Nanostructure Synthesis and Fabrication
Room 113-115 - Session NS-MoA

2D Materials

Moderators: Yo-Sep Min, Konkuk University, John Conley, Jr., Oregon State University

1:30pm NS-MoA-1 Low-temperature Growth of 2-D SnS Thin Films by Atomic Layer Deposition, *In-Hwan Baek, J Pyeon,* Korea Institute of Science and Technology, Republic of Korea*; T Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; J Han,* Seoul National University of Science and Technology, Republic of Korea*; C Hwang,* Seoul National University, Republic of Korea*; S Kim,* Korea Institute of Science and Technology, Republic of Korea

Many efforts have been dedicated to 2-D metal chalcogenides because of their characteristic properties which can hardly be expected from bulk materials. A challenging task for implementation of 2-D metal chalcogenides in emerging devices is to synthesize the well-crystallized layer on large area substrates at low temperatures which are compatible with the current fabrication processes for electronic devices are. SnS, a p-type layered semiconductor with high hole mobility, is a promising candidate for the realization of the large-area growth at low temperature because of its low melting point ($882^{\circ}C$). Several techniques such as spray pyrolysis, chemical vapor transport, sulfurization and e-beam evaporation have been introduced to synthesize 2-D SnS thin films. However, There are difficulties in synthesizing phase-pure SnS thin films because tin sulfides exist in various phases such as SnS, Sn_3S_4, Sn_2S_3, and SnS_2.

Here, we demonstrate a successful synthesis of single phase and impurity-free p-type SnS thin films using an ALD technique at low temperatures (< $240^{\circ}C$). The use of a Sn precursor with an oxidation state of +2, bis(1-dimethylamino-2-methyl-2propoxy)tin(II), enabled the synthesis of single phase SnS(II) thin films at temperatures ranging from $90^{\circ}C$ to $240^{\circ}C$, which is an exceptionally wide window for an ALD process. The SnS grain size increased with increasing the growth temperature. It was also found out that the SnS van der Waals interlayers were well aligned in parallel to the substrate at $240^{\circ}C$. Impurities such as carbon, oxygen, and nitrogen were negligibly detected in the SnS(II) films and other phases such as Sn_2S_3 and SnS_2 are not incorporated. Furthermore, we investigated the feasibility of the SnS(II) thin films as a functional material in emerging devices such as thin film transistors and gas sensors.

1:45pm NS-MoA-2 Atomic Layer Deposition of 2D Semiconductor SnS_2, *Miika Mattinen, P King, L Khriachtchev, K Meinander,* University of Helsinki, Finland*; J Gibbon, V Dhanak,* University of Liverpool, UK*; J Räisänen, M Ritala, M Leskelä,* University of Helsinki, Finland

Two-dimensional (2D) materials have attracted broad interest due to their unique properties and wide range of applications stemming from their layered crystal structures. In particular, semiconducting 2D materials, such as MoS_2, have been extensively studied for applications including field-effect transistors (FETs), photodetectors, catalysis, energy storage, and sensing. Tin disulfide (SnS_2) has recently emerged as a promising alternative for MoS_2 as a 2D semiconductor. It has an indirect band gap ranging from 2.2 eV in bulk[1] to approximately 2.6 eV in monolayer[2] and it has shown performance comparable to MoS_2 in FET and photodetector applications.[3] Furthermore, SnS_2 appears to have potential for low-temperature processing compared to the dichalcogenides of refractory metals, such as MoS_2.

We have developed a new process for atomic layer deposition of 2D SnS_2 films using tin(IV) acetate and H_2S at 150 °C combined with mild post-deposition annealing at 250 °C in H_2S/N_2 atmosphere. Deposition of continuous, uniform, and conformal ultrathin (2 to 11 monolayers) SnS_2 films is demonstrated for the first time (Supplementary Figure 1). The annealed films exhibit good crystallinity with the expected, layered SnS_2 structure and are very smooth, stoichiometric, and show n-type semiconducting behavior (Supplementary Figure 2). Using the present method, SnS_2 films can be deposited on a range of different substrates.

[1]Burton et al., *J. Mater. Chem. A*, **2016**, *4*, 1312–1318

[2]Ye et al., *Nano Res.,* **2017**, *10*, 2386-2394

[3]Huang et al., *ACS Nano,* **2014**, *8*, 10743–10755

2:00pm NS-MoA-3 Wafer-scale Growth of Single Phase SnS_2 Thin Films by Atomic Layer Deposition, *Jung Joon Pyeon, I Baek,* Korea Institute of Science and Technology, Republic of Korea*; T Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; J Han,* Seoul National University of Science and Technology, Republic of Korea*; C Kang, S Kim,* Korea Institute of Science and Technology, Republic of Korea

Two-dimensional (2-D) metal chalcogenides have received great attention because of their unique characteristics which are not expected from bulk materials. In order to implement the 2-D materials in nanoelecronic devices, it is imperative to develop a facile route for large-area synthesis with precise thickness controllability and excellent uniformity in a temperature range compatible to common fabrication processes for electronics. SnS_2 is great a great candidate material for meeting the above conditions. Because the melting point(T_m) of SnS_2 is $860^{\circ}C$, lower than that of other 2-D mateirals such as MoS_{-2} and WS_2 (>1000 $^{\circ}C$). The low meliting point of SnS_2 renders the high crystallized growth below $400^{\circ}C$ that satisfies the device process temperature. In addition, this material has a few hundreds of $cm^2V^{-1}s^{-1}$ and shows a indirect band gap ~ 2.4 eV, lager than that MoS_2 and WS_2. This larger band gap of SnS_2 allows that higher on/off current ratio and lower leakage currents of off state. Also SnS_2 materials is environmental friendly, abundant materials and nontoxic. However, tin sulfides exist various crystal phases such as SnS_2, SnS, and Sn_2S_3. The important point is that the electronic properties of tin sulfides are strongly dependent on the crystal phase. Therfore, it has been challenging to synthesize the pure SnS_2 single phase without the other crystal phase.

Here we demostrated a useful technique to form single phase SnS_2 thin films by Plasma Enhanced Atomic Layer Deposition (PEALD). The SnS_2 thin films were grown by PEALD using unstable 2^+ Sn(dmamp)$_2$ source and H_2S plasma. All the processes were performed below such a low temperature of $300^{\circ}C$, which is compatible to current fabrication processes for electronic devices. Despite of low temperature, our SnS_2 has van der waals interlayer structure and these films have single phase of n-type SnS_2 without no oher phase. In addition, this method achieved great uniformity over large area (4-inch Si wafer) and excellent step coverage on the 3D structure. Moreover, field effct transtor devices using single phase SnS_2 channel layers were investigated. We expect that this SnS_2 process would provide decisive opportunities for realizing next genenration nano electronic devices.

2:15pm NS-MoA-4 ALD Tin Sulfide Thin Films and Their Device Applications, *Hyeongsu Choi, S Shin, J Lee, H Park, N Lee, C Jung, H Cho, H Jeon,* Hanyang University, Republic of Korea

Tin disulfide (SnS_2) and tin monosulfide (SnS), two representative tin sulfide materials, are emerging as two-dimensional (2D) materials after appearances of graphene and black phosphorus. SnS_2, an n-type semiconductor, has hexagonal structure that individual layers consisting of three atomic planes, such as CdI_2. It has been studied, due to the same crystal structure and similar semiconductor characteristics with transition metal dichalcogenides(TMDCs) . In the case of SnS, it has been attracting attention as an absorber layer of solar cell due to its appropriate band gap and absorption coefficient. Recently, SnS is also studied as a 2D material due to orthorhombic double layer structure like black phosphorus. However, very few studies have been done to obtain tin sulfide thin films with current thin film fabrication methods such as chemical vapor deposition (CVD) and atomic layer deposition (ALD).

In this study, we will present about results of high crystalline tin sulfide thin films deposited by ALD method. High crystalline SnS_2 thin films were obtained by phase transition from the high crystalline SnS thin films. SnS thin films were deposited on Si/SiO_2 substrate with tetrakis(dimethylamino)tin ($Sn[N(CH_3)_2]_4$, TDMASn) and hydrogen sulfide (H_2S) at 170°C, and subsequent H_2S annealing was performed in the tube furnace at 450°C. We then characterized the crystal structures, chemical bonding states, and optical band structures with XRD, XPS, TEM and UPS. In addition, we fabricated the field effect transistors (FETs) with SnS and SnS_2 thin films, and compared their switching device characteristics. Consequently, changes in the crystal structure and chemical state from SnS to SnS_2 were examined by XRD and XPS, respectively. After transition from SnS to SnS_2, the optical bandgap was measured and increased from 1.35 to 2.70 eV, but absorption coefficient decreased from ~10^5 to ~10^4 cm^{-1} at visible region. Transition of electrical characteristic from p-type to n-type were also observed, and highly crystalline orthorhombic and hexagonal layer structures of two tin sulfide thin films were directly shown in the images of high resolution-transmission electron microscopy (HR-TEM). The electrical characteristics of FETs of SnS and SnS_2 thin films showed on-off

current ratios of 8.8 and 2.1 x 10^3 and mobilities of 0.21 and 0.014 cm²/Vs, respectively. These deference of switching device characteristics will be discussed based on the major carrier concentrations of the SnS and SnS_2 thin films.

