Thin Films Division
Room 101A - Session TF-TuM

Emerging Applications for ALD

Moderators: Arrelaine Dameron, Forge Nano, Qing Peng, University of Alabama

8:00am TF-TuM-1 Atomic Layer Deposition of the Metal Pyrites FeS₂, CoS₂, and NiS₂, *Xinwei Wang,* Shenzhen Graduate School, Peking University, China

The pyrite-type transition-metal disulfides (MS_2, M = Fe, Co, Ni) form a series of compounds that are highly interesting in many aspects. These compounds share the same cubic pyrite crystal structure but differ in the progressive increase of an anti-bonding *d* electron in the conduction band, and as a result, the metal pyrites exhibit very diverse and intriguing electrical magnetic properties from diamagnetic semiconductive to itinerant-electron ferromagnetic and to antiferromagnetic semiconductive. This diversity of the material properties has not only offered a model system platform for fundamental science studies but also enabled tremendous engineering possibilities for practical applications, such as solar cells, lithium/sodium-ion batteries, and electrocatalytic hydrogen evolution, oxygen evolution, and oxygen reduction.

In this presentation, we will show our latest progress on the development of atomic layer deposition processes for the metal pyrites of FeS_2, CoS_2, and NiS_2 (*Angew. Chem.Int. Ed.* 2018, doi:10.1002/anie.201803092). We use the metal amidinate compounds as the precursors for the metals and H_2S plasma as the sulfur source, and we will show that the deposition processes for FeS_2, CoS_2, and NiS_2 all follow ideal layer-by-layer ALD growth behavior over a wide temperature range to produce fairly pure, smooth, pyrite-structure metal disulfide films. We will further show that the ALD FeS_2, CoS_2, and NiS_2 films can be conformally deposited into deep narrow trenches with aspect ratios as high as 10:1, which thereby highlights the broad and promising applicability of these ALD processes for conformal film coatings on complex high-aspect-ratio 3D architectures in general.

8:20am TF-TuM-2 Atomic Layer Deposition of Yttrium Fluoride and Yttrium Oxyfluoride Films with Tunable Stoichiometry, *Jasmine Wallas*[1], *J Murdzek, D Lancaster, A Cavanagh, S George,* University of Colorado at Boulder

YF_3 and YO_xF_y are materials with excellent chemical and thermal stability. YF_3 and YO_xF_y have both demonstrated exceptional corrosion resistance to highly reactive plasmas. In this work, YF_3 atomic layer deposition (ALD) was developed using tris(butylcyclopentadienyl) yttrium and HF-pyridine as the reactants. The ALD of YO_xF_y alloys was also demonstrated with tunable control of the oxygen and fluorine stoichiometry. This tunable control was difficult because of the rapid exchange of oxygen by fluorine in Y_2O_3 and YO_xF_y alloys during HF exposures.

In situ quartz crystal microbalance (QCM) analysis of YF_3 ALD revealed linear mass changes and self-limiting behavior using tris(butylcyclopentadienyl) yttrium and HF-pyridine as the reactants. The mass gain per cycle (MGPC) was 21.5 ng cm⁻² at 225°C. The growth rate of YF_3 ALD was also determined to be 0.3 Å per cycle by ex situ X-ray reflectivity analysis. Energy dispersive spectroscopy (EDS) of a cross-section of the YF_3 film yielded a uniform 3:1 ratio of F:Y with low impurities.

YO_xF_y alloys were deposited using H_2O together with the tris(butylcyclopentadienyl) yttrium and HF-pyridine reactants. However, control of the composition of the YO_xF_y alloys was complicated by the facile exchange of oxygen by fluorine during the HF exposures. The oxygen/fluorine exchange was most obvious during HF exposures on Y_2O_3 ALD films when a large mass gain was observed during fluorination. The Y_2O_3 fluorination reaction is believed to be: $Y_2O_3 + 6\ HF \rightarrow 2\ YF_3 + 3\ H_2O$. In addition to the large mass gain, the presence of fluorine throughout the entire film was revealed by X-ray photoelectron spectroscopy (XPS) measurements with depth-profiling. The XPS depth-profiling results are consistent with rapid fluorine diffusion in the Y_2O_3 and YO_xF_y films.

