

Emerging Materials

Room On Demand - Session EM1

Molecular Layer Deposition

EM1-1 Gas Phase Phosphane-ene Polymer Film Depositions, Peter Gordon, Carleton University, Canada; **P. Ragogna,** University of Western Ontario, Canada; **C. McGuinness,** Solvay; **S. Barry,** Carleton University, Canada

Phosphane-ene polymers are a new class of soft material with a wide variety of characteristics. They exhibit orthogonal reactivity for functionalization, polyelectrolyte behavior, and oxygen and metal scavenging¹⁻³. These versatile polymers are highly tunable and structurally diverse, depending on the choice of phosphine and cross-linker^{4,5}.

Previously reported solution-phase synthesis of phosphane-ene polymers⁶ have been adapted to a molecular layer deposition (MLD) process. The solution-phase synthetic method employs a photo-initiated radical-assisted polymerization, and we have adapted an A-B-C MLD pulse sequence that includes a plasma step to produce gas-phase radicals. These radicals serve as surrogates for the photo-initiator in the solution-phase method, generating surface-bound radical sites that promote reactivity to generate the polymer. This hypothesis is supported by an absence of film growth if the plasma pulses are omitted.

Thin polymer films were deposited on silicon substrates at 40°C. An optimized pulse sequence of 0.1 s pulse isobutyl phosphine with a 149 s chamber residence time, 60 s argon plasma, 1.0 s tetramethyltetravinylcyclotetrasiloxane with a 149 s residence time, and a 10 s nitrogen purge was used. At a plasma power of 600 W, uniform phosphorus-containing films with a growth per cycle of 0.8 Å and an RMS roughness of 8 nm were produced. Composition has been characterized by XPS, TOF-SIMS, Auger sputtering, and PM-IRRAS. Roughness and growth per cycle were measured with AFM. These properties can be tuned by varying plasma power, yielding a reliable method for fabricating thin phosphane-ene films from gas phase reagents in a stepwise fashion.

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EM1-2 Atomic/Molecular Layer Deposition of Ordered 1D Coordination Polymer Thin Films With Adjustable Electric Conductivity, Mikko Nisula, Ghent University, Belgium; **A. Karttunen,** Aalto University, Finland; **E. Solano,** ALBA Synchrotron Light Source, Spain; **P. Kaur,** A. Devi, Ruhr University Bochum, Germany; **G. Tewari,** M. Karppinen, Aalto University, Finland; **M. Minjauw,** H. Jena, P. Van Der Voort, C. Detavernier, Ghent University, Belgium

The prospect of introducing tuneable electric conductivity in hybrid metal-organic coordination polymers could be of high interest for future nanoelectronic applications. As the electronic properties of these materials are strongly dependent on their microstructure, robust synthetic routes for thin films with high degree of ordering and well-controlled thickness are needed not only for practical applications but also for fundamental understanding of transport phenomena in conductive coordination polymers.

In this respect, atomic/molecular layer deposition (ALD/MLD) is uniquely suited for the fabrication of high-quality coordination polymers thin films. While the technique is already established for passive coatings such as barrier layers, intrinsically conductive materials could be achieved by broadening the range of available ALD/MLD processes to redox non-innocent molecules.

With this goal in mind, we investigate the deposition of hybrid thin films based on several dithioamides (DTOA) with Cu as the metal site. The good overlap between the Cu d-orbitals and the frontier orbitals of the sulphur-containing ligand should be beneficial towards charge

delocalization and electric conductivity. The redox-active DTOA ligands open up the possibility of further tuning the thin film properties by adjusting their oxidation state.

High out-of-plane ordering is observed in the resultant thin films suggesting the formation of a well-ordered secondary structure by the parallel alignment of the 1D polymer chains. As postulated, we show that the electrical conductivity of the thin films is highly dependent on their oxidation state. The as-deposited films are nearly insulating with electrical conductivity below 10^{-10} S/cm with semiconductor-like temperature dependency. By taking advantage of the catalytic properties of the open Cu nodes, we utilize H₂ at elevated temperature to partially reduce the thin films. With N,N'-dimethyldithiooxamide as the ligand, the reduction leads to an increase in the electrical conductivity by 8 orders of magnitude. In this high-conductance state, the thin films exhibit metallic temperature dependency of conductivity. On the other hand, with diethyl- and dipropyl variants, the conductance remains unchanged. With the help of DFT modeling, we link the observed conductance increase to combined structural change and charge carrier injection. Namely, we observe the formation of a half-filled conduction band that arises from the formation of extended (-Cu-S)_n conduction pathways between neighbouring polymer chains.

EM1-3 Oxidative Molecular Layer Deposition of Conjugated Amine Polymer Thin-Films, Quinton Wyatt, M. Vaninger, T. Heitmann, H. Kaiser, M. Young, University of Missouri, Columbia

Electrically-conductive and redox-active polymers such as polyethylenedioxythiophene (PEDOT), polypyrrole (PPy), and polyaniline (PANI) have applications in flexible electronics, energy storage, electrochemical desalination, and chemical sensors. In each of these applications, delivering conformal, thin-film polymer coatings is attractive to provide lower weight, faster charging, and higher sensitivity. Unfortunately, traditional approaches for polymer synthesis struggle to deliver uniform thin film coatings onto 3D substrates. In general, molecular layer deposition (MLD) is an attractive route for the formation of these polymer coatings because MLD growth involves alternating self-limiting surface reactions and inherently provides uniform coatings on 3D substrates. Previous work reported a scheme for MLD of conductive and redox-active polymers employing sequential doses of monomers and a chemical oxidant (MoCl₅), termed *oxidative MLD* or "oMLD," and demonstrated the formation of PEDOT films using this approach. In this report, we expand on this prior work and study oMLD of amine-containing conductive and redox-active polymers including PPy, PANI, and their derivatives using alternating exposures of monomers and MoCl₅ oxidant. We perform both in-situ and ex-situ experimental measurements to study the growth behavior of these polymers, and identify unexpected monomer-dependent growth. We also measure the conformality and the electrical and electrochemical properties of the resulting films. We find that pyrrole and substituted-aniline both undergo self-limiting surface reactions to form conformal, electrically-conductive and redox-active polymer films. We also identify that copolymer alloys of PPy and substituted-PANI growth chemistries yield improved electrochemical properties over isolated monomer chemistries. Our results provide new insights into the oMLD growth mechanism in general, and offer the prospect for molecular-level control of conjugated polymer structures delivered in a conformal, thin-film geometry.