2:30pm NS-MoA-5 Synthesis of 2D MoS_2 and MoS_2-Graphene Heterojunction by Atomic Layer Deposition, *Youngjun Kim, D Choi, W Woo, J Lee,* Yonsei University, Republic of Korea*; G Ryu, Z Lee,* Ulsan National Institue of Science and Technology, Republic of Korea*; J Ahn, J Park, H Kim,* Yonsei University, Republic of Korea

The effective synthesis two-dimensional molybdenum disulfides (2D MoS_2) with atomically controlled thickness is essential for their use in electronic devices. In this work, 2D MoS_2 was grown directly on SiO_2 and Graphene using Atomic Layer Deposition (ALD) with MoF_6 and H_2S. We investigated the growth characteristics of the Molybdenum precursor (MoF_6) by Raman spectroscopy and microscopy. By using MoF_6 precursor, 2D MoS_2 synthesized also on the graphene forming MoS_2/graphene heterostructure. The optical microscopy, Raman spectroscopy, photoluminescence (PL), X-ray photoemission spectroscopy (XPS), and transmission electron microscopy (TEM) measurements indicate that the ALD MoS_2 is layered structure with good uniformity, stoichiometry and controlled layer number. Furthermore, we demonstrated the electrical properties of 2D MoS_2 and optical characteristics of MoS_2/Graphene 2D heterostructure. This fabrication process could also provide an opportunity for the production of burgeoning MoS_{-2} and other Transition Metal Dichalcogenides (TMD) for nanoelectronics and optoelectronics.

2:45pm NS-MoA-6 Atomic Layer Deposition of MoS_2/WS_2 Nanolaminates from bis(tert-butylimido)-bis(dialkylamido) Compounds and 1-Propanethiol, *Berc Kalanyan*, *J Maslar, B Sperling,* National Institute of Standards and Technology*; R Kanjolia,* EMD Performance Materials

Layered two dimensional (2D) transition-metal dichalcogenides (TMDs) are finding use in nanoelectronic and optoelectronic applications due to their thickness dependent optical and electrical properties. Scalable fabrication of TMD-based devices requires deposition routes that can produce continuous and uniform films with sub-nanometer thickness control. Atomic layer deposition (ALD) is a highly promising route for the synthesis of 2D TMDs and heterostructures due to digital thickness control achieved by sequential self-limiting chemistry. Another advantage of ALD is that thickness control and the structural development of the films can be decoupled by separating the deposition and crystallization steps. We take advantage of these process attributes to prepare ALD MoS_2/WS_2 nanolaminates that would be otherwise difficult to grow by conventional chemical vapor deposition approaches. We have recently characterized the self-limiting deposition of MoS_2-containing amorphous films from bis(tert-butylimido)-bis(dialkylamido)Mo and 1-propanethiol. Using the homologous W precursor, we now report on the development of MoS_2/WS_2 nanolaminates, which offer a convenient means to tune the optical and electronic properties of few-layer TMD systems.

We deposited thin films using $(N^tBu)_2(NMe_2)_2M$ and 1-propanethiol, where M=(Mo,W), at wafer temperatures of 300°C to 400°C on SiO_2/Si substrates. As-deposited and sulfur annealed films were evaluated using spectroscopic ellipsometry, grazing incidence X-ray diffraction (GIXRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and cross-sectional transmission electron microscopy (TEM). As-grown films were an amorphous matrix of metal sulfides mixed with unreacted ligands, evident as carbon and nitrogen impurities as measured by XPS. As-deposited films were annealed to produce $2H-MoS_2$ and $2H-WS_2$ under a sulfur atmosphere, which also removed residual ligands. Nanolaminates were prepared by alternating the injections of the two metal precursors at a fixed Mo:W ratio to achieve different film compositions. The overall Mo:W ratio in the film was found to follow the pulsing ratio of the two metal precursors. Upon annealing at 850°C, we obtained films that exhibit Raman modes associated with $2H-MoS_2$ and $2H-WS_2$, suggesting that distinct phases, rather than a solid solution, were favored. Relative changes in the overall Mo:W composition were also maintained in the annealed films, indicating that final material properties in TMDs could be controlled by implementing ALD nanolaminates. We will also discuss the implications of film incubation during laminate cycling and subsequent effects on film chemistry.

3:00pm NS-MoA-7 Wafer-scale MoS_2 Monolayer Grown on SiO_2/Si Substrate by Modified Atomic Layer Deposition, *Dae Hyun Kim*, *D Kim, T Seok, H Jin, T Park,* Hanyang University, Republic of Korea

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) have gained great attention due to its potential applications in electronic and optical devices. Among the 2D-TMDCs family, MoS_2 monolayer has been extensively studied due to high carrier mobility over 200 cm²v⁻¹s⁻¹and flexibility. The electronic band structure is transformed from indirect (~1.2 eV) to direct (~1.9 eV) with decreasing the thickness of MoS_2 from bulk to mono layer (0.6 nm), that is suitable for electronic and optical applications. However, most of studies on 2D MoS_2 have utilized small flakes prepared by mechanical exfoliation and chemical vapor deposition with a transfer technique onto SiO_2 substrate due to the difficulty of direct growth of uniform MoS_2 monolayer on SiO_2 substrate.

In this study, an uniform MoS_2 monolayer was grown directly on 4-in. SiO_2/Si substrate by modified atomic layer deposition technique with extremely-precise thickness controllability and uniformity, which were confirmed by various tools such as Raman shift, photoluminance (PL) mapping and atomic force microscopy. The detailed experimental results will be presented.

3:15pm NS-MoA-8 X-ray Absorption Spectroscopy of Amorphous and Layered ALD Molybdenum Sulfide Films Prepared using MoF_6 and H_2S, *Steven Letourneau,* Boise State University*; M Young,* Argonne National Laboratory*; N Bedford,* National Institute of Standards and Technology*; Y Ren, A Yanguas-Gil, A Mane, J Elam,* Argonne National Laboratory*; E Graugnard,* Boise State University

Atomic layer deposition of molybdenum disulfide has recently been demonstrated using various chemistries. Many of these ALD processes, when performed at low temperatures, yield amorphous films and require annealing to obtain layered MoS_2. Raman spectroscopy is one of the most widely used characterization techniques for 2D materials, but these amorphous structures typically do not show the in-plane and out-of-plane vibrational modes of a layered structure. Characterizing these amorphous films is difficult, but crucial if ALD is to succeed in making monolayer or few layer MoS_2. In this work, we use X-ray absorption spectroscopy (XAS) and pair distribution function (PDF) measurements to investigate the as-deposited structure of ALD MoS_2 films prepared using MoF_6 and H_2S at 200°C. Model fits of the extended X-ray absorption fine structure (EXAFS) regime were used to infer the local coordination around the Mo atom centers. While the Mo-S coordination in ALD MoS_2 films seems to fit well with MoS_2 reference structures, the Mo-Mo coordination number was much lower than expected. In addition, PDF measurements performed to examine the bonding pairs suggested small clusters of trigonally prismatic MoS_2 with polysulfides forming between the sulfur atoms. Annealing these films at 400°C in H_2S yielded layered MoS_2, which was confirmed by transmission electron microscopy and X-ray photoelectron spectroscopy, suggesting that thin, layered MoS_2 films are possible using MoF_6 and H_2S.