Various super-cycles were employed to obtain YO_xF_y alloys with particular F:O ratios. The most reliable method for composition control was defined by performing HF exposures between intervals of Y_2O_3 ALD. The number of Y_2O_3 ALD cycles and the length of the HF exposure could be varied to produce YO_xF_y alloy films with tunable and consistent composition as measured with XPS depth-profiling. The growth rate of the YO_xF_y alloy films was dependent on the number of Y_2O_3 ALD cycles before the HF exposures. The super-cycles with a larger number of Y_2O_3 ALD cycles before the HF exposures produced higher growth rates resulting from the higher growth rate of 0.8 Å per cycle for Y_2O_3 ALD.

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8:40am TF-TuM-3 Synthesis of Single Phase Two-dimensional SnS₂ by Plasma-enhanced Atomic Layer Deposition, *J Pyeon, I Baek,* Korea Institute of Science and Technology; *T Chung,* Korea Research Institute of Chemical Technology; *J Han,* Seoul National University of Science and Technology; *C Kang, SeongKeun 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. A challenge in implementing 2-D metal chalcogenides in emerging devices is to synthesize a well-crystallized layer over large areas at temperatures compatible with current fabrication processes. Tin disulfide, a n-type layered semiconductor, is a promising candidate for realizing large-area growth at low temperatures because of its low melting point. However, tin sulfides exist in various phases such as SnS, Sn_2S_3, and SnS_2. It is challenging to form a single phase SnS_2 at low temperatures.

Here, we demonstrated the synthesis of high-quality SnS_2 by plasma-enhanced atomic layer deposition (PEALD). All the processes were performed below 300 °C, which is compatible with current electronic devices. Stoichiometric SnS_2 films were formed. It was verified from various techniques such as Raman spectroscopy, x-ray photoelectron spectroscopy, and x-ray diffraction that a single phase of SnS_2 was formed. It was found that the microstructure of the SnS_2 films was strongly dependent on the growth temperature. Vertically aligned SnS_2 flakes were observed in the SnS2 grown at relatively high temperatures (210 - 270 °C). Through a two-step process – a seed layer growth at low temperature (150 °C) and a main layer growth at high temperatures (240 – 270 °C), well crystallized SnS_2 layers were aligned in parallel to the substrate. Moreover, the properties of field-effect transistor using the SnS_2 films were investigated. A high on/off ratio of ~ 10^6 and a moderate field-effect mobility of ~ 1 cm²/Vs were achieved from the devices utilizing SnS_2 grown by PEALD.

9:00am TF-TuM-4 Phase Selective, Low Temperature Growth of TiO2 by Atomic Layer Epitaxy, *Jason Avila, D Boris, S Qadri, J Freitas, S Walton, C Eddy Jr., V Wheeler,* U.S. Naval Research Laboratory

Atomic layer deposition (ALD) of TiO_2 has been widely explored recently due to its promise in non-volatile resistive switch, high-k gate dielectric, solar cell, and photocatalytic applications. This growth method has become increasingly useful as device dimensions are reduced and non-planar complexity is increased. To facilitate epitaxial films at low growth temperatures (T_g), many have investigated plasma, laser or photon, or electron enhanced ALD processes. Specifically for TiO_2, it would be beneficial to selectively grow epitaxial anatase or rutile phases in order to tailor optical, catalytic and electrical properties for the required application. Typically, TiO_2 phase selectively is attained by varying the underlying substrate, Ti and/or oxidation precursor, or T_g. However, here we demonstrate phase selectivity of high quality epitaxial TiO_2 films simply by adjusting plasma gas composition, pressure and Tg.

A Veeco Fiji G2 reactor was used to deposit TiO_2 films on different sapphire orientations (c-, m-, a-) with tetrakis(dimethylamido)titanium (TDMAT) and either Ar/O_2 or pure O_2 plasma at 100-350° C. Previous reports indicate that tuning the ion energy, specifically through substrate biasing, can influence TiO_2 film crystallinity and phase [1]. The high pumping speed and large gas flow range available in this specific ALD system provides a wide variation in operating pressures (7-100's mTorr), which effectively allows tuning of plasma characteristics. Operating at relatively low pressures (9-21mTorr) resulted in a significant flux (0.5-1.5x10¹⁹ m⁻²s⁻¹) of energetic ions (30-50eV), with both the flux and energy decreasing as the pressure is increased. The low pressure conditions yield high-quality epitaxial films at all temperatures, which differs from previous reports using these specific precursors [2,3] likely due to these unique plasma conditions.