EM1-6 Converting Molecular Layer Deposited Alucone Films into Al₂O₃/alucone Hybrid Multilayers by Plasma Densification, Juan Santo Domingo Peñaranda, Ghent University, Spain; **M. Nisula,** Ghent University, Finland; **S. Vandenbroucke,** M. Minjauw, Ghent University, Belgium; **J. Li,** Ghent University, China; **A. Werbrouck,** J. Keukelier, Ghent University, Belgium; **A. Pitillas Martínez,** IMEC, Spain; **J. Dendooven,** C. Detavernier, Ghent University, Belgium

Alucones are one of the best-known films in the Molecular Layer Deposition (MLD) field, mainly due to their flexibility, but their stability in air is a concern. On the other hand, Al₂O₃ offers very low water vapour transmission rates (WVTRs), at the expense of strain sensitivity even for thin layers. As a consequence, alucone/Al₂O₃ nanolaminates withhold potential for synergistic behaviour. The impermeability of Al₂O₃ will impede moisture from entering the stack and, when it enters, it will encounter an alucone structure where it will absorb. Therefore, these nanolaminates can create a very tortuous path for water molecules and may lower the effective diffusion constant to the substrate.

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In this work, we prove that alucone/ Al₂O₃ nanolaminate synthesis can be successfully performed by alternating alucone MLD growth with static O₂ plasma exposures. Upon plasma treatment, only the top part of the alucone is densified into Al₂O₃, while the rest of the film remains relatively unaltered. X-ray reflectivity (XRR) and x-ray photoelectron spectroscopy (XPS) depth profiling show that the process yields a bilayer structure, which remains stable in air. Fourier-transform infrared spectroscopy (FTIR) measurements show that Al₂O₃ features are generated after plasma treatment, while the original alucone features remain, confirming that plasma treatment results in a bilayer structure. Also, an intermediate carboxylate is created near the interface. Calculations of Al atom density during plasma exposure point towards a partial loss of Al atoms during plasma treatment, in addition to the removal of the glycerol backbone.

The effect of different process parameters has been studied. Densification at the highest temperature possible (200°C) has the best alucone preservation without hindering its thermal stability. In addition, operating at the lowest plasma power is found the most beneficial for the film, but there is a threshold that must be surpassed to achieve successful densification. About 70% of the original alucone film thickness can be expected to remain after densification, but thicker films may result in more diffuse interfaces. Additionally, this process has also been successfully performed in multilayers, showing potential for encapsulation applications.

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Emerging Materials

Room On Demand - Session EM11

Emerging Materials Poster Session

EM11-1 Strategies for High-Quality Nitride and Oxide Stacks by Plasma ALD, Yi Shu, Oxford Instruments Plasma Technology, UK; **F. McGuire**, Oxford Instruments Plasma Technology; **A. Kurek, O. Thomas**, Oxford Instruments Plasma Technology, UK; **H. Knoops**, Oxford Instruments Plasma Technology, Netherlands

Many applications in industry require the deposition of nitrides and oxides with high purity and with high-quality interfaces. The focus of most atomic layer deposition (ALD) studies is on the deposition of a single layer in a dedicated deposition chamber. This contribution highlights a set of strategies for high-quality nitride and oxide stacks deposited by ALD in a single run in a single chamber. As an example, an HfO₂/SiN_x multilayer is demonstrated with <5% oxygen in the nitride.

Low oxygen content is a challenge for nitride deposition, especially when lines and chambers might contain oxygen and water traces from a previous deposition. To demonstrate a high-quality oxide and nitride stack, HfO₂ using TDMAHF and O₂ plasma and SiN_x using BTBAS and N₂ plasma are employed. The depositions are carried out in a FlexAL system in a single run and to get the best SiN_x the residence time was minimized by a combination of turbo pumping, chamber heating and pressure and flow control.¹ For other ALD nitride processes substrate biasing could be employed to lower oxygen content, but in the case of SiN_x this is less effective.² When switching from oxide to nitride deposition, the following strategies are employed:

1. Strong purging and pumping of any gas lines that could contain oxygen or oxygen byproducts.
2. TDMAHF precursor pulses to scavenge possible oxygen byproducts.
3. Plasma treatment of the chamber and wafer surface.

After the subsequent deposition of the nitride the surface is exposed to a plasma post-treatment to further densify the material and protect it against oxidation. Using this strategy an alternating stack of HfO₂ and SiN_x was deposited with individual layer thicknesses of 20 nm. XPS depth analysis indicated that even with this relatively fast switching, oxygen content levels <5% were obtained for SiN_x (XPS analysis by Dr. Shihong Xu, nanoFAB Centre, University of Alberta). This example and general strategies for such oxide and nitride stacks will be presented.

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EM11-2 Compositionally Graded Laminate ALD Films, Alexandru Pavel, V. Vorsa, Greene Tweed, Inc.

To prevent contamination of microelectronic devices during semiconductor processing, chamber components of semiconductor tools are often coated with high purity ceramic coatings such as alumina or yttria that exhibit high resistance to plasma erosion in halogen environments. However, even these materials exhibit erosion over time leading to lower yield and costly down time, especially as the industry moves to smaller node sizes.

To overcome these limitations, there has recently been a major effort to find new coating materials and processes leading to improved plasma erosion resistance. There are now emerging plasma-resistant coatings deposited by atomic layer deposition (ALD). Advantages of ALD include conformal, dense, and pinhole-free film that can coat complex 3D shapes and high-aspect ratio holes.

One weakness with many coatings, including ALD, is the transition from one material composition to another. For example, the transition from substrate to film or from one film composition to another. Typically, in ALD, the film-substrate interface transitions abruptly within an atomic spacing of 1-2 Å. This can lead to high stress gradients confined to a narrow planar region potentially leading to poor film adhesion, especially where smooth surfaces and large CTE mismatches are present.

To overcome this drawback, ALD films can be deposited in such a way (US20200131632A1) that the composition is smoothly transitioned from one material to another, thus avoiding narrowly confined stress gradients. In this work, we present plasma resistant multi-layer coatings that exhibit excellent bonding of films to substrates formed by gradually varying the chemical composition from substrate to film and from one film type to another in a technique called Compositionally Graded Laminates (CGL). Examples of Compositionally Graded Laminate films of Y₂O₃-Al₂O₃, Y₂O₃-SiO₂, and Y₂O₃-ZrO₂ systems will be presented.