Nanostructure Synthesis and Fabrication
Room 113-115 - Session NS-TuM

Nanostructures I

Moderators: Seong Keun Kim, Korea Institute of Science and Technology (KIST), Mato Knez, CIC nanoGUNE

10:45am NS-TuM-12 The Precise Tailoring of Catalyst Interface by Atomic Layer Deposition, *Yong Qin,* Institute of Coal Chemistry, Chinese Academy of Sciences, China **INVITED**

The active sites of the supported nano-catalysts may include the surface sites of the metal nanoparticles and the interface sites between the metal nanoparticles and the support. The metal-support interfaces considerably affect the catalytic performances, and in many cases, are even more effective than the surface sites. Therefore, the precise tailoring of the surface/interface structure is the most important approach to improve the catalytic performance, especially the selectivity of heterogeneous catalyst. Surface modification and encapsulation of the metal nanoparticles are used extensively for the surface/interface tailoring. In order to obtain highly effecient catalyst and understand the catalytic mechanism, it is critically important to precisely control the particle size distribution, the location and content of the modification materials, and the composition and microstructure of the interface. However, in general, it is difficult to regulate these parameters accurately by traditional methods, such as chemical vapor deposition, sol-gel method, precipitation, impregnation, and so on. Atomic layer deposition (ALD) is an advanced thin-film technology, which possesses thickness control at the atomic level, excellent uniformity and conformality, and good reproducibility. In view of the limitations of traditional methods on the tailoring of the surface/interface structures, we developed new methods for the controllable synthesis of metal nanoparticles, dense/porous oxide films, and carbon films by ALD. Based on these synthesized materials, the tailoring of the surface/interface structure were performed by coating, ultrathin coating, confining in nanospace, ultrathin coating of confined catalyst, and assembling of double-interface structure. These catalysts were characterized and evaluated deliberately, and the mechanisms of how the surface/interface structures affect the catalytic performances were discussed. These results will provide new guidance for the design and synthesis of highly effective catalysts.

11:15am NS-TuM-14 Improving the Anti-sintering Ability of Au/TiO$_2$ Catalysts by Constructing Semi-embedded Structure via Selective Atomic Layer Deposition, *Yuanting Tang, X Liu, B Shan, R Chen,* Huazhong University of Science and Technology, China

Au nanoparticles are very active for various important catalytic reactions, such as CO oxidation, partial oxidation of hydrocarbons and so on [1]. However, Au nanoparticles are highly susceptible to sinter at elevated temperature, which leads to serious decrease in catalytic activity . In this work, TiO$_2$-Au/TiO$_2$ catalysts are fabricated with semi-embedded structure via area selective atomic layer deposition (ALD). The area selective ALD method is realized through passivation of metal nanoparticles with self-assembled monolayers [3]. CO oxidation is performed as probe reaction. The results show that TiO$_2$-Au/TiO$_2$ catalysts exhibit outstanding room-temperature CO oxidation activity even after calcination. The key feature of the embedded structure lies in its ability to anchor Au nanoparticles and effectively limits the growth of Au nanoparticles via strong metal–oxide interactions, while still leaving active metal facets exposed. The reported method shows great potential for the simultaneous enhancement of thermal stability and activity of precious metal nanoparticles.

[1] Liu X, He L, Liu Y M, et al., *Accounts. Chem. Res.* 2014, 47, 793.

[2] Valden M, Lai X, Goodman D W, *Science*, 1998, 281, 1647.

[3] Liu X, Zhu Q, Lang Y, et al., Angew. Chem. Int. Ed. 2017, 56, 1648

11:30am NS-TuM-15 Tuning of Boron Nitride Nanotubes, Nanopores and Nanoporous Membranes by ALD, *Matthieu Weber, B Koonkaew, S Balme,* Institut Européen des Membranes, France*; I Utke,* EMPA, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; F Picaud,* Université Bourgogne Franche-Comté, France*; I Iatsunskyi, E Coy,* Adam Mickiewicz University in Poznan, Poland*; D Cornu, P Miele, M Bechelany,* Institut Européen des Membranes, France

In this presentation, we report the design and the fine-tuning of boron nitride nanotubes, nanopores and nanoporous membranes by atomic layer deposition (ALD).

First, we developed an ALD process based on the use of BBr$_3$ and NH$_3$ as precursors in order to synthesize BN thin films. The deposited films were characterized in terms of thickness, composition, microstructure and mechanical properties.[1,2]

Next, we report the scalable synthesis of BN nanotubes that can be tuned in terms of diameters dimensions through a novel and easy route combining ALD and annealing steps. Carbon nanofibers templates are used as initial supports. In order to obtain the crystallization of BN and to eliminate the carbon initial supports, the samples were first placed at a temperature of 1350°C in nitrogen atmosphere for 5 hours, and then annealed at 600°C for 4 hours in air. The inner diameter can be controlled by choosing the initial carbon nanofibers supports. High resolution TEM imaging has been carried out to characterize the obtained BN nanotubes. The self-limiting reactions of ALD provide a clear control over the diameter thickness of the BN layer deposited with sub-nanometer accuracy as a steady-state ALD growth of ~0.8 Å/cycle has been observed on all our samples. The self-supported BN nanotubes synthesized present good mechanical properties and are easy to handle. Furthermore, the sorption performances of the BN nanotubes have been assessed, and the results showed that the nanotubes absorb up to 110 times their weight in oil while repelling water. These proof-of-concept results are thus very promising for water purification purposes.

For the first time, this BN ALD process was also used to tune the diameter of fabricated single transmembrane nanopores by adjusting the BN thickness and to enable studies of the fundamental aspects of ionic transport on a single nanopore. At pH=7, we estimated a surface charge density of 0.16 C.m^{-2} without slip and 0.07 C.m^{-2} considering a reasonable slip length of 3 nm. Molecular dynamic simulations performed with experimental conditions confirmed the conductivities and the sign of surface charges measured.[2] The high ion transport results obtained and the ability to fine-tune nanoporous membranes by such a scalable method paves the way towards applications such as ionic separation, energy harvesting and ultrafiltration devices.

1 Weber M et al. Boron Nitride Nanoporous Membranes with High Surface Charge by Atomic Layer Deposition,

ACS Applied Materials and Interfaces 9, 19, 16669 (2017).

2 Weber M et al. Mechanical Properties of Boron Nitride Thin Films Prepared by Atomic Layer Deposition. *CrystEngComm*, 19, 6089 (2017).

Nanostructure Synthesis and Fabrication
Room 104-106 - Session NS+ALE-TuA

Nanostructures II + ALE

Moderators: Robert Clark, TEL Technology Center, America, LLC, Yong Qin, Institute of Coal Chemistry, Chinese Academy of Sciences

4:00pm NS+ALE-TuA-11 Atomic Layer Etching and Chemical Vapor Etching of 2D Materials and Metal Oxide Films using MoF$_6$-H$_2$O, *Anil Mane, D Choudhury, S Letourneau, J Elam,* Argonne National Laboratory

To meet the milestones outlined in the semiconductor technology roadmap, precisely controlled layer-by-layer etching processes for metal oxides are required to enable the fabrication of 3D-semiconductor microelectronic devices. In addition, 2D-layered transition metal dichalcogenides (TMDs) with tunable electronic properties exhibit attractive material properties and are under intense investigation as alternatives to silicon. Therefore, integration of 2D-materials with compatible dielectric metal oxide growth as well as etching can pave the way to successful device fabrication. Moreover, both selective material growth and selective etching are required for the cost effective manufacturing of advanced microelectronics.

Here we have developed etching processes using alternating exposures to molybdenum hexafluoride (MoF$_6$) and H$_2$O vapor for ALD grown metal oxides and 2D-TMDs. The MoF$_6$-H$_2$O precursors offer several advantages including low cost, low processing temperature, and rapid and effective etching spanning the range from continuous etching to atomic layer etching (ALEt).

We have used in-situ quartz crystal microbalance (QCM) and Fourier-transform infrared spectroscopy (FTIR) measurements to monitor the deposition and etching of the metal oxides and 2D-TMDs layers. Next, the etched metal oxides and 2D-TMDs thin films were analyzed by spectroscopic ellipsometry to determine the thickness and refractive index, and the composition was determined by X-ray photoelectron spectroscopy (XPS). These ex-situ measurements confirmed the etching behavior findings from our in-situ studies. Here we will discuss the details of the MoF$_6$-H$_2$O based etching chemistry.

4:15pm NS+ALE-TuA-12 Membranes by Atomic Layer Deposition: Design and Applications, *Mikhael Bechelany,* Institut Européen des Membranes, France **INVITED**

Atomic layer deposition (ALD) is a thin film technology that in the past two decades rapidly developed from a niche technology to an established method. It proved to be a key technology for the synthesis of ultrathin film, the surface modification and the fabrication of complex nanostructured materials as well as the membrane tuning. [1]

In this work, we will give an overview about our activities on ALD, from the design of nanomaterials to membrane applications. After a short introduction to ALD, the versatility of the technique for the fabrication of novel nanolaminates thin films [2] and functional nanomaterials [3, 4] will be showed. Selected examples, focused on its use for the engineering of nanostructured functional materials and membranes targeting applications in energy (osmotic energy, biofuel cells and gas separation), environmental ((bio)-sensor and water purification) and health (DNA and proteins sensing) fields [5-9] will be discussed.

