ALD Applications
Room Grand Ballroom H-K - Session AA1-WeA

ULSI, Display, Optics, Metamaterials, and Bio Applications
Moderator: Charles Dezelah, ASM

1:30pm **AA1-WeA-1 Synthesis of Low-k SiCNO Thin Films by Plasma-enhanced Atomic-molecular Layer Deposition with Tetra-isocyanate-silane (TICS) and Phloroglucinol (Phl)**, *G. Baek, J. Park, G. Park,* ***Haelin Yang,*** Hanyang University, Korea

Recently, as the nanoelectronics manufacturing process is ultra-miniaturized, high-level patterning technology is increasingly required. The "edge placement error(EPE)" accumulated during the repeated patterning process in back-end-of-line (BEOL) causes shorting or high resistance. To solve the EPE problem, a fully self-aligned via (FSAV) design is essential, and FSAV can be realized by increasing the spacing between the via and the metal line by using low-k materials[1]. Two ways to reduce the dielectric constant k are to reduce the number of dipoles in the film and to reduce its polarizability. The dielectric constant can be reduced by fabricating a film with almost perfect non-polar binding (ex, C–C) through the hybrid of SiO_2 and organic polymer. Therefore, it is essential to research a new molecular layer deposition (MLD) thin film fabrication process that can hybridize with Si-based atomic layer deposition (ALD). For nano scale thin film deposition, various Si precursor synthesis results have been reported for ALD SiO_2 and SiN_x thin film fabrication, and high-quality thin film fabrication is being studied through plasma enhanced atomic layer deposition (PEALD) application. Development of the MLD process using Si precursors is difficult to secure due to very low reactivity with organic precursors.

In order to induce Si-based PEALD and MLD hybrid processes, the surface adsorption reactivity of organic precursors should be increased. In this study, PEALD and MLD hybrid processes were developed using Tetra-isocyanate-silane (TICS) as a Si precursor and Phloroglucinol (Phl.) as an organic precursor for low-k material fabrication. The activation layer was fabricated with PEALD SiN_x using N_2 plasma to improve the hydroxyl reactivity. Subsequently, the SiCNO thin film was successfully fabricated through the Phl. MLD process with tri hydroxyl group. X-ray photoelectronic spectroscopy (XPS) has been used for analyzing SiCNO film composition. As the process temperature increased, the SiN_x surface oxidation was induced more strongly, and the nitrogen composition in the thin film decreased while the oxygen composition increased. Through I-V and C-V measurement, SiCNO deposited at 300 °C has a leakage current (at 1MV/cm) of 1.02 10^{-9} A/cm² and dielectric constant k of 3.02 compared to SiO_2 (k of 3.9).

[1] Yu, Xiaoyun, et al. "Area-selective molecular layer deposition of a silicon oxycarbide low-k dielectric." Chemistry of Materials 33.3 (2021): 902-909.

1:45pm **AA1-WeA-2 Performance and Thermal Stability Improvement of Vertical-Channel Thin-Film Transistor by Controlling Deposition Temperature of Gate Stack Prepared by Atomic Layer Deposition**, ***Dong-Hee Lee,*** Kyung Hee university, Korea (Democratic People's Republic of)*; Y. Kwon, N. Seong, K. Choi,* NCD. Co., Korea (Democratic People's Republic of)*; S. Yoon,* Kyung Hee University, Korea (Democratic People's Republic of)

Vertical-channel structure is one of the promising candidates for scaling down the oxide semiconductor thin-film transistors (TFTs), in which the active channel and gate stack are formed along the vertical sidewall, as shown in Fig. 1a. Thus, the channel length of vertical-channel TFT (VTFT) can be shortened to nanometer regime by reducing the spacer thickness. An ALD technique is completely compatible with manufacturing the oxide VTFTs in terms of conformal deposition, and the device feasibilities of VTFTs using the ALD In-Ga-Zn-O (IGZO) channels have been well demonstrated. However, in lots of works, the impact of deposition temperature (T_D) for the gate stack on device performance have rarely been investigated. Considering that the IGZO channels can be sensitively influenced during the ALD process of gate stack, the T_D is one of the most critical process parameters determining device operation as well as thermal stability of the IGZO VTFTs. In this work, we focused on the relationship between the T_D and VTFT performance from the perspective of thermal stability at various post-annealing temperatures.

