties. Therefore, studies on interface structures and electrical interface properties are necessary. This paper aims to grow Y_2O_3 film by atomic layer deposition (ALD). It can produce high quality, high smooth surface and good stoichiometry Y_2O_3 film due to the self-limited growth mechanism. In this work, Pt/Y_2O_3/GeSn and Pt/Y_2O_3/GaAs capacitors similar to MOSFET gate stack process were fabricated. High interface states density and capacitor leakage current can be reduced by chemistry treatment. Capacitance-voltage (C-V) was done to discuss the electrical characteristics, such as equivalent oxide thickness (EOT), hysteresis reduction.

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AA-MoP-8 Carbon Textile Decorated with Redox-Active Vanadium Hybrid for Flexible Supercapacitors*,* ***Do Van Lam****, S Lee, J Kim,* Korea Institute of Machinery and Materials

We demonstrate that, via V_2O_5 coating by low temperature atomic layer deposition and subsequent pyrolysis, ubiquitous cotton textile can readily turn into high-surface-area carbon textile fully decorated with pseudocapacitive V_xO_y/VC widely usable as electrodes of high performance supercapacitor. We found that carbothermic reduction of V_2O_5 ($C + V_2O_5 \rightarrow C' + VC + CO/CO_2(g)$) leads to chemical/mechanical activation of carbon textile, thereby producing high-surface-area conductive carbon textile. In addition, sequential phase transformation and carbide formation ($V_2O_5 \rightarrow V_xO_y \rightarrow VC$) occurred by carbothermic reduction trigger decoration of the carbon textile with redox-active V_xO_y/VC. Thanks to the synergistic effect of electrical double layer and pseudocapacitance, the supercapacitors made of the hybrid carbon textile exhibited far better energy density with excellent cycling stability than the carbon textile simply undergone pyrolysis. Our method could open up a promising and facile way to synthesize hybrid electrode materials for electrochemical energy storages possessing advantages of both electrical double layer and pseudocapacitive material.

AA-MoP-9 MAPS (Mecaro's Advanced Precursors System)-Ti Series: Atomic Layer Deposition of TiN or TiO_2 Films Using New Titanium Precursors*,* ***Ho Hoon Kim****, D Lee, S Cheon, Y Yoo, S Ha, J Kim, Y Byun,* MECARO Company, Republic of Korea

Size decrease demand in semiconductor devices has been increased for the last few decades. A thinner barrier layer with high uniformity and conformality and also excellent step coverage is needed for optimum layer filling.[1] For these reasons, atomic layer deposition (ALD) has been introduced as a method to deposit conformal thin films in a structure having high aspect ratio, and the famous materials deposited by ALD are Al_2O_3, HfO_2, ZrO_2, ZnO, and TiN. Selection of appropriate precursor plays a critical role in the success of final ALD process since high temperature deposition is required, high thermal stability precursors are required as well. Titanium dioxide (TiO_2) is an attractive candidate for several thin film applications, such as high dielectric constant material for electronic devices. TiO_2 is also a constituent of several important multi-metal oxide systems, such as strontium titanates (STOs), barium strontium titanates (BSTs), and lead zirconium titanates (PZTs), for dielectric and ferroelectric applications.[2] ALD processes for producing metal containing thin films comprise feeding into a reaction space vapor phase pulses of metal containing cyclopentadienyl-based ligands precursors as a metal source material. The quest for alternatives to cyclopentadienyl-based ligands has led to *N*-centered donor ligands in various fields of organometallic and coordination chemistry.

In this work, series of titanium complex (MAP-Ti series) having amine derivative have been synthesized and characterized as new precursors for ALD. The one of these new compounds was found to have properties well-suited for use as precursors for ALD of thin films. It has high volatility, high thermal stability, and high reactivity. The experimental details of film deposition and characterization will be reported briefly.

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AA-MoP-10 MAPS (Mecaro's Advanced Precursors System): Atomic Layer Deposition of TaN and NbN Thin Films using Noble Metal Precursors*,* ***Woori Bae****, Y Byun, S Cheon, H Kim, M Kim, S Ha, J Kim,* MECARO Company, Republic of Korea

New materials are needed to meet the requirements of the continuous downscaling of microelectronic devices. The copper-based interconnects in the next generation ultra large scale integration (ULSI) microelectronics is creating significant challenges for new barrier materials. Transition metal nitrides or metal silicides are considered the most promising diffusion barrier materials[1] for next generation ULSI microelectronics. In this work, tantalum and niobium nitride films were deposited with reducing agent or plasma and characterized, using newly designed MAP-Nb01 and MAP-Ta01 precursors which are characterized by various spectroscopies. The main goal of the present study was to deposit Nb and Ta metal nitride films by atomic layer deposition (ALD)[2,3] method. Films deposited by ALD have excellent conformality and large area uniformity in addition to accurately controlled film thickness.

Protonated lithium amides together with other synthetic strategies have been extensively used to generate the imido ligand, neutral niobium and tantalum complexes have been synthesized and their functionalities were used as both ancillary and reactive sites. The diffusion barrier performance and gate electrode properties of TaN and NbN will be described in some detail. After an account of the experimental details of film deposition and characterization, the results will be reported briefly.

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AA-MoP-11 The Impact of O_2/N_2 Ratio in O_3 Based TiO_2-Active Layer in Vacancy-modulated Conductive Oxide*,* ***Elie Schapmans****,* IMEC, Belgium

Ozone is an effective oxidant used in atomic layer deposition of dielectric oxides. At imec, we have successfully developed ALD processes such as TiO_2 ALD with both O_3 and H_2O. The O_3 based TiO_2 process resulted in high k Rutile phase when grown on Ru substrate or Anatase phase when grown on TiN substrate [1]. In both cases, applications in microelectronic devices have been demonstrated such as in MIM capacitors [1] and a resistive switching memory device with nonfilamentary switching mechanism called Vacancy-modulated conductive oxide VMCO [2]. Thermal ALD films were grown on blanket Si 300mm diameter wafers in a cross flow single wafer reactor at 250°C and 210°C deposition temperatures using Ti(OCH3)4 and O_3 as precursors. O_3 was delivered at a fixed density of 225g/m^3 and formed with a different O_2/N_2 ratio. The TMEIC O_3 generator made it possible to explore a complete range of O_3, formed from N_2 free up to highly N_2 doped O_3 at a fixed O_3 density. The saturation behavior and the growth per cycle of TiO_2 film were determined prior to the integration in the VMCO stack. This stack consists of a 10nm PVD TiN bottom electrode, a 5-10nm amorphous Si barrier layer followed by a ~ 8nm TiO_2 switching layer and 100nm PVD TiN top electrode. We observed a gradual increase in growth rate by lowering the N_2 gas flow used for O_3 generation, up to a value of 0.04nm/cycle in the case N_2 free O_3 based TiO_2. The growth rate also slightly decreases with deposition temperature reduction from 250°C to 210°C. All TiO_2 films were amorphous as deposited regardless the N_2/O_2 ratio or deposition temperature employed. (Fig1) However, significant differences can be demonstrated via electrical measurements depending on the process conditions. In terms of breakdown voltage, we see an improvement of more than 1V with an high N_2 flow during O_3 generation at 210°C. The robustness of the stacks decreases in the case of N_2 free O_3 based TiO_2.(Fig2)

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AA-MoP-12 Effect of O_2 Plasma Exposture Time on Al_2O_3/Si Interface Properties during Al_2O_3 Formation using PAALD

Kwan Hong Min, Korea Institude Energy Reseach, Republic of Korea*; J Lee, M Jeong, S Choi,* Korea Institute of Energy Research, Republic of Korea*; M Kang, J Lee, S Park,* Korea Institute Energy Research, Republic of Korea*; D Kim,* Korea University, Republic of Korea*; H Song,* Korea Institute Energy Research, Republic of Korea

Thermal ALD and PAALD(Plasma Assisted ALD) are widely used as methods for Al2O3 deposition on Si surface. PAALD has the advantage of faster deposition rate compare to thermal ALD. On the other hand, it has disadvantage of the damage to Si surface because of plasma intensity as reaction energy for O2 dissociation. In this study, the effect of O2 plasma exposure time on Si interface was investigated. O2 plasma exposure time was varied from 0.5 to 10 second. Passivation properties such as carrier lifetime, implied voltage were measured by Qusai-Steady-State Photoconductance(QSSPC) and interface properties were analyzed by Capacitance-Voltage(C-V) characteristics. According to increasing O2 plasma exposure time, it is confirmed that passivation properties were decreased. Especially, 'hump' property was observed, which is known to be caused by the interface trap during C-V measurement at low frequency. Therefore, we could expect that the interface properties would be decreased. To confirm interface properties, fixed charge density and interface trap density of Al2O3/Si interface were extracted by C-V and conductance method. As a result, it was found that an increase of O2 plasma exposure time little affected on the fixed charge density but the interface trap density was much affected. Therefore, optimization of plasma condition is important for Al2O3 deposition using PAALD.

AA-MoP-13 Effect of Mechanical Stress on Ferroelectric Properties of Fully-Atomic Layer Deposition Processed TiN/$HfZrO_x$/TiN Stacks

C Choi, ***Myeong Gyoon Chae,*** Hanyang University, Republic of Korea

Due to the device scaling limit, alternative materials and device structures have been investigated to continue performance enhancement and power consumption reduction. Among them, Ferroelectric Random Access Memory (FeRAM), Ferroelectric Field Effect Transistor (FeFET), and Negative Capacitance Field Effect Transistor (NC-FET) are being actively researched as promising alternatives to present DRAM, FINFET, and NAND Flash. As a result, ferroelectric materials have garnered strong interest further. In the early step of research, conventional ferroelectric materials (PZT, BTO, SBT) were actively studied. However, due to poor scalability and bad electrical stability such as higher leakage and breakdown, which are considered as fundamental problems of these materials, CMOS-compatible hafnium dioxide (HfO_2) based ferroelectric materials have been emerging actively.

In this study, we fabricated all atomic layer deposition (ALD) processed ferroelectric capacitor based on doped-HfO_2. To investigate the effect of mechanical stress on ferroelectricity, top electrode titanium nitride (TiN) thickness was controlled. In the case of a device with a thicker TiN, a larger switching polarization and lower ferroelectric saturation voltage were observed compared to a device with a thin TiN. It can be seen that the thick electrode acts as a stressor to inhibit the formation of the monoclinic phase during crystallization and generates a ferroelectric orthorhombic phase. Our finding indicates that performance of ferroelectric materials based devices can be improved by enhanced ferroelectricity as a result of optimizing mechanical stress and thermal budget.

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AA-MoP-14 Atomic Layer Deposition of SnTe for Dopant Application of Phase-change Materials

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A phase-change random access memory (PCRAM) is one of the most promising candidates for the next-generation non-volatile solid-state memory. PCRAM is known for its low cost, high stability, and high compatibility with complementary metal–oxide semiconductor (CMOS) technology. Nevertheless, there are some commercialization issues that must be met such as reduction of switching power, faster phase transition speed, the stable resistivity in the amorphous state. Incorporation of phase-change materials (PCM) with 3D fabrication technology is another challenge to increase the memory density. The 3-D vertical structure was suggested for highly integrated array of cells in vertically integrated structure.[4] In this vertical geometry, atomic layer deposition (ALD) can deposit a PCM film with its excellent step coverage due to the self-limiting growth mechanism.

In this work, an ALD process to form SnTe films was developed . According to the previous reports[1-2], SnTe is proposed as a dopant or superlattice material to increase switching speed and reduce switching power owing to the weaker bond strength of Sn–Te (359.8 kJ mol−1) compared to the Ge–Te (397 kJmol−1).[3] Relatively weak bond strength in phase change material could significantly increase the crystallization speed. Also, the resistivity in an amorphous state can be decreased with increasing Sn content.[5] Precursors of $[(CH_3)_2N]_4Sn$ and $(Me_3Si)_2Te$ were adapted for SnTe deposition. The process was studied in detail to verify the ALD behavior of SnTe film. Figure 1 shows that the growth of SnTe film was saturated at around 30 $ng\cdot cm^{-2}cy^{-1}$. Sn:Te ratio of the film was also saturated at the slightly Te-rich condition. $Ge_xSn_yTe_z$ ternary deposition was performed using $GeTe_2$ to confirm the doping possibility of Sn. $GeTe_2$ was deposited with $Ge(Oet)_4$ and $(Me_3Si)_2Te$ precursors for Ge and Te.[6] Figure 2 shows the $Ge_xSn_yTe_z$ ternary deposition results through the alternating deposition sequences of the $GeTe_2$ and SnTe layers. Apart from the initial conjecture, the film composition lye on $GeTe_2$-$SnTe_2$ tie line rather than $GeTe_2$-SnTe tie line, suggesting that the complicated chemical interaction is involved in the ternary film growth. Detailed discussions on the growth behavior will be made in the presentation.

AA-MoP-15 Atomic-Layer-Deposited LiAlO Protective Layer for Li Metal Anode in Li-ion Secondary Batteries

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Li metal anode for Li-ion secondary batteries has been recently developed to enhance the battery performances. However, the physicochemical instability of Li causes a dendrite formation at the electrode surface by electrochemical reaction with electrolyte during charging/discharging cycle. Even though several protective layers were suggested, most of them have common problems of conformality and low conductivity. To address this problem, we suggest atomic-layer-deposited (ALD) Li-Al-O protective layer which is free from physicochemical degradation by lithiation during charging/discharging cycle. The addition of Li ions to metal oxides such as Al_2O_3 tends to increase the ionic conductivity.[1] ALD Li-Al-O thin films with various compositions were grown by repeated sub-cycle of ALD LiOH and Al_2O_3, and thickness was measured by spectroscopic ellipsometry (Fig. 1). The process temperature was controlled below 100°C for avoiding degradation of Li metal during ALD. The composition of thin films was estimated by X-ray photoelectron spectroscopy. The ionic conductivity of thin films was measured by electrochemical impedance spectroscopy. The experimental results will be presented in detail.

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AA-MoP-16 Effect of Growth Temperature on the Structural and Electrical Properties of i-ZnO by Atomic Layer Deposition Method, ***Yeonbae Shin***, *V Arepalii, J Kim,* Cheongju University, Republic of Korea

Highly resistive i-ZnO can play a critical role to prevent leakage current paths from CIGS thin film solar cells. In this work, we demonstrated the effect of growth temperature on the structural and electrical properties of i-ZnO using atomic layer deposition (ALD) method on to both Si (100) and soda lime glass (SLG). The deposited films were characterized by performing scanning electron microscopy (SEM), X-ray diffraction, UV-Visible spectroscopy, and four-point probe measurements. The four-point probe measurement revealed that samples grown at 80 showed higher resistivity of 10^6 Ω.cm whereas sample grown at 180 showed low resistivity of 10^{-3} Ω.cm. We will further discuss the device characteristics of CIGS solar cells with using both highly resistive and low resistive ZnO.

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Keywords: ZnO, ALD method, solar cells, growth temperature

AA-MoP-17 Atomic Layer Deposition of GeSe Films with Discrete Feeding Method for Ovonic Threshold Switch, ***Woo Hyun Kim***, *C Hwang,* Seoul National University, Republic of Korea

Phase-change Random Access Memory (PcRAM) is a strong candidate for the next-generation memory with characteristics of non-volatility, fast operating speed, and low power consumption. To overcome the existing limitations in the memory density of the PcRAM in 2D structure, the 3D-stackable memory of the crossbar array has been proposed as a promising solution. Despite the advances in 3D structural designs to scale down the memory, sneak current that frustrates accurate reading/writing of data in each cell remained a critical issue. The selector devices such as a P-N junction diode, metal-insulator-metal diodes, Ovonic Threshold Switch (OTS) have been devised to minimize these errors in operation.

Among the options for the selector device, OTS based on the volatile voltage snapback effect of amorphous chalcogenides possesses several desirable characteristics: bidirectional switching, processability for 3D structure and controllable threshold voltage. Among the materials that can be used as OTS, GeSe has strong glass forming ability (T_{cry}~340 ºC) compared to GeTe (T_{cry}~150 ºC) with a simple binary composition. Here, a new method for depositing GeSe films by Atomic Layer Deposition (ALD) was described in which $HGeCl_3$, $[(CH_3)_3Si]_2Se$ were used as Ge-, Se-precursor, respectively. The precursors formed the films through a ligand exchange reaction at a low substrate temperature of 70-150 °C . However, the pseudo-saturation behavior of the ALD, which takes a long time to achieve the saturation growth rate, was observed due to the physisorbed precursor and byproduct molecules on the reaction sites. To overcome slow saturation and excessive use of the Ge-precursor, we applied Discrete Feeding Method (DFM) where $HGeCl_3$ was supplied multiple times consecutively with subdivided pulse times. The ALD without DFM refers to a conventional ALD process where Ge and Se pulse and purge were injected alternatively. The ALD with DFM, by comparison, divides the total Ge pulse and purge times into several shorter times. DFM led to saturation of GeSe growth rate at a much shorter total injection time of Ge precursor and improved the morphological/chemical qualities and electrical performance of the film. Also, these GeSe films exhibit short switching time of ~40 ns, ON/OFF ratio of ~10^7, the selectivity of ~10^4, and the OTS behavior consistent with the modified Poole-Frenkel (PF) mechanism in the OFF state. The ALD method of GeSe films will contribute to the fabrication of 3D integration memory as selector device for preventing sneak current.

AA-MoP-18 Low-temperature Atomic Layer Deposition of Hafnium Oxides using NH_3 as the Catalyst., ***Nak-Kwan Chung***, *Y Kang, S Kim, J Yun, J Kim,* Korea Research Institute of Standard and Science (KRISS), Republic of Korea

We have presented low-temperature preparation of hafnium oxides (HfO_2) by atomic layer deposition (ALD). The hafnium oxide thin films were deposited from tetrakis ethylmethylamino hafnium (TEMAHf) as the Hf precursor, ozone (O_3) as the reactant, and NH_3 as the catalyst on 200 mm silicon wafers at substrate temperatures from 50 to 300°C. The properties of HfO_2 films were investigated by scanning electrom microscopy, X-ray photoelectron spectroscopy, and X-ray deflection. The quality of the films formed at low temperature of 50°C using the combination of O_3 and NH_3 compares well with deposition at higher temperatures (350°C) using O_3 only.

AA-MoP-19 Electrical Properties of Al-doped $SrTiO_3$ Films Grown by Atomic Layer Deposition on Ru Electrodes, ***Sang Hyeon Kim***, *C An, D Kwon, S Cho, S Cha, C Hwang,* Seoul National University, Republic of Korea

Atomic layer deposition (ALD) of Al-doped $SrTiO_3$ (STO) dielectric thin films were investigated in metal-insulator-metal capacitors for the dynamic random access memory application. STO thin films exhibit much higher dielectric constant compared with currently used ZrO_2-based films, but the leakage current density is higher due to their low band-gap energy. To decrease the leakage current density, several cycles of ALD-Al_2O_3 were inserted at the bottom portion of the STO film. Leakage current was increased with increasing insertion amount of Al_2O_3 for 2 ~ 5 cycles, and STO (110) peak on XRD was broadened as the Al_2O_3 layer was inserted. This is due to the deteriorated crystallization of the STO film during the ALD, which required higher post-deposition annealing (PDA) temperature. The higher PDA temperature induced nano-cracking of the STO film, which caused the leakage current increase. Therefore, only one cycle of the Al_2O_3 layer was adopted. The STO ALD was performed using $Sr(^iPr_3Cp)_2$ and $Cp^*Ti(OMe)_3$ [$Cp^* = C_5(CH_3)_5$] as the Sr- and Ti-precursors, using H_2O and O_3 as the oxygen source of the SrO and TiO_2 sub-layer growth, respectively, at a substrate temperature of 370°C, according to the previous report. [1] $Al(CH_3)_3$ and O_3 were used for the Al_2O_3 ALD.

The investigation of the Al_2O_3 cycle insertion position from the bottom of the film to the top of the film showed that top insertion exhibited the leakage current reduction effect while maintaining the crystallinity of the entire STO thin film. As a result, the leakage current of the STO thin film with a thickness of 9nm decreased from 10^{-6} A/cm^2 to 10^{-8} A/cm^2 at 0.8V. The achieved minimum attainable equivalent oxide thickness (EOT) of the (top) RuO_2/STO/Ru (bottom) capacitor was ~0.7 - 0.8nm, with an acceptable leakage current density (~2.7 X 10^{-8}A/cm^2), which was possible in the films with thicknesses > ~12nm without the Al-doping. Compared with the Al-doping effect in TiO_2 [2], the same process induced a much more obvious degradation in the crystallinity of the STO, when the Al_2O_3 layer was inserted within the bulk STO layer. Further examination results of the physical and chemical properties of the Al-doped STO film will be presented.

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AA-MoP-20 Temperature Effect on Thermally Grown AlN Films by Atomic Layer Deposition, ***Yong Kim***, *M Kim, H Yun, W Jeong, B Choi,* Seoul National University of Science and Technology, Republic of Korea

Studies of resistive random access memory (RRAM) have been vigorously conducted due to advantages, such as low operating voltage, high reliability, and simple structure. Until now, most of the switching materials used in RRAM are oxide materials owing to its stability and abundance in nature. However, nitride materials, such as AlN, GaN, TaN_x as well as Si_3N_4 have been also confirmed to show resistive switching characteristics. Among them, AlN-based switching materials showed resistive switching phenomena with low energy and high speed by formation of Al-rich conducting channel owing to the generation of nitrogen vacancies. Moreover, AlN has a large band gap (~6.2eV), high thermal conductivity and dielectric constant. Therefore, AlN can be applied for high-k gate dielectric material, various functional layer and resistive switching layer for RRAM applications.

In this study, AlN thin film is deposited by thermal atomic layer deposition (ALD) that is self-limiting deposition technique through the ligand exchange of the precursor molecules and surface functional groups. This process uses the Trimethylaluminum (TMA) and NH_3 as a metal precursor and reaction gas, respectively. The growth rates according to growth temperatures are shown in Fig. 1(a), at the wafer temperature of 265, 274, 287, 307, and 335°C. The inset of Fig. 1(a) shows Arrhenius plot (1000/T) of the growth rate. Through the slope of this fitting line, the reaction activation energy of AlN (~55 kJ/mol) can be obtained. Physical and chemical properties of AlN films grown at the different temperatures are investigated by X-ray diffraction (XRD), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). Fig. 1(b) shows the average concentration of each element in the AlN thin film. Decrease of oxygen and increase of nitrogen concentration can be observed as the deposition temperature increases. Also, the electrical properties of AlN films having the Al/AlN/Pt structure are studied. The DC I-V and J-E curve of the device are measured at room temperature. As a result, the conduction mechanism for the device is well fit into the Poole-Frenkel emission, where trap site can be attributed to the point defect, such as O_N and V_{Al} according to the trap depth energy.

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AA-MoP-21 Ultrathin ALD Ru Film Deposition using Discrete Feeding Method (DFM) and Electric Field Assisted ALD (EA-ALD)

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Ruthenium (Ru) has been considered as a promising electrode material for next generation semiconductor devices due to its low resistivity (~ 7 μΩ · cm), high oxidation resistance, and existence of conductive oxide phase, RuO_2 (~ 30 μΩ·cm). **[1]** As a complicated 3-dimensional integration scheme has been developed recently for improving the degree of device integration, ultrathin (< 5 nm) and uniform Ru metal electrode is required. Even though atomic layer deposition (ALD) of Ru film was employed, it is difficult to achieve ultrathin and continuous thin film due to its island growth nature at the initial stage of growth. **[2]**

In this work, we demonstrate efficient Ru film growth using discrete feeding method (DFM) and electric field-assisted ALD (EA-ALD) technique, which enabled to reduce the critical thickness of continuous metal thin film by improving chemical adsorption efficiency and surface coverage at the initial stage of thin film growth. DFM eliminates the physisorbed precursor molecules on the chemisorbed screening the active sites for the following precursor molecules by using cut-in purging during a metal precursor pulse, which increased the density of Ru nuclei at the initial growth stage resulting in a lower resistivity. **(Fig.1)** EA-ALD enhances the nucleation of Ru by attracting the precursor molecules onto a substrate with the help of electric field applied to the substrate during precursor pulse. As a result, layer density of the Ru film increased, and thus the resistivity significantly decreased. **(Fig.2)**

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AA-MoP-22 Formation of Antireflection Structures on Silicon Substrates in Near-infrared Region using AlO_x/TiO_x Bilayer Grown by Atomic Layer Deposition

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Antireflection (AR) layers on Si were investigated for potential application in optical communication in the wavelength range of 1270–1330 nm. Essential Macleod program was used to find the optimal thickness of the AR structures using AlO_x/TiO_x bilayer schemes. Achievement of the reflectance less than 0.5% was simulated using AlO_x/TiO_x AR structures. For experimental demonstration, atomic layer deposition (ALD) was used for the growth of AlO_x and TiO_x. Average reflectance of 0.2% was achieved in the wavelength ranging from 1270–1330 nm using ALD-AlO_x/TiO_x on Si. Despite the low reflectance of 0.2%, transmittance of ~88%, which is slightly lower than expected, was obtained. Additional air annealing at 300 ^{o}C for 2 hr enabled the crystallization of amorphous TiO_x into anatase phase and it led to the improvement in transmittance up to ~99%. X-ray photoelectron spectroscopy analysis revealed that the oxidation state of Ti in TiO_x influences the absorption in the near-IR region.

AA-MoP-23 Optimization of RuO_2 Thin Films on NiO Nanostructures by Atomic Layer Deposition for Hybrid Capacitor

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Developments of high-performance electrochemical energy storage device is a vital issue in world wide. Electrochemical supercapacitors are one of the most promising energy storage devices in comparison to lithium-ion batteries because it can provide a higher power density, faster charge/discharge rate, and longer working lifetime. In this regard, intense effort has been focused on the fabrication of electrical double layer supercapacitors (EDLC) based on porous carbonaceous materials for commercialization, but this storage system limits the specific capacitance relative to their theoretical value. However, faradic pseudocapacitors based transition metal oxides or mixed oxides provide much higher specific capacitance than EDLC due to superior redox process for charge storage at the surface as well as near the surface of the active electrode. However, nanostructured NiO on Ni foam has been considered as a one of the promising pseudocapacitor materials. Unfortunately, it suffers from stability of the nanostructures during charge and discharge resulting the lower cycle life. Anyhow, ability to control the issue atomic scale thin layer coating of other metal oxides or nobel metal oxides on the surface of NiO is an efficient approach. In this respect, one of the most powerful technique for atomic scale coating is atomic layer deposition (ALD). Herein, we demonstrate the use of ALD for ultrathin RuO_2 coating on surface of three dimensional NiO nanostructure for supercapacitor application . The optimum coating thickness (~ 20 nm) of RuO_2 provide improved electrochemical performance with enhanced cycling stability. We demonstrate that RuO_2 not only prevents the nanostructures of NiO during charge and discharge process but also facilates charge transport and electrolyte diffusion. The sample shows an ultrahigh specific capacitance 1060F/g.

AA-MoP-24 Screening of ALD Barrier Materials Towards use in LED Lightning

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Atomic layer deposition (ALD) technique has traditionally been used for controlled deposition of high quality thin films for the semiconductor industry. One of the fields benefiting from ALD technology that has been growing very rapidly recently is optoelectronics, including LEDs. Yole development has forecasted that the market of packaged LEDs will exceed 20 B$ by year 2020 [1].

Fabrication of high performance LEDs requires the use of sensitive materials that can limit the operating lifetime of the device due to insufficient passivation from the environment. Before the materials can be implemented to commercial products, these materials need to be protected from damage caused by environment or next process steps. Conformal, uniform and pin-hole free ALD thin film can give a perfect solution for achieving this when properly designed.