[1] **Advanced Materials**, 2012, 24, 1017

[2] **J. Phys. Chem. C**, 2016, 120, 5124–5132

[3] **Nano Energy** 1 (2012) 696

[4] **Nanoscale** 7 (2015) 5794

[5] **Journal of Materials Chemistry A**, 2016, **4**, 6487-6494

[6] **Journal of Materials Chemistry A**, 2016,4, 17686-17693

[7] **Biosensors and Bioelectronics**, 2017, 92, 763–769

[8] **Journal of Materials Chemistry A**, 2014, 2 (48), 20650 – 20658

[9] **ACS Appl. Mater. Interfaces**, 2017, 9, 16669–16678

4:45pm NS+ALE-TuA-14 Field-effect Transistor using Two-dimensional Electron Gas in ALD Al$_2$O$_3$/TiO$_2$ Ultrathin (<10 nm) Film Heterostructure Interface, *Tae Jun Seok, Y Liu,* Hanyang University, Republic of Korea; *H Jung, S Kim,* Ajou University, Republic of Korea; *D Kim,* Hanyang University, Republic of Korea; *S Kim, J Jang,* Korea Basic Science Institute, Republic of Korea; *D Cho,* Chonbuk National University, Republic of Korea; *S Lee,* Ajou University, Republic of Korea; *T Park,* Hanyang University, Republic of Korea

Recently, two-dimensional electron gas (2DEG) has attracted great attention due to the observation of 2DEG at various heteroepitaxial perovskite oxide interfaces. Typically, epitaxial LaAlO$_3$/single-crystal SrTiO$_3$ (LAO/STO) heterostructure shows high density of electrons ($\sim 10^{13}$-10^{14} cm^{-2}) confined at the oxide interface, where the density is about ~ 100 times higher than those of a typical semiconductor interface ($\sim 10^{11}$-10^{12} cm^{-2}). Despite its high electrical performance, process schemes are not suitable for practical device applications because of their high cost in the production of the oxide single crystal and epitaxial layer. Although the formation of 2DEG using γ-Al$_2$O$_3$ and amorphous LAO with Al$_2$O$_3$ over-layers on STO substrate was demonstrated recently, single crystalline STO substrates are still required. Therefore, 2DEG at an oxide interface has not been realized *via* a mass-production compatible thin film deposition process, in contrast to 2DEG at the semiconductor interfaces.

In this work, we demonstrate a realization of 2DEG at the interface in an extremely thin film (< ~ 10 nm) heterostructure comprised of two binary oxide stacks of Al$_2$O$_3$/TiO$_2$ *via* atomic layer deposition (ALD) on a SiO$_2$/Si substrate without using an oxide single crystal or epitaxial substrate. The Al$_2$O$_3$/TiO$_2$ heterostructure was composed of a few nm-thick amorphous Al$_2$O$_3$ over-layer and poly-crystalline anatase-TiO$_2$ bottom layer. We achieved high electron density ($\sim 10^{13}$-10^{14} cm^{-2}) and mobility (~ 4 cm^2/V·s) in the 2DEG at the interface of ultrathin Al$_2$O$_3$/TIO$_2$ heterostructures, comparable to those obtained from epitaxial oxide heterostructures. More importantly, we demonstrate a new type of field-effect transistors (FETs) using Al$_2$O$_3$/TiO$_2$ heterostructures with a high on-current (I_{on}, > 12 A/m), high on/off current ratio (I_{on}/I_{off} > $\sim 10^8$), low off current (I_{off}, $\sim 10^{-8}$ A/m), and low sub-threshold swing (SS, ~ 100 mV/dec.), which outperforms the oxide heterostructure-based FETs reported so far. Ultrathin (< ~ 7 nm) TiO$_2$ bottom layer in the proposed Al$_2$O$_3$/TiO$_2$ heterostructure prone to be fully depleted, allows an extremely low I_{off}, high I_{on}/I_{off} ratio and low SS with maintaining high I_{on} *via* 2DEG channel with a high carrier density at the interface. The proposed new-type devices would provide a great opportunity for practical applications and mass-production of 2DEG devices, allowing a multi-level three-dimensional (3D) integration scheme. The detailed experimental results including new materials systems will be presented.

5:00pm NS+ALE-TuA-15 Increased WS$_2$ Crystal Grain Size by Controlling the Nucleation Behavior during Plasma Enhanced Atomic Layer Deposition, *Benjamin Groven, A Nalin Mehta,* KU Leuven, Belgium; *H Bender, J Meersschaut, T Nuytten, T Conard, A Franquet, W Vandervorst, M Heyns, M Caymax, I Radu, A Delabie,* IMEC, Belgium

Two-dimensional (2D) transition metal dichalcogenides such as molybdenum and tungsten disulfide (MoS$_2$, WS$_2$) emerge as semi-conducting three-atom-thick layers that are widely applicable, for example as the complement of Si in ultra-scaled nanoelectronic devices at the back-end-of-line (BEOL) [1]. To exploit the potential of 2D layers in BEOL structures, they need to be grown using manufacturable deposition techniques in a highly crystalline structure with control over the orientation of the basal plane at low deposition temperatures (< 450°C).

When grown by atomic layer deposition (ALD) for atomistic growth control and compatibility with temperature sensitive structures, the crystallinity and structure of 2D materials is determined by the nucleation mechanisms, which are currently not yet understood. In our earlier work, polycrystalline WS$_2$ with well-controlled composition (S/W ratio ~ 2) and 2D structure was grown by PEALD from WF$_6$, H$_2$ plasma and H$_2$S on Al$_2$O$_3$ at 300°C [2]. The WS$_2$ layers suffered from a nanocrystalline grain structure (< 20 nm).

In this work, we show that the WS$_2$ crystal grain size can be increased from ~ 20 nm to beyond 200 nm by lowering the nucleation density. The latter is achieved by using a starting surface with a lower reactivity towards the PEALD precursors (i.e., thermally grown SiO$_2$), and by enhancing the mobility of the adsorbed species at higher deposition temperature (< 450°C) and reactor pressure (Figure 1).

By analyzing the morphology of the WS$_2$ crystals, we derive a qualitative model for the nucleation behavior of WS$_2$ during the PEALD process. The SiO$_2$ starting surface is less reactive to the PEALD precursors compared to

Al$_2$O$_3$ starting surfaces, which results in growth inhibition on SiO$_2$. The PEALD precursors preferentially adsorb on the existing WS$_2$ nuclei. In combination with enhanced surface diffusion of the adsorbed species across both the SiO$_2$ starting surface as well as the growing WS$_2$ nuclei, lateral growth from WS$_2$ crystal edges is promoted which maximizes the WS$_2$ crystal grain size and develops a strong (0002) texture.

This work demonstrates how insight in the nucleation behavior of 2D materials can be used to increase the crystal grain size and control the basal plane orientation during ALD. A better understanding of these nucleation mechanisms is crucial to advance the field of ALD of 2D materials.

[1] 47th IEEE European Solid-State Device Research Conference (ESSDERC) **2017**, pp. 212–215. T. Schram, et al.

[2] *Chem. Mater.***2017**, 29 (7), 2927–2938. B. Groven, et al.

5:15pm **NS+ALE-TuA-16 Controlling Material Properties of Nanostructured WS$_2$ during Plasma ALD for Improved Electrochemical Performance***, Shashank Balasubramanyam, L Wu, V Vandalon, M Verheijen, E Kessels, J Hofmann, A Bol,* Eindhoven University of Technology, Netherlands

Transition metal dichalcogenides like WS$_2$ are promising candidates for sustainable production of H$_2$ through electrochemical hydrogen evolution reaction (HER), when engineered into nanostructures with exposed reactive edge sites. Controlling the various parameters during the plasma exposure step of plasma-enhanced ALD (PEALD) allows tailoring of material properties which can influence the HER performance. In this work, we demonstrate a novel approach to maximize the density of reactive edge sites in nanostructured WS$_2$ by tuning the composition of co-reactant gas mixture during the plasma exposure step of PEALD.