In addition to the semiconductor industry, this technique may be used to prepare and/or to coat substrates that form components useful in a variety of industries, especially those where components may be exposed to high temperatures and/or corrosive chemicals. For example, Compositionally Graded Laminates may be used on components that are found in equipment or devices used in aerospace, energy storage, pharmaceutical production, food processing, oil field applications, military and/or maritime applications, industrial manufacturing, and scientific and/or diagnostic instrumentation.

EM11-3 In Situ Electrical Conductance to Measure Vapor Phase Infiltration (VPI) Doping Kinetics of Semiconducting Polymers, Kristina Malinowski, S. Gregory, O. Hvidsten, A. Jungreis, M. Losego, Georgia Institute of Technology

This poster will show our development of *in situ* electrical conductance measurements during vapor phase infiltration (VPI) of polyaniline (PANI) thin films with titanium tetrachloride (TiCl₄) to achieve electrical doping. *In situ* measurements during vapor phase processes provide abundant information about reaction kinetics and mechanisms that could not be acquired with *ex situ* data alone. The field of vapor doping semiconducting polymers lacks a robust understanding of doping mechanisms and their respective kinetics. Therefore, the vapor doping community stands to benefit from the implementation of *in situ* measurements. Here, we demonstrate how *in situ* conductance correlates with *ex situ* characterization and propose a sequence of *in situ* doping mechanisms. Dosing and holding TiCl₄ in a chamber where hydroxyl groups are present can lead to both oxidative and acid doping of PANI films. The TiCl₄ vapor can directly oxidatively dope PANI while the HCl byproduct of TiCl₄+ -OH can lead to acid doping. During the first dose and hold of TiCl₄, *in situ* conductance measurements show that varying the TiCl₄ dose pressure changes the rate and total conductance. Then, purge, pump and isolate steps remove untrapped TiCl₄ from the chamber. Dosing and holding H₂O allows further acid doping, oxidative dedoping and oxide formation. Acid doping is in competition with dedoping and oxide formation to increase and decrease conductance, respectively. The *in situ* conductance measurements show decreasing conductance rates with increasing initial TiCl₄ pressures, suggesting that acid doping dominates at low pressures and dedoping and oxide formation dominates at high pressures. The *ex situ* characterization of the thin films validates these suggested mechanisms. Opposite pressure-conductance correlations between the TiCl₄ dose and H₂O dose present an opportunity for optimizing PANI conductivity, aided by a thorough understanding of *in situ* kinetics. PANI doping can be further controlled by managing the reactor wall chemistry. If the reactor is first

exposed to a precursor reactive towards hydroxyls but does not create an acid byproduct (for example trimethyl aluminum, TMA), then the walls can be passivated. Consequently, when TiCl_4 is dosed, it does not react with the passivated walls, and HCl is not formed, so only oxidative doping occurs. During the subsequent water dose, the potential for acid doping is reintroduced through HCl formation within the film. *In situ* measurements demonstrate that this effectively isolates the two doping mechanisms. Thus, *in situ* measurements show promise in aiding design of complex processes for vapor doping of conductive polymers.

EM11-4 Atomic Layer Deposition of Yttrium Oxide using a Liquid Yttrium Precursor, Y-08. M. Kim, EMD Performance Materials, Korea (Republic of); S. Lee, EMD Electronics, Korea (Republic of); M. Fang, J. Aldo, J. Woodruff, R. Kanjolia, EMD Performance Materials; Bhushan Zope, EMD Electronics, USA; S. Ivanov, EMD Performance Materials

Yttrium Oxide (Y_2O_3) films deposited by ALD have been extensively studied as a promising high-k material for future device manufacturing such as in MOSFETs or memory applications due to its wide band gap (~ 5.5 eV), high permittivity (>10), and high thermal stability. Pure or doped Y_2O_3 containing films have also been used in other applications such as in solid oxide fuel cells, protective coatings, photonics, and quantum information processing.

Herein, we report the studies of atomic layer deposition (ALD) of Y_2O_3 thin films using a newly developed volatile, scalable, liquid yttrium precursor, Y-08, with ozone and/or water as co-reactants.

A comparison of oxygen sources shows that “ozone followed by water” leads to a higher growth per cycle $\{0.81 \text{ \AA}/\text{cycle}\}$ compared to either ozone-alone $\{0.51 \text{ \AA}/\text{cycle}\}$, or water-alone $\{0.16 \text{ \AA}/\text{cycle}\}$. The ALD window starts at 310°C on the system tested, and the growth/cycle is $1.09 \text{ \AA}/\text{cycle}$ when saturation is achieved with both the Y-08 and oxygen sources doses. The refractive index ranges from 1.90 to 1.95. XPS analysis confirms that the bulk of film consists of exclusively oxygen and yttrium; but there was some carbon contamination on the film surface.

An yttrium oxide film deposited on a via with 20:1 aspect ratio (1800-nm deep, and 90-nm wide) shows excellent conformality when characterized by SEM (Figure 1), with film thickness ranging between 22.5 and 26 nm outside the via (Figure 2a), and 23 and 26 nm at the via bottom (Figure 2b).

We demonstrate that the liquid nature and high volatility of our new yttrium precursor promotes easier precursor delivery and more controllable ALD processes for manufacturing good quality Y_2O_3 thin films for future semiconductor applications.

EM11-7 Direct sALD of MOF: An Improvement in the Nucleation Behavior, Maissa Barr, S. Nadiri, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany; D. Chen, P. Weidler, Karlsruhe Institute of Technology (KIT), Germany; S. Bochmann, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany; H. Baumgart, department of Electrical and computer Engineering, Germany; j. Bachmann, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany; E. Redel, Karlsruhe Institute of Technology (KIT), Germany

Metal organic frameworks (MOFs), can be described as crystalline three-dimensional porous solids, with a high surface area, which have attracted considerable attention in a wide range of applications e.g. in catalysis, hydrogen storage, gas-separations, thermoelectric applications or as chemical sensors. Up to the present time, low-temperature methods had to be used to grow MOFs thin films today by conventional solution-based techniques. However, traditional growing methods from solution like spin-coating, spray-coating or dip-coating generates MOFs thin films with a rather low film quality and an alarming lack of a precise film thickness control under 1 nm, which renders them unsuitable for most industrial applications and severely limits their future application potential.

Atomic layer deposition (ALD) provides this capability, but is limited by the necessity to use gaseous precursors in vacuum conditions at temperatures above 100°C . However hybrid organo-metallic compounds such as the MOFs are not accessible by ALD due sensitivity to temperature.