SiO_2 and SiNx by PECVD and Al_2O_3 by ALD are the most common inorganic barrier materials used in microelectronics and in LED-technology. SiO_2 is a rather poor barrier against moisture and can only be used for insensitive devices or in combination with other layers. SiNx is absorbing in the blue / UV wavelength regime and therefore limited in its use for optical devices. Al_2O_3 is a good barrier, but because of its refractive index right between silicon and GaN, it is not optimal for this purpose. In addition its chemical instability limits its use within the process flow of LED manufacturing. Currently there is no barrier film or stack available that fulfills all requirements for LED manufacturing in an ideal way. In the literature different kinds of thin film materials are described that have promising properties, but there is no systematic study that covers all relevant materials and all important properties.

In our work we have made material screening and process development in order to choose the best solutions for LED applications. The PICOSUN™ R-200 Advanced ALD system was used for the depositions. The selected materials included Al_2O_3, Ta_2O_5, SiO_2, Nb_2O_5, TiO_2, HfO_2, ZrO_2, and Y_2O_3. Deposition temperature varied from 100°C to 250°C. The film properties such as morphology, crystallinity, porosity, refractive index, absorption, transmittance, WVTR, composition, breakdown field strength, leakage current and WER were studied to evaluate material compatibility for LED lighting.

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AA-MoP-25 Investigation of Band Structure on Amorphous Zinc Tin Oxide Thin Films Grown by Atomic Layer Deposition for Cd-free $CuGaSe_2$ Solar Cells

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Thin film photovoltaic cells require a buffer layer in a window layer stack to prevent unfavourable conduction band line-up which causes interface recombination. Zinc tin oxide (ZTO) has recently attracted great attention as an alternative buffer layer, since this material exhibits some advantages over the existing CdS. However, their work function which is an essential parameter for band alignment at equilibrium has not been characterized in detail. Here, we investigated compositional, structural and optical characteristics of ZTO thin films to construct the band diagram for films with different Sn contents.^{1} The relationship between the different Sn contents of ZTO films and the performance of $CuGaSe_2$ (CGS) solar cells are also examined. ZTO films were grown at 150 °C by atomic layer deposition (ALD) using tetrakis(dimethylamido)tin(IV), diethylzinc, and water. The ZTO films were amorphous and exhibited wider optical bandgaps of 2.95–3.07

eV than that (2.45 eV) of CdS. Chemical structure and work function analysis were performed by X-ray photoelectron spectroscopy and Kelvin probe force microscopy, respectively. It indicated that the incorporation of Sn into ZnO strongly influenced the content of oxygen vacancies and work function which is related to carrier concentration. In addition, we found an optimal composition for high solar cell conversion efficiency. The band diagram of the ALD-ZTO films will be useful to understand the band alignment of a photovoltaic cell with a buffer layer of ZTO film.

AA-MoP-26 Optical and Electronic Properties of ALD-grown TiO_2 Films on a Thin Glass Substrate for Applications in Photocatalysis*, Yoon Sang Lee, O Kwon, Y Kim,* Ajou University, Republic of Korea

Anatase TiO_2 films were grown on thin glass substrates using titanium tetraisopropoxide (TTIP) and H_2O as precursors. The as-grown TiO_2 films on the glass substrates were transparent up to the thickness of about 100 nm and found to exhibit anatase phase with a good crystallinity. For a potential application in photocatalysis with a maximum use of visible light, the films were subject to post-nitridation processes under the flow of ammonia at elevated temperatures up to about 600°C. Under the process condition, the films were found to undergo nitridation toward titanium oxynitrides with a varying degree of N content and the enhanced visible absorption. The optical abaorption properties were systematically measured to exhibit enhanced aborption in the visible region depending on the degree of nitridation. The bonding structure and and detailed distribution of nitrogen in the films were further evaluated by x-ray photoelectron spectroscopy. The results confirmed the existence of substitutional and interstitial nitrogen species in the film and their relative concentrations were found to be strongly dependent on the process condition. Depth distribution of these N species was further analyzed and used to explain the changes in the optical properties of the films. Finally, photodegradation efficiency of the films under the visible light was also evaluated.

AA-MoP-27 Atomic Layer Deposition as a Tool to Influence the Sintering of Ni Nanoparticles Supported in the Mesopores of SBA-15*, Piyush Ingale, C Guan, R Naumann d'Alnoncourt, A Thomas,* Technische Universität Berlin, Germany*; F Rosowski,* BASF SE, Germany

Nickel-based catalysts are typically used for the production of synthesis gas by reforming reaction[1]. Dry reforming of methane is an attractive reaction for production of synthesis gas by reduction of carbon dioxide. However, Ni nanoparticles (NPs) used in DRM reaction suffer from severe coking and sintering at high temperature which leads to decreased activity of the catalyst[2,3]. The challenge is to synthesize a catalyst with a high Ni loading and dispersion that is stable under reaction conditions. A high internal surface area makes SBA-15, a material based on uniform hexagonal pores with narrow pore size distribution, a well-suited support material for highly dispersed metal catalysts. By the addition of fluoride ions and variation of ageing time during synthesis, SBA-15 with large mesopores and a reduced fraction of micropores is accessible[4]. Large mesopores allow modification of the catalyst via ALD. Our goal is to investigate the influence of thin alumina layers deposited via ALD of TMA/H_2O on the sintering behaviour of Ni NPs supported in the mesopores of SBA-15.

ALD was carried out in a thermal magnetic suspension balance and a fixed bed reactor[5]. Different catalysts were prepared via ALD of TMA/H_2O on Ni/SBA-15 catalysts as shown in figure 1. The thin alumina layers were deposited either before impregnation of the support with NiO NPs or after impregnation of SBA-15 with NiO NPs. The high temperature applied for NiO reduction and during catalytic testing introduces porosity into the deposited alumina layer, due to shrinking and cracking, making Ni accessible for the gas phase. Strategy C (see Fig.1) aims at producing Ni NPs inside of porous alumina cavities.

The catalysts were tested for activity and stability during dry reforming of methane at different temperatures (500°C-800°C). Sintering of Ni NPs was investigated using XRD and TEM before and after catalysis, and after thermal treatment in different gas atmospheres.

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AA-MoP-28 Metal-doped HfO_2 for Ferroelectric Tunneling Junction Applications using Atomic Layer Deposition*, Chi Thang Nguyen,* Incheon National University, Korea

Conventional non-volatile memories have separate storage of information and transmission of signals. Therefore, there are many difficulties in improving the fabrication steps and operation speed of the devices. In order to overcome these technical limitations, recently, studies on ferroelectric memory devices have been actively conducted. Typically, a metal/ferroelectric layer/metal (MFM) structure has been used for ferroelectric tunnel junction (FTJ) and in addition, a semiconductor bottom layer is used to improve on/off ratio by formation of a Schottky barrier across the ferroelectric-semiconductor junction. However, the on/off ratio of the metal/ferroelectric/semiconductor (MFS) structure is still insufficient to be used for a non-volatile memory device. Recently, in a report, ferroelectric-antiferroelectric properties were switched by controlling doping ratio in a thin HfO_2 layer with specific elements. In this work, atomic layer deposition (ALD) method is used to precisely control specific metal dopants during the HfO_2 deposition cycles, and the electric properties of the metal-doped HfO_2 are investigated in different doping conditions. To understand the results, microstructure and chemical composition of the metal-doped HfO_2 are correlated with theoretical calculation results by density functional theory (DFT).

AA-MoP-29 Atomic Layer Deposition of Al- and Ga-doped HfO_x Films for Resistive Switching Layer*, Sungyeon Ryu, S Oh,* Seoul National University of Science and Technology, Republic of Korea*; W Park, S Kim,* SK Hynix, Republic of Korea*; B Choi,* Seoul National University of Science and Technology, Republic of Korea

Bipolar type resistive switching random access memories (RRAMs) utilized by TaO_x and HfO_x as switching materials, have been demonstrated superior to unipolar type RRAMs owing to the low switching current and better reliability. Likewise TaO_x switching layer, bias-polarity-dependent valence change mechanism in HfO_x is attributed to the repeated generation and rupture of conducting filaments (CF), which could be the clusters of oxygen vacancies (V_o). It has been reported that crystalline HfO_2 film could not create enough oxygen vacancies for resistive switching.1) Crystalline HfO_2 RRAM may cause higher forming voltage, which in turn, device variability could be worse or even catastrophic breakdown could be happen. To change the structure of the film, defect engineering by doping has been deliberately investigated by using various methods, such as, co-sputtering, implantation, thermal and photo-assisted diffusion, etc.

In this study, Al- and Ga-doped HfO_x films are grown by using atomic layer deposition (ALD) to change the structural and chemical properties of HfO_2 film. Tetrakis(ethylmethylamino) hafnium (TEMAH), trimethyl aluminum (TMA), and cyclic dimethylamide gallium ($Ga(NMe_2)_3$) are used as Hf, Al, and Ga precursors, respectively, and H_2O as oxidant gas. Al-doped HfO_2 film was deposited at 250℃, while Ga-doped HfO_2 film was deposited at 200℃ to protect thermal decomposition of Ga source. XRD, SEM, EDS, AES, and XPS are used to examine the structural and chemical properties of the film. The device having TiN contact-plug with 50 to 2000-nm-diamenter formed in SiO_2 inter-layer is fabricated. Electrical property is measured by semiconductor parameter analyzer (HP-4155) and function generator (AFG-3102) for DC and AC measurements. Dopant concentration and location are controlled by the ALD cycle ratio and sequence. Through Al doping, pristine resistance and forming voltage of the device are increased with increasing Al cycle ratio as shown in Fig 1(a) and (b). On the other hand, Ga-doped HfO_2 device shows forming-free and reverse switching polarity as shown in Fig. 1(c). The resistive switching characteristics caused by internal structure of Al- and Ga-doped-HfO_2 films will be presented in detail.

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AA-MoP-30 Synthesis of Well-Defined PO_x/V_2O_5 Powder Catalysts *via* Atomic Layer Deposition*, Kristian Knemeyer,* Technische Universität Berlin, Germany*; V Strempel,* BASF SE, Process Research and Chemical Engineering*; C Schulz, J Xie, R Naumann d'Alnoncourt,* Technische Universität Berlin, Germany*; M Driess,* Institut für Chemie, Germany*; F Rosowski,* BASF SE, Germany

The selective oxidation of n-butane to maleic anhydride (MAN) is an industrial process with a world capacity of over 1 Mt/year. In this highly complex reaction the catalyst plays an essential role for the conversion of butane and selectivity towards MAN. Suitable catalysts for this reaction consist of vanadium, oxygen, and phosphorous, such as vanadyl pyrophosphate $(VO)_2P_2O_7$. Vanadium oxides without phosphorous are total oxidation catalysts with minor selectivity towards MAN.

This paper focusses on the modification of V_2O_5 by depositing various amounts of PO_x via ALD. Subsequent catalytic testing in selective oxidation of n-butane was applied to investigate the influence of P on catalytic performance. The ALD process was carried out in a magnetic suspension balance (MSB)[1][2] to determine ideal ALD conditions and to prove self-limiting growth. Samples with varying amounts of PO_x on V_2O_5 were prepared by performing different ALD cycle numbers with subsequent calcination at 450°C in synthetic air. The as prepared samples were characterized and tested in an automated parallel reactor set-up. ICP-OES analysis show a steady increase of P amount with ALD cycle number but the growth per cycle decreases. No significant loss of P was obtained during calcination or during the reaction, which is in contrast to wet impregnated and subsequent calcined PO_x/V_2O_5 catalysts.[3] Catalytic testing shows a huge influence of P on the selectivity towards MAN. Pure V_2O_5 is a total oxidation catalysts with a selectivity <5 % to MAN at low conversion and temperatures, whereas adding P leads to a high increase of selectivity. Conversion is barely influenced by adding phosphorous.

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AA-MoP-31 Use of New Cyclopentadienyl Tris(dimethylamino) Based Zirconium Precursors for the Leakage Current Reduction of Atomic Layer Deposited ZrO_2- Thin Films

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ZrO_2 materials have attracted a great deal of attention as they are widely used in the $ZrO_2/Al_2O_3/ZrO_2$ (ZAZ) structure of DRAM capacitors and their mixture with HfO_2 exhibit promising ferroelectric properties. Decreasing the off-state leakage characteristics of DRAM capacitors with ZrO_2 materials is critically important for further scaling, which can be aggravated by subsequent high-temperature annealing for crystallization. Hence, reduction of the leakage current can be expected if the thermal budget is lowered by inducing in-situ crystallization during a high-temperature atomic layer deposition (ALD) process followed by low-temperature post-deposition annealing (PDA). Recently developed New Cyclopentadienyl Tris(dimethylamino) based Zirconium (PCp -Zr) is used as a Zr precursor since it has higher thermal stability compared with the conventional Cp-Zr or amide-based precursors. O_3 was used as an oxygen source and, ALD was performed at 300°C and 350°C on the sputtered TiN substrates, which were relatively higher than the conventional ALD temperatures between 250°C and 280°C. Capacitance-voltage (C-V) characteristics were measured at the as-deposited state and after the PDA at different temperatures of 450°C, 500°C, and the dielectric constant was obtained from the slopes of the equivalent oxide thickness vs. physical oxide thickness plots. For the ALD temperature of 300°C, the achieved dielectric constant for the as-deposited film, and after the PDA at 450°C, 500°C was 27.3, 28.9, and 29.1, respectively. The corresponding values of the film grown at 350 ^{o}C were 41.3, 22.9, and 29.1, respectively, suggesting that the increasing ALD temperature was not as efficient as expected initially. The leakage characteristics were confirmed by current-voltage measurements at thicknesses between 5.7 nm and 9.8 nm under the specified annealing conditions. As a result, the leakage current density of 10^{-7} A/cm^2, which is a necessary condition of DRAM capacitors, was obtained for all of the conditions at 0.8 V. Further research will be necessary to fully explore the potential of this newly developed precursor.

AA-MoP-32 Control of Refractive Index by Atomic Layer Deposition on Various Textile Surfaces

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Attempts to integrate various electronic systems and sensors into textiles have been made for future wearable electronics. Conducting textile which is a key component for these wearable electronics is usually called electronic textiles (e-textiles). Since most of conventional textiles are electrically insulator, conducting materials, such as metals, should be added to textiles during or after synthesis processes of textile. In the aesthetic point of view, however, the addition of metal for fabrication of e-textiles has a big disadvantage that is grey and black color of textile from the reflection and scattering of metal components. In addition, the conventional dying technology could not be applied to the e-textile systems after addition of metals due to lack of surface chemical species which are bonded to dye molecules. In our recent paper, we reported that conventional cotton textiles were successfully changed to e-textiles by Pt coating by atomic layer deposition (ALD), and we have produced color coated e-textiles by depositing oxide multilayer thin films. In order for color coated electronic fibers to be used in real life, however, they must have physical and chemical stabilities, in addition, wide compatibility on various textiles. In this work, we fabricated color coated electronic fiber by depositing Al_2O_3/TiO_2 on various electronic fibers to confirm not only the mechanical environment such as tensile, shrinkage and friction which can be exposed in daily life but also the chemical stability due to acid base exposure. By ensuring the mechanical and chemical stability of color coated electronic filaments, it is expected that electronic filaments can be applied to a wider range of applications in the near future.

AA-MoP-33 Zinc Tin Oxide Thin Films Grown by Atomic Layer Deposition for Charge-Trap Flash Memory

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As the further scale down of the 2-D planar memory device is challenged by various technical limits including cell-to-cell interference, 3-D memory devices such as vertical-NAND (V-NAND) flash [1, 2, 3] have been proposed as the new effective way of memory density increase. Concerning the transistors in these V-NAND devices, however, the single crystal Si transistors in 2D planar devices was replaced with poorly crystallized poly-Si. However, the low carrier mobility of this poly-Si channel imposes a fundamental limitation to further increase in the integration density. In this regard, the amorphous oxide semiconductor (AOS) grown by atomic layer deposition (ALD) has been proposed as one of the most promising alternative techniques owing to its high mobility, excellent step coverage and low-temperature growth characteristics. [4, 5]

In this work, therefore, n-type zinc tin oxide (ZnSnO) thin films were prepared via ALD with the various film thickness and the atomic ratio of zinc to tin to achieve higher carrier mobility and stable transistor operation. ZnSnO ALD was performed by the alternation of ZnO (with DEZn) and SnO_2 (with TDMASn) ALD cycles in proper ratio utilizing O_3 as the oxygen source. The electrical performance of ZnSnO films was estimated by fabricating bottom-gated thin film transistors where the heavily-doped p-Si was the gate, and thermally growth 100nm-thick SiO_2 was the gate oxide, as shown below. Finally, the charge-trap memory devices were fabricated using ALD ZnSnO film as the channel layer, and low-pressure chemical vapor deposited Si_3N_4 as the charge trap layer. The program/erase characteristics of the fabricated devices were analyzed.

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AA-MoP-34 Protective Layer TiO_2/Pt/C Catalyst for Excellent Durability deposited by Fluidizing Bed Reactor Atomic Layer Deposition

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Proton Exchange Membrane Fuel Cell (PEMFC) is one of the most promising power sources ranging from portable electronic devices to automobile industry because of its advantages such as low operating temperature, fast start-up and sustained operation at high current density. In PEMFC, the challenges for the commercialization are to resolve the high cost and low durability of Pt catalyst which currently is used. As common synthesis for Pt catalyst, Wet process such as electrodeposition, Electroless can make thresholds due to the long process term, pre-treatment and, un-uniform Pt size and distribution leading to decrease of Pt/C utilization. To resolve these problems, dry based-technique for Pt catalyst must be developed. Among dry based-methods, ALD (Atomic Layer Deposition) is the prominent method due to the excellent uniformity, accurate thickness control and island -shaped growth of noble metal at the initial stage. In addition, fluidizing bed reactor can be introduced to the atomic layer deposition for more excellent uniform Pt/C and mass production.

In this work, to improve the cost and durability, protective layer/Pt/C structure was deposited and optimized in situ process by using fluidizing bed reactor ALD. TiO_2/Pt (30wt%) on carbon black powder was successfully deposited using TTIP, H_2O for $TiO-_2$ and $MeCpPtMe_3$ precursor and O_2 reactant for Pt by using the fluidizing bed reactor ALD. ALD cycle is changed from 0 cycle to 10cycle to optimize the thickness. Loading, particle size and distribution were investigated by TGA, STEM measurement. With increasing the $TiO-_2$ ALD cycle on Pt/C, overall TiO_2/Pt loading increased regularly and particle size have no big change due to the ultra $TiO--_2$ thin film. From TEM-EDS, TiO_2 was selectively positioned around Pt, making the TiO_2 shell/Pt core. After 1000 Cycle ADT(Accelerated degradation test), TiO_2(10cycle)/Pt/C prepared by ALD shows good and stable durability.

AA-MoP-35 Atomic Layer Deposition of Si-doped HfO_2 Thin Film by using $HfCl_4$, $SiCl_4$ and H_2O for FeRAM Device Application*, Se-Won Lee, M Kim,* Versum Materials Korea, Republic of Korea*; M MacDonald, X Lei,* Versum Materials, Inc.*; Z Zhu, A Yoon,* Lam Research Corp*; H Yoo, D Suh, Y Choi,* SK Hynix Inc

Recently, next-generation memory devices such as PRAM, ReRAM and FeRAM have been widely studied to replace conventional DRAM and NAND flash devices. Especially, FeRAM has high potential that it can achieve fast write/erase speed, compatible integration (3-D stack architecture) and low power consumption. There are a number of materials that demonstrate ferroelectric properties, among which silicon doped hafnium oxide (Si:HfO_2) is one of promising ferroelectric materials because it operates at very thin thickness (about 5~10 nm) without losing its functional properties and has excellent compatibility [1].

In this study, we have investigated thermal ALD of Si:HfO_2 using $HfCl_4$ and $SiCl_4$ precursors with H_2O as an oxygen source at deposition temperatures 250°C and 300°C, and also studied ferroelectric characteristics of MFM FeRAM device structure with various Si doping concentrations (about 2, 4 and 6 mol % Si). To control mol % Si in the HfO_2 films, we used a 3-step Si precursor pulsing method including sub-cycle and main-cycle such as [(HfO_2 x m sub-cycle/ SiO_2 x 1 sub-cycle /HfO_2 x m sub-cycle) x n main(super)-cycle] (see the Fig.1 below). For example, (HfO_2 x 9 cy /SiO_2 x 1 cy /HfO_2 x 9 cy) x 5 cy at 250°C resulted in ~4 mol% Si. SiO_2 sub-cycle number was fixed at 1 cycle for all films. XPS was used to measure contents of Si, Hf and impurities of resulting Si:HfO_2 films. No Cl and C impurities were found in the film, and O content was ~65 at%. FE properties were measured after rapid thermal process (RTP) at 600°C for 20 sec or 800°C for 1 sec.

With samples deposited at 300°C, good FE characteristics were achieved. Wake-up property remained after RTP at 600°C for 20 sec and it disappeared after RTP of 800°C for 1 sec conditions. Remnant polarization (P_r) value of 16 $\mu C/cm^2$ and coercive electric field (E_c) of 1.1 MV/cm was achieved with the 2.5 mol % Si sample after 800°C annealing process. 600°C annealing temperature is not enough to activate 5.6 mol% Si sample and it showed anti-FE characteristics at 800°C annealing temperature. However, in the 250°C deposited samples, poor FE characteristics were obtained. With RTP condition of 600°C for 20 sec, all samples were not activated enough to show FE characteristics. Over annealing temperature of 800°C, 4.0 mol% Si samples showed FE properties, but also showed high leakage current (see Fig.2 below).

In summary, we have demonstrated that the 2.5 mol % Si in Si:HfO_2 samples deposited using $HfCl_4$, $SiCl_4$, and H_2O are the most effectual FE material, because the FE characteristics is superior to those of other samples.

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AA-MoP-36 Combining ALD with Pulse Current Electroplating of Gold to Deposit on the Wall of High Aspect Ratio Silicon Grating*, Tae Eun Song, H Han,* National NanoFab Center (NNFC), Republic of Korea*; S Jung, S Kim,* Yeungnam University, Republic of Korea*; C Ahn,* National NanoFab Center (NNFC), Republic of Korea

Deposition on the wall of high aspect ratio silicon grating with gold is a frequent requirement in the fabrication of X-ray phase contrast imaging technique as well as micro-electronic components and other fabrication processes[12]. Utilizing Silicon grating etched by deep reactive ion etching have been fabricated in silicon wafers. Electroplating of gold in silicon grating with a high aspect ratio greater than 40 over a grating area of 10 cm * 10 cm require conductive supports which were created by uniformly depositing Ru on the silicon by Atomic Layer Deposition (ALD). Moreover pulse current electroplating led to uniformly deposit gold on the wall of silicon grating for such structures[345].

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AA-MoP-37 Atomic Layer Deposition of Ru Metal Thin Film with Substrate-Dependent Growth Behavior on Ta_2O_5 Substrate*, Cheol Hyun An,* Seoul National University, Republic of Korea*; W Lee,* Northwestern University*; S Kim, D Kwon, S Cha, S Cho, C Hwang,* Seoul National University, Republic of Korea

The growth of Ru noble metal has been studied for several purposes such as catalyst, an oxygen diffusion barrier layer or electrode materials due to its electrical properties and chemical stability. Especially, Ru metal is also nominated for an electrode of the capacitor in DRAM due to its high work function which could reduce the leakage current of the capacitor. For applying Ru electrode on capacitor under 20nm, atomic layer deposition (ALD) of Ru film is inevitable since its precise thickness controllability and high conformality. The ALD growth of Ru metal has been progressed using various Ru precursors, most of those are metal-organic (MO) precursor which have carbon containing ligands. Also, the ALD methods with MO precursors have difficulties on the nucleation of Ru metal on a substrate and show long incubation time which induces less conformal film surface.

In this study, the RuO_4 and N_2/H_2 gas were used in ALD process of Ru metal thin film as a precursor and reactant gas, respectively. The RuO_4 precursor, which has small molecular size and high volatility, is adaptable for depositing Ru metal on the narrow and complex structure. Moreover, the Ru film deposited by RuO_4 precursor could have low carbon impurity since any carbon atom is contained in the precursor and oxygen atoms are only ligand atoms. The ALD growth of Ru film with RuO_4 has been reported before, but it was examined mainly on Si substrate. However, the growth behavior of the Ru film on transition metal oxides needs to be examined for the DRAM capacitor application. Therefore, growth behavior of Ru film on the Ta_2O_5 substrate was confirmed in this study. The self-limited growth was observed with RuO_4 precursor feeding time as conventional ALD method, while 2-step saturation behavior was observed versus N_2/H_2 reactant gas feeding time. Moreover, the growth per cycle of Ru films were higher than conventional ALD studies. Since this unideal growth behavior was not observed on inert Au substrate under the same deposition conditions, the growth mechanism was further examined by X-ray analysis and secondary ion mass spectroscopy. Apart from the general assumption of the inactive role of stable bottom Ta_2O_5 layer, it showed catalytic properties for precursor absorption and film formation. During N_2/H_2 reactant gas exposure, the Ta_2O_5 film was reduced to Ta metal phase which migrated towards the growing Ru surface. The catalytic activity of Ta atoms on the chemical adsorption of multiple layer of RuO_4 molecules was considered to be the plausible mechanism of the unideal growth behavior. Nonetheless, the abnormal growth did not influence the electrical properties and physical properties.

AA-MoP-38 Forming of Conformal Multilayer on Periodic Microstructures for Solar Selective Absorption*, Makoto Shimizu, H Akutsu, S Tsuda, M Kumano, H Yugami,* Tohoku University, Japan

Solar absorbers are a key component in solar thermal utilization systems such as concentrated solar power generation (CSP) and solar thermal chemical conversion systems. For using solar energy effectively, the enthalpy of sunlight should be utilized up to the maximum extent possible. The operating temperature of solar thermal systems such as CSP systems is increasing. Regarding high-temperature usage, to create microstructures on-top of metal surfaces is a promising technology.

Typically, these materials are able to possess spectrally selective absorption properties for high-temperature usage. However, this technique is typically not well-suited because deep microstructures should be required to attain high spectrally selective absorption properties. In this study, we investigated high spectrally selective absorption properties; i.e., broad and high-absorptance in a short wavelength range and low emittance in a long wavelength range, with shallow honeycomb array cylindrical-microcavities coated by metal-dielectric multi-layers.

Honeycomb array cylindrical microcavities were fabricated on tungsten substrate with interference lithography and multi-layers consisting of platinum nano-film sandwiched by Al_2O_3 layers were created for a uniform coating via atomic layer deposition. Due to high conformal multilayer on the cylindrical microcavity thanks to characteristics of ALD method, absorptance spectrum is well consistent with the simulated result. A solar absorptance value of 0.92 and a hemi-spherical total emittance value of 0.18 at 700^{o}C was determined from the fabricated solar selective absorber. Additionally, thermal stability of up to 700^{o}Cwas confirmed in vacuum a pressure range of 1 Pa.

AA-MoP-39 Ti-doped ZnO Films Grown by Atomic Layer Deposition for Solar Cell Applications*, **Ji Hye Kim**, C Kim, H Park, Z Urrehman,* ISAC Research Inc., Republic of Korea

Transparent conductive oxides(TCOs) are widely used in various industry such as displays, solar cells, thin-film-transistors. Zinc oxide(ZnO) based semiconductors has been extensively studied due to their high optical transmission and electrical conductivity and lower material cost. Furthermore, for flexible optoelectronics in future, it is desired to prepare TCOs as low temperature as possible. Among various deposition techniques, doped ZnO thin films were deposited by atomic layer deposition (ALD) due to low temperature growth, excellent step coverage, good conformality.