For the fabrication of IGZO VTFTs, a vertical sidewall was formed by patterning the PECVD SiO_2 spacer (150 nm) intervening between the ITO source and drain layers. Then, an IGZO (In:Ga:Zn=1:1:2, 5 nm) was deposited by ALD using triethyl indium (TEIn), In-Ga bimetallic, diethyl zinc (DEZn), and O_3 as source of In, Ga, Zn and O, respectively. The gate stack composed of Al_2O_3 protection layer (PL, 5 nm) and gate insulator (GI, 15 nm) was prepared by ALD at different T_D's of 200 (Dev. A), 250 (Dev. B), and 300 °C (Dev. C). Finally, gate electrode and contact pads were formed with Al-doped ZnO deposited by ALD. Figs. 1b and 1c show an optical image and a device layout of the VTFTs. To examine the thermal stability of the fabricated VTFTs, post-annealing was carried out in O_2 ambient with increasing the temperature up to 300 °C.

Fig. 2a shows the transfer curves of the fabricated VTFTs. The overall device performance was found to be enhanced with increasing the T_D and the Dev. C showed the highest current drivability (44 µA/µm). Even after post-annealing at 300 °C, all the VTFTs showed sound thermal stability (Fig. 2b) with excellent operational stability (Figs. 2c, 2d). It was noteworthy that the current drivability of Dev. C amounted above 55 µA/µm (Fig. 3a), which is remarkable improvement in the bench-mark plot shown in Fig. 3b. The T_D could be verified to have crucial impact on the current drivability of thermally-stable IGZO VTFTs. These achievements in device operation provide a path towards the highly-functional IGZO VTFTs.

2:00pm **AA1-WeA-3 Sequential Design of PEALD In-Ga-Zn-O Active Layer: Sub-cycle Engineering of Indium Oxide Layer for Highly Stable TFT**, ***Taewon Hwang,*** *H. Yang, Y. Kim,* Hanyang University, Korea*; T. ONO, S. KAMIMURA, A. EIZAWA, T. TERAMOTO, C. DUSSARRAT,* Air Liquide Laboratories, Japan*; J. Park,* Hanyang University, Korea

Oxide semiconductors such as In-Ga-Zn-O (IGZO) are attracting considerable attention as active layers of next-generation displays such as AR/VR and automotive displays due to their excellent characteristics such as low leakage current, low deposition temperature, large area uniformity, and compliance mobility. For the application of 3D integration such as Fin-FET and memory/logic technology, atomic layer deposition (ALD) is a suitable method because it has the advantages of smooth surface, accurate thickness control in nanoscale, and conformal coating in complex structures due to its self-limiting characteristic. Furthermore, controlling the ALD sequence facilitates controlling the composition of the multi-component oxide semiconductor. In our previous study, we fabricated Indium-rich IGZO TFT with high mobility (≥70 cm²/Vs) by controlling the indium sub-cycle of the ALD sequence[1]. However, it shows that excessive indium content can cause device degradation due to large carrier concentrations and crystallinity. This crystallinity-related device degradation needs to be solved for the application to future technology. We chose an advanced channel design to get the film with improved electrical properties by controlling the sub-cycle of the ALD sequence.
In this study, we suppressed the crystallinity of IGZO by inserting gallium and zinc layers into the indium layer through sequential design, and the electrical/reliability of the device was also evaluated. We confirmed that the indium crystallinity was suppressed as the interlayer of IGZO increased using the sequential design. As the indium crystallinity was suppressed, the roughness of the thin film was decreased by ~35 %, and the oxygen-related defect was also reduced. Furthermore, by adding an inter-layer to the Indium layer of IGZO, the S.S. reduced by ~45 % (from 0.42 V/decade to 0.23 V/decade), and the threshold voltage shift under PBS 3,600 s is decreased from 3.75 V to 0.83 V. The Sequential design method could be a breakthrough in improving the performance of the oxide semiconductor.

Reference

[1] Sheng, Jiazhen, et al. "Amorphous IGZO TFT with high mobility of∼ 70 cm2/(V s) via vertical dimension control using PEALD." ACS applied materials & interfaces 11.43 (2019): 40300-40309.

2:15pm **AA1-WeA-4 Bilayer Channel Combination Strategy via Atomic-Layer Deposition of In-Sn-O/In-Sn-Zn-O Structures for Highly-Functional Oxide Thin-Film Transistors**, ***SHIN HO NOH,*** Kyunghee University, Republic of Korea*; Y. Kwon, N. Seong, K. Choi,* NCD Co. Ltd, Korea*; S. Yoon,* Kyunghee University, Republic of Korea

The introduction of a bi-layered channel structure is considered a highly effective approach to improve the device performance of oxide TFTs, which is composed of stacked 'prompt' and 'prime' channel layers with higher and lower carrier concentrations, respectively, owing to the impact of 2-dimensional electron gas (2DEG) formation at hetero-interfaces, leading to synergic roles in enhancing the carrier mobility and operation stability of the oxide TFTs. In this work, by means of ALD, a unique bilayer channel configuration exploiting In-Sn-O (ITO) prompt and In-Sn-Zn-O (ITZO) prime layers, where cationic compositions of each layer were carefully controlled and determined for realizing high-performance oxide TFTs showing both benefits of higher mobility and better stability.

Fig. 1 shows a schematic cross-section of the ITO/ITZO TFTs with overall process conditions of active channel compositions for single-layer and bilayer channel configurations. Bi-layered prime ITZO (7 nm) and prompt ITO (3 nm) thin films were successively deposited in ALD chamber at 150 ^{o}C. Cationic compositions of ITZO layers were adjusted by controlling the sub-cyclic ratios (TEIn:TDMASn:DEZn) to 2:1:2 and 2:1:4. Alternatively, the sub-cycles (TEIn:TDMASn) was fixed as 6:1 for the preparation of ITO layer.

Figs. 2a and 2b show the transfer characteristics of the fabricated ITZO and ITO/ITZO TFTs, respectively. Dev-C and Dev-D with bilayer channel configurations exhibited sound TFT operations, even though the turn-on positions were shifted in negative direction. While the field effect mobility (μ_{FE}) of the Dev-B was estimated to be only 23.0 cm^2/Vs, the μ_{FE} of the Dev-D was significantly improved above 30.8 cm^2/Vs. Figs. 3a-3d shows the variations in transfer curves with stress time evolution for the Dev-B and Dev-D, respectively. Noticeably, the Dev-D exhibited the shifts in threshold voltages of +0.05 and -0.07 V under positive- and negative-bias stress conditions, respectively, declaring stronger immunity against gate bias stress than the Dev-B. In other words, the implementation of hetero-junctions with 2DEG was verified to provide easier path of conduction electrons with simultaneously suppressing the charge-trapping events at front-channel interfaces. As results, the introduction of ALD-derived ITO prompt layer was found to enhance the device performance of conventional devices using ITZO single-layer channel.Consequently, the enhancement in device performance obtained from the ITO/ITZO bilayer channel TFTs clearly claim that the engineered bilayer channel configurations designed by the ALD process can extend the application fields of oxide TFTs.

2:30pm **AA1-WeA-5 Elaboration of Refractory Metamaterials by Atomic Layer Deposition for Tuning Thermal Emission at High Temperature***,* ***Syreina Sayegh,*** European Institute of Membranes, France*; A. NZIE,* CEMHTI, France*; M. Bechelany,* European Institute of Membranes, France*; O. ROZENBAUM,* CEMTHI, France*; Q. FLAMANT,* Saint Gobain, France

At high temperature, thermal radiation accounts for a large part of the heat transfer. Therefore, the ability to tune thermal emission is paramount to improve energy efficiency when heating and cooling. It is also one of the keys for converting efficiently heat into electricity in a thermophotovoltaic system.

Electromagnetic properties of natural materials are mainly determined by their chemical composition. The metamaterial approach provides additional degrees of freedom for tailoring these properties by playing on the internal structure. This accrued flexibility is of particular interest for the design of thermal emitters: it allows full spectral control and impedance matching with free space, thereby maximizing the emission for a chosen wavelength range.

Unfortunately, most existing metamaterials rely on metals with a low melting point such as gold or silver. So far, the attempts to realize refractory metamaterial emitters relied either on refractory metals (e.g. Ta, Mo, W) or on nitrides (e.g. TiN, AlN, ZrN). These materials do have high melting points but are prone to oxidation which limits their operating temperature in air.

In this presentation, we will show how using innovative fabrication approaches such as Atomic Layer Deposition (ALD) and making the proper choice for associating a conducting and a dielectric material allows elaborating refractory metamaterials with tunable emissivity in the near infrared (NIR) that can operate in air at temperatures exceeding 1000°C.

2:45pm **AA1-WeA-6 Optical Properties of Interconnected Plasmonic Nanostructures with sub-10 Nm Nanogaps by Area-Selective Atomic Layer Deposition***,* ***Brian Willis,*** *R. Raman, J. Grasso,* University of Connecticut

Nanostructures made of materials such as Cu, Ag, and Au have plasmonic resonances in the visible and near infrared spectral regions. These resonances enhance light - matter interactions by concentrating electric fields around nanostructures. Enhanced electric fields are useful for applications in spectroscopy, catalysis, and photodetection. Electric fields are especially strong in nanogaps between closely spaced particles, and there has been significant work to devise nanofabrication techniques to control interparticle distances with nanometer precision. The majority of work in plasmonics has investigated particles in solution or nanostructures deposited onto surfaces without electrical connections, but adding electrical contacts adds new functionality. In particular, adding electrical interconnects to plasmonic nanostructures provides opportunity for nanoscale light emitters and detectors, as well as energy harvesting. In this work, we investigate the design and fabrication of arrays of interconnected plasmonic nanostructures with sub-10 nm nanogaps. FDTD simulations model optical extinction properties of nanostructures fabricated on glass substrates, and ALD experiments create nanostructures with tunable nanogap spacing. We use glass substrates with nanostructure templates made by conventional nanofabrication methods, and subsequently coat those nanostructures with conformal layers of Cu by ALD to control interparticle distances. Cu ALD occurs selectively on Pd, and nanostructure templates are coated with Pd to promote growth. Selective area growth ensures that neighboring nanostructures remain electrically isolated. This configuration allows for electrical measurements during irradiation with light, see attached figure. Compared with Cu and Au, Pd is a poor plasmonic material, but Pd is necessary for promoting Cu growth. In this talk, we investigate several different approaches using both homodimers and heterodimers with different Au/Pd combinations. Optical extinction measurements reveal how plasmonic resonances evolve when Cu layers are added and nanogaps shrink. FDTD simulations provide insight to how complex changes of nanostructure size, thickness, and shape affect plasmonic properties. We also investigate how interconnect designs perturb plasmonic resonances compared to isolated nanorods. Our findings show that ALD can achieve sub-10 nm nanogaps for interconnected designs with plasmonic properties similar to isolated nanostructures, and that the process can scale to large arrays of devices. Results show that it should be possible to create electro-optic devices where intense electric fields from plasmonic resonances enable new functionality.