Gas composition during the plasma step also had a substantial effect on growth rate, TiO_2 phase, and strain. At T_g < 300° C, the growth rate was increased from 0.5 to 0.7 Å /cycle by switching from Ar/O_2 to pure O_2. Moreover, an O_2 plasma produced only rutile TiO_2 films, with less strain, independent of growth temperature or underlying substrate orientation. In contrast, films deposited with an Ar/O_2 plasma show a phase dependence on temperature and substrate. Films on c-plane Al_2O_3 go from anatase at T_g

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below 200° C to rutile above 300° C. The films on m-plane Al_2O_3 are rutile independent of temperature.

Profijt et al. *Electrochem. Sol. Stat. Lett.* **15**(2) G1 (2012).

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Maeng and Kim. *Electrochem. Sol. Stat. Lett.* **9**(6) G191 (2006).

9:20am TF-TuM-5 Substrate Biasing During Plasma Atomic Layer Deposition: From Stress-controlled Oxides to Low-resistivity Nitrides, *Harm Knoops,* Oxford Instruments, The Netherlands*; T Faraz,* Eindhoven University of Technology, The Netherlands, Netherlands*; K Arts,* Eindhoven University of Technology, The Netherlands*; S Karwal, M Creatore, E Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands

Thin films grown by plasma atomic layer deposition (ALD) can be strongly influenced by the energy of the ions present during the plasma step. Here we report on how using enhanced energies influence the material properties of many oxides and nitrides.[1,2] To utilize these effects, discussion on promising process schemes and which material properties are key is needed. This work will discuss application relevant aspects and focus on the stress-control of oxides and the reduction of resistivity for nitrides.

Ion energy control during plasma exposure was carried out in a commercial 200-mm remote plasma ALD system (Oxford Instruments FlexAL) equipped with RF substrate biasing. Substrate biasing increased the refractive index of TiO_2 at 300 °C to 2.54±0.03, mass density to 4.2±0.2 g/cm^3, and the crystal phase went from anatase to rutile. ALD of TiO_2 at 150 °C typically yields amorphous films, but using a bias crystalline rutile phase was obtained. Besides these modified material properties the residual stress was altered from tensile (176±50 MPa) to strongly compressive (-2430±50 MPa) and by choosing the bias voltage and duration, a close to zero stress could be achieved (−25±50 MPa). Stress control of oxides on planar surfaces can be beneficial for several devices through: anti-reflective TiO_2 coatings, stressed Al_2O_3/HfO_2 gate oxides, and compressive Ta_2O_5 barrier layers.

For transition metal nitrides, enhancing ion energies was observed to have pronounced effects on chemical composition and microstructure.[1,2] Energetic ion bombardment lowered film resistivity down to 139±10 μΩcm at -187V bias for TiN and increased the crystallinity. The ability to deposit crystalline films on temperature sensitive substrates (e.g., conductive TiN on polymer substrates) could be a benefit for low temperature electronics. Oxygen impurity content was observed to be significantly reduced by substrate biasing. Oxygen contents of 3±2 at. % for TiN and <2 at. % for HfN_x were achieved without taking special care of low oxygen backgrounds. Ar/H_2 plasma with biasing was found to allow removal of surface oxygen, while simply extending the plasma exposure without applying bias did not lead to such removal. The reduction of oxygen content by these plasmas also suggests a possible use in applications as a chemical sputter clean of surfaces. In general the application of biasing brings the processing of plasma ALD closer to the realm of ALE and atomic scale processing. Possible related processing schemes and the general trends for nitrides and oxides will be discussed.