In this work, we investigated the electrical, structural and optical properties of Ti doped ZnO thin films prepared by thermal ALD and plasma enhanced ALD.

AA-MoP-40 Crystal Structure and Electrical Properties Modulation of Al-doped $HfZrO_2$ Thin Films by ALD*, **Seung-Won Lee**, J Ahn, J Choi, C Hyeon,* Korea Maritime and Ocean University, Republic of Korea*; M Ahn, S Jeon,* Korea University, Republic of Korea

As the size of semiconductor device is scaled down, electronic components such as gate oxide, DRAM capacitor are more important for high-k materials. Among the various high-k materials, the oxide thin films based on Zr and Hf can be realized by deposition conditions or by phase stabilizer doping such as monoclinic, tetragonal, cubic. Especially, when having tetragonal phase, it is known to have high dielectric constant about 40. In addition, it has relatively wide bandgap and it is highly compatible with Si integration technology. So, it is applied to high-k device. Recently, $HfZrO_2$ thin films have ferroelectric and anti-ferroelectric properties by Zr content. So, many studies are underway to utilize them for ferroelectric devices. On the other hand, the study on the electrical characteristics of phase transition through thin film doping based on ZrO_2 and HfO_2 has been done. However, the study on change of dielectric constant by doping binary oxide film based $HfZrO_2$ have been deficient compared to applicability.

Therefore, we investigated the sturcture and electric properties of $HfZrO_2$ thin films doped by controlling Al contents. In the process of depositing $HfZrO_2$ thin film using PEALD, the Al dopant was doped by two methods : supercycle and sequential cycle. Then, the characteristics of Al doped $HfZrO_2$ films were observed for ellipsometer, XRD, XPS and semiconductor parameter analyzer.

AA-MoP-41 In situ Capping of VO_x using PEALD of V_2O_5 and/or VN*, **Rémy Gassilloud**, M Fraccaroli, C Charpin,* CEA-Leti, France*; C Vallée,* CNRS-LTM, France

Resistive memories composed of Ta_2O_5/TaO_X dielectrics sandwiched between a TaN cathode and noble-based anode have good potential for use as nonvolatile switch in large-scale integrated circuits [1]. Another group 5 element that shows a pretty good compatibility with standard Si technology and more sustainable than Ta, is Vanadium. Thermal ALD deposition of VO_2 has already been achieved using Tetrakis(EthylMethyl)Amino Vanadium (Air Liquid TEMAV) [2][3]. Many reports discuss on the growth of this material and the required post deposition anneal under O_2 ambient to reach the well-known MIT VO_2(M) monoclinic phases. The required partial pressure of oxygen must be so precise that it restrains its integration in devices [4]. Another solution is to keep VO_2 in its as-deposited amorphous state and use it as oxygen reservoir in a ReRAM based configuration VO_2/V_2O_5, with V_2O_5 as switchable insulator, i.e. through filament vacancies formation. In the meantime, Vanadium nitride has also been developed using the same TEMAV molecule and NH_3 plasma. Resistivity as low as 200 µOhm.cm were obtained for as-deposited VN which is in the range of resistivity values obtained with TaN or even TiN. In this work, we will review and present our results on the ALD deposition of VO_2 amorphous and monoclinicphase using TEMAV and water on 300mm Si. We will extend the work on V_2O_5 deposition using O_2 plasma and show results on in-situ bilayer deposition. We will finally go further on the VN electrode deposition with VO_2/V_2O_5/VN tri-stack fully in-situ deposited.

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AA-MoP-42 PE-ALD for Deposition of TiN as a Refractory Plasmonic Material*, G Dogan, U Sanli,* Max Planck Institute for Intelligent Systems, Germany*; H Karl,* University of Augsburg, Germany*; G Schütz, **Kahraman Keskinbora**,* Max Planck Institute for Intelligent Systems, Germany

Titanium nitride (TiN) was recently proposed as an alternative to gold for high-temperature plasmonic applications such as concentrated solar thermal power generation. The refractory plasmonics material TiN was shown to be more stable than Au after intense laser irradiation.[1] Conformality aspect of atomic layer deposition (ALD) is recently being exploited for fabricating high-quality dielectric nanostructures for applications in optics.[2,3] Therefore, ALD processing of plasmonic materials with a low electrical resistivity and high crystalline quality is a very interesting prospect.

In this work, we have studied the influence of growth conditions on the physical properties of TiN films by analytical techniques including *in-situ* and *ex-situ* spectroscopic ellipsometry (SE), X-ray reflectivity (XRR) and diffraction (XRD), X-ray photoelectron emission spectroscopy (XPS), and four-point probe (FPP) measurements. The TiN thin films were deposited on single crystal silicon substrates at 350°C by plasma-enhanced atomic layer deposition (PE-ALD) using $TiCl_4$ and N_2-H_2 plasma as the precursor and the co-reactant, respectively. *In-situ* SE confirmed ALD type growth and the deposition rate was found to vary between 0.024 to 0.032 nm/cycle depending on the plasma ratio N_2-H_2 and plasma exposure time. The XRD results exhibit a strong (002) texture in the deposited films. The electrical resistivity of the films can be tuned between 1200 to 290 µohm.cm by varying the process parameters. Low resistivity correlates with low chlorine content and large TiN grain size, obtained for films deposited with a plasma-ratio of 7.5 and plasma exposure time of 4 s. We will further discuss how these results can be utilized as a precursor for integration of TiN into nanostructured materials for optical applications.

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AA-MoP-43 Physical Characaterization of Transition Metal Dichalcogenide MoS_2 Thin Films Synthesized by Atomic Layer Deposition*, **Hongguo Zhang**, M Zeng, C McCleese, C Kolodziej, P Lin, K Zhang, C Burda, Q Li, H Baumgart,* Old Dominion University

Transition metal dichalcogenides (TMDC s), such as MoS_2, WSe_2 and $MoSe_2$, exhibit layered structures in which are in-plane covalent bonds are strong and interplane van der Waals forces are relatively weak. This bond structure demonstrates extraordinary in plane thermal, mechanical, electrical, optical properties. The monolayers exfoliated from bulk counterparts, commonly called as two-dimensional (2D) materials, are paid significant attentions due to their unique and tunable material properties: (1) indirect to direct band gap transition when the bulk material is exfoliated to a single layer, making them become ideal quantum well. (2) higher carrier mobility with 100cm^2/Vs. (3) enhanced spin orbit coupling used in spin based electronic devices. These unique properties of 2D TMDCs are promising to be applied in sensors, filed effect transistors, photodetectors, piezoelectric devices and solar cells.

To date, many techniques have been developed for the synthesis of mono and few-layer TMDC films on different substrates, such as pulsed laser deposition (PLD), chemical vapor deposition (CVD). However, very little is known about atomic layer deposition (ALD) synthesis of MoS_2 films there are very only few references. ALD technique exhibits self-limiting atomic layer reactions in each introduced ALD cycle. It can accurately control film layer thickness stoichiometry, composition, uniformity, and sharp interface. Furthermore, ALD also can be used to deposit conformal film onto very complex structures.

Here we report on synthesis of MoS_2 films on Silicon substrates by ALD system. Molybdenum hexacarbonyl ($Mo(CO)_6$) and dimethyldisulfide (CH_3SSCH_3, DMDS) are employed as the chemical ALD precursors for Molybdenum and Sulfur, respectively. Generally, 20 sccm N_2 was used as a carrier gas for the precursors. The growth temperature was set at 200, 230 and 250^{o}C. The crystallinity of as-deposited MoS_2 thin film could be improved by post-annealing under saturated sulfur vapor. The Raman spectroscopy analysis show the MoS2 thin films demonstrate the characteristic of E12g and A1g Raman modes. The decay processes and valence band splitting are in accord with the known energy scheme for MoS_2 thin films. A band gap of about 1.8 eV of MoS_2 thin film is in the range of 1.1 eV (bulk MoS_2) to 1.9 eV (monolayer MoS_2). The band gap of ALD MoS_2 thin films is much closer to the monolayer limit than to the bulk limit.

AA-MoP-44 Synthesis of ALD Iridium Thin Films on 3-D Fabricated Monel K-500 Steel Samples*, P Oelslager,* ***Helmut Baumgart,*** Old Dominion University

Iridium (Ir) thin films have been extensively investigated for a variety of applications. Ir is a potential optical material for Fresnel zone X-ray microchannel plates, inductive grid filters, and potential electrode materials. It is also a noble metal making it well suited to corrosion resistance in harsh environments

Atomic Layer Deposition (ALD) is considered a modification of chemical vapor deposition (CVD), where two different chemical precursors are pulsed separately into a reactor chamber one at a time, requiring two self-limiting surface chemical reactions to occur on the substrate. It is possible for ALD technology to synthesize high quality materials over large areas at low temperature. ALD technology has numerous advantages over conventional thin film deposition techniques. ALD can precisely control film layer thickness, stoichiometry, composition, and uniformity, and produce sharp interfaces in nanolaminate structures. ALD can also be used to deposit conformal films onto very complex surface morphology structures

In this work, iridium metal films were deposited on silicon (Si) and Monel K-500 alloy substrates by ALD using Iridium (III) acetylacetonate known as Ir(acac) or $[CH_3COCH{=}C(O\text{-})CH_3]_3Ir$ as precursor, and industrial grade O_2 as oxidizing reactant. The solid Ir precursor was heated to 150°C, and the substrate temperature was varied to establish an optimum growth window. The lowest temperature in which Ir growth was is 200°C, and the thin film growth rate increased as a function of temperature up to 250°C. Higher temperatures have not yet been attempted due to equipment constraints. The Monel K-500 steel alloy flat discs were cut from commercially available Monel K-500 bars of ~1 inch diameter.

In this study we report on the successful synthesis of Ir metal films on both Si and Monel K-500 substrates by ALD system with $Ir(acac)_3$ and Oxygen between 200 and 250^{o}C. Detailed characterization has been performed using X-ray diffraction (XRD), atomic force microscopy (AFM), and field emission scanning electron microscopy (FE-SEM) of samples which have been notched with focused ion beam (FIB) techniques for cross-sectional film thickness measurements. The XRD and FE-SEM results reveal that the ALD Iridium thin film are polycrystalline at deposition temperatures based on Volmer–Weber island growth mode. Heterogeneous nucleation on Si and Monel K-500 alloy surfaces and yielded excellent surface coverage and does not require special surface treatments.

AA-MoP-45 Precursor Dependent Optical Properties of ALD TiO_2*,* ***Ritwik Bhatia,*** Veeco-CNT

There has been increased interest in the use of atomic layer deposition for optical applications due to the ability of ALD to uniformly coat curved substrates and ease of scale up of ALD to large batches and/or large substrates. Many optical designs require alternating layers materials with low and high refractive index. TiO_2 is a material of interest in optical coatings due to its high refractive index (~ 2.4) and transparency across most of the visible spectrum (band gap ~ 3eV). However, TiO_2 can be absorbing in the visible region (sub-band gap) absorption, typically attributed to oxygen vacancies.

In this work we discuss the optical properties of TiO_2 and how they depend on deposition parameters like precursor type, deposition temperature and precursor exposure. We have found that TiO_2 deposited with tetrakis(dimethylamino)titanium (TDMATi) and water is absorbing across the visible spectrum, while TiO_2 from titanium chloride ($TiCl_4$) and water is transparent across the visible region - only showing the expected band edge absorption ~ 400nm. Further, we investigate the processing parameters required to make TiO_2 from TDMATi less absorbing.

AA-MoP-46 Accurate Modeling of the Gate Leakage Currents in Metal-Insulator-Semiconductor (MIS) Devices using Ultra-thin High-k Oxides*,* ***Hector Uribe-Vargas****, J Molina-Reyes,* National Institute of Astrophysics, Optics and Electronics

Ultra-thin high-k oxides are widely used in advanced CMOS technology in order to continue scalability and to increase performance. Nevertheless, as the devices reach the nanometer regime, accurate predictions ensuring long-term operation of these devices is now more complicated due to several physical and electronic considerations: 1) precise atomic control of the high-k material in the ultra-thin regime (thickness, stoichiometry, dielectric constant, etc), 2) excessively large gate leakage current levels, 3) appearance of several conduction mechanisms able to degrade the performance and reliability of the devices, 4) interfacial defects at the high-k/silicon interface and 5) low thermodynamic stability of the high-k materials after being exposed to the inherent thermal treatments during several Front-End-Of-Line (FEOL) or Back-End-Of-Line (BEOL) stages.

In order to contribute to better predictions of electrical performance and reliability characteristics, this work carefully reviews the conduction mechanisms in Metal-Insulator-Semiconductor (MIS) devices fabricated using ultra-thin Al_2O_3, and TiO_2 (less than 10 nm in thickness for each dielectric) deposited by atomic-layer deposition (ALD). This deposition technique has excellent conformality, outstanding control (to atomic level) on the thickness and stoichiometry, interface quality with the semiconductor substrate, and low deposition temperature ($T \leq 250°C$) for these metal oxides, assuring high reproducibility for each device.

After fabrication, MIS devices were electrically characterized using standard Ig-Vg, C-V, Ig-Vg-temperature measurement conditions in order to determine the precise carrier conduction mechanism for each dielectric under different conditions of substrate passivation (by using a chemical oxide SiO_x) and post-metallization annealing (PMA). The experimental measurements were compared with semi-empirical tunneling models like direct tunneling (DT), Ohmic conduction (OC), Poole-Frenkel emission (PF), Trap-Assisted Tunneling (TAT), Schottky Emission (SE) and Fowler-Nordheim tunneling (FN). Physical parameters such as effective mass, barrier height (SE and FN), and trap energy level were extracted and then compared with simulations using MATLAB and SILVACO software. All values were compared with those found in literature, having excellent agreement. The accurate identification of self-consistent conduction models for the gate leakage current in MIS devices allows for better performance/reliability predictions before degradation or failure of these devices and this is possible due to the high quality of the ultra-thin high-dielectric constant materials enabled by thermal ALD.

AA-MoP-47 Optimization of Microwave Generated Surfatron for Wafer-scale Plasma Enhanced ALD System*, J Kim,* ISAC Research Inc., Republic of Korea*; A Poruba,* SVCS Process Innovation s.r.o., Czech Republic*; M Cada,* Institute of Physics of the Czech Academy of Sciences, Czech Republic*;* ***Hyung Sang Park,*** ISAC Research Inc., Republic of Korea*; J Dolak,* SVCS Process Innovation s.r.o., Czech Republic

With the continued down scaling of devices and structure changed to 3-dimensional, new ALD processes are in great demand. Microwave surfatron plasma is considered new plasma source because it enables very low-temperature deposition and good film quality due to its low electron temperature and higher plasma density. For adopting surfatron plasma source to new ALD system, it is essential to understand the physical properties of generated plasma with the varying gas atmosphere. Also we are requested to achieve acceptable homogeneity on wafer-level area. Thus, in this work, we investigated plasma parameters with various gas, pressure, flow and various distances from the plasma outlet with optimized design of plasma nozzle. Furthermore, we will present the preliminary results of TiOx layers achieved with this tool.

AA-MoP-48 Grow of GaN Thin Films over a Si/Al_2O_3 Stack by Thermal and Plasma Enhanced Atomic Layer Deposition as MOS Structure*,* ***Joaquin Alvarado,*** University of Puebla, Mexico*; M Chavez,* CINVESTAV-IPN, Mexico*; D Cortes,* University of Puebla, Mexico*; S Gallardo,* CINVESTAV-IPN, Mexico*; L Martinez, S Alcantara,* University of Puebla, Mexico

Atomic layer deposition (ALD) is a promising technique because highly uniform films can be obtained and allows an excellent growth control [1,2]. Oxides (eg. Al_2O_3) and III nitrides (InN, AlN and GaN) can be obtained with ALD technique . These features make ALD technique a candidate for manufacture high-electron-mobility-transistors (MIS- HEMTs) and metal-oxide-semiconductor high-electron- mobility-transistors (MOS-HEMTs) [3]. Metal-insulator-semiconductor (MIS) structure using Al_2O_3 and GaN as a dielectric and semiconductor respectively obtained by Atomic layer deposition has received much attention because the Al2O3/GaN structure provides low leakage current, whereas GaN layer offers higher mobility than Metal Oxides layers.

Experimental

GaN and Al_2O_3/ GaN layers were carried out at 400°C using both Thermal and Plasma Enhanced Atomic Layer Deposition (PEALD). First, 50 cycles of Al_2O_3 were deposited at 150°C, thermal ALD Al_2O_3 cycle consist of (a) pulse of Trimethyl Aluminium (TMA), (2) Ar purge, (3) H_2O pulse and (4) Ar purge. Furthermore, 1000 cycles of GaN were deposited with PEALD, where each cycle consist of (1) pulse of Trimethylgalium (TMG), (2) Ar purge, (3) N_2 plasma and (4) Ar purge. Base pressure was 150 mTorr. Two structures were obtained Si/GaN and Si/Al_2O_3/GaN and Ohmic contacts of Ti/Al/Ti/Al/Ti/Au (50/30/50/30/60) metals were deposited through evaporation.

Results.

Fig. 1 shows the XRD pattern of GaN and Al_2O_3/GaN films, the peak located at 34.5° (002) confirms the hexagonal phase of Gallium Nitride [4], whereas no peaks of Al_2O_3 are present, which indicates that Al_2O_3 is amorphous.

Fig. 2 shows the results of X-ray reflectivity (XRR) for (a) Si/GaN (b) si/AL_2O_3/ GaN, XRR data indicate the thickness of GaN and GaN/Al_2O_3 layers are 40 nm and 60 nm respectively. The inset figure shows the critical angle (c_a), where the precise position was determined by the minimum of the first derivative. Also the mass density obtained was 6.04 g cm^{-3}. Atomic Force Microscopy, Scanning Electron Microscopy as well as Transmittance and Absorbance characteristics of these films grown at different temperatures will be included.

On the other hand, Fig. 3 shows the C-V and G-V characteristics of Si/Al_2O_3/GaN stack at three different frequencies; thanks to this figure it will be possible to evaluate the insulator-semiconductor interface.

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**AA-MoP-49 Reduction of Hysteresis in p-Type Atomic Layer Deposited SnO Thin Film Transistors by Adopting Interfacial Layers*, Younjin Jang*, *J Kim, E Hwang, S Lee, S Jeon,* Seoul National University, Republic of Korea*; J Han,* Seoul National University of Science and Technology, Republic of Korea*; C Hwang,* Seoul National University, Republic of Korea

Oxide thin film transistors (TFTs) have made impressive progress using n-type oxides such as a-IGZO, ZnO, and SnO. However, realizing the complementary metal oxide semiconductor circuit using all oxide TFTs was retarded by lack of high-performance p-type oxide semiconductors. Recently, tin monoxide (SnO) was suggested as a promising p-type material for high hole mobility due to its valence band structure [1]. To date, the SnO thin films were mainly deposited by magnetron sputtering method, but a recent study showed a possibility of fabricating a p-type SnO thin film using atomic layer deposition (ALD) method. Although it showed superior TFT performances compared to the previous results, electrical properties of ALD SnO TFTs have not been sufficiently analyzed yet [2]. In this work, the interfacial layer effects on the hysteresis of p-type SnO TFT were investigated.

p-Type SnO thin films were grown by the atomic layer deposition (ALD) using Sn(dmamp)$_2$ (bis(1-dimethylamino-2-methyl-2- propoxy) tin(II)) and H_2O as the Sn and O sources at 200 °C on SiO_2/p^{++}-Si substrate. To investigate the interfacial effects on hysteresis behaviors, and the Al_2O_3 interfacial layer (IL) grown by ALD (thickness from 2.5 to 5 nm) was inserted between the SnO active layer and the SiO_2 gate oxide layer. Various heat treatments on ILs by rapid thermal annealing (RTA) were carried out.

By optimizing the gas atmosphere of RTA process, a significant decrease in the hysteresis was observed (from 4 V at no IL to 2 V at 2.5 nm-thick IL). It seems that oxygen treated IL reduced the defects close to the channel, which contributed to the reduction of hysteresis. Also, it was confirmed that the hysteresis characteristics were further improved by increasing IL thickness from 2.5 nm to 5 nm. Possible origin of hysteresis would be related to Si diffusion to the SnO layer during the deposition process, but more detailed investigation of hysteresis mechanism is necessary.

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AA-MoP-50 The Impact of ALD ZrO_2 Gate Insulators on Indium Tin Zinc Oxide (ITZO) Thin Film Transistor Applications*, Wan-Ho Choi*, *H Jung, J Sheng, J Lee, J Park,* Hanyang University, Republic of Korea

High-k dielectric materials have been extensively studied in the memory semiconductor and display industries. Especially in the field of displays, high-k materials should be studied for low-voltage operation. Especially, the solution process has been mainly studied for the high-k material for the low voltage drive transistor. However, due to the leakage current of the solution process and limitations of the device behavior, it is necessary to study the high-k dielectric layer using atomic layer deposition (ALD) to obtain excellent insulating layer characteristics. In this study, ZrO_2 films were deposited at various temperatures by ALD. The MIM and MIS structures were fabricated using the deposited ZrO_2 thin films to investigate the dielectric properties of the films. In order to measure the performance of the device, a thin film transistor(TFT) of back-channel-etching (BCE) structure using In-Sn-Zn-O (ITZO), which is a high mobility oxide semiconductor, was fabricated. The ZrO_2 thin films used in each structure were deposited at 100 nm and their thicknesses were measured by spectroscopic-ellipsometry (SE). Leakage current density of 200,250 and 300ºC is 7.5´10^{-8}, 2.9´10^{-8} and 3.6´10^{-8} and k value is 17.4, 21,4 and 23.0, respectively . TFT with ZrO_2 showed mobility of 23.4, 7.0, and 4.16 at 200, 250, and 300 ºC and hysteresis of 0.13, 0.02, and 0.04 with subthreshold swing of 0.19, 0.15, and 0.16, respectively. And the constant current stress (CCS) test was conducted to confirm the suitability as a driving transistor. The higher the deposition temperature of ZrO_2, the better the reliability. XRD analysis was carried out to examine the crystallinity of the ZrO_2 thin film. XPS analysis of the ZrO_2 surface was also performed to study the origin of the performance difference of the device depending on the deposition temperature. Comparing the surface composition through XPS, the ZrO_2 thin film deposited at 200°C showed more than two times higher composition of Carbon than the other temperature set. Due to this impurity, defect-assist leakage mode is dominent and that increase the leakage current density. The XPS O1s spectra show that the O-deficient peak associated with Vo is the highest in the thin film deposited at 200°C, indicating that the mobility of the device is high and the reliability is poor. We confirmed the suitability of ZrO_2 as a dielectric layer of TFT deposited at over 250°C.

AA-MoP-51 Templated Carbon Nanotube Growth from Reduced NiO Atomic Layer Deposition*, Erin Cleveland*, *K Perkins, P Campbell, A Friedman,* U.S. Naval Research Laboratory

Carbon nanotubes (CNTs) have drawn great attention due to their exceptional thermal, electrical, and mechanical properties. Owing to their unique mechanical properties, CNTs are promising as reinforcement for nanocomposite materials. CNTs have been widely studied using a variety of different growth techniques, including catalytic CVD. In CVD, metal catalytic nanoparticles deposited on substrates from solution or spontaneously formed through nucleation of films formed by physical vapor deposition (PVD) techniques such as sputtering or evaporation are exposed to a gaseous carbon precursor at elevated temperatures. The catalytic particles decompose the precursor, giving rise to surface C and H atoms, with subsequent growth of CNTs from the particle surface.

In general, the size of the catalyst particle rules the diameter and type of carbon nanotube. Large catalyst particles typically result in multi-walled CNTs, which may be relevant to applications benefiting from their mechanical properties. However, a key requirement for growing single walled CNTs is that the catalyst particles be extremely small, typically only a few nanometers in diameter. Uniform and reproducible deposition of such small particles requires careful process control. More importantly, due to PVDs' line-of-sight constraint, these techniques struggle to conformally deposit material on 3D architectures.

A potential solution to these challenges is the use of atomic layer deposition (ALD) for catalyst preparation. ALD uses self-limiting chemistries to deposit thin films in a layer-by-layer fashion with atomic level thickness control and unprecedented uniformity and conformality. A high temperature H_2 anneal step that is part of the CNT synthesis process can subsequently be used to reduce a metal-oxide film into a catalytic metal. In contrast to physical deposition techniques, ALD is capable of coating complex 3D structures with atomic level precision.

In this paper we investigated the use of NiO ALD reduced to metallic Ni for the catalytic growth of CNTs within the confines of a high aspect ratio nanoporous template. Thin films of NiO were deposited using Ni(amd) and

H_2O and reduced in a post-deposition low temperature H_2 anneal. After reduction, films became very granular with increased surface roughness of ~1.6 nm RMS. CNTs grown with ethylene within 5 µm dia. pores exhibited small diameters, well below the pore size. Since grain size of the catalytic metal has a direct effect on the diameter and type of the subsequent CNT growth, different reduction methods were investigated, such as reduction temperature, time and the use of an in-situ H_2 plasma during the ALD deposition.

AA-MoP-53 Atomic Layer Deposition of Titanium Oxide using Heteroleptic Titanium Precursors with a Linked Ligand*, **Seongyoon Kim**, J Kim, J Gu, H Kim, H Jung,* Sejong University, Republic of Korea*; M Park, J Park,* Hansol Chemical, Republic of Korea*; W Lee,* Sejong University, Republic of Korea

Titanium oxide and Ti-based perovskites have been continuously studied for application to DRAM capacitors as high-permittivity materials. ALD technology has replaced PVD and CVD to provide excellent step coverage, accurate film thickness control, and highstoichiometry film quality. The most popular titanium precursors are tetrakis(dimethylamino)titanium (TDMAT) and titanium tetraisopropoxide (TTIP), and the ALD TiO_2 films using those precursors showed narrow ALD temperature window with the maximum ALD temperature of approximately 200°C. In general, higher deposition temperature improves the physical and electrical characteristics of the dielectric film, such as film density, stoichiometry, and purity. However, the ALD precursors decompose at higher temperatures, resulting in poor step coverage and high impurity concentration. Therefore, we need titanium precursors with excellent thermal stability together with high reactivity and sufficient volatility. It was reported that thermal stability of TDMAT is improved by replacing an alkylamine group with a cyclopentadienyl to form tris(dimethylamino)cyclopentadienyl titanium [1]. In the present study, we investigated the ALD of titanium oxide using heteroleptic titanium precursors with a linked ligand. A heteroleptic precursor with alkylamino groups was compared with alkoxy groups. Saturation dose and the ALD temperature window were determined by measuring growth rate with different precursor feeding times, oxidizing agent feeding times, and the process temperatures. The reaction mechanism was studied by using in-situ Fourier transform infrared spectroscopy and quadrupole mass spectroscopy. The physical and electrical properties of the deposited films were also characterized.

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AA-MoP-54 *Ex-Situ* Grown Low-Temperature SiN_x on GaN with Crystalline Interfacial Layer using Hollow Cathode PEALD*, **Xin Meng**, J Lee, A Ravichandran, Y Byun, J Lee, A Lucero, S Kim,* The University of Texas at Dallas*; M Ha,* Myongji University, Republic of Korea*; C Young,* The University of Texas at Dallas*; B Hwang,* Dow Chemicals*; J Kim,* The University of Texas at Dallas

In this work, we report *ex-situ* grown low-temperature SiN_x on GaN with ~1.5 nm crystalline interfacial layer (CIL). The 2.8-2.9 Å d-spacing indicates that the CIL is β-phase Si_3N_4. The SiN_x was grown by hollow cathode plasma-enhanced atomic layer deposition (PEALD) [1]. Tris(dimethylamino)silane (3DMAS) and a remote N_2 plasma were used as the silicon precursor and the nitrogen co-reactant, respectively. Though the growth temperature was as low as 300°C, we obtained excellent film properties comparable to those of high-quality thermal SiN_x films grown at a temperature above 700°C. Owing to the effective passivation of dangling bonds and nitrogen vacancies by the crystalline interfacial layer, GaN MIS-HEMTs with PEALD SiN_x gate dielectric shows excellent threshold voltage (V_{th}) stability (ΔV_{th}<0.3 V) under positive/negative bias stress.

We also compared with other devices using different ALD-grown gate insulators (15 nm), including (a) SiN_x using pentachlorodisilane (PCDS) and N_2/NH_3 plasma, (b) SiN_x using hexachlorodisilane (HCDS) and N_2/NH_3 plasma, and (c) Al_2O_3 using trimethylaluminum (TMA) and H_2O. Of all the devices, PCDS-SiN_x/GaN MISHEMTs exhibited both a highest on/off ratio (~10^{10}) and a negligible V_{th} instability (ΔV_{th}<0.1 V) under a large gate bias stress of 7 V. The extraordinary results suggest an excellent interface of the gate dielectric stacks, as well as negligible bulk traps inside the PEALD SiN_x layer.

The authors would like to acknowledge Dr. Scott Butcher (Meaglow Ltd.) for the technical discussions on the use of hollow cathode plasma source.

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AA-MoP-55 Composition Adjustment of Zn(O, S) Buffer Layer on CIGS Solar Cell by Atomic Layer Deposition*, **Yu-Hsuan Yu**, N Koothan,* Instrument Technology Research Center, Republic of China*; W Xu,* National Tsing Hua University, Republic of China*; C Kei, M Shiao,* Instrument Technology Research Center, Republic of China*; C Lai,* National Tsing Hua University, Republic of China

Depositing Zn(O, S) thin film as the Cd-free buffer layer is an important topic in CIGS solar cells since it offer the potential enhancements for either low cost and good for environment. The band gap and the optical properties, which is crucial to the buffer layer, is controlled by the element composition of Zn(O, S) thin film. In this study, In this study, we deposited ZnO and ZnS thin films by atomic layer deposition(ALD). We deposited ZnO thin film by using diethyl Zinc((C_2H_5)2Zn, DEZ) and H_2O and the ZnS film was deposited by using DEZ and H_2S. And the Zn(O, S) buffer layer was fabricated y alternately depositing ZnO and ZnS thin films. We can control the oxygen/sulfide composition in the Zn(O, S) thin film by changing the cycle ratio of ZnS and ZnO. The properties of Zn(O, S) films were measured by ellipsometry, SEM, XRD and XPS. We also deposited Zn(O, S) films with different O/S composition on CIGS absorber. The device performance were measured by current-voltage measurement.

AA-MoP-56 Effect on Low Plasma Damage by ALD Deposition of Silicon Heterojunction Solar Cell*, **Hyeongsik Park**,* Sungkyunkwan University (SKKU), Republic of Korea*; H Kim,* Incheon National University, Republic of Korea*; Y Kim,* Sungkyunkwan University (SKKU), Republic of Korea*; K Lim,* JUSUNG Engineering, Republic of Korea*; J Kim,* Incheon National University, Republic of Korea*; J Yi,* Sungkyunkwan University (SKKU), Republic of Korea

We report regarding ZnO back reflector by atomic layer deposition (ALD) on a silicon heterojunction solar cell with the rear-emitter structure. ALD ZnO can reduce a plasma damage on silicon heterojunction after an ITO deposition and be leading to maintaining the open circuit voltage. The current density has different around 1 mA/cm^2 led to the cell efficiency depending on a ZnO back reflector. We achieved the efficiency of 22.4% having a ZnO back reflector without a change of open circuit voltage (V_{OC}: 723 mV) and fill factor (FF: 76.8%) as compared the reference specimen (V_{OC}: 723 mV, FF: 76.4%).

AA-MoP-57 A Study on the Mechanical and Electrical Properties of Atomic and Molecular Layer Deposited ZnO – Zincone Alloy Thin Films with change of Molecular Backbone Structures.*, **Seung Hak Song**, S Hwang, B Choi,* Korea University, Republic of Korea

The interposition of zincone thin films into ZnO thin films can improve the properties of structures. Zincones are fabricated by the reactions between zinc reactants and organic precursors. Zincones have a different backbone structures depending on organic precursors, for example, zincone thin films which deposited by the reactions between diethylzinc (DEZn) and ethylene glycol (EG) precursors have a –O-CH2-CH2-O- backbone structures. The reactions between DEZn and hydroquinone (HQ) fabricate zincone thin films that have aromatic backbone structures. The rigid and conjugated structure of HQ is expected to produce durable and electrically conductive materials. In this study, the differences of mechanical and electrical properties between ZnO – zincone (EG) and ZnO-zincone (HQ) alloy thin films were measured. The critical tensile strain and elastic modulus of the thin films were measured using micro tensile tests. Electrical conductivity and sheet resistances were also measured. The structure and growth rates of thin films were investigated using x-ray diffraction and ion mass spectrometry methods.

AA-MoP-58 ALD and Nanocellulose Based Sensors for Ultra-low Power, Room Temperature Ozone Gas Monitoring for Respiratory Ailments and Wellness Management*, A Tanneeru, T Flewwellin, A Young, M Daniele, V Misra, **Bongmook Lee**,* North Carolina State University

Ultra low-powered gas sensors for environment and breath monitoring, can help us tackle health conditions like asthma, emphysema, chronic bronchitis by monitoring for permissible levels of gases like ozone in the atmosphere. The sensitivity of these sensors should be in the 50-100ppb concentration range to detect ozone in the atmosphere so as to avoid exacerbating these chronic conditions. Traditional sensing methods of high temperature heating of the substrate (200^0C-450^0C), consume high-power and are therefore not compatible with wearable technology for long-term gas monitoring. We have demonstrated highly sensitive, selective sensors with low power consumption and room-temperature operation, by depositing nanoscale thick metal oxide layers ALD technique on Si/SiO_2 substrate. Nanocellulose is a material has several advantages such as bio-compatibility, high mechanical ruggedness, high surface area, thermal stability and flexibility. It also has a conformal adherence to epidermal surfaces without adhesives via Vanderwaals forces and is less susceptible to degradation due to mechanical stress. In this work we report ultra-low power room temperature sensing of ozone gas, by atomic layer deposited (ALD) tin oxide sensing layer on a nanocellulose substrate. The sensor fabrication started with a nanocellulose substrate produced by oven drying cultured bacteria over glass slides. A 6nm sensing layer of SnO_2 was deposited by atomic layer deposition with Tetrakis (dimethylamino tin (IV) – $Sn[N(CH_3)_2]_4$) precursor at 200°C, with a 20nm ALD Al_2O_3 interlayer to ensure electrical isolation with substrate. Titanium (20nm)/Gold (250nm) electrodes were deposited by e-beam evaporation. The sensors were tested for response to ozone in 25 to 100 ppb concentration range in a humidity and temperature controlled testing chamber. UV LED with a 5-10% duty cycle was used to reset the resistance to the baseline value keeping the total power consumption under 200uW. The flexible ozone sensor shows highly sensitive and selective responses from 25 parts per billions (ppb) to 100 ppb. This ultra-low power, highly selective and sensitive nano-scale thick ALD deposited ozone sensor can be integrated with a highly bio-functional nanocellulose substrate in the flexible system. Combined with the body powered, battery-free and wearable health monitoring systems as developed at NSF-ASSIST center, this has a potential to play a key role in management of respiratory ailments

AA-MoP-59 Plasma-enhanced Atomic Layer Deposition of Ruthenium Thin Film using (p-cymene)(dimethyl-hexadiene)Ruthenium*, J Choi,* UP Chemical Co., Ltd., Republic of Korea*; S Kim,* Sejong University, Republic of Korea*; B Yoo, W Han, **Wonyong Koh**,* UP Chemical Co., Ltd., Republic of Korea*; W Lee,* Sejong University, Republic of Korea

The resistivity of copper interconnect increases rapidly as the linewidth decreases beyond 30 nm due to the sidewall scattering of electrons. The resistance of copper interconnect increases even further because it is hard to scale the thickness of barrier and cladding layers. In addition, the maximum allowable current density in high-performance logic devices will be limited by the electromigration failure of scaled copper interconnects. These problems can be solved by replacing copper by an alternative metal. Ruthenium and cobalt are attracting attention as candidate conductor materials because they have shorter mean free paths of electrons and higher melting point compared with copper. They can also improve the resistivity by reducing the barrier thickness because they do not attack the lower layer. Atomic layer deposition (ALD) is a promising method for gapfilling of damascene pattern or the conformal deposition of a seed layer for electroplating. The most popular co-reactant in ALD ruthenium is O_2. However, the drawback of O_2 is the formation of the insulating layer by oxidation the underlying layers, resulting in high resistance. In the present work, therefore, we studied the plasma-enhanced ALD (PEALD) of ruthenium thin film using (p-cymene)(dimethyl-hexadiene)ruthenium and non-oxidizing co-reactants, the mixtures of N_2 and H_2 or NH_3. Ruthenium thin films were grown in a showerhead-type cold-wall PEALD reactor. The growth rate, composition, and resistivity of the deposited films were investigated with varying co-reactant and plasma condition.

AA-MoP-60 Low Temperature Plasma Enhanced Atomic Layer Deposition of SiO_x Films using New Divalent Si Precursor for Thin Film Encapsulation*, **Jung-Hoon Lee**, J Lee, W Choi,* Hanyang University, Republic of Korea*; J Park,* Hansol Chemical, Republic of Korea*; J Park,* Hanyang University, Republic of Korea

Silicon dioxide (SiO_2) is a well-known dielectric material, which have been used for semiconductor industries such as gate dielectric, gate spacer and deep shallow trench.

Besides, SiO_2 attract its attention as a promising material for thin film encapsulation (TFE), organic devices such as light emitting diode, photoelectric device need encapsulation layer to prevent degradation of organic materials caused from oxygen and water vapor. Conventionally, SiO_2 films are deposited by chemical vapor deposition (CVD), sputtering and thermal evaporation. The above methods have some problem for TFE such as high growth temperature, poor step coverage, point defect. Plasma enhanced atomic layer deposition (PEALD) method is popular that can achieve high quality SiO_2 without defect at relatively low temperature.

In our study, SiO_x thin film was deposited by PEALD method using N,N'-tert-butyl-1,1-dimethylethylenediamine silylene as a precursor, oxygen plasma as a reactant. PEALD processes show surface limit reaction behavior as increase precursor dose with constant purge time 10s during processes. Also, it exhibited significant process window in the temperature range of 80-200°C with negligible ble carbon, nitrogen impurity concentration. Film thickness, refractive index of SiO_x thin films are investigated using spectroscopic ellipsometry (SE) and films have about 1.45-1.5 refractive index value which is correspond to SiO_2' refractive index although we used divalent precursor. Due to low temperature process, SiO_x thin films are deposited on polymer substrate under 120°C and Water vapor transmission rate (WVTR) is measured by Ca-test method. As a result, we can compare the WVTR properties of SiO_x depending commercial precursor and new divalent precursor.

AA-MoP-61 Atomic Layer Deposited Tungsten (W) Thin Films using Fluorine-free W Precursors*, S Kim, **Min Young Lee**, T Kim,* Yeungnam University, Republic of Korea

The tungsten films have good properties such as relatively low resistivity (bulk resistivity: 5.6μΩ·cm), low reactivity with oxygen, and good step coverage deposited by chemical vapor deposition method. So, it has widely investigated in semiconductor device technologies including the word lines and bit lines of memory devices. However, with the continuous shrinkage and novel 3D structure with high aspect ratio of device, a conformal deposition technique on a high aspect-ratio trench and hole structure with excellent uniformity of thickness and process controllability is essential. In these respects, atomic layer deposition (ALD) for these materials have been drawn much attention because ALD uses a self-limiting film growth mode by surface-saturated reaction, which enables atomic scale control of the film thickness with excellent step coverage. The WF_6 precursor was commonly used as a precursor for atomic layer deposition but this process using WF_6 precursor has some problems. It has long incubation time and additional pretreatment carried out. Furthermore, fluorine remaining in the tungsten film made critical damage on underlying substrate. To solve these problems, we report the plasma-enhanced ALD (PEALD)-W and thermal ALD-W processes using two kinds of fluorine-free precursor, an inorganic WCl_5, and a novel tungsten metalorganic precursor with various reactants. For example, tungsten thin films using WCl_5 precursor were deposited by using showerhead type ALD reactor (ALD, Lucida-M100, NCD technology) with H_2 plasma as a reactant. The deposition temperature's range is from 200 to 350°C. We check the grazing incidence angle (q = 3°) XRD patterns of the typical PEALD-W film deposited on SiO_2 substrate. Five peaks from primitive cubic-structured beta tungsten were clearly shown. T he properties of PEALD-W and thermal ALD-W films with deposition conditions have been evaluated by using various tools; resistivity by 4-point probe and XRR(or X-SEM), step coverage by XTEM, phase using XRD, composition by SIMS, and chemical bonding by XPS.

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AA-MoP-62 Low Temperature Atomic Layer Deposited MoN_x as an Efficient Cu-diffusion Barrier*, S Kim, **Tae Hyun Kim**, D Nandi,* Yeungnam University, Republic of Korea

A deposition technique with extremely precise control over film thickness, the low deposition temperature and non-corrosive by products (like acids) during deposition are the essential criteria for an efficient barrier layer. To address all of these issues, molybdenum nitride (MoN_x) is deposited at a relatively low temperature (175-300°C) by atomic layer deposition (ALD) using molybdenum hexacarbonyl [$Mo(CO)_6$] as a novel precursor for Mo and ammonia gas (NH_3) as reactant. The as-grown MoN_x are mostly amorphous, however poor nano-crystalline *h*-MoN phase formation is evident from the deposition temperature of 250°C and beyond. The lowest resistivity less than 6000 μΩ-cm for as-deposited film reflects the suitable properties of these MoN_x films to be used as barrier material. Nevertheless, X-ray diffraction (XRD) analysis also reveals that the crystallinity could be enhanced by post-annealing from 500°C to 700°C that converts the film into cubic-Mo_2N phase as well. Corresponding with this, the film resistivity was decreased to ~4000 μΩ-cm. The properties of as-deposited and annealed films are further well-characterized by secondary-ion mass spectroscopy (SIMS), X-ray photo electron spectroscopy (XPS), Rutherford back-scattered spectroscopy (RBS) etc. Two set of ALD-MoN_x films (~4 nm) grown at 225 and 275°C are tested as a diffusion layer against Cu. It is observed that the film deposited at higher temperature acts better for this purpose. The possible reason for this might be the higher density of the ALD-MoN_x films grown at 275°C compared to the films deposited at 225°C.

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AA-MoP-64 State Key Laboratory of Digital of Manufacturing Equipment and Technology, School of Mechanical Science and Engineering,Huazhong University of Science and Technology*, Qinyong Xiang*, *B Zhou, K Cao, B Shan, R Chen,* Huazhong University of Science and Technology, China

$CsPbX_3$ (X=Cl, Br, I) lead halide perovskite quantum dots (LHPs) have attracted great attention due to their excellent optical properties, such as tunable wavelength, narrow emission, and high photoluminescence quantum efficiency [1]. However, When LHPs are exposed to external environment (humanity, heat and light), the degradation of LHPs occurs and leads to the photoluminescence quenching [2-3]. In this work, alumina shell is deposited by atomic layer deposition to stabilize $CsPbBr_3$ QDs-silica nano luminescent sphere. The $CsPbBr_3$ QDs are coated with nanoscale Al_2O_3 layers with excellent uniformity and the aggregation of QDs are also avoided during ALD process. The as prepared $CsPbBr_3$ QDs-silica nano luminescent spheres not only retain the high photo luminescent quantum yields, but also exhibit excellent stability in water and heat. Further characterizations results show that Al_2O_3 coating effectively avoids the destruction of QDs' crystalline structure in water and thus enhance the stability. This method is potentially applicable to the stabilization of other QDs such as CdSe, InP and PbS and backlight devices.

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AA-MoP-66 Research on Properties of Protective Film Deposited on Silver Hat with Large and Complex Morphology at Low Temperature*, Yang Liang,* *L Lina,* Kaili University, China

Sulphides and oxides formed on the surface of silver hat will degrade the appearance seriously.To solve the problem,Al2O3 protecting film was deposited on silver hat for anti-tarnishing by thermal atomic layer deposition technique with $Al(CH_3)_3$ and H_2O as precursors at low substrate temperature. The film with thickness uniformity less than 6.8% has been successfully prepared on both the internal and external surfaces of silver hat by designing and using a dispersal device to make the gas flow uniform. Some small particles appearing on the surface of the film disappear by optimizing process parameters. The x-ray diffraction test shows that the film is amorphous at 120°C. The x-ray photoemission spectroscopy and scanning electron microscopy-energy dispersive spectrometer test show that the atomic ratio and weight percent of oxygen to aluminium for the Al_2O_3 film are 1.52 and 0.86 respectively. The accelerated corrosion experiment, diffuse reflection test and color difference calculation show that the protecting film with thickness of 30nm has a satisfactory anti-tarnishing effect and produces no effect on the appearance of silver ornament.

AA-MoP-68 Fabrication of Microchannel Plate (MCP) using 3D Printing and ALD Coatings*, Anil Mane,* *L Xia, J Xie, R Wagner, H Nicholson, M Pellin, J Elam,* Argonne National Laboratory

Microchannel plates (MCPs) are 2D-electron amplifiers with high gain (10^3-10^5) used in a variety of commercial applications including night vision and particle detection. Traditional MCPs are made with lead glass capillary arrays with millions of pores of size from a few to tens of microns diameter [1]. A pair of MCPs sealed in a package under ultra-high vacuum with a photocathode window is the basis for photodetectors that provide picosecond time resolution and sub-millimeter spatial resolution. Recently, MCPs have been fabricated using non-lead micro capillary array (MCA) glass substrates functionalized by ALD coatings with dramatically larger area and improved properties compared to lead glass MCPs [2]. 3D printing may provide a more flexible and cost effective route for producing micro capillary array substrates. To explore this approach, we used a 3D printer based on 2-photon polymerization with ~50 nm spatial resolution to fabricate capillary arrays ~1 cm^2 in area. We functionalized these 3D printed substrates with ALD resistive coatings composed of a W-Al_2O_3 nanocomposite, and MgO secondary electron emission layers [2, 3]. These 3D printed MPCs show gain and spatial uniformity comparable to the MCA glass MCPs. Here we will discuss the synthesis, characterization, and testing of MCPs using 3D printed structures and ALD functionalization. 3D printed MCP substrates offer the possibility of significant cost savings in materials and labor compared to MCA glass. More importantly, 3D printing can easily create tailored structures not possible using conventional techniques, and this will facilitate new applications for MCP technology.

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AA-MoP-69 Zn-doped TiO_2 Hollow Fibers Fabricated by ALD Nanolamination for Photocatalysis*, Li-Chen Wang,* National Tsing Hua University, Taiwan, Republic of China*; W Liu, C Su, T Perng,* National Tsing Hua University

Recently, one-dimensional (1D) materials such as SnO_2, ZnO, and TiO_2 nanowires or nanotubes have attracted immense attention due to their unique and tunable optical, magnetic, electrical, and chemical properties. Tremendous attempts, therefore, have been made to refine these properties by incorporating various ions into the 1D nanomaterials for application in photocatalysis. In this study, we demonstrated a controllable synthesis of Zn-doped TiO_2 (Zn-TiO_2) hollow fibers as a photocatalyst by atomic layer deposition (ALD) via nanolamination for hydrogen evolution and continuous-flow dye degradation. Herein, diethyl zinc (DEZ), titanium tetrachloride ($TiCl_4$) and H_2O were utilized as precursors of Zn, Ti, and O in the ALD reaction, respectively, to fabricate laminated layers of ZnO and TiO_2 on hollow polysulfone fibers (PSFs). The laminated composite was then annealed to remove the PSF and get a uniform doping of Zn in TiO_2. It was revealed that the photocatalytic efficiency of the Zn-TiO_2 hollow fibers could be affected by the concentration of Zn (*X*z) and the film thickness of Zn-TiO_2. The *X*z could be precisely controlled by the cycle numbers of DEZ/H_2O (N_z) and $TiCl_4$/H_2Ocycles (N_T) in a supercycle (N_z+N_T), and the film thickness of Zn-TiO_2 could be determined by the number of supercycles (n(N_z+N_T)). More importantly, this dry process to deposit Zn-TiO_2 thin film with perfect conformality on the porous PSF template offers a large surface area for the novel nanostructured photocatalyst. The structure of interconnected Zn-TiO_2 nanotubes inside the fiber wall benefits efficient trapping of the reflected photons within the hollow fibers, further improving the photocatalytic efficiency of hydrogen evolution and continuous-flow dye degradation.

AA-MoP-70 Co Decorated Ni/Al_2O_3 Catalysts Fabricated via Atomic Layer Deposition with Coking and Sintering Resistance Towards Dry Reforming of Methane*, Kun Cao,* *M Gong, J Yang, J Cai, B Shan, R Chen,* Huazhong University of Science and Technology, China

The advances in natural gas recovery have drawn much attention to dry reforming of methane (DRM) with carbon dioxide.[1] Nickel is an effective component for the reforming of methane in terms of the catalytic activity and cost, while Ni is plagued by deactivation due to sintering and heavy coking in the catalytic environment.[2] It is necessary to tune the catalytic structure and add the properties of high resistance to sintering, hot spot formation, and coke deposition, to the Ni catalysts. In this work, a mesh-like cobalt oxide coating structure is prepared on Ni nanoparticles via atomic layer deposition. The CoO /Ni catalysts demonstrate both good coking eliminable and sintering resistance ability compared with supported Ni nanoparticles catalysts and CoO /Ni catalysts prepared by incipient wetness method. Co oxide layer is deposited on Ni nanoparticles with discontinuous structure. The mesh-like coating layer could inhibit continuous carbon nanotubes formation, meanwhile CoO deposited on Ni surface partly passivates the coking sites also eliminate carbon formation. In addition, the coating layers provide physical barriers that anchor Ni nanoparticles and improve the sintering resistance.

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AA-MoP-71 Atomic Layer Deposition of Y:ZrO_2 on Nanoporous Silver for Thermally Stable Solid Oxide Fuel Cell Metal Cathodes*, Hyung Jong Choi,* *K Bae,* Korea University, Republic of Korea*; D Jang,* Korea university, Republic of Korea*; G Han, J Koo, J Shim,* Korea University, Republic of Korea

Solid oxide fuel cells (SOFCs), which produce electricity by converting chemicals directly into electrical energy, are attracting much attention due to their high efficiency and fuel flexibility. Since low-temperature SOFC (LT-SOFC) has a short start-up time and a wide selection of SOFC materials, studies are under way to lower the SOFC operating temperature (<500°C). However, by reducing the operating temperature, the oxygen reduction reaction (ORR) kinetics on the cathode sharply diminishes and degrades the overall electrochemical performance of the LT-SOFC. Therefore, for a high-performance LT-SOFC, it is essential to develop a cathode having high ORR activity.

Metal-based materials can be considered as LT-SOFC cathodes. For example, platinum (Pt) is the representative fuel cell cathode material because it has the excellent ORR activity when comparing to others. However, the cost of Pt is very high due to low reserves which hinders the widespread use of Pt. Silver (Ag) can be a potential alternative cathode material because it is much cheaper than Pt and has high oxygen solubility and diffusivity. However, Ag can be thermally agglomerated at the operating temperature of LT-SOFC due to the rapid reduction of AgO_x to Ag and the low melting point. Thermal agglomeration of Ag can destroy the overall microstructure of the cathode and reduces the three-phase boundary of Ag, the active site for ORR. As consequence, the long-term performance of LT-SOFC using Ag cannot be guaranteed.

In this study, we propose a method to fabricate a thermally stable metal cathode by coating a nanoscale $Y:ZrO_2$ (YSZ) thin film on Ag surface using atomic layer deposition (ALD). ALD allows precise control of thickness in atomic-scale while enabling uniform YSZ coatings on nanoporous Ag structures. Electrochemical performance experiments showed that a surface treated Ag cathode showed a power density comparable to a porous Pt cathode. Also, during long-term testing, the Ag coated with ALD-YSZ exhibited a stable current, but a bare Ag cathode showed abrupt deterioration. Through scanning electron microscopy, we found that the bare Ag cathode agglomerated severely while the surface-coated Ag could retain its nanoporous structure after the test. Thus, we can conclude that the electrochemical performance of Ag can be enhanced by ALD-YSZ capping on the surface that can preserve the nanoporous structure of the cathode at LT-SOFC operating temperatures.

AA-MoP-72 Plasma Enhanced Atomic Layer Deposition of Co-C Thin Film as Hydrogen Evolution Electrocatalysts*, **Qi Peng Fan**, Z Liu, Q Chen, Z Wang, L Sang,* Beijing Institute of Graphic Communication, China

In recent years, transition metal carbides (TMCs) have attracted increasing interest in the fields of mechanics, biomedicine and nanomagnetism due to their scientific and industrial importance. Among these transition carbides, cobalt carbide is one of important TMCs because of its excellent magnetic properties, which is identified as an alternate to rare earth magnets. Beside this, cobalt carbide was also studied as a promising catalysis for the dehydrogenation of ethanol to acetaldehyde, the production of lower olefins from syngas and low temperature water-gas shift. The present study reports the deposition of cobalt carbide films by the technique of plasma enhanced atomic layer deposition (PEALD). Bis(N,N-diisopropylacetamidinato)-cobalt（Ⅱ）($Co(^{ipr2}AMD)_2$) was used as cobalt and carbon precursor, and hydrogen plasma as reactive agent. The PEALD process is able to produce smooth, pure, and low resistivity Co-C thin films with an ideal selflimiting ALD growth fashion. Co-C thin films with a uniform thickness can be found throughout the entire trench with an aspect ratio as high as 20:1.The influences of the precursor pulse time, deposition temperature and input power on the growth rate of Co-C thin films were investigated. When the deposition temperature is 80℃ and the input power is 60 W, the saturated growth rates of the films are 0.065 nm/cycle . XRD and XPS measurements suggest that these films are composed of the amorphous phase. The ALD-synthesized Co-C/carbon cloth catalyst acted as efficient electrocatalyst for HER at low overpotential ($\eta_{10\ mA\ cm-2}$=182 mV) with long-term stability (keeping the activity at least 48 h) in 1 M KOH.

AA-MoP-73 TiO_2 Layer by Low Temperature Atom Layer Deposition for Perovskite Solar Cells*, Q Chen, **Yumeng Wang**, D Wang,* Beijing Institute Of Graphic Communication, China

In PSCs, the n-type electron transport layer (ETL) plays an important role in extracting photo-induced free electrons and suppressing front-surface.The simplification of perovskite solar cells (PSCs) which replaces the mesoporous electron selective layer (ESL) with a planar one is advantageous for large-scale manufacturing and greater selection of flexible substrates.Toward this end, we utilize thermal atomic layer deposition (T-ALD) to deposit ultra-thin (20nm) compact TiO_2 underlayers at 140℃ low-temperature as an eletron transporting layer in planar halide perovskite solar cells.Herein we regulate the electron transport layer energy level by plasma treatment to maintain good carrier extraction.When replacing Sol-gel method with thermal atomic layer deposition,the fabrication of our perovskite solar cells was conducted at low temperatures, which should simplify manufacturing of large-area perovskite devices that are inexpensive and perform at high levels.

