

Live Session

Room Live - Session LI2-TuM

Technical & Poster Sessions: Tuesday Live

Moderators: Harm C.M. Knoop, Oxford Instruments Plasma Technology, The Netherlands, Paul Poodt, Holst Centre / TNO

10:00am **LI2-TuM-7 Welcome and Introduction**, *C Detavernier, J Dendooven*, Ghent University, Belgium; *Paul Poodt*, TNO/Holst Center, Netherlands; *E Kessels*, Eindhoven University of Technology, Netherlands; *H Knoop*, Oxford Instruments Plasma Technology, Netherlands; *J de Marneffe*, IMEC, Belgium

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10:15am **LI2-TuM-8 Thermal Atomic Layer Deposition of Noble Metal Films Using Non-Oxidative Coreactants**, *Charles H. Winter*, Wayne State University

Atomic layer deposition (ALD)^{1,2} growth of noble metal (Ru, Os, Rh, Ir, Pd, Pt, Ag, Au) films is almost universally carried out by treatment of a volatile organometallic or metalorganic precursor with O₂ or ozone at temperatures of 200 °C or higher.³ These processes lead to combustion of the organic ligands of the surface-bound metal precursors, affording a metal oxide layer, water, and CO₂. At temperatures above about 200 °C, the noble metal oxides decompose to the metals. By this general approach, thin films of Ru, Os, Rh, Ir, Pd, and Pt can be deposited. Despite the success of these existing ALD processes for noble metal films, O₂ and ozone are strong oxidants and can oxidize sensitive layers in microelectronics devices, such as W metal, TiN, and TaN.⁴ Thus, combustion-based ALD processes using O₂ or ozone are unlikely to be suitable for depositions on easily oxidized substrates. Herein, we will describe our efforts to develop alternative, non-oxidizing co-reactants for the thermal ALD of noble metal films. We will overview the growth of Ru metal films using (η⁴-2,3-dimethylbutadiene)(tricarboxyl)ruthenium (Ru(DMBD)(CO)₃) with 1,1-dimethylhydrazine and several other N-based molecules.⁵ With 1,1-dimethylhydrazine, an ALD window was observed from 200 to 210 °C, with a growth rate of 0.42 Å/cycle. X-ray photoelectron spectroscopy revealed >90% Ru metal in the films, with N (~7%) as the only significant contaminant. Annealing of these films under various atmospheres led to low resistivity, high purity Ru films. We will also report the thermal ALD growth of Re metal films, using Re precursors and nitrogen-based co-reactants.

1. M. Leskelä and M. Ritala, *Angew. Chem. Int. Ed.* **42**, 5548–5554 (2003).
2. S. M. George, *Chem. Rev.* **110**, 111–131 (2010).
3. J. Hämäläinen, M. Ritala, and M. Leskelä, *Chem. Mater.* **26**, 786–801 (2013).
4. S.-J. Lee, S.-H. Kim, M. Saito, K. Suzuki, S. Nabeya, J. Lee, S. Kim, S. Yeom, and D.-J. Lee, *J. Vac. Sci. Technol. A* **34**, 031509 (2016).
5. S. Cwik, K. N. Woods, M. J. Saly, T. J. Knisley, and C. H. Winter, *J. Vac. Sci. Technol. A* **38**, 012402 (2020).

10:45am **LI2-TuM-10 Mixing It Up: Tuning Atomic Ordering in 2-D Mo_{1-x}W_xS₂ Alloys by ALD**, *Jeff Schulpen, E Kessels, V Vandalon, A Bol*, Eindhoven University of Technology, Netherlands

In this contribution, we show how ALD can be used to finely tune the atomic ordering of transition metal dichalcogenide alloys, while at the same time exerting excellent control over their alloy ratio. Transition metal dichalcogenides (TMDs) such as MoS₂ and WS₂ are promising for many applications ranging from photonics and nano-electronics to photovoltaics and catalysis. Tailoring the properties of these materials is often desired for specific applications. An effective method of enabling such tunability of these materials is by alloying multiple TMDs. Conventionally, investigations on alloys focus on how their properties change as a function of the alloy ratio, i.e. the abundance ratio of the constituents of the alloy. However, alloys also have another degree of freedom, namely their atomic ordering. This ordering can range from random to clustered, and controlling this parameter could enable additional tuning of the properties of TMD alloys.