[1]Faraz et al., *ACS Appl. Mater. Interfaces* **10**, 13158 (2018)

[2]Karwal et al., *J. Mater. Chem. C***6**, 3917 (2018)

9:40am TF-TuM-6 Development of Novel Superconducting ALD Films for Astronomy Applications, *Frank Greer, P Day, B Eom, H Leduc,* Jet Propulsion Laboratory, California Institute of Technology

Future sub-millimeter telescopes and spectrometers have the potential to revolutionize our understanding of the formation of the modern universe. Sub-millimeter astronomy can probe the fine structure of the cosmic microwave background, giving glimpses into the early universe immediately following the Big Bang. Recent advances in design have enabled the production of large arrays of cryogenically cooled superconducting detectors with sufficient sensitivity for photon counting applications. Transition edge sensors (TES) and other types of detectors, fabricated from thin films of metal nitrides such TiN, NbN, TaN, VN, and their mixtures, are cryogenically cooled to just below their superconducting transition temperature. Photons in the X-ray or sub-millimeter wavelength range can be detected because their absorption will cause the temperature of an appropriately designed TES array element to rise just enough to cause

it to have a finite resistance. However, while conventional deposition processes such as physical sputtering have been sufficient for small area arrays and proof of concept sensors, critical parameters such as the superconducting transition temperature are strongly sensitive to film thickness, stochiometry, and interface quality. Therefore, as the size of an individual detector array or the number of detector arrays on a wafer increases, it becomes more and more difficult to fabricate them with sufficiently uniform response in sufficient quantity to populate the focal plane of a large telescope. We are utilizing the uniformity and compositional control provided by atomic layer deposition to overcome these limitations for the fabrication of transition edge sensors as well as other applications requiring superconducting thin films.

11:00am TF-TuM-10 Atomic Layer Deposition of Cobalt Nanoparticles, *Gerben van Straaten, E Kessels, M Creatore,* Eindhoven University of Technology, The Netherlands, Netherlands

Cobalt nanoparticles (NPs) with well-defined sizes are highly sought after for a variety of catalytic processes. For example, cobalt NP catalysts for the Fischer-Tropsch process, used in industry to upgrade coal and natural gas into fuels, show a sharp maximum in activity for a particle diameter of ca. 8 nm[1]. Such size-sensitive catalytic processes require conformal deposition of cobalt NPs throughout porous substrates, requirements that can potentially be met by ALD.

ALD of catalytic platinum-group metal NPs with narrow size distributions has been exhaustively studied. However, compared to these systems, ALD of cobalt metal NPs is much more challenging due to their high reactivity. To our knowledge, Co NPs have only been obtained by reduction of ALD-deposited Co_3O_4 NPs [2] or by reduction and subsequent melting of ALD-deposited Co_3O_4 layers [3].

In this contribution, we demonstrate for the first time the direct deposition of Co NPs using Plasma-Enhanced ALD (PEALD)[4]. Cobaltocene ($Co(C_5H_5)_2$) is evaporated at 80°C and dosed for 6s onto an SiO_2 surface held at 250°C. Then, exposure to a remote, inductively coupled plasma fed with NH_3 ($1*10^{-2}$ mbar, 100W) takes place for 10s. After each step, 4s of purging takes place, and saturation of all steps was verified with in-situ Spectroscopic Ellipsometry (SE). By means of TEM we find that Co NPs synthesized via this process consist of a metallic core and an oxide shell formed by air exposure, and that their growth takes places in 3 stages. In the initial stage, up to 150 cycles, a homogeneous coverage of small NPs occurs, with an average diameter of less than 1 nm. Then, after 150 cycles, a second population of larger NPs starts to develop, which increase rapidly in size while retaining a narrow size distribution. After ca. 250 cycles this secondary population is fully developed, with a mean diameter of 7.5 nm and a width of 1.7 nm, but the initial population of small NPs remains, yielding a bimodal size distribution. Growth of this secondary population continues up to ca. 550 cycles, at which point we find from in-situ SE that the NPs coalesce into a continuous film. Preliminary GIXRD and XPS analysis reveals that this film consists of crystalline β-Co but that up to 10 at% of C and N can be present in the film.

Experiments are ongoing to test the catalytic activity of Co NPs synthesized via this method towards the Fischer-Tropsch reaction.