AA-MoP-74 Oxides Encapsulation for Surface Passivation of Aluminum Nanoparticles via Atomic Layer Deposition*, **Jiawei Li**, K Qu, J Zhang, X Liu, R Chen,* Huazhong University of Science and Technology, China

Aluminum nanoparticles have attracted great attention for energy storage applications such as solid fuels, aerospace propulsion etc.[1,2] However, Al nanoparticles are easy to be oxidized by moisture and oxygen in ambient condition, which leads to the decrease of energetic metallic Al component. The surface passivation is necessary to enhance the stability of Al nanoparticles for practical applications. This work develops an oxide-encapsulation method for Al nanoparticles via atomic layer deposition to enhance their stability. Different types of oxides are encapsulated on Al nanoparticles. It is found that Al nanoparticles coated by ZrO_2 exhibit excellent corrosion resistance ability against hot water-bath compared with Al_2O_3 coating. The failure mechanisms of Al_2O_3 coating are studied. The generated hydrated oxide such as AlOOH reacts with active Al are responsible for the perforation of Al_2O_3 thin film. For ZrO_2 coating, denser ZrO_2 thin films and the generated interfaces between native Al layers enhance the stability of Al nanoparticles significantly.

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AA-MoP-75 Atomic Layer Deposition of Titanium Oxide-based Electrocatalysts for Li-O Battery*, **Yongliang Li**,* Shenzhen University, China

$Li-O_2$ batteries have been attracted worldwide research interests and considered to be the potential alternatives for the next-generation devices. Nitrogen doped carbon nanofibers (N-CNFs) prepared by electrospinning are used as flexible substrate and the TiO_2-based layers are coated by atomic layer deposition (ALD) and are employed as electrocatalysts for $Li-O_2$ batteries. The TiO_2-based electrocatalysts deliver a high specific capacity, improved round-trip efficiency and good cycling ability. The superior electrochemical performance can be attributed to the superior catalytic activity of TiO_2-based electrocatalysts toward oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) during the discharge/charge processes. This work paves a way to develop the catalyst materials for the future development of high-performance $Li-O_2$ batteries.

AA-MoP-76 Fabrication of Pt Nanoparticles on VN@TaC Porous Structure by Forced-Flow ALD for Proton Exchange Membrane Full Cell*, **Li-Chuan Tsai**, T Chin, T Perng,* National Tsing Hua University

Proton exchange membrane fuel cell (PEMFC) is considered as a promising clean energy because it can convert hydrogen and oxygen into electricity and the only byproduct is water which does not pollute the earth. In PEMFC, Pt is commonly used as the catalyst. In order to maximize the Pt catalytic activity, extensive studies have been made on uniform deposition of nano-sized Pt particles on the catalyst support. Herein, we report a controllable fabrication of Pt nanoparticles on our homemade VN@TaC porous structure by a forced-flow atomic layer deposition (ALD) process for PEMFC. TaC porous structure was first synthesized by a salt flux method, and it showed good electric conductivity, large surface area, and high stability which are the three indispensable requirements for the PEMFC catalyst support. It was then deposited with VO_x by a sol-gel method, followed by reduction in an ammonia atmosphere to form VN@TaC. Here, VN can act as not only a catalyst support but also a cocatalyst for PEMFC, which can enhance the performance of PEMFC with less Pt. For the forced-flow ALD process, the sample powder of VN@TaC was dropped on a glass microfiber filter which was then placed on a stainless steel mesh in the reaction chamber. The precursors, $MeCpPtMe_3$ and O_2, were forced to flow perpendicularly through the filter so that the Pt particles could be more uniformly deposited on VN@TaC than by conventional horizontal flow ALD. The Pt particles were semispherical and 3-6 nm in diameter. For comparison, Pt was also deposited by forced-flow ALD on TaC and VN. All of the three samples, i.e., Pt@TaC, Pt@VN, and Pt@VN@TaC, loaded with approximately 5% Pt, demonstrated higher specific power density than commercial electrode (20% Pt loading on carbon black). More importantly, Pt@VN@TaC showed better performance than Pt@TaC and Pt@VN, that is attributed to the synergistic effect between TaC and VN.

AA-MoP-77 Atomic Layer Deposition of TiO_2 Thin Films on Aluminium Foil: Material Properties and Application as Protective Layer for Food Packaging, *V Dias,* Universidade do Vale do Paraíba, Brasil; ***Rodrigo Pessoa,*** *A Lobo, F Marciano,* Universidade Brasil, Brasil; *H Maciel,* Instituto Tecnológico de Aeronáutica

Several types of coatings have been used for corrosion protection of food packaging [1]. The CO_2-containing beverages such as beer and carbonated drinks have acidity and chlorides in the composition and, when packed in Al cans, can promote the corrosion process by encountering the Al material. To prevent this, commercial Al cans are coated internally by synthetic resins that aims to protect the Al surface from direct contact with the beverage. However, when the resin is not applied correctly or when the Al can undergo mechanical impact or elevated temperatures, the occurrence of localized corrosion is verified due to the presence of pinholes, cracks or grains boundaries in the coatings [2]. In food packaging, the application of ALD technique has already been discussed for the protection and increase of shelf life of products such as paperboard used in food packaging with Al_2O_3 and TiO_2 coatings. However, the synthesis of protective thin films using the ALD process in the field of aluminum cans for carbonated beverages have not yet been reported. The aim of this work was to investigate the TiO_2-covered Al foil properties and evaluate its electrochemical behavior using as electrolyte a commercial beer. The samples were separated into three groups: (i) Al foil, (ii) commercial resin coated Al foil and (iii) Al foil coated with TiO_2 film obtained from ALD process using Beneq TFS-200 equipment. $TiCl_4$ and H_2O were used as precursors at 100ºC, while the reaction cycle number ranged from 500 to 2000. The corrosion resistance was carried out in a potentiostat / galvanostat AUTOLAB302N (Metrohm). The commercial beer was used as electrolyte. RBS, FT-IR and SEM were performed in TiO_2/substrates to investigate the GPC, elemental composition, chemical bonding and surface morphology. The electrochemical impedance spectroscopy (EIS) tests were performed on open circuit potential during 1h. From the potentiodynamic polarization, the corrosion and passivation potential of each sample were measured. To analyze the film strength, the protection efficiency was calculated for each sample. SEM images show that the films tend to follow the substrate surface roughness, even at high film thickness. The EIS results demonstrate an increase of up to five times in the corrosion resistance of aluminum when coated with TiO_2, when compared with bare aluminum foil. The EIS analyses focus on understanding the kinetics of the corrosion process and correlate with film properties.

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AA-MoP-78 Atomic Layer Deposition of Nitrogen-incorporated MoO_x Films: Electrical and Electrochemical Properties, ***Arpan Kumar Dhara,*** *D Saha, S Sarkar,* Indian Institute of Technology Bombay, India

Oxynitrides or nitrogen incorporated oxides of transition metals are rapidly gaining attention in materials research because of their tunable electrical and optical properties. They offer usage in variety of applications like photocatalysis, phosphors, electrochemical energy storage, magnetic materials etc. Primary changes in the material properties after incorporation of nitrogen occur due to the difference in electronegativity, electronic charge and polarizability between oxygen and nitrogen atoms. However, effective and homogeneous doping in the host material is a major practical issue till date. Constructive ways to increase the conductivity without significantly altering the material's chemical properties after doping are still a challenge. Usually nitrogen incorporation is carried out by annealing oxides under NH_3 or N_2/H_2 gas environment. In such circumstances the metal ions are sensitive to reduction which results in the formation of undesirable phases in the doped materials. Also the possibility of dopant inhomogeneity is a major drawback towards obtaining good quality doped materials.

Here we report, amorphous nitrogen-incorporated molybdenum oxide (MoO_x:N) thin films synthesized by atomic layer deposition (ALD) at relatively lower temperature of 170ºC. One ALD cycle of molybdenum nitride (MoN_x) is sandwiched for nitrogen incorporation between two MoO_x layers. The concentration of nitrogen is controlled by varying the ratio of MoO_x/MoN_x layers. Quartz crystal microbalance (QCM) measurement is carried out to study the mass change after every single precursor dosed into the reactor. Secondary Ion Mass Spectra (SIMS) shows the presence of nitrogen throughout the deposited films. Hence uniform inclusion of N-atom is adequately achieved at the reaction temperature. It is observed that conductivity of MoO_x films increase with increase in nitrogen concentration. Room temperature and low temperature electrical properties of different films are also studied in detail to understand the transport mechanism with and without nitrogen incorporation.

Both pristine and N-incorporated MoO_x are deposited on high surface area MWCNTs and applied as anode material in lithium ion batteries. As expected, addition of nitrogen helps to improve the electrochemical performance because of the increased ionic and electronic conductivity.

AA-MoP-79 Deposition of Multi-Component Amorphous Oxide Semiconductor for the Oxide Thin-Film Transistors, ***Jong Beom Ko,*** *S Lee, S Park,* Korea Advanced Institute of Science and Technology, Republic of Korea

Amorphous oxide semiconductor (AOS) thin films are appropriate candidate for the driving devices of the high-end display due to their several important advantages. Mostly, to obtain amorphous phase of oxide semiconductors, two or more cations with different atomic sizes and ionic charges are mixed, and various kinds of AOS materials with multi-component system are reported including IZO, ZTO and ITZO. The most of multi-component of AOS materials are deposited by physical vapor deposition, especially sputter. However, it may cause non-uniformity of electrical characteristics in large area due to heterogeneous distribution of O_2 plasma. In contrast, the atomic layer deposition (ALD) is superior method to deposit films with good uniformity.

In here, the IZO and ITZO films were deposited with plasma-enhanced ALD (PEALD) by feeding metal precursors and oxidize with O_2 plasma. We successfully deposited different composition of IZO and ITZO for the semiconductor and applied to the TFTs. To control the composition of AOS films, the feeding dose of indium precursor was modified while fix the dose amount of another precursor.

From the XRD pattern, we confirm that the phase of the IZO and ITZO films deposited by PEALD was amorphous which appropriate to the active layer due to good electrical characteristics. The composition of the IZO and ITZO films also investigated by means of XPS. As the dose of the indium precursor increase, the indium composition in IZO and ITZO also increase. The different composition of the IZO and ITZO films were applied to the BGBC TFTs as the active layer, and their electrical characteristics were investigated. The linear mobility of the TFTs with IZO was about 18cm^2/Vs and the mobility value was increased as the indium composition of IZO increased. The turn-on voltage (V_{on}) of the IZO TFTs was -1V and it shift to the negative direction as the indium composition increase. For the TFTs with ITZO, the field effect mobility and V_{on} were about 30cm^2/Vs and -1V, respectively. For the measurement of stability at the bias and temperature stress condition, the devices were biased with +20V and -20V at 60^{o}C condition during the 10000 sec. The transfer curve of IZO TFTs were barely shifted during the stress, however, the transfer curve of the ITZO TFTs were shifted about 0.5 and -1V after positive and negative bias, respectively. From the research, we found the feasibility of applying the PEALD process for the multi-component AOS for the oxide TFTs. The composition of the AOS films was easily controlled and showed different electrical properties depending on the composition.

AA-MoP-80 Identification and Improvement of Reliabilities on Oxide Semiconductor TFTs with Al_2O_3 Gate Insulator Layer Deposited by Various Atomic Layer Deposition Process, ***Kyoungwoo Park,*** *G Jeon, S Lee, J Ko, S Park,* Korea Advanced Institute of Science and Technology, Republic of Korea

Among the backplanes for the next generation display, the oxide semiconductor TFTs is receiving the most attention because of its characteristics such as high mobility, high stability, scalability, low process temperature and high transparency. However, due to the intrinsic problem of oxide semiconductors caused by oxygen and hydrogen species, it is hard to control reliabilities under various stress conditions. One of the most effective ways to improve this reliability is defect passivation by hydrogen. However, previous studies have shown that hydrogen can act positive or negative roles in oxide TFTs.

In order to overcome these issues, we investigated the causes of degradation of oxide TFTs by applying Al_2O_3 gate insulator layer (GI) deposited by various atomic layer deposition (ALD) methods using trimethylaluminum (TMA). ALD method was used to determine the factors affecting the positive bias temperature stress (PBTS) and negative bias illumination stress (NBIS) reliabilities by varying the reactants such as H_2O and O_2 plasma in Al_2O_3 GI deposition. In case of TFT with Al_2O_3 deposited by using H_2O reactant, it shows very stable characteristics under PBTS due to hydrogen passivation, however, NBIS has shown unstable results. On the contrary, TFT with Al_2O_3 deposited by using O_2 plasma reactant, it exhibited stable NBIS characteristics but exhibited very unstable PBTS due to plasma-related defects. From the above results, we have confirmed that the hydrogen may passivate the defects at the shallow level, and may also generate the new defects at the deep level in oxide semiconductors. And the influence of hydrogen on the characteristics of oxide TFTs was confirmed by controlling the amount of hydrogen by varying the deposition temperature of Al_2O_3 GI. As a result of measuring the electrical properties of these TFTs with the various deposition temperature of Al_2O_3 GI, there was no significant difference between the devices. However, it was confirmed that the hydrogen contents decreased as the deposition temperature of Al_2O_3 increased, and the NBIS instability was improved from -4.36V to -2.48V. In addition, photoluminescence (PL) analysis results of Al_2O_3 thin films with the various deposition temperature shown that as the number of hydrogen increases, new peaks are generated at the deep level. From the above results, we have confirmed that excessive hydrogens influx can generate new defects at the deep level, which can degrade NBIS reliability.

Based on these results, we will propose the way to improve reliabilities of oxide semiconductor TFTs via GI process optimization.

ALD Applications

Room 107-109 - Session AA1-TuM

Memory Applications: RRAM & Neuromorphic, MIM Capacitors

Moderators: Shi-Jin Ding, Fudan University, Jaeyoung Ahn, Samsung Electronics

8:00am **AA1-TuM-1 Using ALD to Engineer Metal/Insulator/Metal Devices*, John Conley, Jr.,*** Oregon State University **INVITED**

Simple thin film metal-insulator-metal (MIM) devices find application as capacitors (MIMCAPs) in the back-end-of-line (BEOL) of integrated circuits, as tunnel diodes for optical rectenna based IR energy harvesting, in IR detector arrays, in large area macroelectronics, as building blocks for hot electron transistors, and as selector devices to avoid sneak leakage in resistive memory (RRAM) crossbar arrays. This invited talk will highlight how atomic layer deposition (ALD) insulators, nanolaminates, and metal electrodes can be used to engineer interfaces, materials phases, energy barriers to electron transport, turn-on voltage, and non-linearity and asymmetry of current and capacitance vs. voltage characteristics of MIM and MIIM devices [1-7].

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8:30am **AA1-TuM-3 Impact of Metal Nanocrystal Size and Distribution on Resistive Switching Parameters of Oxide-based Resistive Random Access Memories by Atomic Layer Deposition*, Chang Liu,*** *Y Cao, A Li,* Nanjing University, China

Resistive random access memory (RRAM) devices are promising candidates for nonvolatile-memory (NVM), analog circuits, and neuromorphic applications. The mainstream resistive switching mechanism of RRAM is the formation and rupture of nanoscale conductive filament (CF) inside the insulation layer. However, the random nature of the nucleation and growth of the CFs leads to dispersed resistive switching (RS) parameters, which is a major challenge for oxide-based RRAM applications. The introduction of metal nanocrystals (NCs) has been confirmed to improve electrical uniformity of oxide-based RRAM devices significantly.

In this work, we focused on the impact of metal NCs size and distribution on the RS performances of oxide RRAM by atomic layer deposition (ALD) based on experiment results and theoretical calculation. The dependence of ALD cycles of 50~130 during Pt or $CoPt_x$ NCs growth on the RS parameters of Al_2O_3 memory units has been evaluated systematically. Both memory cells with embedded Pt or $CoPt_x$ NCs show similar trends: with increasing ALD cycles, the forming voltage, set/reset voltage, low resistance state/high resistance state, and resistance ratio firstly decrease and then increase. And in the middle region of about 90 and 100 cycles, the lower RS parameters are obtained with flat change and better RS properties. When ALD cycles exceed a critical value of about 110 to 120, the RS parameters suddenly become large with degraded RS performances due to percolation effect. The impact of metal NCs size and distribution on local electric field strength of RRAM devices has been calculated by using the finite element method. Although all metal NCs with various sizes enhance the electric field strength compared to at the planar region, only metal NCs with proper grain size and areal density ($9\ nm/6{\sim}10\times10^{11}/cm^2$ in this work) can effectively produce stronger localized electric field at the tip of metal NCs, leading to optimal RS behavior.

Keywords: resistive random access memory, metal nanocrystals, atomic layer deposition, electrical uniformity

8:45am **AA1-TuM-4 Epitaxial Electronic Materials by Atomic Layer Deposition*, Peter J. King,*** *M Vehkamäki, M Ritala, M Leskelä,* University of Helsinki, Finland

ALD has already delivered unparalleled thickness, conformality and composition control in thin films - enabling the continued scaling of MOSFET and DRAM devices to feature sizes previously thought impossible. Additionally, ALD is now a feature defining tool, using the self-aligned layer principle to set the tolerance of device dimension into the nanoscale.

More control is available from the technique in films that are single crystal and registered to the substrate. The advantages here are improved materials properties and better-defined interfaces for improved device properties.

This talk will explore epitaxial layers produced by ALD, and the possibility of growing multi-layer products with the rationale of enabling future electronic devices. Oxide conductor/semiconductor epitaxial multi-layers will be discussed and the advantages and limitations of ALD examined in this context.

Figure 1 presents a TEM measurement of a 8.5 nm $LaNiO_3$ layer deposited on $SrTiO_3$ substrate, demonstrating epitaxial registration after annealing. The film forms anti-phase boundaries to alleviate the strain from the slightly different lattice parameters and lattice types of the integrated films ($LaNIO_3$ is a rhombohedral crystal and forms a pseudocubic epitaxial relationship with the substrate). In this pseudocubic arrangement films are limited to <10 nm in alternating layers, above this thickness the epitaxy is lost and a polycrystalline product results.

9:00am **AA1-TuM-5 Scaling Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ for Back -end of Line Integration*, Jaidah Mohan,*** *S Kim,* The University of Texas at Dallas*; S Summerfelt,* Texas Instruments, USA*; J Kim,* The University of Texas at Dallas

Although ferroelectric random access memory (FRAM) is the most energy efficient memory device (which can operate at <2 V), it has currently reached its scalability limit at the 130 nm node because of two primary reasons: (i) ferroelectric properties could not be demonstrated below 70 nm in conventionally used $Pb(Zr,Ti)O_3$ (PZT) and (ii) It was impossible to demonstrate reliable ferroelectric performance in trenched or stacked capacitors [1-3]. Further, all conventional memory devices are fabricated in the front-end of line making fabrication and scaling more tedious. In the recent years, Ferroelectricity in doped HfO_2 has attracted much attention because of its simplicity in fabrication using atomic layer deposition (ALD), silicon compatibility, ability to scale down <10 nm and its 3D integration capability [1]. Also, the Ferroelectric properties can be obtained at a temperature of 400°C, making it suitable for back-end of line (BEOL) integration.

In this study, the ferroelectric properties of $Hf_{0.5}Zr_{0.5}O_2$ (HZO), deposited using ALD (Cambridge Nanotech Savannah S100) was evaluated, scaling down up to 5 nm. HZO was deposited using TDMA-hafnium ($Hf[N(CH_3)_2]_4$), TDMA-zirconium ($Zr[N(CH_3)_2]_4$), and O_3 as the Hf-precursor, Zr-precursor and oxygen source respectively at 250°C. Blanket TiN (90 nm thick) electrodes were deposited before and after the HZO deposition as it is believed that the stress exhibited by TiN helps HZO to crystallize into a ferroelectric phase [3]. Then, rapid thermal annealing was done at 400°C in an N_2 atmosphere for 60 s to crystallize the HZO films. A conventional photo-lithography/etching process was used to make capacitors of different diameters. After performing the “wake-up” field cycling, polarization-electric field hysteresis and pulse read/write tests were performed to extract the ferroelectric polarization. 10 nm HZO showed very large polarization ($2P_r \sim 45\ \mu C/cm^2$), saturating at ~1.5 V compared with 7 nm HZO ($2P_r \sim 37\ \mu C/cm^2$ and V_{sat} ~1.2 V) and 5 nm HZO ($2P_r \sim 8\ \mu C/cm^2$ and V_{sat} ~1 V). Nevertheless, scaling HZO and reducing the operating voltage lower than 1 V can benefit the development novel FRAM. It was also seen that further annealing of the 5 nm HZO at 450°C increased the $2P_r$ to ~20 $\mu C/cm^2$ while maintaining the low saturation voltage. Hence, 5 nm HZO annealed at a low thermal budget (450°C)can be a prospective next generation non-volatile ferroelectric memory with back end of line integration capability.

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9:15am **AA1-TuM-6 Atomic Layer Deposition Processes for Logic Device Applications*, Bong Jin Kuh,*** Samsung Electronics **INVITED**

9:45am **AA1-TuM-8 Effect of ZrO_2 Capping-layer on Ferroelectricity of $Hf_xZr_{1-x}O_2$ Thin Films by ALD using Hf/Zr Cocktail Precursor*, Takashi Onaya,*** Meiji University, Japan*; T Nabatame,* National Institute for Materials Science, Japan*; N Sawamoto,* Meiji University, Japan*; A Ohi, N Ikeda, T Chikyow,* National Institute for Materials Science, Japan*; A Ogura,* Meiji University, Japan

Ferroelectric $Hf_xZr_{1-x}O_2$ (HZO) thin films are considered to be promising candidates for future memory device applications such as FeRAM and FeFET, due to its stable ferroelectricity even in extremely thin region (~10 nm) and CMOS compatibility [1]. The HZO films with HfO_2/ZrO_2 nano-laminate structure were typically deposited by the layer-by-layer ALD process [2]. The nano-laminate structure still remains an issue of an ideal ferroelectric HZO film formation. In this study, we investigate the characteristics of the HZO single film deposited by ALD using Hf/Zr cocktail precursor, and discus the effect of a nano-crystallized ALD-ZrO_2 as a capping-layer on the crystallization and ferroelectricity of the HZO films.

The HZO, ZrO_2, and HfO_2 films were deposited on Si/SiO_2 substrates by ALD at 300°C using $(Hf/Zr)[N(C_2H_5)CH_3]_4$ (Hf/Zr = 1/1) cocktail, $(C_5H_5)Zr[N(CH_3)_2]_3$, and $Hf[N(C_2H_5)CH_3]_4$ precursors, respectively, and H_2O gas. The TiN/HZO/ZrO_2/TiN capacitors with a ZrO_2 capping-layer (Cap-ZrO_2) were fabricated as follows: A HZO film was deposited on the TiN bottom-electrode (BE-TiN) by ALD at 300°C. The thickness of the HZO film was varied from 7.5 to 25 nm by changing the number of ALD cycles. Next, a 2-nm-thick ZrO_2 capping-layer was deposited on the HZO film by ALD at 300°C. After that, the annealing was carried out at 600°C for 1 min in a N_2 atmosphere. TiN top-electrodes (TE-TiN) were then fabricated on the ZrO_2 capping-layer by DC sputtering. The TiN/HZO/TiN capacitors (w/o) were also prepared under the same process.

The growth per cycle of the HZO, ZrO_2, and HfO_2 films were estimated to be 0.065, 0.043, and 0.073 nm/cycle, respectively, from the relationship between the number of ALD cycles and the film thickness. The Hf:Zr ratio in the HZO film was estimated by EDS analysis to be 0.43:0.57. Noted that the maximum remanent polarization ($2P_r = P_r^+ - P_r^-$) (23 $\mu C/cm^2$) of the Cap-ZrO_2 capacitor with a 10-nm-thick HZO film was approximately 2 times larger than that (12 $\mu C/cm^2$) of the w/o capacitor. The $2P_r$ of both capacitors decreased as the HZO thickness increased. Moreover, the ratio of ferroelectric orthorhombic phase of the Cap-ZrO_2 capacitor was significantly larger than that of the w/o capacitor. Therefore, we found that the ZrO_2 capping-layer plays an important role for the HZO formation with ferroelectric orthorhombic phase. Based on these experimental results, a HZO film with superior ferroelectricity can be obtained by using ZrO_2 capping-layer.

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ALD Applications
Room 107-109 - Session AA2-TuM
Photo-Chemical Energy

Moderators: Jae Young Hur, Cheonnam National University, Xueliang (Andy) Sun, University of Western Ontario

10:45am **AA2-TuM-12 Efficient Photoelectrochemical H_2 Generation using Molybdenum Disulfide Film on Black Si Photocathode *via* Wafer-scale Atomic Layer Deposition*, Dae Woong Kim,*** *D Kim, T Park,* Hanyang University, Republic of Korea

The hydrogen is an energy source spotlighted as an eco-friendly environmental fuel to replace fossil fuels. Photoelectrochemical (PEC) water splitting is one of the most promising methods for producing such hydrogen. However, high cost of noble metal catalysts such as Pt and low stability of Si photocathode need to be overcome. MoS_2 is an earth-abundant and low-cost electrocatalyst material for hydrogen evolution enabling to substitute for noble metal catalysts. [1] Atomic layer deposition (ALD) is proposed as a reliable and atomic scale-adjustable process for growing MoS_2 directly on Si photocathode with an exact thickness and composition. Furthermore, wafer-scale uniformity of the film even on a complicated nanostructure facilitates a mass production.

In this work, ALD amorphous MoS_2 film was grown on Si photocathode forming a Schottky junction at the interface of MoS_2/Si photocathode, which reduced the overpotential and improved stability of Si photocathode resulting in improved photovoltaic characteristics. Figure 1 shows typical photoelectrochemical current density curves of the PEC cells with MoS_2 layers with various thicknesses. Detailed experimental results will be presented.

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11:00am **AA2-TuM-13 Junction Interface Passivation by ALD in CIGS Solar Cells*, Wei-Lun Xu,*** National Tsing Hua University, Republic of China*; N Koothan,* Instrument Technology Research Center, Republic of China*; J Huang,* Institute of NanoEngineering and MicroSystems*; Y Yu,* Instrument Technology Research Center, Republic of China*; C Ke,* Instrument Technology Research Center*; C Lai,* National Tsing Hua University, Republic of China

Increasing the efficiency of CIGS solar cells is of a crucial topic. One way of increasing the performance of CIGS solar cells is to grow a passivation layer between the CIGS and the buffer layer. The chemical and charge property of passivation layer is used to reduce the recombination between p-type and n-type and helps to increase the efficiency but the layer has to be grown in a certain way that it does not affect the current flow between the absorber layer and buffer layer. Also, the texture of the junction passivation layer has to be maintained to have a better interface. The ALD technique is known for its uniformity and conformal coverage, therefore the junction layer was deposited by ALD without needing any additional patterns. For the first time, we explore the effect of junction interface passivation with different materials including HfO_2 and AlO_x. The mechanism of the passivation effect is discussed in detail. Based on the results, suggestion for the best practice for the passivation is also discussed.