In this perspective, we have transferred the principles of ALD to precursors dissolved in liquid solvents. The ‘solution ALD’ (sALD) method can be implemented in a variety of microfluidic or slot-die processing devices. We have demonstrated that the principles of classical, gas-based ALD —self-limiting surface reactions— are reproduced in sALD. sALD shares the fundamental properties of standard ‘gas ALD’ (gALD), in particular the self-limiting surface chemistry and the ability to coat deep pores in a conformal manner. Furthermore, sALD allows the experimentalist to design new, advantageous, reactions of known semiconductors (oxides, heavier

chalcogenides), or to deposit materials otherwise inaccessible to ALD altogether, such as polymers, ionic solids, and metal-organic frameworks. They may be obtained in highly pure, crystalline form at room temperature, either as planar films or as conformal coatings of porous substrates. Based on these advances, we have been able to make the first sALD-derived MOFs.

EM11-10 Thermal ALD Growth of Ir and IrOx Films Using (MeCp)Ir(COD) and Oxygen, Guo Liu, J. Woodruff, EMD Electronics, USA; T. Okamura, Merck Performance Materials Ltd, Japan; D. Moser, R. Kanjolia, B. Zope, EMD Electronics, USA

Iridium is a noble metal with low oxygen permeability, high chemical stability and high work function. It is one of the most corrosion resistant metals and has a lower bulk resistivity ($\sim 5.0 \mu\Omega\text{-cm}$) than Ru ($6.8 \mu\Omega\text{-cm}$). Due to these unique properties, iridium has been investigated for potential applications in semiconductor devices as gate electrodes, a seed layer or Cu diffusion barrier. On the other hand, IrO_2 can be converted into Ir metal by H_2 reduction, and IrO_2 nanoparticles are some of the best catalysts with potential applications for oxygen evolution in electrolyzers, metal-air batteries, and photoelectrochemical water splitting.

Various Ir precursors have been reported for ALD and CVD growth of Ir and IrO_2 films (1,2). O_2 is the most common oxidizer. Among the known ALD Ir precursors, the cyclodienyl-based (RCp)Ir(COD) (R=Me, Et) have very high thermal stability, and the liquid (EtCp)Ir(COD) precursor has been studied extensively (3,4), while the low melting-point ($\sim 40^\circ\text{C}$) MeCp analogue, (MeCp)Ir(COD), has not received much attention although it is easier to synthesize and has a higher thermal stability than (EtCp)Ir(COD). We have studied the ALD growth behavior of Ir and IrO_2 films using (MeCp)Ir(COD) and O_2 on a number of oxide and metal nitride surfaces in a wide temperature range up to 425°C . High purity Ir films with low O and C have been obtained on oxide and nitride substrates with resistivity down to $\sim 16 \mu\Omega\text{-cm}$ under various deposition conditions as shown in Fig. 1. The growth behavior on oxide surfaces is more complex. IrOx formed under certain conditions with notably higher resistivities. For examples, IrO_x formed at $\sim 350^\circ\text{C}$ with O_2 on Al_2O_3 as shown in Fig. 1.

References:

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Emerging Materials

Room On Demand - Session EM2

Organic-Inorganic Hybrid Materials

EM2-1 Toward Industrially Viable ALD/MLD Nanolaminate Films for Flexible Electronics, Jesse Kalliomaki, T. McKee, Picosun Oy, Finland

Foldable phones are now a commercially available product, with some manufacturers already several generations into the product cycle. Use of thin film encapsulation solutions (TFEs) in organic electronic manufacturing (OEM) has become more common as they are lighter and enable folding and stretching of a device, unlike conventional encapsulation methods. The commercial demand has created a large driving force to develop the quality, reliability, and process flow integration of TFEs to enable future product iterations. Inorganic films, such as those generally associated with atomic layer deposition (ALD) are vital building blocks for electronic devices due to the variety of properties they offer to a fabrication scheme. One of the main reliability issues TFEs face is that inorganic films are susceptible to crack under mechanical stress, compromising the barrier performance and cutting the lifetime of the device short. [1]

One approach to address this issue is the nanolamination of dense inorganic layers deposited with ALD for enhanced barrier performance, with organic or hybrid molecular layer deposition (MLD) layers to offer enhanced flexibility [2, 3]. To be an industrially viable solution both components of this process need to be scalable to large substrate sizes, have reasonable deposition time and show good stability in ambient conditions. The more studied MLD processes have been shown to be prone

to degradation in ambient atmosphere and quickly lose their beneficial properties [4].

We present process development results from a MLD hybrid with several different inorganic linkers deposited in Picosun R-200 advanced ALD reactor on 200 mm Si substrates. The hybrid films analysed with spectroscopic ellipsometer and Drop Shape Analyzer show excellent large area uniformity at OEM friendly temperature of 90 °C. Long term stability was studied with XPS and FTIR in addition to the previously mentioned methods and demonstrates excellent film stability after months of ambient ageing.

Industrially viable MLD processes can be a valuable tool to have in the fields of OEM and flexible electronics. In this work we show that industrial-scale ALD reactors are capable of producing MLD and ALD layers in the same chamber with low thermal budget and that ALD/MLD nanolaminates (Fig 1) can be easily deposited in a single process step on a large-scale substrate, a process that has a potential as a TFE solution.

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EM2-2 Antibacterial Alumochitin Thin Films Grown by Molecular Layer Deposition, Karina Ashurbekova, CIC nanoGUNE BRTA, Spain; K. Ashurbekova, Dagestan State University, Russian Federation; A. Muriqi, Tyndall National Institute, University College Cork, Ireland; L. Barandiaran Larrea, CIC nanoGUNE BRTA, Spain; B. Alonso Lerma, CIC nanoGUNE BRTA, Spain; I. Saric, University of Rijeka, Croatia; E. Modin, CIC nanoGUNE BRTA, Spain; R. Perez-Jimenez, CIC nanoGUNE BRTA, IKERBASQUE, Spain; . Petravic, University of Rijeka, Croatia; M. Nolan, Tyndall National Institute, University College Cork, Ireland; M. Knez, CIC nanoGUNE BRTA, IKERBASQUE, Spain

Natural chitin and chitinoid materials have outstanding physical and biological properties, which inspired us to develop a process for biomimetic chitinoid organic and hybrid organic-inorganic thin film growth by Molecular Layer Deposition (MLD).

