Tuesday Afternoon Poster Sessions, July 31, 2018

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 $[(CH_3)_3Si]_2Te$ 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 $ng\cdot cm^{-2}cy^{-1}$ 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 shows$\sigma=pO_2^{1/4.05}$ with a positive slope under low pressure region for the BiOCl and $\sigma=pO_2^{1/5}$ 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_2O_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 $(C_2H_5)_2Zn$ 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_2O_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_2O_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_2O_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_2O_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_2O_3, grown by ALD, enables the high temperature cabonization 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.

Author Index

Bold page numbers indicate presenter

— A —
Ahn, J: NS-TuP-4, 1
— B —
Banerjee, P: NS-TuP-8, 2
Baumgart, H: NS-TuP-9, **2**
Bose, R: NS-TuP-14, **3**
Browning, N: NS-TuP-8, 2
— C —
Chen, X: NS-TuP-9, 2
Choi, B: NS-TuP-3, 1
Choi, J: NS-TuP-4, **1**
Choi, S: NS-TuP-3, **1**
— E —
Elias, M: NS-TuP-11, 2
— F —
Feigelson, B: NS-TuP-10, 2
— G —
Greenberg, B: NS-TuP-10, **2**
— H —
Han, J: NS-TuP-3, 1
Hegemann, D: NS-TuP-11, 2
Hwang, C: NS-TuP-7, 1
Hwang, J: NS-TuP-6, **1**
Hyun, C: NS-TuP-4, 1
— J —
Jang, E: NS-TuP-13, **3**
— K —
Kaushik, P: NS-TuP-11, 2
Kim, D: NS-TuP-3, 1
Kornelius, N: NS-TuP-5, 1
Krayev, A: NS-TuP-8, 2
— L —
Lee, S: NS-TuP-4, 1
Lin, P: NS-TuP-9, 2
Liu, H: NS-TuP-12, **2**
Long, N: NS-TuP-2, **1**
— M —
Mehdi, L: NS-TuP-8, 2
Michal, L: NS-TuP-11, 2
Michalicka, J: NS-TuP-11, 2
Michlicek, M: NS-TuP-11, 2
Myung, Y: NS-TuP-8, **2**
— P —
Park, G: NS-TuP-5, **1**
Park, J: NS-TuP-8, 2
Park, T: NS-TuP-13, 3
Park, Y: NS-TuP-1, **1**
— S —
Shin, S: NS-TuP-3, 1
Song, W: NS-TuP-8, 2
Sung, M: NS-TuP-1, 1; NS-TuP-6, 1
— T —
Thomas, A: NS-TuP-5, 1
— W —
Wollmershauser, J: NS-TuP-10, 2
— Y —
Yang, L: NS-TuP-8, 2
Yoo, C: NS-TuP-7, **1**
— Z —
Zajickova, L: NS-TuP-11, **2**
Zhang, K: NS-TuP-9, 2