11:15am **AA2-TuM-14 Spatial Atomic Layer Deposition: Up-scalable Route of Metal Oxide Functional Layers for High Efficient and Stable Perovskite Solar Cells and Modules*, Valerio Zardetto,*** TNO/Holst Center, Netherlands*; M Najafi, D Zhang,* ECN, Netherlands*; F Di Giacomo,* TNO/Holst Center*; I Dogan,* TNO/Holst Center, Netherlands*; W Verhees,* ECN, Netherlands*; A Senes, H Lifka, H Fledderus, F van de Bruele,* TNO/Holst Center, Netherlands*; S Veenstra,* ECN, Netherlands*; R Andriessen,* TNO/Holst Center, Netherlands*; P Poodt,* Holst Centre - TNO, Netherlands

Atomic layer deposition (ALD) technique is well acknowledged to fabricate dense, conformal, uniform films over large area with an accurate control of the deposited thickness. ALD has been widely explored in several applications including photovoltaics (PV). In the last 5 years, organometallic halide perovskite solar cells (PSCs) attracts the interest in the PV community, due to the rapid increase in power conversion efficiency (PCE). However, the high performance has been achieved adopting lab scale techniques such as spin coating on small area (< 0.2cm^2).[1] In order to move PSC towards commercialization, large area sheet-to-sheet (S2S) and/or roll-to-roll (R2R) deposition methods are required. Whilst ALD technique has been adopted to deposit several functional metal oxides layers,[2] low deposition rates and the presence of expensive vacuum systems are not desired in the case of a low cost photovoltaic technology based on in-line large area manufacturing processes. Atmospheric pressure spatial atomic layer deposition (s-ALD) can couple the benefits of conventional ALD technique with high deposition rates and the absence of vacuum systems.[3]

In this contribution, we demonstrate the beneficial effect of the introduction of n-type s-ALD layers such as ZnO, TiO_2 and SnO_2 in the perovskite "p-i-n" planar perovskite solar cell. The presence of the s-ALD layer is found crucial to replace the conventional metal top electrode with a semitransparent sputtered ITO, which is required for hybrid tandem PV architectures (i.e., in combination with silicon solar cells). The s-ALD layer prevents sputtering damages during ITO deposition, enabling devices with efficiency up to 17% on small area (0.04 cm^2) and up to 13.5% on an integrated series connected mini-module (4 cm^2). The presence of the s-ALD layer increases the device stability during thermal aging tests. Our standard PSC degrades extremely fast when stressed at 85°C in N_2 environment, losing 90% of the initial performance (PCE_0) after 500hrs. The introduction of s-ALD ZnO enables the device to retain more than the 80% of the PCE_0 after 900hrs. Furthermore, we explored the deposition of s-ALD layers n-type layers in "p-i-n" PSC where the p-type contact and the intrinsic perovskite films have been deposited via S2S slot-die technique. We observe that s-ALD SnO_2 process delivers higher performance (16%

with Al electrode, and 14% with sputtered ITO) with respect to the s-ALD-free PSC (15% with Al contact).

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11:30am **AA2-TuM-15 Applications of Atomic Layer Deposition in Solar Energy Conversion***, **Xianglin Li**, Z Wang, H Fan, A Tok,* Nanyang Technological University, Singapore

Atomic layer deposition (ALD) provides a unique tool for the growth of thin films with excellent conformity and thickness control down to atomic levels. The application of ALD in solar energy research has received increasing attention in recent years. The research focus of our work is focused on the fabrication, surface passivation of nanostructured photoelectrodes based on ALD technique. Various of “host & guest” type composite photoanodes have been designed and fabricated for efficient photoelectrochemical (PEC) water splitting based on ALD. In such a design, a highly porous and conductive nanostructures act as the “host” skeleton it provides direct pathways for faster electron transport, while the conformally coated semiconductor layers act as the “guest” absorber layer. For example, 3D FTO/FTO-NR/TiO_2 composite invers opal structure, Nb--SnO_2 nanosheet/TiO_2 and Nb--SnO_2 nanosheet/Fe_2O_3 heterostructures were designed for PEC water splitting application. Also the ALD thin layer surface passivation and ALD ZnSnO, Zn(O, S) Cd-free buffer layers for CIGS solar cells were studied. Challenges and future directions of ALD in the applications of solar conversion will be discussed.

11:45am **AA2-TuM-16 Inorganic Charge Transport Layers Grown via Atomic Layer Deposition for Highly Stable and Efficient Perovskite Solar Cell***, **Seongrok Seo**, S Jeong, C Bae, N Park, H Shin,* Sungkyunkwan University, Republic of Korea

Despite the high power conversion efficiency (PCE) of perovskite solar cells (PSCs), poor long-term stability is one of the main obstacles preventing their commercialisation. Several approaches to enhance the stability of PSCs have been proposed. However the accelerating stability test of PSCs at high temperature under the operating conditions in ambient air remains still to be demonstrated. Herein, we show interface engineered stable PSCs with inorganic charge transport layers (*p*-NiO and *n*-Al:ZnO grown *via* atomic layer deposition (ALD)). First of all, NiO has been chosen as hole transporting layers due to its a wide band gap (~3.6 eV) and *p*-type semiconducting porperties. It also has good optical transparency and high chemical stability, and thus has the capability aligning the band edges to the perovskite ($CH_3NH_3PbI_3$) layers with efficient energy transfer. Ultra-thin and un-doped NiO films with much less absorption loss were prepared by ALD with highly precise control over thickness without any pinholes. Thin enough (5–7.5 nm in thickness) NiO films with the thickness of few time the Debye length (L_D = 1–2 nm for NiO) show enough conductivities achieved by overlapping space charge regions. Second, t he highly conductive Al doped ZnO films have been chosen as an efficient electron transporting layers while acting as dense passivation layers. This layer prevents underneath perovskite from moisture contact, evaporation of component, and reaction with a metal electrode. Finally the inverted-type PSCs with inorganic charge transport layers exhibited a PCE of 18.45 % and retained 86.7 % of the initial efficiency for 500 hours under continuous 1-sun illumination at 85 °C in ambient air with electrical biases (at maximum power point tracking).

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ALD Applications
Room 113-115 - Session AA-TuA
Active Matrix Device and Material

Moderators: Soo-Hyun Kim, Yeungnam University, Ganesh Sundaram, Ultratech

4:00pm **AA-TuA-11 Amorphous In-Ga-Zn-O Thin-Film Transistor-Based Nonvolatile Memory Devices***, **Shi-Jin Ding**,* Fudan University, China **INVITED**

In recent years, amorphous indium-gallium-zinc-oxide (a-IGZO) thin-film transistor (TFT) nonvolatile memor ies have been widely researched as next-generation memory devices for flexible electronic systems and transparent panel systems. This is because a-IGZO has many advantages over conventional amorphous or polycrystalline silicon, such as high electron mobility, good uniformity, low processing temperature, and transparency in the visible region of the spectrum.

In this talk, I will talk about several types of a-IGZO TFT memory devices: (1) the a-IGZO TFT memory device with ALD Zn-doped Al_2O_3 charge storage layer. It exhibited fast programming characteristics and very good electron retention. The light emitting from a halogen tungsten lamp could be used to erase the programmed device, and the monochromatic light-assisted electrical erasing could increase the erasing efficiency, which was further enhanced with reducing the wavelength of the monochromatic light; (2) The a-IGZO TFT memory device with ALD Pt or Ni nanocrystals. It exhibited a high programming efficiency, and the programmed device could be erased efficiently by UV light or bias-assisted monochromatic light; (3) multi-level cell a-IGZO TFT memory with an IGZO or ALD ZnO charge trapping layer. When the fresh device was programmed at a positive or negative gate bias, a positive or negative threshold voltage shift was obtained compared with the fresh device. Therefore, a large memory window was achieved at relatively low operating voltages. Moreover, the memory device demonstrated electrically programmable and erasable characteristics between different states as well as good data retention.

In conclusion, the above memory devices could have promising applications in one-time programmable memory, light-erasable memory, UV detectors and electrically programmable and erasable memory.

4:30pm **AA-TuA-13 Atomic Layer Deposition of Elemental Tellurium for Composition Tuning Of Ovonic Threshold Switching Materials***, **Stephen Weeks**, G Nowling, V Adinolfi, V Narasimhan, K Littau,* Intermolecular, Inc.

Recent work on resistive switching based non-volatile memory (NVM) technologies has shown their potential for use in next generation data storage applications. In these next generation applications, NVM devices are required to be packed densely in cross-bar memory arrays that require a selector device, such as the ovonic threshold switch (OTS), in series with the memory element to minimize parasitic currents in the memory array.[1] To be cost competitive, the NVM architecture must also be of a high areal density, making three dimensional (3D) integration of both the memory and selector active layers attractive. To obtain this, there is a need for the development of atomic layer deposition (ALD) processes for the materials used in both the memory and selector elements deployed in these memory arrays.

In this work, we focus on the $GeTe_x$ material system. This system is known to exhibit phase change memory (PCM) behavior near the GeTe composition[2] and OTS behavior at the $GeTe_x$(x=4-6) compositions.[3,4] While a number of processes have been reported demonstrating the ALD of GeTe,[5,6] to date no report exists of ALD for the OTS relevant range of this material system, $GeTe_x$(x=4-6). Here, we report for the first time the ALD of elemental tellurium and use this process to tune the composition of $GeTe_x$. Elemental Te ALD was accomplished by reacting $[(CH_3)_3Si]_2Te$ with the alkoxide $Te(OC_2H_5)_4$. The Te deposition was observed to be conformal (see supplemental information). We discuss growth and nucleation behavior of ALD Te observed on Si, TiN, and GeTe substrates. Beyond this, we report the development of a TeO_2 ALD process utilizing $Te(OC_2H_5)_4$ and H_2O to encourage Te growth on surfaces where island like nucleation is observed to limit film closure. Finally, we deposit ALD GeTe using the recently reported $HGeCl_3$+$[(CH_3)_3Si]_2Te$ process of Gwon et al.[6] and utilize the ALD Te process to increase the Te content of the film to compositions relevant for OTS applications. These results provide a pathway towards using conformal elemental Te to tune the composition of chalcogenide films deployed in PCM and OTS applications using an all ALD approach.

References:

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4:45pm **AA-TuA-14 Plasma Enhanced Atomic Layer Deposition of Low Temperature Silicon Nitride for Encapsulation Layer using Novel Silicon Precursor***, **SungGi Kim**, S Jang, J Park,* DNF Co. Ltd, Republic of Korea*; H Jeong,* DNF Co. Ltd*; J Park, G Park, S Lee, M Kim,* DNF Co. Ltd, Republic of Korea

OLED(Organic Light Emitting Diode) has characteristics of self-emission, high-speed response, wide viewing angle, ultra-thin type, and high image quality, and is the spotlight in the display field. However, in the case of an OLED device, there is a problem that the lifetime is shortened and the device performance is lowered due to deterioration and oxidation of a light emitting material and an electrode material due to oxygen and moisture. In order to overcome these disadvantages, encapsulation techniques capable of blocking oxygen and moisture are very important in OLED devices. Recent thin encapsulation technology and hybrid encapsulation technology in flexible OLED panels. Thin film encapsulation technology is used by laminating organic film, inorganic film or inorganic film. Typical inorganic films include Al_2O_3, SiO_2, and SiN_x.

In this paper, a silicon nitride film was deposited with NH_3 and N_2 PEALD (plasma enhanced atomic layer deposition), using a new silicon precursor (Figure 1) on PEN (polyethylene naphthalate) films at various RF time conditions. The PEALD one cycle is made of 6 steps (Si precursor - Purge - NH_3 Reactant - Reaction Purge - N_2 Reactant - Reactant Purge) and the deposition temperature is 90℃. The encapsulation layer property was measured by WVTR(Water Vapor Transmission Rate) using a MOCON AQUATRAN Model 2 and the measurement time is over 100 hours. The deposited silicon nitride film with a 300Å thickness showed excellent WVTR characteristics below 1.00 x 10^{-4} g/m^2·day. It looks like a saturation behavior at above 300Å thickness, but we expect to be lower. Because it was measured below the detection limit (1.00x10^{-4}g/m^2•day) of MOCON AQUATRAN Model 2.

5:00pm **AA-TuA-15 Atomic Layer Delta Doping and Deposition of Ultrathin Metallic TiN-based Channel for Room-temperature Field Effect Transistor***, **Yu-Tung Yin**, P Cheng, C Wang, T Chang, T Shen, Y Cai, M Chen,* National Taiwan University, Republic of China

Under sub-10 nm technology node, the metallic channel transistors have been proposed as one of the possible candidates. However, the conductivity modulation in metallic channels can only be observed at low temperature, which is usually below 100 K. By using the atomic layer delta doping and deposition (AL3D) technique, the thickness and electron concentration of oxygen-doped TiN metallic channel has been precisely controlled, and the room-temperature field effect and modulation of the channel conductivity on TiN metallic channel were achieved in this study. The reduction in electron concentration and the blue shift of absorption spectrum were observed with the decrease of the channel thickness, which can be explained by the onset of quantum confinement effect. Similarly, the oxygen incorporation using the AL3D tehnique also results in the reduction in electron concentration and the blue shift of absorption spectrum, which can be deduced from the increase of the interband gap energy due to the oxygen oncorporation. Since the electron concentration was significantly modulated by the AL3D process, the screen effect was dramatically suppressed in the oxygen-doped TiN metallic channel. In addition, owing to the quantum confinement effect and the suppressed screening effect, the modulation of channel conductivity from the gate electric field can be achieved at room temperature in the precisely controlled oxygen-doped TiN ultrathin-body channel with the thickness down to 4.8 nm and the oxygen content up to 35%.

5:15pm **AA-TuA-16 Influences of Annealing Conditions on Characteristics of Sn-doped Zinc Oxide Thin Film Transistors Fabricated by Atomic Layer Deposition***, **Tao Wang**, H Lu, J Yang, W Liu, S Ding, D Zhang,* Fudan University, China

Transparent oxide semiconductors employing a tin-doped zinc oxide (TZO) thin film generated via atomic layer deposition (ALD) at low temperature (150°C) are investigated for their feasibility into high performance thin film transistor (TFT). The resistivity of the as-deposited uniform TZO film is as low as 1.9×10^{-2}Ω cm. The carrier concentration is high up to 4.9×10^{19}cm^{-3} and the optical transparency is greater than 80% in visible range. The TZO thin film transistors exhibit excellent electrical and optical properties. In addition, the insights into the dependency of the impurities within the channel layer upon thermal annealing of the oxide film are presented. Studies towards an optimized annealing temperature (300°C) result in a high device performance in enhancement mode with a field effect mobility (μ_{FE}) of 13.7cm^2/Vs and a subthreshold swing (S.S.) of 0.15V/dec. The performance of the TZO TFTs relies on carriers and defects in SnZnO and near the back-channel surface of SnZnO as well as the quality of the gate dielectric/SnZnO interface. Compared with the pristine devices, the TFT performance turned out to be dependent on the annealing temperature because of growing grain size and decreasing interface defects. These findings on the influence of annealing conditions allow for a better understanding on the formation of the active semiconductor channel and serve towards the applicability of ALD based transparent oxide semiconductors in next generation electronics.

ALD Applications

Room 116-118 - Session AA1-WeM

Display Device and Material

Moderators: Kwang Soo Lim, LG Display, Chang-Yong Nam, Brookhaven National Laboratory

8:00am **AA1-WeM-1 Growth Of Indium Oxide Thin Films Based On A Plasma Enhanced Atomic Layer Deposition Technique*, Joaquin Alvarado, L Martinez,*** University of Puebla, Mexico*; M Chavez,* CINVESTAV-IPN, Mexico*; S Alcantara, D Cortes,* University of Puebla, Mexico*; S Gallardo,* CINVESTAV-IPN, Mexico

Indium oxide is a wide band-gap transparent n-type semiconductor with a body centered cubic structure (a=1.012 nm) and relatively high electrical conductivity, in its non-stoichiometric form it has been widely used in the microelectronic field for gas sensors, window heaters, solar cells, memory devices, transistors, chemical and biosensors, transparent conducting electrodes, some types of batteries, hot mirrors, and also for transparent electronics [1].

It is expected that lowering the film dimensions or increasing the surface-to-volume ratio of the material can improve the performance of those applications; thus, several researchers worldwide have dedicated considerable efforts to the synthesis of In_2O_3 nanostructures such as nanowires, nanoparticles and thin films with a few nanometers of thickness [2].

Considering a homogeneous deposition, in this work we present a comparison of the growth of In_2O_3 thin films by thermal ALD and plasma enhanced atomic layer deposition PEALD at different temperatures, where we expect to get optical and/or electrically favorable layers to improve the performance of solar cells as well as a capacitor in order to use it as the base of a cost effective thin film transistor (TFT) suitable for radiation sensors (x-rays, alpha and gamma radiation) at low temperatures.

Figure 1 left shows that quite similar transmittance is obtained between In_2O_3 layers deposited by both ALD methods at the same temperature, where the ones deposited at 150ºC shows high transparent layers. Also, Figure 1 right depicts the absorbance of these layers as well as its band-gap, which is close to 3.2eV. Furthermore, Tauc plot calculation allows extracting a correct band-gap for each sample, being the layers grown by thermal ALD the ones that present higher band-gap that the ones grown by plasma. We will also present optical, electrical and elemental characterizations such as XRD, SEM, Transmittance, Reflectance, SIMS, AFM, Profilometry, C-V Curves and I-V Curves to explain the characteristics and applications of the material.

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8:15am **AA1-WeM-2 Large-Area Atmospheric Pressure Spatial ALD for Display Applications***, C Frijters, F van den Bruele, A Illiberi,* ***Paul Poodt,*** Holst Centre - TNO, Netherlands **INVITED**

Atmospheric pressure Spatial ALD (sALD) is able to deliver high deposition rates while maintaining the advantages of conventional ALD, such as low defect density, high conformality and thickness uniformity. First industrial applications of Spatial ALD include passivation of c-Si solar cells and roll-to-roll manufacturing of flexible barrier foils. An emerging application for Spatial ALD is flat panel (OLED) displays. Examples include semiconducting and dielectric layers for use in thin-film transistors, and thin-film encapsulation for flexible OLED displays. As today's displays are fabricated using glass panels in the order of several square meters, a remaining challenge is the development of large-area Spatial ALD deposition technology that is able to combine high throughput with uniform performance across very large areas.

We are developing large-area Spatial ALD technology, and as a first step between the lab and the display fab, we have installed a large area Spatial ALD sheet-to-sheet tool which can handle up to 400x325 mm^2 sized substrates. With this tool we are able to deposit uniform films across a deposition width of 400 mm. The whole tool is operated under an atmospheric pressure but inert N_2 environment. The tool can be used to deposit a variety of materials using both thermal and plasma-enhanced Spatial ALD. We will present the basic deposition performance of the tool in terms of thickness- and compositional uniformity. Large-area thickness non-uniformities of less than 1% are achieved for several oxide materials. Next, we will focus on two display-related applications: thin-film encapsulation of OLED devices, and high mobility InZnO and InGaZnO semiconductors for thin-film transistors. We will explain the requirements, the deposition process and the performance of the deposited films. Finally, the challenges in up-scaling Spatial ALD to plate sizes of 1.5 m and beyond will be discussed.

8:45am **AA1-WeM-4 Amorphous Indium Zinc Tin Oxide (IZTO) Semiconductor Materials and the Associated Thin Film Transistor Properties Deposited by Atomic Layer Deposition*, Jiazhen Sheng,*** *T Hong,* Hanyang University, Republic of Korea*; J Lim,* Samsung, Republic of Korea*; J Park,* Hanyang University, Republic of Korea

Oxide semiconductor thin film transistors (TFTs) have been extensively researched as a backplane technology in display industry. Comparing to the indium gallium zinc oxide (IGZO) which has been widely used as TFT active layer ma terial, indium zinc tin oxide (IZTO) has been suggested as a promising material due to its attractive performance, including relatively high mobility (>25cm^2/Vs) and superior stability. Relying on the self-limiting reaction, the atomic layer deposition (ALD) takes advantage of uniformly depositing the films over large areas with precisely controlled thickness that makes ALD become a promising technology to apply in thin film transistor, including of active layer fabrication. In this research, the ALD Sn doped IZO thin film was first investigated, which was deposited using the concept of "super-cycle" – IZO (1 cycle InOx – 1 cycle ZnO), IZTO111 (1 cycle InOx – 1 cycle ZnO – 1cycle SnOx) and IZTO112 (InOx 1 cycle – 1 cycle ZnO – 2cycle SnOx). It is found, by doping with SnOx, the band gap structure, micro-structure as well as the electrical characteristics were changed. Then, the bottom gate top contact IZO, IZTO111 and IZTO112 thin film transistors were fabricated by ALD process. The devices with Sn doped IZO active layer exhibited increased mobility (27.8cm^2/Vs for IZTO111 and 22.7cm^2/Vs for IZTO112) and stability under positive bias temperature stress (threshold voltage shift of 1.8V and 0.7V) than IZO TFTs (mobility of 18.0cm^2/Vs and threshold voltage shift of 2.2V). The flexible ALD IZTO TFT also fabricated on the PI substrate, and 200,000 cycles bending test was processed to investigate the degradation mechanism of flexible ALD TFT under mechanical stress.

9:00am **AA1-WeM-5 Evaluation of Si precursor for SiO_2 OLED Encapsulation by PEALD*, GunJoo Park,*** *J Park, B Yang, S Kim, J Park, S Jang, S Lee, M Kim,* DNF Co. Ltd, Republic of Korea

OLED devices are made up of organic compounds, which are excited to emit light due to the nature of the material. In this excited state with high energy, it easily reacts with moisture and oxygen. When the OLED element reacts with moisture and oxygen, problems such as decrease in luminance, increase in voltage, and poor emission occur.

Recently, TFE (Thin Film Encapsulation) technology has been used to overcome this problem. The OLED encapsulation technology using a thin film can provide the display flexibility and effectively prevent the infiltration of air and moisture into the organic layer of the OLED device, which is suitable as a next generation display encapsulation film.

In this paper, NSi-01 and 1N5 precursors were applied to thin film encapsulation technology for next generation OLED devices, and low-temperature SiO_2 deposition process by PEALD method was developed. In both precursors, SiO_2 deposition conditions were similar, and RF dosage experiments confirmed their suitability as ALD precursors.

High growth rate of 1.95 Å / cycle and 2.65 Å / cycle (Fig.2) and formation of pure silicon oxide film free of impurities were confirmed (Table.1).

The density of the SiO_2 thin film was 2.23 g / cm^3 (Table.2) for both precursors, and the bulk SiO_2 density was 2.6 g / cm^3, indicating that an amorphous SiO_2 thin film was formed. The encapsulation layer affects the image quality and brightness of the display when the visible light transmittance is decreased. In the case of the precursor used in this experiment, the visible light transmittance was 99% at a thickness of 700Å (Table.2). It can be seen that there is no difference in image quality or brightness after applying the encapsulation layer .

The moisture permeability, which is the core of the encapsulation layer, varies with RF time and thickness. In case of NSi-01 with a thickness of 700Å, the RF time was 0.9 seconds at 4.6 × 10^{-3} g / m^2-day. In case of 1N5, the RF time was 1.5 seconds at 5.0 × 10^{-3} g / m^2-day Sufficient RF dosage is required compared to NSi-01. However, in case of 1N5, high film growth rate was confirmed compared to NSi-01, and the actual process time was confirmed to be similar. We also confirmed the excellent WVTR characteristics of 5.5 × 10^{-3} g / m^2-day even at a thin thickness 500Å (Fig.6), thus confirming the possibility of the next generation OLED element encapsulation film precursor.

9:15am **AA1-WeM-6 Hydrogen Barrier Properties of ALD Al_2O_3 with Different Oxidants***, H Kim,* ***Yujin Lee****, T Nam, S Seo, C Lee,* Yonsei University, Republic of Korea*; J Yang, D Choi, C Yoo, H Kim,* LG Display

Amorphous In-Ga-Zn-O (a-IGZO) semiconductors have been used as an active channel material in high mobility, flexible, and transparent thin film transistors (TFTs), but it is highly influenced by the external environment. To protect from it, plasma-enhanced chemical vapor deposition (PECVD) SiN_x deposited using SiH_4/N_2O is commonly used as the encapsulation film. In this process, however, the amount of hydrogen was introduced to backchannel.[1] It is well known that the hydrogen in an oxide semiconductor acts as a shallow donor by ionizing and bonding with oxygen to form hydroxyl bonds. It makes the oxide TFT very conductive and causes it not to show an on/off property.[2] Therefore, appropriate hydrogen barrier is required to prevent hydrogen incorporation into the IGZO channel, but there is a lack of systematic research on it.

In this study, Al_2O_3 was deposited on the a-IGZO TFT by atomic layer deposition (ALD) using trimethylaluminum(TMA) with water or O_3, as the precursor and oxidant, respectively, at low temperature (about 60°C). First, we fundamentally investigated the characteristics of Al_2O_3 according to the oxidant. The composition of the Al_2O_3 was different depending on the oxidant used in the ALD process. Based on this, we analyzed the effect of these characteristics on hydrogen barrier properties by using transfer curve and stress test of device. As a result, the device in which the Al_2O_3 was deposited exhibited excellent hydrogen barrier properties as compared with the bare device. There was no device degradation after the hydrogen treatment, which suggested the possibility of enhancing the device reliability in mass production in the future.

Reference

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9:30am **AA1-WeM-7 Flexible Al_2O_3/Organic Multilayer Moisture Barrier Films Deposited by Spatially Resolved ALD Processes in a Single Chamber***,* ***Sang Heon Yong****, S Kim, Y Choi, H Hwangbo, H Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Thin film encapsulation (TFE) is one of essential technologies required for flexible organic light emitting diode (OLED) display devices. It is well known that organic materials are easily damaged by moisture and oxygen when plastic films are adopted for substrates. Atomic layer deposition (ALD) processes on plastic films demonstrated superior moisture barrier property to other inorganic barrier deposition processes.[1] However, extremely low throughput of ALD processes is a big huddle for commercialization and active research on 'spatial ALD' process is underway to enhance throughput. [2] To improve the barrier property further and to increase flexibility of barrier films simultaneously, various multilayer structures have been reported with various inorganic and organic layers. Since the multilayer structure consists of several thin films, the diffusion path of the barrier film can be increased and flexibility can be increased by reducing the bending stress of thin films. [3]

In this study, we deposited Al_2O_3 and organic layers in a single spatially-resolved processing chamber and demonstrated multilayer structures to achieve high barrier property and flexibility. The water vapor transmission rate (WVTR) of Al_2O_3 single thin films decreases significantly above 10nm thickness as shown in Figure 1. Organic layers were also deposited in the same chamber by plasma-enhanced chemical vapor deposition. About 20nm or thicker organic layers are required to improve the barrier film flexibility in this experiment. The total of 21 layers of Al_2O_3 and organic layers are deposited alternately and WVTR of 8.5 10^{-5} g/m^2·day was achieved. The WVTR increases by 10%, 21% and 32% in 3cm, 1.5cm and 1cm bending radius, respectively.

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9:45am **AA1-WeM-8 Optimization of Film Structure by Stress Engineering for Flexible Thin Film Encapsulation***,* ***Ju-Hwan Han****, D Choi, J Lee, K Han, J Park,* Hanyang University, Republic of Korea

Flexible electronics are focused recently as future-oriented devices such as light emitting device, sensing device and photoelectric cell. One of critical issues is a rapid degradation by oxygen and water vapor in flexible organic light emitting diodes (OLEDs) devices. Thus, thin film encapsulation (TFE) process is highly recommended to protect the OLEDs from water vapor and also preserve their flexibility. The inkjet printing and PECVD methods have been comerciallized to make orgniac/inorganic hybride layer. Unfortunately, they have some limits on flexible OLEDs; not only poor step coverage and particle issues but also cracking films under mechanical stress conditons. Atomic Layer Deposition (ALD) can be a promising candidate to solve the above issues.

In this study, we optimized the TFE layer via the stress engineering using organic/Al_2O_3 ALD hybrid films. In order to suggest optimized structure for flexible gas diffusion barrier layer, we investigated water vapor transmission ratio (WVTR) of the layer under the bending stress as a function of thickness of substrate, thin film and additional layer on the thin film. With additional layer of similar thickness to the substrate, the degradation of TFE layer is minimum (W/W_0 ~ 1.08, bending radius of 2.5mm). And there was almost no degradation of TFE layer with more than 2 dyads of organic/Al_2O_3 layer (W/W_0 ~ 1.01, bending radius of 2.5mm). As a result, optimized TFE layer structure using inorganic/organic layer showed not only improved moisture barrier property, but mechanically robust behavior after bending stress.

