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

AA+AF+EM

Moderator: Iian Buchanan, Versum Materials, UK

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

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

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

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

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

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

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

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

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

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

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

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

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

[1] US patent # US 9828673 B2.

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

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

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

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

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

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

Reference:

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

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

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

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

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

[1] J. W. Elam *et al.*, *Chem. Mater.***15**, 3507 (2003).

[2] M. Retala and Markku Leskelä, *Handbook of Thin Films* Volume 1, 103 (2002).

[3] Y. H. Lin *et al.*, *Materials***8**, 7084 (2015).

[4] S. Y. Wu *et al.*, *Microelectron. Eng.***147**, 310 (2015).

[5] T. W. Chang *et al.*, *Microelectron. Eng.***178**, 199 (2017).

[6] Y. H. Chang *et al.*, *Microelectron. Eng.***88**, 440 (2011).

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