1. Den Breejen, J. P. *et al. J. Am. Chem. Soc.***131,** 7197–7203 (2009)

2. Taheri Najafabadi, A. *et al. Appl. Catal. A Gen.***511,** 31–46 (2016)

3. Thissen, N. F. W. *et al.Carbon N. Y.***121,** 389–398 (2017)

4. Lee, H.-B.-R. & Kim, H. *Electrochem. Solid-State Lett.***9,** G323 (2006)

11:20am TF-TuM-11 Atomic Layer Deposition of Ni-Al-O Catalysts for Water Oxidation, *Jon Baker, J Schneider, J Singh, A Mackus, S Bent,* Stanford University

Electrical energy storage has emerged as an important challenge for societies moving away from fossil fuels toward more renewable sources (e.g. solar and wind) that are intermittent in nature. To rely only on solar and wind for electricity, large scale energy storage systems are required. Among several potential solutions, one promising strategy is to store excess electrical energy in the form of chemical bonds, through electrochemical production of fuels. In particular, electrochemical water splitting enables the production of hydrogen gas as a chemical fuel from excess electrical energy. However, a major drawback of this strategy is the low efficiency of the oxygen evolution reaction (OER).

To improve the efficiency of the OER, understanding why certain catalysts perform well is a powerful tool in designing new catalysts with better properties. Atomic layer deposition (ALD) has emerged as a strong platform to study catalysts due to its ability to deposit films that are compositionally

well-defined. For electrochemical systems, ALD has the added benefit of high uniformity, conformality and precise thickness control; these attributes can minimize potential confounding effects like resistive and mass transport losses, which may affect measurement of a catalyst's intrinsic activity. In this work, we study the effect of aluminum on Ni-Fe-OOH catalysts. While Ni-Fe-OOH catalysts have been reported to have high activity for the OER (nearly independent of synthesis method), the impact of aluminum on this catalyst is not yet well understood, with a wide range of OER activities reported. By using ALD, ternary films of Ni-Al-O were deposited. Introduction of iron was achieved through electrolyte iron-doping, enabling the formation of the quaternary Ni-Al-Fe-OOH catalyst. Electrochemical characterization of sufficiently thin films found that aluminum improved the turnover frequency of Ni-Fe-OOH catalysts by a factor of 3-4. By carefully controlling composition of the catalyst, the effects of aluminum and iron were independently studied. In iron-free catalysts, aluminum was found to improve OER activity; however, its improvement in activity was small compared to the effect of iron. In addition, thickness dependent studies were performed to understand how morphology and synthesis method may impact observed activity. For Ni-Al-Fe-OOH catalysts, a strong thickness dependence in the OER activity was observed. Characterization of the catalysts *ex situ* and under OER operating conditions reveal the likely cause of this thickness dependence is the observed changing morphology of the film with increasing thicknesses.

11:40am **TF-TuM-12 Atomic Layer Deposition of Bismuth Vanadate Photoanodes**, *Sudarat Lee, A Bielinski, S Esarey, J Brancho, B Bartlett, N Dasgupta,* University of Michigan, Ann Arbor

Bismuth vanadate (BVO) has been widely studied as one of the most promising photoanode materials for photoelectrochemical (PEC) water splitting, owing to a bandgap of 2.4 eV and favorable band positions for water oxidation. However, while BVO has the potential for high anodic photocurrents, it is often limited by electron-hole separation, charge transport, and water oxidation kinetics, requiring development of nanostructured electrode architectures to optimize performance.

Here we demonstrate a new method for fabricating tunable BVO photoanodes deposited by atomic layer deposition (ALD). We present the first deposition of ALD BVO using $Bi(OCMe_2iPr)_3$ as the bismuth source, vanadium(V)oxytriisopropoxide as the vanadium source, and water as the oxidant. The choice of this recently developed Bi precursor provides full control of Bi:V stoichiometry in contrast to the use of earlier Bi precursors such as triphenylbismuth[1], while also providing a per cycle growth rate that is more than three times higher than previous reports.