ALD Applications
Room 116-118 - Session AA2-WeM
Flexible Application

Moderator: Jin-Seong Park, Hanyang University

10:45am **AA2-WeM-12 A Condense Polymer-inorganic Hybrid Nanolayer with Extremely Low Gas Transmission Rate Behavior and Ultra-flexible Nature***,* ***Myung Mo Sung****,* Hanyang University, Republic of Korea

Hermetic sealing is an important technology to isolate and protect air-sensitive materials, and a key issue to develop foldable and stretchable electronic devices. We reported an ultrahigh gas-proof polymer hybrid nanolayer, prepared by filling the free volume of the polymer with Al O by using gas-phase atomic layer infiltration. The free-volume-free polymer-inorganic hybrid shows extremely low gas transmission rate behavior, which is below the detection limit of the Ca corrosion test (< 10 g m day). Furthermore, due to the ultra-thin complete hybrid of polymer-inorganic materials, the polymer hybrid nanolayer has ultra-flexible nature, which is useful as hermetic sealing for stretchable and foldable electronic devices.

11:00am **AA2-WeM-13 SiN-Al_2O_3 Nano-laminates Fabricated with Combination of CVD-ALD Method for Encapsulation of Highly Stable Flexible OLED Electronics***,* ***Huizhi Yang****, Y Li, Y Liu, K Cao,* Huazhong University of Science and Technology, China*; H Hsu, J Huang,* Wuhan China Star Optoelectronics Technology Co., Ltd (CSOT), China*; R Chen,* Huazhong University of Science and Technology, China

The expansion demand for wearable and flexible electronics based on organic light emitting diode (OLED) displays have attracted great attention. Flexible OLED displays, however, widely utilize materials that are sensitive to oxygen and water which causes performance degradation or failure during usage. It is imperative to develop reliable and efficient thin film encapsulation methods to improve the stability and meet the requirements of miniaturization, flexibility and low cost.

This work focuses on the design and fabrication of nano-laminates SiN-Al_2O_3 encapsulation films for high stable flexible OLED electronics with the combination of plasma enhanced chemical vapor deposition (PECVD) and spatial separated atomic layer deposition (S-ALD) methods. SiN layer is deposited on OLED devices with ~1 um thickness via PECVD, after which ~20 nm Al_2O_3 is deposited on the SiN layer with S-ALD. The service life of encapsulated devices is tested under heat/humid environment. The failure time of nano-laminates SiN-Al_2O_3 encapsulated device is enhanced ~10 times compared with SiN or Al_2O_3 coating alone. The coating layers configurations play an important role in determining the encapsulation ability. It is found that the SiN layer fabricated by PECVD contains large amount of pinholes and defects. After very thin layer of Al_2O_3 deposited, most of defects are passivated and the water-oxygen resistance ability is enhanced significantly.

11:15am **AA2-WeM-14 Thermoelectric Device Based on ALD/MLD-grown ZnO and ZnO:benzene Thin Films on Flexible and Textile Substrates**, ***Giovanni Marin**, M Karppinen,* Aalto University, Finland

We have fabricated simple flexible thermoelectric devices on different substrates, such as plastics, flexible glass and different textiles, using ALD-grown ZnO and ALD/MLD-grown coatings as the active thermoelectric materials. In the hybrid ZnO:benzene superlattice thin films monomolecular benzene layers are inserted in between ZnO blocks of varying thicknesses to block the thermal conductivity.[1], [2]

The thermoelectric performance of the devices with the different ZnO and ZnO:benzene layer structures were tested with an applied (cross plane) temperature varying between 30 and 100°C at the bottom side of the substrate. The voltage generated by the device with the varying temperature was measured for both open-circuit and with a load of 1.4 Ω. The hybrid ZnO:benzene devices exhibited enhanced performances compared to those based on plane ZnO.

The final goal of our work is in wearable devices fabricated on textile. Such devices would enable energy harvesting from human body heat to power small sensors (constant medical monitoring) without the need of changing batteries. The current results based on simple model device architectures have provided us useful knowledge and guidelines towards this final goal.

11:30am **AA2-WeM-15 Transparent Graphene Heater Improved by Defect Healing of Metal Atomic Layer Deposition**, ***Hyun Gu Kim**, W Kwon, T Im, M Khan,* Incheon National University, Republic of Korea*; H Choi,* Yonsei University, Republic of Korea*; W Kim,* Chonbuk National University, Republic of Korea*; J Chung,* Soongsil University, Republic of Korea*; H Lee,* Incheon National University, Republic of Korea

Graphene has been widely applied for various applications, such as flexible display, energy device, and transparent electrode due to its superior properties over bulk materials in transparency, flexibility, and electrical conductivity. Until now, many methods to synthesize graphene have been reported, such as physical exfoliation, epitaxy, chemical vapor deposition (CVD), and chemical reduction of graphene oxide (GO). Since the chemical reduction of GO has a high rate of obtaining graphene as a single layer, it can be used in a wide variety of applications through the formation of a complex with other materials as well as high compatibility with mass production. In many cases, however, the reduced GO (RGO) is not completely reduced and many defects are left, so there is a disadvantage that reliability such as electrical properties is deteriorated. When the GO is reduced to RGO, the functional groups of the graphene surface remain or are not restored to the original structure of the graphene. In order to avoid such problem, researches for improving the conductivity by healing defects of RGO have been reported in recent years. In this study, a selective metal deposition process by atomic layer deposition (ALD) was applied on the surface of RGO to study the defect healing of RGO. Since the ALD process involves deposition only through a surface reaction, it is able to perform selective deposition at defective sites that have a relatively high energy. The surface coverage of Pt deposited on RGO was analyzed by using various analytical methods, including field emission electron microscopy (FE-SEM), X-ray photoelectron spectroscopy (XPS), and THz spectroscopy. In order to confirm the defect healing effect, the thermal characteristics of the heater were prepared by using a transparent graphene heater before and after healing the defect. In addition, the self-healing of damaged self-healing polymers was studied suing the thermal properties of the heater.

11:45am **AA2-WeM-16 Surface Modification Studies and Stabilization of Perovskite Quantum Dots with Atomic Layer Deposition**, ***Binze Zhou**, Q Xiang, K Cao, R Chen,* Huazhong University of Science and Technology, China

Perovskite quantum dots (QDs) have received extensive attention for potential display applications, due to their excel lent prop erties for high photoluminescence, tunable wavelength, and narrow emission wavelength [1]. However, perovskite QDs are very sensitive to air, and hot/humid atmosphere which tend to failure in practical applications.[2,3] In this work, atomic layer deposition (ALD) is applied to modify and encapsulate the surface of perovskite QDs with thin layers of oxides to enhance the stability during usage. To study the surface interaction mechanisms of ALD precursors with the ligands of perovskite QDs, in-situ characterizations such as quartz crystal microbalance (QCM), infrared spectrometer (IR) are applied to monitor the ALD process. It is found that process parameters, such as deposition temperature, precursors and pulse time are critical to its surface modification behavior. Higher temperatures resulted in etching or replacing the surface ligands of perovskite QDs by ALD precursors. At room temperature, the perovskite QDs films can be stabilized effectively with just few cycles of oxide passivation, and the light emitting diode's performance has also enhanced.

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ALD Applications

Room 107-109 - Session AA3+AF+EM-WeM

AA+AF+EM

Moderator: Iian Buchanan, Versum Materials, UK

8:00am **AA3+AF+EM-WeM-1 Fabrication of TiO_2 Interconnected Nanotubes by ALD and Synthesis of g-$C_3N_4/Au/TiO_2$ Heterostructure for Photocatalytic Water Splitting**, ***Li-Chen Wang**, L Tsai, C Liu, T Perng,* National Tsing Hua University, Republic of China

Recently, the catalysis science has ascended to a new horizon due to the advent of novel nanotechnologies such as atomic layer deposition (ALD) with the capability of fabricating a marvelous panoply of nanomaterials. The sequential and self-limiting gas-solid surface reactions of the ALD process enable to deposit extremely conformal and ultrathin film on a wide variety of templates, favoring the innovative design of various nanostructured photocatalysts. Herein, we report a controllable fabrication of a hybrid photocatalyst comprising graphitic carbon nitride (g-C_3N_4), Au nanoparticles, and TiO_2 hollow fibers for photocatalytic water splitting. Titanium tetrachloride ($TiCl_4$) and H_2O were used as precursors for the ALD process to uniformly deposit a thickness-controllable TiO_2 thin film on hollow polysulfone fibers (PSFs). In order to minimize the e^--h^+ pair recombination, the TiO_2 hollow fibers were further decorated with Au nanoparticles by chemical reduction and then coated with a g-C_3N_4 nanolayer by pyrolysis of urea at a certain elevated temperature. For comparison, Au/TiO_2 hollow fibers and Au/g-C_3N_4 nanosheets were also prepared and individually used as photocatalysts for water splitting. It was demonstrated that the photocatalytic efficiency of the g-$C_3N_4/Au/TiO_2$ heterostructure could be influenced by the thickness of the TiO_2 thin film which can be tailored by the ALD cycle number. TiO_2 with perfect conformality on the porous PSF template also offers a large surface area of the hybrid catalyst and efficient trapping of the reflected photons within the interconnected nanotubes of the hollow fibers. More importantly, the surface plasmon resonance (SPR) effect of Au nanoparticles and the g-$C_3N_4/Au/TiO_2$ heterostructure that could effectively increase the separation of e^--h^+ pairs further enhance the photocatalytic efficiency of g-$C_3N_4/Au/TiO_2$ for water splitting when compared to those of Au/TiO_2 and Au/g-C_3N_4.

8:15am **AA3+AF+EM-WeM-2 Nano-energetic Materials Fabricated by Atomic/Molecular Layer Deposition**, ***Hao Feng***, Xi'an Modern Chemsitry Research Institute, China

As key components to improve energy densities, metal nanoparticle based energetic materials are widely used in many energetic systems, for example, as additives for propellants and explosives. Metal nanoparticle based energetic materials have fairly large surface areas and are extremely reactive. Proper surface modification improves the safety and stability of these materials and may also enhance their energy releases. By applying atomic layer deposition (ALD) or molecular layer deposition (MLD), surfaces properties of the metal nanoparticles can be dramatically changed and their energy release patterns can be effectively tuned at minimum losses of the energy densities.

Zr nanopowder is a very promising high energy metal fuel. However, this material is extremely sensitive to electrostatic discharges, which greatly jeopardizes its applications. By applying ALD/MLD surface modification, metallic Zr nanoparticles can be encapsulated by uniform layers of metal oxides, polymers, or carbon. The thicknesses of the encapsulation layers can be precisely controlled. The electrostatic sensitivity of Zr nanoparticles can be tuned in a wide range by varying the type and thickness of the ALD coating, which significantly enhances the safety in handling, storage, and utilization of this high energy material.

Metal nanoparticle based thermite materials feature very exothermic solid-state redox reactions. However, reaction rates of traditional thermite mixtures are limited by reactant diffusion velocities. Core-shell structured nanothermite materials can be synthesized by depositing certain types of metal oxides (oxidizers) on Al nanoparticles. The oxidizer layers deposited on the Al nanoparticles are conformal and their thicknesses can be precisely controlled by adjusting the number of ALD cycle. Reaction rates of the core–shell structured nanothermites synthesized by ALD are several times faster than the mixture of nanopowders. The enhanced reaction rate is ascribed to the intimate fuel-oxidizer contact as a result of the exquisite core–shell nanostructure and excellent conformity of the oxidizer shells.

8:30am **AA3+AF+EM-WeM-3 Atomic Layer Deposition of Alumina on Lactose Particles for Modified Release: Effect of Co-reactants and Substrate Crystallinity***, **Damiano La Zara**,* Delft University of Technology, Netherlands*; D Zhang, M Quayle, G Petersson, S Folestad,* AstraZeneca, Sweden*; J van Ommen,* Delft University of Technology, Netherlands

Atomic layer deposition (ALD) is an established technique for the synthesis of thin films for various applications ranging from semiconductors to energy storage devices. Recently, it has been gaining attention in the pharmaceutical field to modify the particle properties, for example the drug release. Compared to the conventional methods of drug particle coating, ALD has a number of advantages: control over the amount of deposited material, conformality, and its solventless nature. A few studies about ALD of metal oxides, including Al_2O_3, TiO_2 and ZnO, on acetaminophen, lactose and budesonide particles showed that the deposition of nanoshells can effectively slow down the drug release. However, the dependence of the film growth on pharmaceutical particles on the ALD operating conditions has not yet been investigated. Furthermore, the relationship between the properties of the coating (e.g, uniformity, conformality) and the dissolution behaviour of the resulting core-shell structures is not clear. Therefore, as the dissolution profile strongly depends on the coating quality, understanding how process parameters (e.g., number of cycles, co-reactants and substrate surface) affect the coating uniformity and conformality is crucial.

In this work, we study the effect of co-reactants, namely H_2O and O_3, on the Al_2O_3 growth on two kinds of lactose particles (i.e., fully crystalline lactose and crystalline lactose with micronization-induced amorphous surfaces) and evaluate the dissolution behaviour. The ALD process is carried out at ambient conditions in a fluidized bed reactor for a low number of cycles (i.e., from 4 to 14) using trimethylaluminum (TMA) as a metal precursor. Time-of-flight secondary ion mass spectrometry and Transmission Electron Microscopy (TEM) show that TMA/O_3 ALD on crystalline lactose particles offers greatly improved control over the coating uniformity and conformality compared to TMA/H_2O ALD. In fact, by causing severe agglomeration of the particles, water deteriorates the fluidization quality and thus the homogeneity of the coating process. In-vitro dissolution tests reveal more sustained release for the O_3-based process than for the H_2O-based one, thus underlining the benefit of O_3 in providing uniform and conformal coatings. However, little to no difference between TMA/O_3 and TMA/H_2O ALD is observed on lactose particles with amorphous surfaces. In fact, such amorphous surfaces firstly are inherently inhomogenous across the particles and secondly present micropores, as suggested by BET measurements. This inevitably leads to non-conformal films regardless of the co-reactant and moreover results in both surface and subsurface growth.

8:45am **AA3+AF+EM-WeM-4 A High Vacuum Plasma Enhanced Atomic Layer Deposition System for Depositing Very Reactive Metals***, **Feng Niu**,* SVT Associates, Inc.

Most of metal elementals deposited by ALD or PEALD so far are less electropositive or relatively stable. Very reactive metals which are defined as highly electropositive elements(electronegativity c <1.8) including alkaline, alkaline earth, group III, some transition and rare earth metals are needed for applications such as batteries, improved adhesion, barriers, etc.. However they have been proved very difficult to deposit in a conventional thermal ALD or PEALD reactor due to thermodynamic limitation, impurity requirements and unavailability of proper precursors and reducing agents.

A new high vacuum PEALD system achieving base pressure at level of 10^{-8} Torr range with a high efficiency hydrogen plasma source was developed and applied to deposit highly reactive metals. The system has demonstrated deposition of pure Mg metal using commercially available Bis(ethylcyclopentadienyl) magnesium ($Mg(CpEt)_2$).[1] Self-limiting performances of Mg was evaluated(Figure1).Results for film characterizations such as surface morphology by atomic force microscopy (AFM), and film composition especially O impurity by x-ray photon-electronic spectrometer (XPS) (Figure2) will also be presented. A binary sequence surface chemistry is suggested that the hydrogen radicals serve to strip the ligands from the metal precursor according to the general overall reaction scheme: $Mg(CpEt)_2+H_2$*--Mg+2HCpEt.

This system should also be excellent for deposition of many other very reactive metals such as Sr, Ba, Ti, Nb, Zr, Hf, Li, Na, etc., and for borides, carbides and nitrides where the materials are extremely sensitive to contaminants such as oxygen, moisture, carbon oxides, etc…

[1] US patent # US 9828673 B2.

9:00am **AA3+AF+EM-WeM-5 Plasma Properties of High Pressure ALD***, C Qu,* University of Michigan*; **Pulkit Agarwal**, Y Sakiyama, A LaVoie,* Lam Research Corp.*; M Kushner,* University of Michigan

Plasma enhanced atomic layer deposition (ALD) of high quality dielectric films ultimately depends on controlling the fluxes of plasma produced reactive species onto the substrate and into features. In a typical plasma enhanced ALD cycle of SiO_2, the Si-containing precursor is usually deposited in a non-plasma environment. The oxidation step is then conducted by an oxygen containing plasma such as Ar/O_2. In order to produce high fluxes of the oxidizing radicals, which requires high power deposition, while having ion energies onto the wafer with below-damaging energies, the capacitively coupled plasmas are typically operated at pressures of many Torr. Theses pressures with high power produce high radical fluxes, while the collisional nature of the sheath results in low ion energies. There are several challenges in optimizing this system, including uniformity of reactant fluxes, controlling ion energies and minimizing damaging UV/VUV fluxes.

Results from a computational investigation of high pressure capacitively coupled plasmas designed for plasma enhanced ALD of SiO_2 will be discussed, with the goal of providing insights to the tradeoffs to simultaneously optimizing deposition conditions. Consequences of varying fluxes on uniformity of deposition in moderate aspect ratio features will also be discussed. The modeling platforms used in this study are the Hybrid Plasma Equipment Model (HPEM) and the Monte Carlo Feature Profile Model (MCFPM). The example system uses Ar/O_2 mixtures at pressures of 1-5 Torr, with power deposition of up to a few kW. The fundamental plasma properties of this operating regime (e.g., plasma and radical densities, electron temperature, reactive fluxes to the substrate, sources of ionization), ion energy and angular distributions (IEADs) to the substrate will be discussed. Feature scale modeling will correlate the reactive fluxes to deposition uniformity.

* Work supported by LAM Research Corp. and the DOE Office of Fusion Energy Science.

9:15am **AA3+AF+EM-WeM-6 Remote Plasma Atomic Layer Deposition of Gallium Oxide Thin Films using Trimethylgallium and Oxygen Plasma***, H Hao, Y Shen, J Zhang, **Xiao Chen**,* Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, China

Because of its large band gap and many other excellent properties, gallium oxide (Ga_2O_3) is being considered as an important oxide semiconductor for large power transistors, UV optoelectronics and solar cells, etc. Particularly, amorphous Ga_2O_3 is now attracting great interest as gate dielectric and surface passivation layer in transistors. In this work, we have deposited high quality Ga_2O_3 thin films by remote plasma atomic layer deposition (RP-ALD) with trimethylgallium (TMGa) and oxygen plasma. The deposition rate was constant at 0.36Å/cycle within a wide process window from 100 to 400 ℃. X-ray photoelectron spectroscopy (XPS) indicates the presence of gallium, oxygen, and carbon elements with content of ~37.4, ~54.5 and ~8.1 at % respectively in the Ga_2O_3 thin films deposited on silicon substrate at 250℃. The carbon impurity in the film was reduced by ~ 34% comparing with previous reported results[1]. Atomic force microscopy shows smooth surface morphology with a small root-mean-square roughness of 0.156nm. Furthermore, Ga_2O_3 films were successfully deposited on silicon, sapphire and GaN surfaces, indicating the low substrate selectivity that is beneficial to the III-V device fabrication . X-ray diffraction reveals no any crystallization happened in the amorphous Ga_2O_3 films after annealed at a high temperature up to 900℃, under O_2 atmosphere for 90 sec in a rapid thermal annealing system. The excellent thermal stability and high uniformity of Ga_2O_3 thin films deposited by RPALD are very critical to further improve the stability of III-V devices.

Reference:

1. Donmez, I.; Ozgit-Akgun, C.; Biyikli, N. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **2013,** 31, (1), 01A110.

9:30am **AA3+AF+EM-WeM-7 Impact of Substrate Biasing during Plasma-enhanced Atomic Layer Deposition on Dielectric Breakdown of Al_2O_3 Thin Film***, **Hyun Soo Han**, M Winterkorn, Y Kim, K Lee, T Yong, K Bae, W Park, P Schindler, F Prinz,* Stanford University

The plasma as reactants in atomic layer deposition process enables a great flexibility in processing conditions and a wide spectrum of material properties. In this study, we demonstrate the tunable electrical property of Al_2O_3 thin film through the substrate biasing during the plasma-enhanced atomic layer deposition. We modulate the substrate bias voltage from 0 to 150 V and evaluate its impact on growth per cycle, mass density and electrical breakdown strength. By applying substrate bias of ~ 20 V during the deposition, an impressive breakdown strength of 0.96 V/nm is achieved, which is approximately 11% higher value than that of the film prepared without substrate bias. Our results demonstrate that the plasma energy control via substrate biasing in the plasma-enhanced atomic layer deposition process is able to be a promising technique in optimizing materials' properties for various electronic or optoelectronic devices.

9:45am **AA3+AF+EM-WeM-8 Growth Mechanism of High-k Y_2O_3 on GaAs(001)-4×6 using *in-situ* Cycle-by-Cycle ALD and Synchrotron Radiation Photoelectron Spectroscopy***, C Cheng,* National Chia-Yi University, Republic of China*; **Wan-Sin Chen**, Y Cheng, L Young, H Wan,* National Taiwan University, Republic of China*; C Yang,* National Tsing Hua University, Republic of China*; K Lin,* National Taiwan University, Republic of China*; T Pi,* National Synchrotron Radiation Research Center, Republic of China*; J Kwo,* National Tsing Hua University, Republic of China*; M Hong,* National Taiwan University, Republic of China

Atomic layer deposited (ALD) high-k dielectrics on semiconductors with thickness from sub-monolayer (ML) to nano-meter (nm) has become a norm in the fabrication of metal-oxide-semiconductor field-effect transistors (MOSFETs).[1,2] The high-performance nano-electronic devices demand scaled-down nm thick oxide layers. Moreover, a low interfacial trap density (D_{it}), the most critical property for the device, depends on the initial oxide growth on semiconductor. Literature contains many studies on ALD oxide films on semiconductors, but few studies have investigated the oxide growth mode in the embryo stage. Thus, the present investigation is motivated to reach the fine region of a single precursor molecule in contact with a single surface atom of a semiconductor substrate. We specifically selected the system of ALD-Y_2O_3 on freshly molecular beam epitaxy (MBE) grown pristine GaAs(001)-4x6. The oxide film is a single-domain single-crystalline cubic phase with a surface normal (110).[3,4] The D_{it} is low of mid 10^{11} $cm^{-2}eV^{-1}$, having a flat D_{it} distribution within the GaAs band gap without a peak bulge in the mid-gap.[5] We have studied the interfacial electronic structure with the film sub-ML to nanometers thick using *in-situ* synchrotron radiation photoelectron spectroscopy (SRPES). In this talk, we will present the growth mechanism of ALD-Y_2O_3 adsorption on GaAs(001)-4×6 with different cycles of deposition in an atomic scale. The pristine p-type MBE-GaAs(001)-4×6 surface was grown in an integrated ultra-high vacuum (UHV) growth/analysis system.[6] After each MBE and ALD deposition, the sample was *in-situ* transferred to National Synchrotron Radiation Research Center (NSRRC) for SRPES measurements with a UHV portable chamber, in which the vacuum is maintained below 5 x 10^{-10} torr. In the embryo stage, we found that $Y(EtCp)_3$ precursors mainly undergo a charge transfer to the faulted As atoms on the GaAs(001)-4x6 surface. Upon H_2O co-reactant deposition, followed N_2 purge, the footed As atoms are readily removed. Moreover, the oxygen atoms in H_2O take over the bonding role with the underneath Ga atoms and lines of Ga-O-Y bonds stabilize the Y_2O_3 film on the GaAs substrate. After one-monolayer Y_2O_3 formed, the coordinatively unsaturated Y-O pairs of Y_2O_3 open the next ALD cycle of alternated $Y(EtCp)_3$ and H_2O process.

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ALD Applications
Room 116-118 - Session AA1-WeA
Energy: Catalysis and Fuel Cells

Moderators: Myung Mo Sung, Hanyang University, Yongfeng Mei, Fudan University, China

1:30pm **AA1-WeA-1 Oleo Sponge: Reusable Sorbent for Oil Spill Cleanup Fabricated using Sequential Infiltration Synthesis***, **Jeffrey W. Elam**, A Mane, E Barry, S Darling, J Avila, J Libera,* Argonne National Laboratory

Crude oil spills in the ocean can be devastating to the environment and extremely expensive to mitigate. Furthermore, while oil on the surface can be removed by skimming or burning, there are currently no technologies for the cleanup of subsurface oil droplets in the ocean. To address this need, we have developed a reusable sorbent material, Oleo Sponge. To synthesize this material, we begin with commercial polyurethane foam, and first treat the foam using sequential infiltration synthesis (SIS). SIS is similar to ALD in that it uses alternating, self-limiting exposures between gaseous precursors and a substrate. However, whereas the ALD substrate is a solid surface, in SIS the substrate is a polymer, and the precursors react on organic functional groups within the polymer to seed the nucleation of metal oxide clusters. We performed in situ infrared spectroscopy and mass spectrometry to elucidate the mechanism for metal oxide SIS within the polyurethane foam, and we have studied the effects of temperature, time, and partial pressure on the resulting SIS deposits. The next step is to graft an oleophilic monolayer onto the SIS-treated foam, either through gas-phase or solution phase treatment. The resulting material is simultaneously hydrophobic and oleophilic, and is able to rapidly extract oil from water. We have performed extensive bench-scale testing using 1” cubes of the Oleo Sponge and found that it absorbs >40x its weight in oil, and can be simply squeezed out and used again. Next, we performed a 10,000 scale up, and tested the material at the Ohmsett facility in Leonardo, New Jersey, using the largest outdoor saltwater tank facility in North America. The Oleo Sponge performed very well in extracting subsurface crude oil and diesel fuel from seawater under realistic conditions.

1:45pm **AA1-WeA-2 Evaluation of Zinc Oxide Fabricated by Atomic Layer Deposition as an Antibacterial Coating under UV Light***, **Gwon Deok Han**, K Park, M Kim, H Choi, J Koo, H Park, J Shim,* Korea University, Republic of Korea

Zinc oxide (ZnO) is widely used as a promising antibacterial agent in environmental remediation processes such as water disinfection and air purification [1]. This is because ZnO has a wide band gap energy (approximately 3.3 eV) which is favorable for photocatalytic reaction. In aquatic environments, ZnO produces reactive oxygen species (ROS) such as superoxide anion, hydroxyl radical, and singlet oxygen based on photocatalytic reaction promoted under UV irradiation. The photo-generated ROS exhibits antibacterial activity against microorganisms such as gram-negative bacteria and gram-positive bacteria. Recently, the improvement of the antimicrobial effect through application of nanoparticle ZnO having a high active surface area has been verified [2]. However, the ZnO nanoparticles have a problem in that the antibacterial ability is lowered due to agglomeration between nanoparticles and weak adhesion to the continuous flow-through reactor in wastewater treatment. Accordingly, immobilization of ZnO on reactor surface is essential.

In this study, we successfully demonstrated that thin-film ZnO fabricated by atomic layer deposition (ALD) exhibits comparable levels of antibacterial activity to commercially available ZnO nanoparticles [3]. We observed that the as-deposited ZnO consisted of closely packed nano-sized grains and firmly attached to the underlying substrate. As an alternative to the particulate photocatalysts, it was confirmed that the thin-film ZnO efficiently adsorbed UV light of 380 nm or less and continuously generated ROS even in repeated use in an aqueous environment. *Staphylococcus aureus* (*S. aureus*) was used as a gram-positive model bacterium for antimicrobial activity evaluation. Finally, we demonstrated that the photo-generated ROS from the thin-film ZnO damage cellular membrane and contribute to the death of *S. aureus*.