3:00pm **AA1-WeA-7 Electrochemically Active Antibacterial Electrodes for Neural Interfacing Applications***,* ***Shahram Amini,*** Pulse Technologies Inc.*; G. Feng, H. Khosla,* Villanova University

Miniaturization and electrochemical performance enhancement of electrodes and microelectrode arrays in emerging long-term implantable neural interfacing devices improves specificity, functionality, and performance of these devices. However, surgical site and post-implantation infections are amongst the most devastating complications after surgical procedures and implantations. Additionally, with the increased use of antimicrobial drugs, the threat of antimicrobial resistance is significant and is increasingly being recognized as a global problem. Therefore, the need for alternative strategies to eliminate post-implantation infections and reduce antibiotic consumption has led to development of medical devices with antibacterial properties. In this work, we report for the first time on the development of antibacterial platinum-iridium electrodes with ultra-high electrochemical performance using a two-step manufacturing process. Electrodes are first restructured using femtosecond-laser hierarchical surface restructuring technology yielding unprecedented performance values that significantly exceed those reported in the literature, e.g. charge storage capacity and specific capacitance were shown to have improved by two orders of magnitude and over 700-fold, respectively, compared to un-restructured electrodes. In the second step of the process, atomiclayer deposition was utilized to deposit conformal copper oxide thin films on the hierarchical surface structure of the electrodes to impart antibacterial properties to the electrodes. Electrochemical, morphological, compositional, and structural properties of the electrodes were studied using a suite of characterization techniques. Last, but not least, the antibacterial properties of the electrodes were also studied, particularly, the killing effect of the antibacterial electrodes on Escherichia coli and Staphylococcus aureus - two common types of bacteria responsible for implantation infections.

3:15pm **AA1-WeA-8 Ultrathin TiO_2 ALD Coatings Strongly Enhance Biological Response of Biomedical Materials***,* ***Jan Macak,*** University of Pardubice, Czechia

TiO_2 surfaces are in general recognized as excellent biocompatible materials owing to their low cytotoxicity, high stability, antibacterial properties, and wetting ability. Among various TiO_2 nanostructured surfaces that show very good cell interactions (various cell types) and osseointegration, anodized TiO_2 nanotube (TNT) layers have emerged as extremely suitable substrates. A pioneering work demonstrated that TNTs with diameter of 15 nm are the most suitable for the growth of various cells [1]. But numerous papers also showed that anodization is a very viable tool for nanostructuring of various biomedical alloys, including frequently used TiAlV.

Recently, we demonstrated that an ultrathin coating on TNT by suitable oxides (e.g. TiO_2) using Atomic Layer Deposition (ALD) can enhance cell growth and adhesion [2]. These properties make them excellent as final surfaces for medical and dental implants based on Ti alloys.

The presentation deals with the comparison of the influence of ultrathin ALD TiO_2 coatigs (achieved by few cycles of TiO_2 ALD process) on TNT layers, reference Ti foils and Ti biomedical alloys for the proliferation of fibroblast, osteoblast and neuroblasts cells. For that Ti sheets and anodized TNT layers with a distinct inner diameter of 12 nm, 15 nm, and 100 nm were used as substrates, as they appear to be the most suitable for cell growth in general [2,3,4]. We investigated the shaping, adhesion, proliferation, and cell density on these substrates.

Moreover, the single-cell adhesion of the cells to the TNTs was studied by the bio-atomic force microscopy (bio-AMF) technique [3]. Last, but not least, black form of TiO^2 nanotubes was investigated for cell proliferation in comparison to classical TNTs [4],

References:

1. Park, J. et al. Small 2009, 6, pages:666 -671.

2. Motola, M. & Rousar, T.; &Macak, J.M. Thin TiO_2 Coatings by ALD Enhance the Cell Growth on TiO_2 Nanotubular and Flat Substrates. ACS Appl. Bio Mater. 2020, 3, 6447−6456.

3. Baishya, K. & Macak, J.M. Bio-AFM exploits enhanced Response of Human Gingival Fibroblast (hGFs) on TiO_2 Nanotubular Substrates with Thin TiO_2 Coatings. 2022, Applied Surface Science, submitted.

4. Sopha, H. & Rousar, T. & Macak, J.M., et al. Comparison of cellular effects between white and black anodic TiO_2 nanotubes, Surface and Coating Technology, 2023, submitted.

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