The BVO films were deposited as a nanolaminate of binary bismuth and vanadium oxides. The films were post-annealed to achieve the photoactive monoclinic $BiVO_4$ phase. Film composition and photocurrent were investigated as a function of deposition pulse ratio and film thickness. The photoactivity of planar ALD BVO was measured in a three-electrode cell under simulated AM1.5G illumination. Sulfite oxidation was used to optimize the BVO deposition conditions independent of co-catalyst performance. We achieved the highest reported photocurrent to date for ALD photoanodes. Using a planar electrode with a 40nm thick BVO film, a photocurrent of >2.6 mA cm^{-2} at 1.23 V_{RHE} was demonstrated for sulfite oxidation and a photocurrent of >1.1 mA cm^{-2} at 1.23 V_{RHE} was demonstrated for water oxidation using an un-optimized cobalt co-catalyst.

ALD provides conformal coverage of high aspect ratio structures. The development of an ALD process for BVO enables core-shell architectures that help address the charge transport and carrier separation challenges by decoupling carrier diffusion and light absorption lengths. To demonstrate this benefit, BVO was deposited on mesoporous tin oxide (ITO) substrates to form 3-D electrode architectures with tunable absorption and charge extraction properties. The photoresponse was enhanced for both sulfite and water oxidation under illumination, demonstrating the power of ALD to improve light absorption and charge extraction in 3-D nanostructured electrode architectures.

*(1)*Stefik, M. Atomic Layer Deposition of Bismuth Vanadates for Solar Energy Materials. *ChemSusChem*

2016, *9* (13), 1727- 1735.

12:00pm **TF-TuM-13 ALD of Cobalt Phosphate Electro-catalyst for Oxygen Evolution Reaction**, *Valerio Di Palma,* Eindhoven University of Technology, The Netherlands*; G Zafeiropoulos, M Tsampas,* DIFFER*; W Kessels,* Eindhoven University of Technology, The Netherlands*; M Creatore,* Eindhoven University of Technology, The Netherlands, Netherlands

Sunlight-driven water splitting is widely investigated through studies addressing both the development of earth-abundant element-based (photo)electrodes, as well as engineering of compact, efficient and inexpensive devices. One important reason that keeps these systems from being of practical use to date is the sluggish kinetics (high overpotential) of the oxygen evolution reaction (OER). OER is a four electron-proton coupled reaction, while hydrogen evolution reaction (HER) is only a two electron-transfer reaction, and hence usually OER requires a higher overpotential [1].

Electro-deposited cobalt phosphate (CoPi) has been reported as a valid OER catalyst (as bare electrode or as cocatalyst in photoelectrodes) and alternative to rare element compounds [2]. In parallel, ALD is rapidly reaching out also to (photo-)electrocatalytic applications [3,4] and in the present contribution we investigate CoPi growth by ALD and its application as OER catalyst. Compared to electrodeposition, ALD offers the major advantage of tuning the electro-catalyst chemical composition, as we demonstrate in this work.

The CoPi process has been developed using an ABCD scheme, where A, B, C and D are the cobaltocene (CoCp), first oxygen plasma (5 s), trimethylphosphate (TMP) and second oxygen plasma (2 s) dosing steps, respectively. The deposition performed at 300ºC results in a growth per cycle of about 1.1 Å, determined by in-situ spectroscopic ellipsometry. Elemental characterization by XPS of the ALD prepared CoPi shows a stoichiometry of $Co_3(PO_{4.3})_2$. The film deposited on FTO/glass is active for OER, as confirmed by cyclic voltammetry. The current density peak measured is about 1.0 mA/cm^2 at 1.4 V vs. NHE (Normal Hydrogen Electrode), comparable to the values reported in literature for electrodeposited CoPi. Furthermore, we investigated the effect of Co-to-P concentration ratio on the OER catalytic activity. To this purpose, the process was modified from the aforementioned ABCD approach into an $(AB)_x(CD)_y$ supercycle approach. The sample prepared with a ratio x-to-y of 12-to-11 showed already a higher current density peak (about 1.2 mA/cm^2 at 1.4 V vs NHE) than the sample deposited without the use of supercycles. This finding highlights the role of Co-to-P concentration ratio on the activity of the catalyst and how the ALD supercycle approach can be adopted to this purpose.

References

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[4] S.C. Riha et al., ACS Nano, 7 (3) (2013) 2396

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