We employ plasma-assisted ALD^{1,2} to synthesize Mo_{1-x}W_xS₂ films using a supercycle approach. The excellent control over the alloy achieved by this method is evidenced by XPS atomic abundance measurements and Raman spectroscopy, both of which indicate that the alloy ratio varies smoothly as

a function of the relative number of MoS₂ and WS₂ cycles. Control over the atomic ordering of the alloys was achieved by manipulating the ordering of the ALD cycles while keeping the alloy ratio fixed. As a function of the ALD cycle ordering, systematic shifts are observed in the lattice vibration frequencies and in the exciton energies by Raman spectroscopy and visible light absorption spectroscopy, respectively. To understand these effects, density functional theory (DFT) calculations were performed on Mo_{1-x}W_xS₂ structures of varying atomic ordering. Through comparison with the DFT results, we interpret our experimental results as indeed arising from the atomic-scale ordering of the alloy films. This supports the idea that ALD can be used to tune the atomic ordering of these materials, adding this parameter to the experimental toolbox for tailoring the material properties of TMDs by ALD.

[1] Sharma, A. Low-temperature plasma-enhanced atomic layer deposition of 2-D MoS₂: large area, thickness control and tuneable morphology. , 8615–8627 (2018).

[2] Balasubramanyam, S. Edge-site nano-engineering of WS₂ by low temperature plasma-enhanced atomic layer deposition for electrocatalytic hydrogen evolution. (2019).

11:00am **LI2-TuM-11 Deposition of Conductive PEDOT Thin Films with EDOT and ReCl₅ Precursors**, *Saba Ghafourisaleh, G Popov, M Leskelä, M Putkonen, M Ritala*, University of Helsinki, Finland

In this study we used the Oxidative Molecular Layer Deposition technique (oMLD) to deposit the most common conductive polymer – PEDOT. PEDOT is the polymer of ethylenedioxythiophene (EDOT, monomer) and has gained a lot of interest in solar energy and battery applications because it is stable, conductive, flexible and transparent. Here we were able to prepare PEDOT thin films by using a new inorganic oxidizing agent rhenium pentachloride (ReCl₅). We extensively characterized the properties of our films with XRD, EDS, SIMS and SEM.

Not many oMLD processes exist. The oMLD of polymers is based on sequential adsorption of the monomer and its polymerization that is induced by oxidation. The challenge in the oMLD of polymers is finding a suitable combination of precursors which is difficult because most organic monomers are non-volatile or unstable at high temperatures. Another challenge lies in finding an agent for oxidizing the organic monomer efficiently. The oxidizing agent should not contaminate the film with impurities, or if impurities are left in the film, they should be easily removed afterwards with post-deposition treatment.

The oxidizing agent used in this process is ReCl₅ which has high thermal stability and high oxidizing ability. 3,4-Ethylenedioxythiophene EDOT is used as the organic monomer. With these precursors PEDOT films were deposited at temperatures in the 125–225 °C range. The polymer films were transparent in the visible region and showed high electrical conductivities.

XRD measurements showed that some rhenium residues were present in the polymer films and after the deposition these impurities segregated on the film surface in the form of rhenium oxychloride particulates. The PEDOT polymer is insoluble in water, whereas rhenium oxychloride is soluble. We post-treated the samples with deionized water. The post-treatment removed the contaminating rhenium impurities.

This work is funded by the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No765378.

11:30am **LI2-TuM-13 Resistless Lithography Based on Local Surface Modification of Halogenated Amorphous Carbon**, *Mikhail Krishtab*, KU Leuven/Imec, Belgium; *T Kulmala, E Cagin*, Heidelberg Instruments Nano, Switzerland; *S Armini*, Imec, Belgium; *S De Gendt*, KU Leuven/Imec, Belgium; *R Ameloot*, KU Leuven, Belgium

The fabrication of nanoscale devices involves multiple lithography steps which define the device's geometry and its performance. Electron-beam lithography and thermal scanning probe lithography (t-SPL) allow routine printing of features down to few tens of nanometers. Both techniques are based on the traditional resist process flow which relies on **bulk** modification of the sensitive layer to form an initial pattern. However, the achievement of the highest possible resolution requires application of very thin resist films thus making the successive pattern transfer particularly challenging. Inspired by the recent advances in the field of area-selective atomic-layer deposition (AS-ALD), we explored an alternative resistless approach based on local **surface** modification of an amorphous carbon film guiding the growth of a hard-mask layer.