H$_2$S+Ar and H$_2$ diluted H$_2$S+Ar were used as co-reactant gas mixtures for tuning the plasma composition during PEALD of WS$_2$. The addition of the strong reducing agent H$_2$ to the H$_2$S+Ar plasma gas mixture can significantly influence the WS$_2$ growth behaviour and resulting material properties. The H$_2$S+Ar plasma yielded a GPC of 0.8Å while the H$_2$S+Ar+H$_2$ plasma increased GPC to 1.4Å for the same metalorganic precursor bis(tertbutylimido)-bis(dimethylamido)-tungsten, at a low temperature of 300°C. Transmission electron microscopy (TEM) studies revealed the growth of WS$_2$ 'nanoflakes' when using H$_2$S+Ar plasma, while H$_2$S+Ar+H$_2$ plasma resulted in the growth of WS$_2$ 'fins'. The nanoflakes comprised of closely packed basal planes with their edges predominantly terminating on the top surface, while the fins appeared to have higher surface area and were observed to taper out on the top surface. Rutherford backscattering spectroscopy studies indicated an excess S content for nanoflakes (S:W=2.2), while a S deficiency was observed for fins (S:W=1.9). In line with TEM studies, X-ray diffraction measurements showed differences in preferential orientation of crystals for nanoflakes and fins.

The HER performance of WS$_2$ nanoflakes was significantly better than of WS$_2$ fins. To reach a current density of 10mA/cm^2, a relatively lower overpotential of ~390mV was sufficient for the nanoflakes while a significantly higher overpotential of ~460mV was required for the fins. In line with HER results, copper underpotential depositions on the respective nanostructures revealed a three-fold increase in the amount of reactive edge sites for nanoflakes when compared with fins. In order t o further enhance the HER performance, catalytically superior WS$_2$ nanoflakes were grown on top of high surface-area WS$_2$ fins. This WS$_2$ stack yielded the best HER performance in our work (overpotential of ~365mV). To summarize, we demonstrate how PEALD can be used as a new approach to nanoengineer and enhance the HER performance of WS$_2$ by maximizing the density of reactive edge sites at low temperature.

Nanostructure Synthesis and Fabrication
Room Premier Ballroom - Session NS-TuP

Nanostructures Synthesis and Fabrication Poster Session

NS-TuP-1 High Sensitive Strain Sensor with Organic Single-crystal Nanowires by Direct Printing, *Yoon Kyoung Park*, *M Sung*, Hanyang University, Republic of Korea

Charge transport properties of organic semiconductors critically depend on their molecular packing structures. Controlling the charge transport by varying the molecular packing and understanding their structure–property correlations are essential for developing high-performance organic electronic devices. Here, we demonstrate that the charge carrier mobility in organic single-crystal nanowires can be modulated with respect to the intermolecular center-to-center distance by applying uniaxial strain to the cofacially stacked crystals. Furthermore, the measured values of charge carrier mobility were in good agreement with theoretical calculations based on charge localized hopping theory. These results provide a definitive relationship between intermolecular packing arrangement and charge transports, which enables a huge improvement in charge carrier mobility for organic single-crystal materials.

NS-TuP-2 Charge-transfer Complex Thin Films with Visible-light Absorption by using Molecular Layer Deposition, *Nguyen Van Long*, Hanyang University, Republic of Korea

A titanium-aryloxide (Ti-Ao) thin films showing high visible-light absorption was fabricated by molecular layer deposition (MLD). The origin of the visible light absorption was ligand-to-metal charge-transfer that is revealed by studying ultraviolet-visible analysis and density functional theory calculations. ZnO/Ti-Ao nano-laminate active channel photo-transistors functioned synergistically with Ti-Ao acting as a visible-light absorber, and ZnO serving as a great semiconductor.

NS-TuP-3 Pretreatment Effect of SnO_2 Layer Coated on Carbon Nanofiber by Atomic Layer Deposition, *D Kim, S Shin, Seok Choi, J Han, B Choi,* Seoul National University of Science and Technology, Republic of Korea

Carbon nanofibers (CNF) are used as active materials for electrodes in various energy devices, such as lithium ion secondary batteries, super capacitors and fuel cells. Recent studies have been proved that nanoscale coatings on carbon nanotubes increase the output and lifespan of the devices owing to the improvement of mechanical and chemical properties. Among the various coating methods, atomic layer deposition (ALD) can conformally adjust the thickness of coating layer without any directional growth. Therefore, it has the advantage of coating on the particle with high aspect ratio, such as CNF, even in nanometers thickness.

In this work, we grow SnO_2 layers having two kinds of morphology on CNF. We compare the reactivity and wettability of precursors and reactant gases as follows; trimethylaluminum (TMA), tetrakis(dimethylamino)tin (TDMASn), $Sn(dmamp)_2$, H_2O, O_3. Since the ALD reaction of TMA, $Sn(dmamp)_2$, O_3 with surface functional group requires the smallest activation energy, it is easier to react with surface functional sites. We also use two types of ALD equipment; Flow-type ALD (static ALD), and fluidized bed reactor type ALD (dynamic ALD). Static ALD is processed at 161℃, 5 cycles by TMA and H_2O as Al_2O_3 reactant, and then followed by 105 cycles of TDMASn and H_2O as SnO_2 reactant. Dynamic ALD is processed at 120℃, 5 cycles by TMA and H_2O as Al_2O_3 reactant, and 150℃ 105 cycles by TDMASn and H_2O as SnO_2 reactant.

According to the TEM analysis, static ALD creates an island-shaped SnO_2, but uniform SnO_2 layer is formed by inserting Al_2O_3 layer. On the contrary, dynamic ALD shows formation of uniform SnO_2 layer irrespective of Al_2O_3 layer. In addition, energy dispersive spectroscopy (EDS) analysis showed more intensive elemental Sn and O signal can be detected from Al_2O_3-coated CNF. XPS analysis reveals that both Sn^{4+} and Sn^{2+} are observed in SnO_2 on CNF by static ALD probably due to the formation of an interfacial layer between the SnO_2/CNF interface. Meanwhile, Sn^{4+} spectra are only shown in SnO_2 on CNF by dynamic ALD. Cyclic voltammetry analysis is performed to characterize the electrochemical properties of SnO_2 coated CNF as an electrode on fuel cell.

NS-TuP-4 Plasma-enhanced Atomic Layer Deposition of Molybdenum Compounds Thin Films Using $Mo(CO)_6$ with Various Plasma Gases, *Jeong-Hun Choi*, *S Lee, C Hyun, J Ahn,* Korea Maritime and Ocean University, Republic of Korea

In recent years, transition metal oxides and dichalcogenides have received much attention due to its attractive properties for a wide range of applications. Among these materials molybdenum compounds were studied most initiatively and achieved considerable progress. Meanwhile, metallic molybdenum is also widely used as conducting materials in many electronic applications. In this study, therefore, optical, structural and electronic properties of metallic molybdenum and its compounds thin films have been investigated. Plasma-enhanced atomic layer deposition (PEALD) was employed to form the uniform Mo, MoO_3, MoS_2 thin films. Especially, When $Mo(CO)_6$ was used as the precursor, different kinds of plasma gases such as O_2, H_2, H_2S and their mixtures for reactant resulted in selective growth of Mo, MoO_3, MoS_2, respectively. Basically, the ALD characteristics with each reactant were studied. The ellipsometry, raman spectroscopy, photo luminescence, X-ray photoelectron spectroscopy, scanning electron microscopy were used to examine film characteristics according to the different precursor combinations and growth conditions. Furthermore, the potential of metallic Mo as well as Mo compounds for device component was investigated.

NS-TuP-5 Fabrication and Characterization of Titanium Disulfide Thin Films by Atomic Layer Deposition, *Gyuhyeon Park*, *N Kornelius, A Thomas,* IFW-Dresden, Germany

Titanium disulfide (TiS_2) is part of the family of layered transition metal dichalcogenides, where each layer consists of edge-sharing TiS_6 octahedra, which leads to strong covalent bonds in plane and weak van der Waals forces out of plane. Because of the uniqueness of the layered structure, TiS_2 enables the formation of various intercalation compounds with guest species such as Na, Li, Mg, and Bi. Therefore, it has potential to adopt to numerous applications, such as thermoelectrics, Lithium ion battery (LIB) or field effect transistor (FET) devices to name a few. In this study, we fabricate TiS_2 by either ALD with H_2S and $TiCl_4$ as precursors or employ sulfurization methods with pre-deposited TiO_2 thin films on various substrates. We will investigate the thermoelectric and electrical properties with a custom setup. This was developed at the IFW in cooperation with Linseis Meßgeräte GmbH in the last years and can simultaneously measure the in-plane electrical and thermal conductivity, the Seebeck coefficient as well as the Hall constant of thin films. Moreover, the result is compared to our previous results of TiS_2 preparation by using CS_2 gas.