Here, we present a new class of organic-inorganic hybrid polymers called "metallo-saccharides", based on sugar-type precursors. For a controlled MLD growth, the hexosamine monosaccharide N-Acetyl-D-mannosamine (ManNAc) was coupled with trimethylaluminum (TMA) repetitively in a cyclic manner for the growth of the hybrid organic-inorganic alumochitin thin films.

The self-limiting behavior of the surface reactions and the growth rate were determined by in-situ quartz crystal microbalance (QCM) and X-ray reflectivity (XRR) studies. The QCM measurements revealed a linear mass increase with the number of MLD cycles. The chemical structures of the coatings were studied with ex-situ X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR). Characterization of the film structure, morphology, and conformality were performed by High-resolution transmission electron microscopy (HR-TEM), showing uniform and conformal alumochitin films wrapping ZrO₂ nanoparticles (NPs).

The chemical interaction between ManNAc and TMA, and the possibility of hybrid alumochitin film formation were modeled by density functional theory (DFT). The computed interaction energies between TMA and ManNAc are negative, meaning that there's a strong interaction between these precursors. Theoretical modeling revealed that the proposed reaction mechanism for the ManNAc/TMA MLD process is energetically favorable.

The evaluation of the antimicrobial activity of the alumochitin thin film against Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) bacteria was assessed. Bacteria attachment and proliferation on glass substrates, covered with MLD film, were analyzed by confocal microscopy. (Fig. 1S in the ESI) Both types of bacteria grow and proliferate on positive control samples, while neither *Staphylococcus aureus* nor *E. coli* bacteria attached to the surface of the alumochitin film. These results show a great antimicrobial activity of alumochitin against gram-positive and gram-negative bacteria, as well as its enormous application potential as bioactive surfaces.

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EM2-3 Mechanics of Flexible ϵ -Fe₂O₃/Organic Superlattice Thin-Film Magnets, Janne-Petteri Niemelä, Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland; A. Philip, G. Tewari, Aalto University, Finland; N. Rohbeck, B. Putz, T. Edwards, Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland; M. Karppinen, Aalto University, Finland; J. Michler, I. Utke, Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The little-known iron(III)oxide polymorph ϵ -Fe₂O₃ has risen intrigue for its ferrimagnetic character and high coercive field, that make it an interesting material for magnetic storage applications.¹ To enhance the appeal of ϵ -Fe₂O₃ thin-film magnets for flexible electronics, tailoring its mechanically rigid character is however desired. Here we demonstrate tailoring of the mechanical properties of ϵ -Fe₂O₃ thin films through insertion of Fe-terephthalate interlayers by using the combined atomic/molecular layer (ALD/MLD) deposition technique.^{2,3}

We deposited ϵ -Fe₂O₃ oxide films, Fe-terephthalate (Fe-TP) hybrid films and ϵ -Fe₂O₃/Fe-TP superlattice thin films using FeCl₃ as the Fe metal precursor, H₂O as the oxygen source, and terephthalic acid as the organic precursor.^{2,3,4} Nanoindentation experiments indicate that the insertion of the Fe-TP interlayers in the ϵ -Fe₂O₃ matrix enables a factor-of-two decrease in elastic modulus for the superlattice films down to 70±20 GPa. In-situ tensile fragmentation testing indicates that the crack onset strain and critical bending radius can be tuned by a factor of three. Modeling of the tensile fragmentation patterns through Weibull statistics shows that cohesive and interfacial shear strain, following the trend for crack onset strain, increase with increasing organic content, while gains for the respective strengths are limited by the simultaneous reduction in elastic modulus. Importantly, we demonstrate through magnetization vs. magnetic field (M-H) measurements that the unique magnetic characteristics of ϵ -Fe₂O₃ are not sacrificed in the superlattices with enhanced mechanical flexibility. Magnetic characterization of strained films indicates absence of catastrophic failure upon fragmentation and modest debonding of the films, while the improved mechanical characteristics for the superlattices translate to improved preservation of the magnetic characteristics.

The present results are interesting for magnetic storage applications in flexible electronics and highlight the potential of the combinatorial ALD/MLD technique for enhancing mechanical properties of—not only inorganic-organic alloys as known from the past⁵—but also of multilayer structures with inorganic layers thick enough to generate usable functionalities.

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EM2-4 Effect of Vapor-Phase Metal Infiltration on Lithography of PMMA Resist for EUV Applications, Su Min Hwang, R. Gummadavally, D. Le, J. Kim, Y. Jung, J. Veyan, University of Texas at Dallas, USA; C. Nam, Brookhaven National Laboratory; J. Ahn, Hanyang University, Korea; J. Kim, University of Texas at Dallas, USA

Due to the limitation of resolution with scaling down of feature size, extreme ultraviolet (EUV) has drawn great attention as the light source for the next-generation lithography process. Unlike the photoresists for UV irradiation, EUV photoresist interacts with secondary electrons. However, the current polymer-based resist has confronted a number of challenges, such as pattern collapsing due to resist thickness, poor EUV adsorption, and etch-selectivity, etc. To circumvent the limitation, research on new materials, particularly metal incorporation with organic resists has been recently reported. With introduction of metal, the hybrid resist can increase the EUV absorption as well as the mechanical stability during the pattern transferring.^{2,3} Among the various synthesis of inorganic-organic hybrid EUV resists, vapor-phase infiltration of metal source into existing organic resist using ALD process can be employed. This *ex-situ* process can avoid the complex chemistry and employ the standard fabrication process.

In this work, we have demonstrated the infiltration of Hf into PMMA e-beam resist using ALD process. The PMMA resist is coated on the Si substrate using a spin-coating technique, followed by exposure of TDMA-HF precursor in the ALD chamber at 85 °C. In XPS gas cluster ion beam depth profile, Hf concentration showed 5 to 10 at. % in PMMA film, implying that Hf is distributed in the PMMA resist. Specifically, we

investigated the effect of metal-infiltrated resists on electron-induced solubility by understanding the change of chemical bonds using an *in-situ* Fourier transform infrared spectroscopy (FTIR) equipped with electron gun capability. Each sample was exposed with electrons with 100 eV, which was similar energy of incident photons from EUV, and characterized the difference of chemical bonds before and after exposure. Based on these theoretical results, pure PMMA and metal infiltrated PMMA was exposed with a variable dose of electrons, followed the developing test with various solvent to investigate the effect of metal infiltration.

This work is funded by Brain Pool Program through National Research Foundation by the Ministry of Science and ICT in Korea (No. 2019H1D3A2A01101691). This work was also partially supported by SRC-NMP program (task# 3035.001).