The approach starts from plasma halogenation of a hydrogenated amorphous carbon film (a-C:H) deposited on top of a desired stack to be

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patterned (Figure 1). The carbon-halogen bonds (C-F, C-Cl) on the surface of the a-C:H prevent ALD growth of an inorganic hard-mask layer. The exposure of the halogenated a-C:H layer to a certain energy source during the appropriate lithography step (heating or e-beam) results in local breaking of the carbon-halogen bonds, which in turn enables the growth of the ALD hard-mask exclusively in the exposed areas. The formed thin hard-mask layer is then used for patterning of the a-C:H by plasma etching.

The complete patterning sequence was demonstrated using Cl₂- and CF₄-plasma treated a-C:H films and ALD TiO₂ (TiCl₄/H₂O) as a hard-mask deposition process. After validating the blocking capability of the 3-5 nm thick halogen-rich a-C:H surface (Figure 2), we studied its sensitivity to e-beam exposure (Figure 3) and its thermal stability (Figure 4). It was found that a relatively high e-beam dose was required to get a degree of surface dehalogenation sufficient for the deposition of a pinhole-free hard-mask layer. In contrast, the low decomposition temperature of the topmost halogen-containing surface groups favored t-SPL lithography. The latter appears particularly efficient when combined with an additional 405 nm laser source, exposure to which enabled fast formation of micron-size TiO₂ patterns. The final aspect of our study concerned the reduction of nucleation defects associated with imperfections of ASD TiO₂ process. The repetitive halogenation treatment and post-deposition plasma etching were tested as defect-reduction strategies.

11:45am LI2-TuM-14 Mimicking Chitin and Chitosan Type of Functionality with Novel Thin Films Grown by Molecular Layer Deposition, Karina Ashurbekova, M Knez, CIC nanoGUNE BRTA, Spain

In a bioinspired approach, we are mimicking naturally occurring materials to fabricate hybrid antibacterial and biocompatible thin films for various applications.

In this work we will present a new process for generating chitin and chitosan type of functionality by Molecular Layer Deposition (MLD). A proposed deposition scheme of the underlying chitin-type of MLD process is presented in Fig. 1. Chitin and chitosan are prominent natural biocompatible and biodegradable polysaccharides that exhibit antimicrobial, antifungal and antiviral properties, which could find application in, for example, food packaging.

For the first time sugar molecules, such as, N-acetyl-D- mannosamine and N-acetyl-D-glucosamine, were used as precursors for MLD. Thionyl chloride was used as a chlorinating agent to bind the sugar molecules to the surface. ATR-FTIR spectra of the N-acetyl-D-Mannosamine/SOCl₂ MLD film show several bands that are characteristic of chitin.

Besides antimicrobial properties, packaging materials require good barrier properties for water vapor and oxygen. In order to create efficient gas diffusion barriers, various metals (Al, Ti and Zn) were grafted to the chain, creating hybrid Chitin-metal surfaces. In-situ Quartz Crystal Microbalance (QCM) studies show a linear mass increase during sequential dosing of N-acetyl-D-mannosamine and trimethylaluminum (TMA) (Fig. 2A) with a total mass gain per cycle (MGPC) of 20 ng/cm² (Fig. 2B).

The obtained hybrid MLD films grown at different temperatures were characterized by ATR-FTIR, X-ray reflectivity (XRR), X-ray photoelectron spectroscopy (XPS), in-situ QCM and Solid-state NMR (ssNMR).

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska -Curie grant agreement No 765378.

12:00pm LI2-TuM-15 Closing Remarks & Sponsor Thank You, C Detavernier, J Dendooven, Ghent University, Belgium; P Poodt, TNO/Holst Center, Netherlands; E Kessels, