

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.

On Demand

In this work, we prove that alucone/ Al_2O_3 nanolaminate synthesis can be successfully performed by alternating alucone MLD growth with static O_2 plasma exposures. Upon plasma treatment, only the top part of the alucone is densified into Al_2O_3 , 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 Al_2O_3 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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Author Index

Bold page numbers indicate presenter

— B —

Barry, S.: EM1-1, **1**

— D —

Dendooven, J.: EM1-6, **1**

Detavernier, C.: EM1-2, **1**; EM1-6, **1**

Devi, A.: EM1-2, **1**

— G —

Gordon, P.: EM1-1, **1**

— H —

Heitmann, T.: EM1-3, **1**

— J —

Jena, H.: EM1-2, **1**

— K —

Kaiser, H.: EM1-3, **1**

Karppinen, M.: EM1-2, **1**

Karttunen, A.: EM1-2, **1**

Kaur, P.: EM1-2, **1**

Keukelier, J.: EM1-6, **1**

— L —

Li, J.: EM1-6, **1**

— M —

McGuinness, C.: EM1-1, **1**

Minjauw, M.: EM1-2, **1**; EM1-6, **1**

— N —

Nisula, M.: EM1-2, **1**; EM1-6, **1**

— P —

Pitillas Martínez, A.: EM1-6, **1**

— R —

Ragogna, P.: EM1-1, **1**

— S —

Santo Domingo Peñaranda, J.: EM1-6, **1**

Solano, E.: EM1-2, **1**

— T —

Tewari, G.: EM1-2, **1**

— V —

Van Der Voort, P.: EM1-2, **1**

Vandenbroucke, S.: EM1-6, **1**

Vaninger, M.: EM1-3, **1**

— W —

Werbrouck, A.: EM1-6, **1**

Wyatt, Q.: EM1-3, **1**

— Y —

Young, M.: EM1-3, **1**