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EM2-5 About the Importance of Purge Time in Molecular Layer Deposition of Alucone Films, *Hardik Jain, P. Poedt*, Holst Centre / TNO, Netherlands

The deposition rate and properties of MLD films are for a large part determined by what happens during the precursor exposure. In some cases, however, the purge step is of equal importance, for example in the MLD of alucone films using trimethylaluminum (TMA) and ethylene glycol (EG). These alucone films tend to be porous in nature due to which the reactants during their exposure step not only react at the film surface but also tend to infiltrate into the film. The outgassing of the infiltrated reactant can take relatively very long thereby becoming the deposition rate limiting step. If enough purge time is not provided for the reactant to outgas, it will lead to an undesirable CVD component alongside MLD in the overall growth. We have investigated the MLD of alucone focusing on the effect of purge time of TMA on the growth kinetics. To avoid any negative impact of the CVD component on the deposition rate and the film's properties, we have also developed a kinetic model to correlate parameters like exposure times, partial pressures, purge times and deposition temperature to the CVD component in the growth. With an intention to improve the outgassing efficiency of TMA, the influence of purge gas flow on the CVD growth component has also been briefly investigated. Finally, we show that using a bulkier precursor like DMAI instead of TMA can overcome the problem of precursor infiltration altogether and increase the deposition rate of alucone processes by at least an order of magnitude.

EM2-8 Low Temperature Alumina and Alucone Multistack by Ald for Flexible and Transparent Gas Barrier Layers, *Shiv Bhudia, N. Adjeroud, R. Leturq*, Luxembourg Institute of Science and Technology (LIST), Luxembourg

Gas permeation barriers are widely employed in many technological applications. From medium barrier properties (Oxygen transmission rate, $OTR \approx 1 \text{ cc m}^{-2} \text{ day}^{-1} \text{ bar}^{-1}$; Water vapour transmission rate, $WVTR \approx 1 \text{ g m}^{-2} \text{ day}^{-1}$) as in the food packaging industry. To very high barrier properties ($OTR \approx 10^{-5} \text{ cc m}^{-2} \text{ day}^{-1} \text{ bar}^{-1}$; $WVTR \approx 1 \text{ g m}^{-2} \text{ day}^{-1}$) such as in flexible organic opto-electronics. Here, it is even more critical to avoid the presence of water and oxygen in the active layer.

Atomic layer deposition (ALD) of amorphous alumina show very promising properties for passivation or encapsulation layer, for gas barrier layers. However, the deposition conditions usually require temperatures above 100 °C or highly oxidative conditions (ozone or oxygen plasma) to obtain reasonable deposition rates and high-density material. And due to its brittle nature, it limits the implementation on rigid or low flexibility substrates. A process for temperature sensitive substrates used in food packaging would be highly welcomed.

In this work, we combined amorphous alumina with alucone, in multi-stack structures on flexible PET substrate for food packaging. The inorganic alumina layer serves as gas barrier layer and the organic alucone layer decouples the adjacent alumina layers, thus avoiding direct passage of the permeant gas through pinholes.

By developing an in-house He permeation tester, we have investigated the physical diffusion of Helium on these structures; and a method of extracting diffusivity and solubility from different substrate thickness is proposed. To further understand the morphology of these layers, we have simulated those structures using Finite Element Method (FEM).

EM2-11 Transport in Vapor Phase Infiltration Processes: Modeling and Measuring Competition between Reactions and Diffusion, *Emily McGuinness, Y. Ren, B. Jean, R. Lively, M. Losego*, Georgia Institute of Technology

Over the past decade, vapor phase infiltration (VPI) has emerged as a technique to create hybrid organic-inorganic materials with a wealth of industrially relevant applications. While the utility of VPI has become clear, the fundamental mechanisms that control the hybrid material structure (and therefore material properties) are complex and not well understood. In this presentation, a reactive-diffusion model is explored that provides insight into how the presence of reactions between polymers and metalorganic precursors modifies the transport behavior of the vapor phase metalorganic molecule through the material. This model is found to not only account for diffusion of the vapor phase metalorganic precursor within the polymer film, but also capture the reaction between the two phases, as well as associated reductions in diffusivity. For example, a hindering factor is established that accounts for the interference of chemically bound precursor with further diffusion of unbound precursor. This parameter captures the orders of magnitude reduction of out-diffusion coefficients as compared to in-diffusion coefficients observed in certain VPI systems. The model is shown to both qualitatively and quantitatively capture and predict VPI behaviors in an experimental case-study of the trimethylaluminum (TMA) / poly(methyl methacrylate) [PMMA] VPI system (**Figure 1**). Parameters extracted from the model can be used to understand the fundamental thermodynamic and kinetic principles that underly the VPI process. For instance, the Damkohler number (a dimensionless value comparing the rate of diffusion to the rate of reaction in a system) for TMA / PMMA at 130 °C is found to be approximately 0.08. This value indicates that diffusion of TMA occurs faster than reactions between TMA and PMMA under these conditions. As a result of this, the TMA / PMMA system is able to exhibit high mass uptake in early times before hindering of the system sets in from the formation of bound precursor. Overall, this presentation will not only introduce a new model capable of capturing the complexities of VPI, but also provide guidelines and a case-study of its utility in experimental parameterization and prediction.

EM2-14 First Principles Study of Reactions in Hybrid Organic-Inorganic Films: The Impact of the Organic Reactant, *Arbresha Muriqi, M. Nolan*, Tyndall National Institute, University College Cork, Ireland

The development of hybrid inorganic-organic films with well-controlled properties is vital for the future of nanotechnology for many applications. Molecular layer deposition (MLD) allows the deposition of hybrid films using sequential, self-limiting reactions, similar to ALD. In this study, we investigate the growth mechanism of different hybrid organic-inorganic thin films by using first principles density functional theory (DFT).

The prototype for MLD hybrid films are composed of thin films of aluminium alkoxides, known as "alucones". We investigated the MLD reaction products between the post-TMA Monomethyl-Al₂O₃ (Al-CH₃-Al₂O₃) and Dimethyl-Al₂O₃ (Al(CH₃)₂-Al₂O₃) surface and diol organic precursors, including ethylene glycol (EG) as well as glycerol (GL). The results show that Al-O formation with release of methane is favorable for all diols. Interaction energies show that longer diols will not maintain an upright configuration compared to lying flat and participating in the "double reaction" where the two terminal -OH groups bind to surface TMA. A detailed comparison of ethylene glycol (EG) and glycerol (GL) precursors is presented to assist the interpretation of experimental findings regarding the differences in the hybrid films grown by EG and GL. EG and GL can lie flat and create double reactions through the two terminal hydroxyl groups. This phenomenon removes active hydroxyl sites for EG. For GL the third hydroxyl group is available and growth can proceed. This analysis shows the origin of differences in thickness of alucones found for EG and GL.