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2:00pm **AA1-WeA-3 ALD Enabled Non-linear Optical Properties at Substrate-film Interfaces***, Z Gao,* Washington University, St. Louis*; M Hussain,* University of Dayton*; D Ceglia,* Aegis Technology Group Inc.*; M Vincenti,* University of Brescia, Italy*; A Sarangan, I Agha,* University of Dayton*; M Scalora,* US Army AMRDEC*; J Haus,* University of Dayton*; **Parag Banerjee**,* Washington University, St. Louis

Metal-insulator and metal-semiconductor interfaces are a technologically important class of interfaces, given their ubiquitous presence in advanced materials and devices. ALD is an enabling synthesis tool for studying such materials systems as the first few monolayers deposited during ALD provide superb control over film thickness and nuclei morphology. Together with theoretical calculations and experimental nonlinear optical measurements, interfacial electronic properties at the nanoscale can be unraveled.

In this talk, the unique nonlinear optical signals generated from Au-Al_2O_3 and Au-ZnO systems will be described and correlated with predictions from hydrodynamic model for free electrons, incorporating quantum tunneling effects. Al_2O_3 and ZnO provide vastly differing nucleation behavior on Au substrates. Further, whereas Al_2O_3 is not known to be a nonlinear optical material, ZnO is strongly non-linear. The nucleation and growth of Al_2O_3 and ZnO on Au are studied using x-ray photoelectron spectroscopy (XPS) and Kelvin-Probe Force Microscopy (KPFM). The results show a clear nucleation followed by growth mechanism for ALD Al_2O_3 on Au, whereas for ALD ZnO on Au, a conformal layer-by layer growth is observed.

Second harmonic (SH) generation and third harmonic (TH) generation of incident light were measured on metal/insulator (MI): Au/Al_2O_3 & Au/ZnO; and metal/insulator/metal (MIM): Au/Al2O_3/Au & Au/ZnO/Au. The MIM was fabricated by coating the surface with gold nanoparticles. Both Al_2O_3 and ZnO films show a common feature for the SH signal in both MI and MIM structures. SH signals monotonically decreases and saturate once the Au surface is fully covered by the ALD film. In the case of Au/Al_2O_3, this allows us to develop a new phenomenological model[1] that estimates the occupancy of delocalized electrons in metal-induced-gap-states (MIGS) at 44%. On the other hand, the TH signal for the MIM case has a maximum that reaches a peak when the ALD film has a sub-nanometer thickness and is fully consistent with the electron quantum tunneling theory. Thus, ALD enables us to measure and understand interfacial electronic properties at the nanoscale for designing and fabricating future nonlinear optoelectronic devices.

References:

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2:15pm **AA1-WeA-4 Bottom-up Fabrication of X-ray Optics using ALD***, **Umut Tunca Sanli**,* Max Planck Institute for Intelligent Systems, Germany*; C Jiao,* Thermo Fisher Scientific, Netherlands*; M Baluktsian, G Schütz, K Keskinbora,* Max Planck Institute for Intelligent Systems, Germany

The interest in X-ray microscopy has gained a rapid momentum especially in the last decade with the emergence of third- and fourth-generation synchrotrons, free electron lasers and new laboratory size X-ray sources. These new advanced X-ray sources require high-performance X-ray optics to study nano-scale structures. One of the most popular X-ray optic is the Fresnel zone plate (FZP), owing to its high-performance, monolithic structure and versatility. A FZP consists of alternating opaque and transparent co-axial annuli, which are the zones of the FZP. The resolution of the FZP is defined by the width of the outermost zone. Fabrication of the FZPs have been mostly relied on e-beam lithography, achieving resolutions down to 20 nm. However, efficient focusing of hard X-rays and resolutions beyond 20 nm requires structures that are extremely challenging to achieve *via* e-beam lithography or any other top-down subtractive method.

In this study, we follow a bottom-up approach and exploit the conformality and precision of ALD to manufacture the extremely challenging FZPs to achieve ultra-high resolution, highly efficient FZPs. Our method consists of three-steps: i) the fabrication of a micro-pillar array using a Plasma Focused Ion beam milling (PFIB), ii) the deposition of the multilayer zones of the FZP *via* ALD on the micro-pillar array and iii) the lift-out of individual FZPs using a FIB lift-out technique. The fabrication of FZPs requires using the ALD at the extreme. We deposit several hundred layers of ceramic materials, with thicknesses of 20-40 nm. The total deposition thickness reaches 6 µm. Due to its conformality, ALD allows multiple pillars to be deposited simultaneously. Hence, virtually unlimited number of FZPs can be fabricated out of one successful deposition. ALD is essential here as it provides the needed precision in zone positions through sequential, self-limiting reactions.

ALD-FZPs resolved 15 nm structures, the best resolution ever obtained via a multilayer FZP. For even higher resolutions, a better control of the interface sharpness, the microstructure, the volumetric mass density, and the chemical composition of the deposited layers become essential. In this study, characterization of the ALD layers via High-resolution Transmission Electron Microscopy (HR-TEM), Electron Energy Loss Spectroscopy (EELS), Energy dispersive X-ray Spectroscopy (EDX) Wavelength-Dispersive X-ray spectroscopy (WDX), X-ray Photoelectron Spectroscopy (XPS) and X-ray reflectometry (XRR) will be presented. Our results confirm that high-quality layers and interfaces are achieved through our ALD processes, required for sub-10 nm resolutions.

2:30pm **AA1-WeA-5 Thickness Optimization of Aluminum Oxide for High Secondary Electron Emission Deposited via Atomic Layer Deposition***,* ***Baojun Yan,*** Institute of High Energy Physics, Chinese Academy of Sciences, China

The performance of traditional electron multipliers, such as microchannel plate and channel electron multipliers, can be improved by coating high secondary electron emission (SEE) layers such as aluminum oxide via atomic layer deposition (ALD). The gain, peak to valley ratio and energy resolution of coated electron multipliers have been greatly improved by our previous study. As we all know, the SEE coefficient is depend on the material thickness if other conditions are fixed. In this study, the thickness optimization of aluminum oxide have been investigated. The aluminum oxide with varied thickness were deposited by ALD, and by comparing the performance of MCPs without and with aluminum oxide, the optimal range of SEE thickness can be obtained.

2:45pm **AA1-WeA-6 Effect of Deposition and Annealing Condition on Atomic Layer Deposited SnO$_2$ for Environmental Ozone Monitoring***, S Mills, V Misra,* ***Bongmook Lee,*** North Carolina State University

Portable and wearable systems to continuously monitor environment pollutants over long periods of time is great interest to correlate an individual's exposure levels to personal health. For example, Asthma is a lifelong respiratory ailment causing wheezing, breathlessness, chest tightness, coughing and degrades the quality of life for the patient. The impact of certain environmental exposures such as ozone and particulate matter are also known to be critical triggers in asthma attacks. Solid-state based thin film sensors are favorable for real-time and long-term environmental monitoring. Among various types of gas sensors, metal-oxide based thin film sensors are widely used but detection of gases relies on high temperatures (>300^{o}C) for sensitivity and selectivity to various gases at the cost of many mW of power. Development of nanoscale metal oxide gas sensors which operate at room temperature is a promising strategy that leads to improved performance and reduced power consumption in the µW range. We have demonstrated that the high sensitivity and room temperature operated an ozone sensor based on atomic layer deposited (ALD) tin oxide (SnO$_2$). This work investigates the processing parameters such as deposition temperature and annealing time and its effects on tin dioxide sensor characteristics. Hall measurements were conducted on the SnO$_2$ films to evaluate the electrical properties as deposition and annealing conditions changed. It was found that the carrier concentration is generally increased with deposition temperature due to carbon impurities in the film at lower deposition temperatures. The electron mobility also increases strongly with deposition or annealing temperature resulting in lower resistivity of the film. It was also found that the SnO$_2$ deposited at 250^{o}C has a crystalline structure confirmed by the XRD but the orientation was not preferable for sensor application. Transient sensor response was conducted for different ozone concentrations varying from 25 parts per billions (ppb) to 100 ppb. Decreasing deposition temperature was found to be associated with decreasing film conductivity, increased ozone response, and increased carbon content. The carbon content was a result of steric hindrance during the deposition process and that the carbon is a substitutional impurity for oxygen in the crystal lattice. This results in the decreased electron concentration and increased ozone response. The effect of annealing temperature was also evaluated. 600C air anneal shows a maximum ozone response. By optimizing deposition temperature and annealing condition, a highly sensitive, selective and room temperature operated ozone sensor is realized.

3:00pm **AA1-WeA-7 Etch Behavior of Ti-based Oxide Grown by Atomic Layer Deposition for Spacer Application***, H Kim,* ***Sanghun Lee****,* Yonsei University, Republic of Korea*; W Lee,* Pusan National University, Republic of Korea*; W Noh, S Gatineau,* Air Liquide Laboratories Korea*; S Kwon,* Pusan National University, Republic of Korea

Thin film grown by Atomic Layer Deposition has been enabled advanced nanopatterning technology such as spacer defined multiple patterning. The main scheme of this patterning technology is using sidewall spacer deposited by ALD as a hardmask.[1] However, usually the high aspect ratio and poor mechanical strength of spacers often causes its collapse problem and this phenomenon was also identified during multiple patterning process.[2] Therefore, the studies for spacer materials that have high etch selectivity and good mechanical properties are required, but there is lack of research on it. In this respect, TiO$_2$ is one of good candidate for spacer materials.[3,4]

Here, we studied on film properties of TiO$_2$ grown by ALD for spacer materials and further investigations for mixture with SiO$_2$ were followed. We observed growth of Ti$_x$Si$_{1-x}$O$_2$ (x=0~1) using Ti(CpMe$_5$)(OMe)$_3$, Ti(O^{i}Pr)$_4$ and H$_2$Si[N(C$_2$H$_5$)$_2$]$_2$ and O$_2$ gas using PE-ALD at low temperature (100 °C). The chemical composition and carbon impurities of the films were analyzed by x-ray photoelectron spectroscopy (XPS), and the nanostructures of the films were analyzed by x-ray diffraction (XRD). And mechanical property of Ti$_x$Si$_{1-x}$O$_2$ films was investigated by nanoindentation. We compared the etch rate of Ti$_x$Si$_{1-x}$O$_2$ films using both dry and wet etching process. As a result, we obtained Ti$_x$Si$_{1-x}$O$_2$ films with various Ti/(Ti+Si) compositions and there was no Ti precursor dependency on dry etch rate which decreases as Ti composition increases. However, both pure TiO$_2$ films were not strippable by diluted HF solution due to its anatase phase. Furthermore, wet etch rate of mixtures were higher than even pure SiO$_2$ film when the films deposited by using Ti(CpMe$_5$)(OMe)$_3$.

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3:15pm **AA1-WeA-8 Scaling Atomic Layer Deposition to Astronomical Sizes: Low-temperature Aluminum Oxide Deposited in a Meter-sized Chamber***,* ***David Fryauf,*** University of California Santa Cruz*; A Phillips,* University of California Observatories*; G Tompa,* Structured Materials Industries Inc.*; N Kobayashi,* University of California Santa Cruz

Atomic Layer Deposition (ALD) is attractive for producing transparent barrier films on metal-coated astronomical mirrors, but to date has been limited to relatively small-sized substrates. A new ALD tool has been designed, constructed, and tested to apply uniform protective coatings over a substrate with 0.9 m diameter. The new tool, nicknamed the Big ALD , employs a novel chamber design which isolates a large substrate surface to be coated by utilizing the substrate as a wall of the reaction chamber. Conceptual design and implementation of this new tool are discussed with potential applications to large astronomical telescope optics, specifically protective coatings for silver mirrors, and other future large structures. To demonstrate the potential of this new design, aluminum oxide was deposited by thermal ALD using trimethylaluminum and water at a low reaction temperature of 60°C. Growth rates, dependent on precursor pulse times and chamber purge times, show that the two half-reactions occur in a saturated regime, which demonstrates typical characteristics of ideal ALD behavior. It is found that uniformity in growth across the chamber, rather than growth rate at a single chamber position, must be studied and optimized to identify saturated growth mode in the Big ALD. Thickness uniformity across a 0.9 m substrate is within 3% of the average film thickness. Aluminum oxide deposition process parameters of the Big ALD are compared with those of a conventional 100 mm wafer-scale ALD tool, and saturated ALD growth over the 0.9 m substrate is realized with a simple scaling factor applied to precursor pulse and purge times. The results show promising application of transparent robust dielectric films as uniform barriers across large optical components scaled to meter-sized and potentially larger substrates.

ALD Applications
Room 104-106 - Session AA2-WeA
Catalytic Application

Moderators: Yongbeom Kim, Hanyang University, Min Hwan Lee, University of California Merced

1:30pm **AA2-WeA-1 Surface Treatment of Solid Oxide Fuel Cell Cathodes by Atomic Layer Deposition***, **Min Hwan Lee,*** University of California Merced **INVITED**

The high operating temperature of solid oxide fuel cells (SOFCs) has limited their lifetime, cost competitiveness, start-up/shut-down speed and applicability to small-scale devices. Reduction of operating temperature, however, results in a dramatic loss of kinetics in both ionic transport and electrode reaction. In particular, sluggish electrode kinetics of oxygen reduction reaction (ORR) at the cathode side has been the main issue to resolve for a decent performance. As ORR of conventional intermediate-temperature SOFCs is often limited by dissociative adsorption and/or transport of electroactive species, an enlargement of catalytically active surface area while minimizing the transport distance is expected to improve the overall ORR kinetics significantly. For this end, a well-dispersed coating of nanoparticle-like catalysts on a cathodic backbone is achieved by e.g. infiltration of proper nitrate solution. The choice of infiltrated material can be mostly based upon catalytic activity and chemical inertness in the given environment, not limited by other criteria such as thermal expansion matching with underlying electrolyte and charge conductivity, which makes the material choice quite flexible. However, the merits of these high surface area structures come with susceptibility to thermal instability caused by particle agglomeration (by ripening and coarsening) during high-temperature operation. In this talk, we will present the application of atomic layer deposition (ALD) to form nanoscale oxide interfaces with platinum or lanthanum nickel ferrite (LNF or $LaNi_{0.6}$ $Fe_{0.4}O_{3-\Delta}$)-based cathodic backbones to tackle the concomitant issue of thermal instability. The impact of ALD treatments on the ORR kinetics, thermal degradation rate and changes in bottleneck process will be also discussed.

2:00pm **AA2-WeA-3 Bottom-Up ALD Engineering of FexCo1-xSy for Electrocatalytic Hydrogen Evolution***, **Wei Xiong,*** Peking University, China

The development of low-cost, efficient electrocatalyst for hydrogen generation from water (HER) is currently a core task for the hydrogen clean-energy technology. Generally speaking, an efficient electrocatalyst requires its bonding strengths with the reaction intermediates to be neither too high nor too low. Accordingly, the specific activity of a catalyst can be optimized by tuning the elemental composition of the catalyst. Experimentally, the tuning of the catalyst composition can be achieved by atomic layer deposition (ALD). Also, ALD allows for highly conformal loading of the catalyst as a thin coating layer onto a mesoscopically rough electrode support, which has a high surface area and therefore can further boost the overall electrocatalytic activity.

In this presentation, we will show a bottom-up strategy for designing an efficient ternary electrocatalyst by ALD.[1] The strategy involves two separate optimization steps: one is to optimize the specific activity of the catalyst material by ALD, and the other is to optimize the geometric structure of the catalyst support by fabricating a carbon nanotube (CNT) network on mesoscopically rough carbon cloth (CC). As an example, we optimize the composition of a promising ternary electrocatalyst of $Fe_xCo_{1-x}S_y$ via ALD, and the optimized $Fe_{0.54}Co_{0.46}S_{0.92}$/CNTs/CC electrode exhibits a fairly low HER overpotential of −70 mV for achieving −10 mA/cm^2 in current density in alkaline solution, which demonstrates the effectiveness of this ALD-based engineering strategy.

Reference

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2:15pm **AA2-WeA-4 Plasma Enhanced Atomic Layer Deposition of Iron Carbide for Electrocatalytic Hydrogen Evolution***, Z Liu, **Yulian Hu**, Q Chen,* Beijing Institute of Graphic Communication, China

A plasma enhanced atomic layer deposition process for depositing iron carbide (Fe_3C) thin films is reported, using bis(N,N'-di-tert-butylacetamidinato)iron(II) and H_2 plasma. The process shows an ideal self-limiting ALD growth fashion with a saturated film growth rate of 0.041 nm/cycle for a fairly wide process temperature window from 80 to 200°C. The surface morphology of iron carbide film is investigated by atomic force microscopy and scanning electron microscopy. X - ray diffraction, X - ray photoelectron spectroscopy and transmission electron microscopy are used to analyze the crystal phase, film composition and microstructure of iron carbide films. Using this ALD process, Carbon cloth could be uniformly and conformally coated by a thin layer of Fe_3C to afford a nanostructured Fe_3C/CC composite. The ALD-prepared Fe_3C/CC composite is demonstrated to show excellent performance for electrocatalytic hydrogen evolution.

2:30pm **AA2-WeA-5 Gadolinia-doped Ceria Thin Film Fabricated by Atomic Layer Deposition for Enhancing ORR Kinetics of LT-SOFC***, **Hwichul Yang**, S Kim, Y Lim, Y Kim,* Hanyang University, Republic of Korea

Ceria(CeO_2)-based material, including gadolinia-doped ceria(GDC), samaria-doped ceria(SDC) and yttria-doped ceria(YDC), has emerged as an electrolyte for low temperature solid-oxide fuel cells(LT-SOFCs) due to the high oxygen ion conductivity and oxygen-reduction reaction(ORR) kinetics compared to yttria-doped zirconia(YSZ) which is a standard electrolyte material for SOFC. Mainly, it has been used as a functional layer on YSZ for enhanced ORR kinetics because it is hard to use ceria-based material as a single electrolyte due to the reduction characteristic in hydrogen environment. Typically, small grain and nanocrystalline structure of this functional layer shows higher ORR kinetics, and thin film fabricated by atomic layer deposition(ALD) is well known for showing that characteristics. In this study, characteristics and effects of GDC functional layer fabricated by atomic layer deposition(ALD) was studied. Surface morphology and crystal structure of ALD/GDC was investigated by physical analysis methods. ALD/GDC functional layer has a small surface grain and nanocrystalline structure, which has lots of oxygen incorporation site and reduces polarization loss. By electrochemical impedance spectroscopy(EIS) method, reduced polarization loss was observed for ALD/GDC-applied cell. Current-voltage characteristic shows enhanced performance of ALD/GDC-applied cell. These results about ALD/GDC indicates that ALD-fabricated functional layer has superior characteristics for SOFC performance.

2:45pm **AA2-WeA-6 Atomic Layer Deposition of Palladium Nanoparticles on Nickel for Direct Methanol Solid Oxide Fuel Cell Catalysts***, **Junmo Koo**, D Jang, H Choi, J Kim,* Korea University, Republic of Korea*; H Jeong,* University of Illinois at Urbana-Champaign*; J Shim,* Korea University, Republic of Korea

Direct usage of methanol as a fuel of solid oxide fuel cells (SOFCs) has several advantages compared to hydrogen gas fuel. Liquide form of methanol enables easy and safe storage, and it can be utilized as fuel without any cumbersome reforming process. These advantages of methanol have drawn much attention in the field of fuel cell society. However, catalyst poisoning originated from residual carbon monoxide and slow reaction of DMSFOC electrode is the most urgent issue of DMSOFC. Among various catalyst for DMSOFC, platinum-ruthenium bimetallic catalyst has shown the best performance for methanol oxidation. High cost of Pt, however, hinders the widespread commercialization of DMSOFC. Recently, nickel is regarded as promising substitute of Pt/Ru catalyst for its reforming performance of alcohol and hydrocarbon and inexpensive price. However, unwanted carbon formation is occurred during electrochemical oxidation of methanol using Ni catalyst. Therefore, nickel-based alloys have been widely studied for the effective oxidation of methanol and avoid unwanted carbon coking of nickel catalyst. Palladium (Pd) is one of the strong candidate material for bimetallic nickel-based catalyst. Previous studies reported the enhanced catalytic activity and unwanted carbon deposition on anode surface originated from the existence of Pd.

Optimum structure of Ni/Pd bimetallic catalyst would be composed of well-dispersed Pd nanoparticles on Ni substrate due to relatively high price of Pd compared to that of Ni. Atomic layer deposition (ALD) was used in order to fabricate Pd nanoparticles because of its unique availability to deposit uniform film even on complex structures. In this study, Ni/Pd bimetallic catalyst for DMSOFC were evaluated by fuel cell performance, electrochemical impedance spectroscopy, and long term-stability. ALD-made Ni/Pd catalyst revealed enhanced performance and stability compared to sputter-made Ni/Pd catalyst, which represents the effectiveness of ALD technique for fabricating surface-modified catalyst with increase surface area for desired reactions.

3:00pm **AA2-WeA-7 Diffusion-Limited Atomic Layer Deposition: Realizing the Encapsulation of Homogeneous Catalysts*, Bin Zhang*,** *S Zhang, H Liang, Y Qin,* Institute of Coal Chemistry, Chinese Academy of Sciences, China

The homogeneous metal complex catalysts play an important role in chemical engineering, biology and medicine industry. The heterogenization of homogeneous metal complex catalystshas performed both advantages of homogeneous (high activity and selectivity) and heterogeneous catalysts (reusability).Generally, the encapsulation of metal complexes via physical adsorption in the pore channels of porous materials is preferred, because it can maintain the properties and freedom of metal complexes. The big challenge is to precisely tailor the pore entrance size of the porous materials. Recently, we have realized the encapsulation of metal complexes into nanochannels of mesoporous materials by building a “hollow plug” at the pore entrance via diffusion-limited ALD[1]. The pore size of the hollow plug is precisely controlled on the sub-nanometer scale by changing the number of ALD cycles to encapsulate various metal complexes with different molecular sizes. Moreover, we have also investigated the effect of ALD parameters and cycles on the activity and reusability of heterogeneous catalysts by the encapsulation. This ALD-assisted encapsulation method has a wide application and can be applied to the encapsulation of most homogeneous catalysts into different mesoporous materials for various heterogeneous reactions.

1. Zhang, S.; Zhang, B.*; Liang, H.; Liu, Y.; Qiao, Y.; Qin Y.* *Angew. Chem. Int. Ed.* 2018, 57, 1091.

3:15pm **AA2-WeA-8 Ultrathin ALD Yttria-Stabilized Zirconia Overcoating on Metal Electrodes for Low Temperature Solid Oxide Fuel Cell*, Byung Chan Yang*,** *D Go, S Oh, J Shin, J An,* Seoul National University of Science and Technology, Republic of Korea

Solid oxide fuel cells (SOFC) have attracted much attention as highly efficient, fuel-flexible, and eco-friendly energy conversion device. However, conventional SOFC have practical issues in applications to various fields due to high operating temperature (up to 1000℃). Recently, studies on low temperature SOFC (LT-SOFC) (≤ 500℃) which can be operated at a relatively low temperature have been actively conducted. However, since it is operated at a low temperature, electrochemical reaction at the electrode is lowered; therefore, the use of noble metal electrode is essential. However, thermal stability, in this case, is also reduced by using noble metal electrode at elevated temperature.

In this study, we show how to improve the thermal stability of metal electrode by depositing yttria-stabilized zirconia (YSZ) overlayer. We have improved the SOFC performance and thermal stability by applying the ultrathin (2-3nm) YSZ overlayer with varying composition. YSZ overlayers were deposited by atomic layer deposition (ALD) on Pt electrodes with 0, 8, 15, 30, and 100 mol% of Y_2O_3-doping in ZrO_2, respectively. Doping level was controlled by the relative cycle ratio between Y_2O_3 and ZrO_2 in of ALD process. Fuel cell performance were analyzed through I-V-P and EIS measurements, and the thermal stability was measured using chronoamperometry. The performance of the reference cell decreased by more than 50% after 10 hours of operation, while that of the cell with YSZ overlayer was maintained at > 90% even after 10 hours of operation. Also, the performance of 8mol%-doped YSZ overlayer was 450℃ to 1.46mW / cm^2, which was not different from 1.4mW / cm^2 of the reference cell. However, the performance of the cell with 15mol%-doped YSZ overlayer was ~10% higher than that of reference cell. These results show that ALD can effectively tune the composition of the 2-3nm-thick YSZ overlayer, which can hugely affect the SOFC performance as well as the thermal stability.

ALD Applications
Room 116-118 - Session AA3-WeA

Functional Film Application

Moderator: Han-Bo-Ram Lee, Incheon National University

4:00pm **AA3-WeA-11 Catalyst Synthesis and Modification via Atomic Layer Deposition: From Supported Metal Catalysts to Complex Systems*, Mar Piernavieja Hermida*,** *R Naumann d'Alnoncourt, K Knemeyer,* Technische Universität Berlin, Germany*; V Strempel,* BASF SE, Process Research and Chemical Engineering*; A Trunschke, R Schlögl,* Fritz Haber Institute of the Max Planck Society, Germany*; M Driess,* Technische Universität Berlin, Germany*; F Rosowski,* BASF SE, Germany

Even though microelectronics has been one of the major adopters of atomic layer deposition (ALD) during the past 20 years, many other applications such as synthesis of battery materials, fuel cells or catalysis have been of increasing interest. A recent review from Junling Lu, Jeffrey W. Elam and Peter C. Stair summarizes the literature reports in the field of catalysis [1]. The vast majority of the cited contributions involve supported metal nanoparticle catalysts. Although in a lesser magnitude, metal oxides have been used as well due to their unique properties.

Our main focus lies on catalysts used for selective oxidation reactions, typically consisting of mixed metal oxides or phosphates. We aim to modify properties of bulk catalysts by changing the catalysts surface via ALD or using ALD for bottom up synthesis of complex systems as mixed metal phosphates or oxides on suitable supports. Thus, our main application of ALD is deposition in a submonolayer regime or deposition of very thin films (< 1 nm) rather than deposition of metal nanoparticles. A small number of ALD cycles can lead to homogeneous coverage of a catalyst surface with adatoms, leading to a higher catalytic performance.

For example, a combination of a thermal magnetic suspension balance and a fixed bed reactor [2] was used to deposit phosphorous on the surface of vanadia, changing its catalytic performance from total oxidation towards maleic anhydride formation [3]. The set-up was also used to deposit different compounds (promotors or poisons) on the surface of vanadyl pyrophosphate to influence its catalytic activity and selectivity. Our next step will be the deposition of vanadium containing layers, e.g. $(VO)_2P_2O_7$ or $VOPO_4$, on a suitable support.

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4:15pm **AA3-WeA-12 Atomically Controllable Ru@Pt Core Shell Nanoparticles Towards PROX’s Reactions Modulated by Pt Shell Thickness*, Yun Lang*,** *K Cao, J Zhang, B Shan, R Chen,* Huazhong University of Science and Technology, China

Preferential oxidation of CO under excess H_2 (PROX) is an effective way to remove CO from steam reforming of hydrocarbons for application in proton exchange membrane fuel cell.[1] For PROX, the bimetallic core shell nanoparticles can tremendously improve total activity and selectivity of PROX reactions[2]. However due to the lack of precise control over the core shell structures, the studies of relationship between PROX reactions with nanoparticles’ structural parameters remain very limited. Herein, we demonstrate synthesis of Ru@Pt core shell nanoparticles using area-selective ALD techniques based on precursors’ partial pressure and deposition temperature adjustment. A near linearly growth rate of Pt on Ru surface monitored with in-situ quartz crystal microbalance indicates well-controlled shell thickness by varying ALD cycles. The catalytic activity and selectivity of Ru@Pt core shell structure are enhanced compared with single component Ru, Pt or alloyed structure, which results from electron transfer from Ru to Pt. The catalytic performance is sensitive with shell thickness that influences the extent of electron modification and lattice mismatch. A monolayer of Pt shell shows optimal catalytic performance and minimal Pt loading. Density functional theory simulations have also been carried out to verify the results.

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