NS-TuP-6 Single-Crystal Poly(3-hexylthiophene) (P3HT) Organic Field Effect Transistor which was used to Fabricate Ammonia Gas Sensor, *Jihee Hwang*, *M Sung,* Hanyang University, Republic of Korea

An ammonia gas sensor which was fabricated based on the P3HT organic field-effect transistor (OFET) in the range of 0.01 to 25ppm. Single-crystal poly(3-hexylthiophene) (P3HT) nanowires (100 nm wide 150 nm high nanowires that were separated a 600nm space) were used as the organic semiconductor (OSC) layer of an OFET with a top-contact geometry. This ammonia gas sensor showed outstanding results such as electrical and sensitivity characteristics. First, electrical properties (high mobility, output signal and on/off ratio) of single crystal P3HT nanowire OFET were around two orders of magnitude higher than those of P3HT thin film OFET. Second, it showed enhanced ammonia sensitivity, around three times higher than conventional P3HT thin film OFET with same geometry. In addition, the reversibility of ammonia response was presented on this OFET, and constant results were obtained in the changes of humidity from 45% to 100%. These excellent performances of P3HT nanowire were presented due to high surface/volume ratio and single crystal characteristics of the P3HT nano wires.

NS-TuP-7 Synthesis of Layered TiTe Thin Films by Atomic Layer Deposition, *Chan Young Yoo*, *C Hwang,* Seoul National University, Republic of Korea

Due to increased research interest in 2-dimensional nanomaterials, single- and multi-layer transition metal dichalcogenide (TMD) nanosheets have attracted considerable attention for their potential use in the fields of catalysis, electronic switching devices, and gas sensors. [1] The key technology for utilizing TMD in various applications is a reliable fabrication of the nanosheets over a large area. Chemical vapor deposition and sulfurization have been introduced for large-area synthesis, but the high-temperature conditions adopted in these methods are not compatible with many of the device fabrication processes, especially on flexible substrates. Therefore, low-temperature atomic layer deposition (ALD) process using

highly reactive precursors has been suggested as an alternative to overcome the thermal limit and to enable the practical use of TMD for electronic devices. [2]

In this report, TiTe$_2$ thin films were deposited by ALD, adopting TiCl$_4$ and [(CH$_3$)$_3$Si]$_2$Te as the Ti- and Te-precursors, respectively. Thermally activated ligand exchange occurred at a substrate temperature of 60~200 C, and the saturated growth rate (at 180°C) was ~15 ng·cm^{-2}cy^{-1} as shown in Figure 1. T he ALD TiTe$_2$ films grown over 180°C showed extraordinary plate-shaped hexagonal TiTe$_2$ grains, parallel to the substrate surface, on Si substrate. They were aligned along the (001) plane, showing sharp (001) family peaks in theta-two theta X-ray diffraction (XRD) as shown in figure 2. Further confirmations of layered growth of the deposited TiTe$_2$ are analyzed by scanning electron microscopy (SEM) and Raman spectroscopy . Tilted and vertically grown plate-shaped grains were confirmed in SEM, but the amount was small, showing no peak in grazing-angle X-ray diffraction (GAXRD). This preference was more pronounced for those deposited on sapphire (0001) substrates, which is attributed to the low atomic mismatch of the same hexagonal crystal structure of sapphire and TiTe$_2$. A bottom-gate thin film transistor (TFT) structure was used to characterize the electrical properties of TiTe$_2$ TFTs. Figure 3 displays the transfer curves of the TFT, showing a typical *p*-type conduction behavior. Although the demonstrated device performance is quite low compared to other *p*-type oxide TFTs, these results demonstrate the feasibility of the atomic layer deposited TMD TFT. Further detailed discussions on such ALD deposition will be made in the presentation.

[1] J. A. Wilson et al., Adv. Phys., 18, 193-335 (1969)

[2] I.H. Baek et al., Chem. Mater., 29 (19), 8100-8110 (2017)

NS-TuP-8 Effects of Vacancies on Electronic and Optical Properties of BiOCl Nanosheets, *Yoon Myung,* Sejong University, Republic of Korea*; W Song,* Washington University, St. Louis*; L Mehdi, N Browning,* Pacific Northwest National Laboratory*; A Krayev,* AIST-NT Inc.*; J Park,* Korea University, Republic of Korea*; L Yang, P Banerjee,* Washington University, St. Louis

In this study, we report conductivity switches from p-type of BiOCl to n-type of black BiOCl with generated oxygen vacancies by UV illumination at the exposed (001) surface. This n-type conductivity occurs by formation of oxygen vacancy at the surface of BiOCl nanosheets, confirmed by XPS spectra that oxygen vacancy gradually increasing as a function of UV illumination time. The raman spectra shows oxygen vacancy related vibration mode was rising under 2 mtorr and low temperature PL, the result reveals decreasing band edge emission of BiOCl due to high density oxygen vacancies placed under conduction band edge of black BiOCl. The oxygen partial pressure dependent electrical conductivity showsσ=pO$_2$$^{1/4.05}$ with a positive slope under low pressure region for the BiOCl and σ=pO$_2$$^{1/5}$ with a negative slope under atmospheric region for the black BiOCl.

NS-TuP-9 Novel ZnO Nanorod Ethanol Sensor using ALD Delta Doping with Al$_2$O$_3$ for Nested AZO Wrap-around Coatings, *P Lin, X Chen, K Zhang, Helmut Baumgart,* Old Dominion University

Metal Oxide Semiconductor (MOS) gas sensors have received significantly attentions as electronic devices for the specifics identification and concentration detection of combustible and hazardous gases. Among various semiconductor materials used in MOS gas sensors, ZnO has been widely used for gas sensor applications due to its good electrical conductivity, wide band gape of 3.37 eV, ~60 meV exciton binding energy, low cost, and high mechanical stability. Currently ZnO ethanol sensors based on nanorod structures have been extensively investigated due to their high electrochemical stability, suitable doping, nontoxicity, and high surface-to-volume ratio. ZnO gas sensors with one-dimensional nanostructures have good performance in terms of their sensing response, response time and recovery time.

In this project, Aluminum doped ZnO (AZO) thin films coated by Atomic Layer Deposition (ALD) was deposited on the surface of the ZnO nanostructure to further enhance its sensing performance. The ZnO seed layers were deposited on Si wafer by ALD with (C$_2$H$_5$)$_2$Zn and DI water as precursors of zinc and oxygen. Hydrothermal method was carried out to grow aligned ZnO nanorods. There was a layer of Al$_2$O$_3$ as sacrificial spacer deposited on the surface of ZnO nanorods by ALD with Al$_2$(CH$_3$)$_6$ and DI water as precursors followed by an additional layer of ZnO thin film synthesized by ALD. To expose the Al$_2$O$_3$ sacrificial spacer layer, Precision Ion Polishing System was employed to remove the top cover of synthesized ZnO nanorods. Then Sodium hydroxide was applied to etch the Al$_2$O$_3$ layer to form ZnO nanorod/nanotube structure. Finally, Al doped ZnO thin films

were deposited on the surface of ZnO nanorod/nanotube by ALD to further enhance its sensing performance to ethanol vapors.

The sensing performance of ZnO nanorod/nanotube to ethanol vapor was investigated by a gas sensor testing system which was home-made with a sealed reaction chamber, ethanol vapor generator, testing circuit, and controlled heating system. The gas sensor testing system interface is operated in LabVIEW program and CompactRio system from National Instruments. The resistant variances of ZnO nanorod/nanotube were measured by the home-made sensor testing system. The demonstrated sensing performance results include the sensing response comparison between ZnO nanorods and ZnO nanorod/nanotube structures before and after ALD coatings with nested AZO films at different temperatures and with various concentrations of input ethanol vapor. The response times and recovery times of ZnO nanorod/ nanotube samples before and after ALD coatings with nested AZO thin films were analyzed to investigate the sensing enhancement.

NS-TuP-10 Crystallization of Nanoparticle Shells Grown by Rotary ALD, *Benjamin Greenberg, J Wollmershauser, B Feigelson,* U.S. Naval Research Laboratory

Rotary ALD, wherein oxide and nitride shells are grown by ALD on nanoparticles agitated in a rotating drum, is an emerging technique for scalable production of a wide variety of core/shell nanoparticles. Due to deposition temperature limitations, the shells are typically grown in the amorphous phase. However, many applications of these particles, including batteries and structural nanocomposites, require crystalline shells. In this work we study the crystallization of ALD-grown shells by post-deposition thermal annealing, an approach rarely examined in detail in the nanoparticle ALD literature, despite the technological potential of fully crystalline core/shell nanoparticles. The crystallization temperature of nanoshells is difficult to predict due to a variety of competing effects of spheroidal geometry. For example, compared to a planar film of the same thickness, a nanoshell has more atoms at the surface but fewer atoms at the film/substrate interface. Using Al$_2$O$_3$ shells as a prototype, we investigate the dependence of crystallization behavior on shell thickness as well as underlying nanoparticle material and size. We characterize shell composition, structure, and morphology by XPS, XRD, and TEM.