We also investigate the growth mechanism of magnesium containing hybrid films known as "magnesicone" from the reaction of EG and GL at MgCp-terminated MgO as a model system. Interaction energies show that while the ligand elimination process is favorable for both precursors, GL species prefers to lie in an upright position and EG prefers to orient in a flat configuration and interacts at the MgO surface, resulting in a thicker GL-based magnesicone compared to the EG-based magnesicone. This is consistent with the experimental findings for magnesicone growth using these precursors.

Finally we study the growth of titanium-containing hybrid organic-inorganic films known as "titanicones". using titanium tetrachloride (TiCl₄) or tetrakisdimethylamido (Ti(TDMA)₄) as metal source

and ethylene glycol (EG) or glycerol (GL) as organic reactants. This investigation contributes to the understanding of growth process of EG and GL based titanicones at different surfaces and is valuable in supporting experimental data on titanicones film growth.

Emerging Materials

Room On Demand - Session EM3

Atomic Layer Epitaxy and Doping

EM3-1 Low-Temperature Dopant-Assisted Crystallization of HfO₂ Thin Films, *Theodosia Gougousi*, Department of Physics, UMBC

We have studied the thermal ALD of HfO₂ on native and chemical oxide GaAs(100) surfaces using various alkylamide precursors. Bright field and HRTEM data for *as-prepared* 12–36 nm HfO₂ films deposited on native oxide GaAs(100) at 250°C from tetrakis ethylmethylamino hafnium (TEMAHF) and H₂O shows that the films are polycrystalline. These films contain several large grains of the order of the film thickness and numerous small crystallites (Figure 1). To clarify the role of the GaAs(100) substrate in the observed HfO₂ film structure an additional set of films was grown on GaAs(100) surfaces that were chemically oxidized. The chemical oxide layer thickness was measured at ~4.6 nm more than twice the thickness of the native oxides. GaAs chemical oxides are similar in composition to the native oxides. HfO₂ films with thickness ~6 nm deposited on the chemical oxide GaAs(100) surfaces are also polycrystalline while ~2 nm of the chemical oxide layer is still detectable at the interface (Figure 2). The presence of the chemical oxide at the interface precludes the direct contact of the HfO₂ layer with the GaAs substrate. Normally, HfO₂ films of such low thickness remain amorphous even after they are subjected to thermal treatment. One of the highlights of alkylamide HfO₂ ALD processes on III-V substrates is the so-called interface cleaning reaction that leads to the gradual consumption of the surface native oxides and results in the formation of a sharp HfO₂/III-V semiconductor interface. We have shown that this interface cleaning reaction is accomplished because the surface native oxides transport to the surface of the growing ALD oxide layer where they react with the precursor to form volatile byproducts that are removed. So, at any point during the ALD process there is mixing of the various III-V oxides in the film but because of the removal mechanism the final ALD film has very low impurity content. We hypothesize that the native oxides lead to the stabilization of the various HfO₂ polymorphs during low temperature thermal atomic layer deposition allowing control of the film microstructure via the deposition process.

Emerging Materials

Room On Demand - Session EM8

Nanolaminates

EM8-1 Properties of Atomic Layer Deposited ZrO₂ or Fe₂O₃ Based Multilayers, *Helina Seemen, K. Kukli, A. Tamm*, University of Tartu, Estonia

Research devoted to the achievement of multiferroic thin-film materials is actual, and the task itself has appeared to be quite challenging. At the same time, it could also be rewarding in the case of success due to prospective applications as these materials are useful for non-volatile memories and electromagnetic sensor materials. In this study, five-layer nanolaminates consisting of alternately deposited ZrO₂ and Co₃O₄ layers, and two-layer structures consisting of Fe₂O₃ film and BiOCl nanoflakes were deposited to explore their potential advanced magnetic properties [1, 2]. The main goal was to achieve a ferromagnetic-like response with the measurable coercivity values getting as high as ten kOe. The Fe₂O₃-BiOCl combination was partly selected due to the possible formation of bismuth ferrite, which is known to be one of the most promising multiferroic materials, at the interfaces.

The ZrO₂-Co₃O₄ 5-layer nanolaminates were grown by atomic layer deposition at 300 °C from ZrCl₄ and Co(acac)₃ as metal precursors and O₃ as the oxygen precursor. The Fe₂O₃-BiOCl two-layer thin-film structures were deposited from FeCl₃, BiCl₃ and H₂O at 375 °C.

The results showed that the multilayers of both studies were crystallized in the as-deposited state. In the ZrO₂-Co₃O₄ 5-layer nanolaminates, the cubic and monoclinic ZrO₂ phases and cubic Co₃O₄ phase were present. Orthorhombic ε-Fe₂O₃ and tetragonal BiOCl phases were detected in the case of Fe₂O₃-BiOCl two-layer thin-film structures. In Table I, selected multilayer structures, their total thicknesses and measured coercivity

values are presented. Magnetic hysteresis loops showed nonlinear and saturative magnetization and measurable coercivity, indicating ferromagnetic-like behaviour at room temperature. The highest coercivity value measured was 9757 Oe (776.4 kA/m), which characterized one particular Fe₂O₃-BiOCl two-layer thin-film structure (Table I). SEM images of this type of multilayer structure are displayed in Figure 1. In the case of the ZrO₂-Co₃O₄ nanolaminates, the coercivity values were 21 and 32 Oe (1.7 to 2.5 kA/m) (Table I). All five layers of the nanolaminates were clearly distinguishable (Figure 2).

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EM8-2 Evaluation of the Near-Zero Temperature Coefficient of Resistivity (nz-TCR) of ALD TiSi_xN Films, *Corbin Feit, S. Berriel*, University of Central Florida; *A. Dhamdhare, B. Nie, H. Cho, H. Kim, S. Chugh, S. Rath, N. Mukherjee*, Eugenius, Inc.; *P. Banerjee*, University of Central Florida

Atomic Layer Deposition (ALD) of ternary TiSi_xN leads to nanocomposites of metallic TiN atomically mixed with insulating Si₃N₄. Formulating TiSi_xN films with various Ti:Si ratios lead to the emergence of a temperature regime where resistivity is independent of thermal drift, denoted as near-zero temperature coefficient of resistivity (nz-TCR). Further, the ease with which nanocomposites of TiSi_xN can be deposited using ALD offer precise tunability in Ti:Si ratio, thickness, mass density, crystallinity and electrical properties.