**NS-TuP-11 Multi-walled Carbon Nanotubes Coated by Atomic Layer Deposition of TiO$_2$, *Lenka Zajickova,* Masaryk University, Czech Republic*; M Elias,* CEITEC, Brno University of Technology, Czech Republic*; P Kaushik,* Masaryk University, Czech Republic*; J Michalicka,* CEITEC, Brno University of Technology, Czech Republic*; L Michal, M Michlicek,* Masaryk University, Czech Republic*; D Hegemann,* EMPA, Swiss Federal Laboratories for Materials Science and Technology

Carbon nanotubes (CNTs) coated with titanium dioxide (TiO$_2$) have become a promising hybrid nanomaterial for a wide range of applications, e.g. photocatalysis, gas sensors, dye-sensitized solar cells and energy storage. These nanostructures combine the high surface area and excellent thermal and electrical conductivity of the CNTs with the high photoactivity and chemical stability of TiO$_2$. In this study multi-walled carbon nanotubes (MWCNTs) were grown by catalytic chemical vapor deposition on Si and Si/SiO$_2$ substrates using Fe catalyst. They were subsequently coated by atomic layer deposition (ALD) of TiO$_2$ from tetrakis(dimethylamido)titanium. Since the ALD is a self-limiting surface process it is important to understand how it proceeds on the inert and nanostructured surface of carbon nanotube forest. Therefore, we tested different plasma modifications of MWCNTs surface (oxygen plasma treatment, carboxyl or amine plasma enhanced chemical vapor deposition) prior to the ALD and also compared thermal and plasma enhanced ALD of TiO$_2$. Pristine and modified MWCNTs were characterized by scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.

NS-TuP-12 ALD on DNA Nanostructures: Application in the Synthesis of Programmably Shaped Carbon Nanostructures, *Haitao Liu,* University of Pittsburgh

DNA nanostructures are versatile templates for low cost nanofabrication. However, their applications in nanofabrication have long been limited to low temperature processes. We show that a thin film of Al$_2$O$_3$, grown by ALD, enables the high temperature carbonization of DNA into carbon nanostructures. Atomic force microscopy (AFM) data showed that carbon nanostructures preserved the shape of the DNA nanostructure. Conductive AFM measurement shows that the carbon nanostructures are electrically conductive.

NS-TuP-13 Multifunctional Ultrathin Coating Layers on Nanoparticles via Atomic Layer Deposition, *Eunyong Jang, T Park,* Hanyang University, Republic of Korea

Industrial applications of nanoparticles have surged recently. In most cases, however, there are difficulties in utilizing nanoparticles itself without any further processing. For example, protective layer coating on metal nanoparticles should be processed to circumvent explosive combustion reaction. Thus, need for development of multipurpose nanoparticles coating techniques, has brought great enthusiasm among researchers. Atomic layer deposition (ALD), a vapor deposition technique, has potential to produce conformal and uniform ultrathin-film on nanoparticles due to sequential self-limiting surface chemical reactions. Being capable of these unique merits, ALD can be introduced to applications including photocatalysts, cosmetics, optical quantum dots and protective layers for various nanoparticles/nanostructures. Herein, we used specially-designed ALD rotary reactor in order to address critical issues in cosmetics and photocatalysis applications. Particularly, in photocatalysis, we deposited TiO_2 and ZnS on $g-C_3N_4$ to reduce recombination rate of charge carriers. In addition, we studied anti-photocorrosion effect of TiO_2 passivation layer on ZnO nanoparticles. In cosmetics application, study on Al_2O_3 blocking barrier for phototoxicity of TiO_2 particles as a sunscreen ingredient was carried out. It was demonstrated that all the nanoparticles with ALD coating layer showed superior properties. Details in each work will be discussed.

NS-TuP-14 Fabrication of Hierarchically Ordered Optically Active Nanocrystal Solids by Surface Passivation using Atomic Layer Deposition of Metal Oxides, *Riya Bose,* University of Texas at Dallas

In order to achieve high efficiency in harvesting solar energy, several types of architectures and active materials have been suggested for photovoltaic devices that may surpass the Shockley-Queisser limit for single p-n junction solar cells. Nanostructured energy transfer (ET) hybrids involving quantum dots (QDs) in conjunction with Si substrate provides an attractive alternative, as excitonic ET and sensitization of Si layer by spectrally tunable QDs with high absorption coefficient eliminates the weak absorption factor in indirect bandgap Si, whereas the high carrier mobility Si component can be used for charge separation and transport. Also, ET instead of charge transfer in quantum dot media revokes the necessity of high charge carrier transport in QDs. Use of a multilayer of different sized quantum dots may further enhance the efficiency of the device by increasing the spectral absorption window. However, the bottleneck for fabrication of multilayer QD films remains the use of solution phase deposition methods, where the solvent in the subsequent step of deposition dissolves the initial layer, until each QD layer is rendered insoluble by means of any surface passivation technique. Again, surface passivation techniques also play a critical role to protect the deposited QD layers from oxidation and deterioration during long-term use. An attractive method to passivate the QD films during the deposition as well as from environmental exposure is to coat them with various metal oxides grown using atomic layer deposition (ALD). Though there are few reports of ALD encapsulation of QD films, they mostly focus on use of the same for charge transfer based devices, as well as few of them report a significant quenching of the photoluminescence intensity after encapsulation. For an efficient ET based QD-Si photovoltaic device however, removal of energy loss channels and preservation of the photoluminescence is necessary. So, we aim to investigate the exact growth mechanism of metal oxide layers by ALD on the surface of QDs and how it, along with the ALD parameters, affect their photoluminescence properties. We start with well-developed QD systems like CdSe-ZnS core-shell nanocrystals and Al_2O_3/ZnO as the metal oxide layers to study the interaction of the ALD precursors with the surface ligands of the QDs with the aid of in-situ FTIR and ex-situ XPS measurements along with the study of the photoluminescence properties of the same. We further aim to extend our study for new generation of multiexciton-bearing QDs, two-dimensional transition metal dichalcogenides and organic-inorganic perovskites, which may provide unique optoelectronic opportunities.

Nanostructure Synthesis and Fabrication
Room 107-109 - Session NS-WeM

Nanostructures III
Moderator: Mike McSwiney, Intel, USA

10:45am NS-WeM-12 DBD Plasma Assisted Atomic Layer Deposition Alumina Barrier Layer and its Applications, *H Wei,* Beijing Institute of Graphic Communication, China*; H Guo,* Qilu University of Technology, China*; L Yang, Z Liu,* **Qiang Chen,** Beijing Institute of Graphic Communication, China

In this paper, the plasma generated by dielectric barrier discharge (DBD) is utilized to assist atomic layer deposition. We compare the discharge properties in low pressure and atmospheric pressure. By optical emission spectroscope (OES) we find the oxide species in two kinds of plasma are different, the atomic oxygen is the major radicals for oxidization reaction in low pressure condition rather than ozone as the oxidant in atmospheric pressure. With these DBD plasma assisted ALD alumina coatings on polyethylene terephthalate (PET) and polylatic acid (PLA) webs as barrier layers are carried out. The Al O component and the surface morphology in two plasmas are compared. The influence of Al O thickness on barrier, mechanical, optical and degradation properties is investigated. It is obtained that the growth rate of Al O coating are 0.12 and 0.23 nm/cycle respectively in low pressure and atmospheric pressure DBD. For same water vapor transmission rate (WVTR) the alumina thickness is thicker in atmospheric pressure deposition Al_2O_3 than that in low pressure deposition Al_2O_3. Atomic force microscope (AFM) and screening electron microscope (SEM) analysis confirm that alumina deposition in atmospheric assisted ALD is loose, as a result, the moisture permeates the barrier layer at a large magnitude.

11:00am NS-WeM-13 Sequential Infiltration Synthesis for sub 20 nm Thermal Scanning Probe Lithography Patterns, *Tero Kulmala, M Spieser,* SwissLitho AG, Switzerland*; B Chan, J de Marneffe,* Imec Vzw, Belgium*; A Knoll,* IBM Research-Zurich, Switzerland

As feature sizes of emerging device concepts in for example nanoelectronics and nanophotonics continuously shrink, a high demand for novel lithography and pattern transfer processes exists. Recently, thermal scanning probe lithography (t-SPL) [1] which relies on the thermal decomposition of thermally sensitive polymer resists, such as polyphthalaldehyde (PPA) has entered the market. Using this technique, single-digit nanometer patterning and pattern transfer [2] as well as superior alignment accuracy [3] and sub-nanometer accurate 3D patterning [4] have been demonstrated. The patterning speed is comparable to high-resolution electron beam lithography [5].

As in all lithographic processes, patterning sub-10 nm features with t-SPL requires use of ultra-thin resist layers which complicates the pattern transfer process. So far, a few nm PVD silicon dioxide layer has been used as a hard mask to enable transferring the PPA patterns into a ~50 nm thick layer of amorphous carbon [6] for further amplification of the shallow t-SPL patterns.

Here, we show how sequential infiltration synthesis (SIS) [7,8] can be used to infiltrate t-SPL patterned PPA with aluminum oxide. We employed a pattern transfer stack consisting of ~10 nm PPA, 6 nm cross-linkable Polystyrene (x-PS) and 13 nm silicon nitride for transferring patterns into silicon. The amount of aluminum oxide infiltration in PPA increases with the number of SIS cycles as verified by energy dispersive spectroscopy carried out in a transmission electron microscope and results in an increase in etching resistance of the material. The resulting patterns were analyzed by atomic force microscopy and cross-section transmission electron microscopy. With an optimized process, patterns with sub-20 nm critical dimension were successfully transferred into Si.

In conclusion, SIS offers an interesting alternative for transferring high resolution patterns written by t-SPL. Furthermore, it eliminates the need for a hard mask layer in the transfer stack, thereby simplifying the process. Moreover, it was shown that such a "soft" transfer stack enhances the resolution of t-SPL patterning to the sub 10 nm range [2].

[1] Ricardo Garcia, Nature Nanotechnology **9**, 577-587 (2014).

[2] Y. K. R. Cho, ACS Nano **11** (2017).

[3] C. Rawlings et al., *ACS Nano***9**, 6188 (2015).

[4] C. Rawlings et al., Scientific Reports **7**, 16502 (2017).

[5] P. Paul et al., *Nanotechnology* **22,** 275306 (2011).

[6] H. Wolf, JVST B (2014).

[7] S. Biswas, US Patent #8,980,418 (2011).

[8] G. N. Parsons, Coordination chemistry reviews **257** (2013).

11:15am NS-WeM-14 Fabrication of BN Coated Carbon Nanostructures using ALD Based on Polymer Derived Ceramics Route, *Catherine Marichy,* Univ Lyon, France*; W Hao,* LMI - UMR CNRS/Univ Lyon 5615, France*; C Journet, A Brioude,* LMI - UMR CNRS/Univ Lyon 5615

Development of sustainable energy as well as environment issues are two of the most important current concerns. In particular, applications in corrosive and/or high temperature treatment such as in heterogeneous catalysis need support with excellent thermal stability and chemical inertness. Boron Nitride (BN) seems thus an excellent candidate; however it is an electrical insulator. Carbon nanotubes, despite their excellent electric properties, suffer of instability under reaction condition at high temperature (>300°C) especially, if the targeted reactions are partial oxidations. Deposition of a very thin BN coating appears an elegant approach to prevent the CNT oxidation while preserving its electric properties [1,2] and access to a support allowing for instance heterogeneous catalysis/electrocatalysis even at high temperature (e.g. 400-700°C). Nevertheless, fabrication of such hetero-structures requires a synthetic approach capable of controlling the size and morphology of the desired materials. Atomic Layer Deposition (ALD) has demonstrated to be an effective approach for surface modification and fabrication of carbon based heterostructures.[3] Currently, BN coating of carbon material by ALD has been poorly investigated. Based on polymer derived ceramic chemistry, a novel two-step ALD approach for BN has been recently reported.[4] Due to its low deposition temperature and non-corrosive precursors, it has been successfully use for BN deposition onto various substrates such as inorganic and polymer nanostructures.[5]

Herein coating of various carbon nanostructures is reported using this new ALD process. As inertness of highly graphitic carbon inhibits the initiation of ALD growth, use of amorphous and graphitized carbon substrates allows studying the impacts of the crystalline nature of the substrate on the coating in term of growth and structure. The obtained BN coated carbon materials are characterized by advanced electron microscopy and related techniques. As a function of the degree of graphitization, nucleation delay and impact on the crystalline quality (amorphous, turbostratic, hexagonal phase) of BN films are observed. Finally, potential of such coating to improve the oxidation resistance of carbon material is demonstrated.

1- Liew K.M., Yuan J., *Nanotechnology*, **2011**, 22 (8), 085701.

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11:30am NS-WeM-15 Atomic Layer Deposition of Lead(II) Iodide, *Georgi Popov, M Mattinen, T Hatanpää, M Vehkamäki, M Kemell, M Ritala, M Leskelä,* University of Helsinki, Finland

Over the years of ALD process development, metal halides have attained the role of classic metal precursors. Lead(II) iodide for instance, was studied as a lead precursor for ALD of PbS.[1] An attempt to deposit these typical precursor compounds might seem as a questionable endeavor at best. However, this is not theoretically impossible, provided that technical challenges, such as the relatively high vapor pressure of the target compound, are addressed. Therefore, it is tempting to explore whether the library of materials that can be deposited by ALD, can be expanded to metal iodides. Our interest in lead(II) iodide has also practical motivation. Lead(II) iodide possesses a two-dimensional structure and a band-gap in the visible range. The material is suitable for photodetectors[2] and lead(II) iodide thin films are an established starting point for preparation of hybrid halide perovskite thin films employed in perovskite solar cells[3].

The ALD process we developed for lead(II) iodide relies on lead(II) bis[bis(trimethylsilyl)amide] as the lead precursor and tin(IV) iodide as the iodine precursor. The process works at low temperatures (< 100°C) and is compatible with a variety of starting surfaces ranging from oxides to metal thin films. We observed saturative film growth with respect to both precursors on substrates selected for detailed study, namely silicon and fluorine doped tin dioxide coated glass. We also noticed a linear relation between the film thickness and the number of deposition cycles. The

process yields crystalline films that show different crystalline textures depending on the nature of the starting surface. We also demonstrate that lead(II) iodide films deposited with this process, when treated with methyl ammonium iodide vapors, convert into a methyl ammonium lead triiodide. Methyl ammonium lead triiodide is a hybrid halide perovskite commonly employed as a light absorber in perovskite solar cells.

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11:45am **NS-WeM-16 Crystalline High-k Dielectric Films on Atmospheric Plasma Treated Graphene by Atomic Layer Deposition**, *Jeong Woo Shin,* Seoul National University of Science and Technology, Republic of Korea*; M Kang,* Kwangwoon University, Republic of Korea*; S Oh, B Yang, K Seong, H Ahn,* Seoul National University of Science and Technology, Republic of Korea*; T Lee,* Kwangwoon University*; J An,* Seoul National University of Science and Technology, Republic of Korea

Graphene has excellent electrical and mechanical properties such as high carrier mobility (~200,000cm^2/Vs), high surface-to-volume ratio, high flexibility and high mechanical property (Young's modulus: ~0.1TPa). Due to these excellent properties, graphene has been extensively studied for flexible electronics and sensors.

However, the basal plane of graphene is known to be chemically inert because of its strong sp^2 carbon bonding. For the fabrication of graphene-based field-effect transistors (GFETs) with high sensitivity and stability, it is important to deposit thin and uniform dielectric films on the graphene surface. Among various dielectric deposition method, atomic layer deposition (ALD) has the advantage of being able to deposit ultra-thin and uniform films. However, the inertness of the graphene basal plane prevents the facile nucleation of ALD dielectric materials on the graphene surface.

In this paper, we demonstrate the deposition of high-quality ALD dielectric films without additional seed layer on the atmospheric oxygen plasma treated graphene while minimizing the structure and electrical degradation. Optical microscope, raman spectroscopy, water contact angle analysis and X-ray photoelectron spectroscopy show that the atmospheric oxygen plasma treated graphene surface become super-hydrophilic. Also, it is confirmed that the uniform and highly crystalline ALD dielectric films deposited at a relatively low temperature (150℃) on the functionalized graphene surface through the atomic force microscopy, field-emission scanning electron microscope and X-ray diffraction analysis. ALD dielectric films on the plasma-treated graphene result in negative shift in the Dirac voltage and the enhanced air stability.

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