Recently, our group explored TiSi_xN films deposited using a Eugenius® 300 mm commercial QXP mini-batch system by modulating the ratio of Ti and Si precursors with NH₃ as a co-reactant. Si-content was varied from 0 at % (pure TiN) to 24.2 at % Si while maintaining thickness ~ 140 nm. The X-ray reflectivity and grazing incidence X-ray diffraction measurements showed a reduction in film density and transition from nano-crystalline to pure amorphous phase with increase in Si-fraction. Spectroscopic ellipsometry revealed the optical constants, composition, and electrical resistivities and were supported by X-ray photoelectron spectroscopy and electrical measurements. Room-temperature resistivity measurements show an increase in film resistivity with increasing at % Si. Temperature-dependent Van der Pauw measurements found a nz-TCR of -23 ppm K⁻¹ in the temperature range of 298 K – 398 K and at 3.4 at % Si content.

We have now discovered that an at % Si = 3.0% induces a nz-TCR of -5.7 ppm K⁻¹ from 80 K – 420 K – one of the best reported nz-TCR values for ALD thin films. Fine tuning the at % Si in TiSi_xN films, possible only via ALD, significantly elongated the temperature window of nz-TCR behavior. Mapping the local conductivity of individual grains through conductive atomic force microscopy (c-AFM) indicated higher resistance at the grain boundaries. The local composition at the grain boundaries may play a major role in determining the nz-TCR behavior of TiSi_xN films. In addition, variable temperature Hall effect measurements were performed to provide deeper insights into the nz-TCR mechanism, decoupling carrier concentration from carrier mobility effects while determining film resistivity.

Compared to other nz-TCR films, which are deposited using physical vapor deposition techniques, ALD based nz-TCR films presents a unique synthesis platform for interconnect technology in topologically complex, 3D devices, circuits and sensors that undergo large temperature variation during operation but need to maintain stability in their electrical characteristics.

Emerging Materials

Room On Demand - Session EM9

Ternary and Quaternary Materials

EM9-1 Substitutional W Doping of MoS₂ for Threshold Voltage Control of Field Effect Transistor, *Hwi Yoon, W. Woo, I. Sohn, Y. Lee, S. Seo, S. Cheong, H. Kim, H. Kim*, Yonsei University, Korea

Two dimensional (2D) layered transition metal dichalcogenides (TMDCs) have attracted great attention owing to its excellent properties such as superior mechanical flexibility, transparency thermal stability, and compatibility to silicon CMOS processes. In particular, molybdenum disulfide (MoS₂) has been extensively studied in recent years. MoS₂ has

been considered as attractive channel material for electronic switch device applications in the form of field-effect transistors (FETs) due to superior electrical properties such as thickness-dependent bandgap, high field-effect mobility, high current on/off ratio ($>10^8$), nearly ideal subthreshold swing (SS). Despite all the advantages of MoS₂ as a promising candidate to replace silicon in such devices, large variations in the threshold voltage (V_{th}) of FET makes difficult it in practical application. The V_{th} of silicon-based semiconductor technology at the 22 nm technology node is 0.289 V for high performance logic and 0.413 V for low operating power logic. In contrast, values of V_{th} of back-gated MoS₂ FETs being reported vary from -30 V to 40 V. In the case of Si-based FET, V_{th} can be easily tuned by doping through ion implantation. However, this method cannot be applied to MoS₂ because energetic processes such as implantation, plasma easily cause damage to MoS₂. In this study, we developed one-step doping process during chemical vapor deposition (CVD) of MoS₂. electrical properties such as carrier density, bandgap and chemical composition tuned according to dopant concentration. In addition, V_{th} modulation of MoS₂ was carried out by using substitutional doping of W. V_{th} of MoS₂ FET has decreased by more than 10 V after doping.

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EM9-2 Atomic Layer Deposition of CuSn_xS_y from Low-Cost Precursors and Its Optical and Electrical Characteristics, Jakub Ostapko, G. Kołodziej, M. Wlazło, CB RTP - Research and Development Center of Technology for Industry, Poland; Z. Starowicz, Institute of Metallurgy and Materials Science, Poland; G. Putynkowski, CB RTP - Research and Development Center of Technology for Industry, Poland

Metal sulfides are of high importance for thin-film photovoltaics applications. Some of the most widely studied structures belong to the quaternary compounds group and play the role of solar cell absorber: CIGS (CuIn_(1-x)Ga_xSe₂) and CZTS (Cu₂ZnSnS₄). The ternary structure, Cu₂SnS₃ (CTS)^[1] has been reported in the literature as a simplified and potential absorber material. Ordinarily, methods different than ALD are used for their synthesis. In case of record CIGS^[2] (23.35% efficiency) and CZTS^[3] (12.6%) cells, DC sputtering and solution approaches were used, respectively.

ALD is dedicated to the preparation of uniform thin films. There are a few reports in the literature concerning ALD synthesis of technologically important ternary^[4–8] and quaternary^[9] sulfides. The ALD synthesis of sulfide-based absorbers is hindered by some limitations: precursor chemical compatibility, including reactivity with the sulfur precursor, parasitic reactions, and the limited volatility of precursors. These limitations are reflected by low growth per ALD cycle. The other aspects that limit ALD utility are high moisture and oxygen sensitivity, and high prices of commercially available metal precursors.

In this study, a new process of ALD deposition of ternary sulfide CuSn_xS_y is presented. The material has been prepared using affordable copper and tin precursors. This is contrasted with the reported ALD processes, which use expensive organometallic reactants as sources of Cu and Sn. The synthesis has been carried out at low temperature. Films of CuSn_xS_y varying in stoichiometry were synthesized. Film morphology, including cross-section imaging, was provided by SEM analysis. The elemental composition was determined by EDS. The results of optical (UV-vis spectroscopy) and electrical measurements (Hall effect, four-point probe) are presented and discussed in the context of the photovoltaic application of ALD synthesized CuSn_xS_y films.

The obtained results highlight the versatility of the ALD technique and provide an example of a cost-effective synthesis of thin-film absorber material.

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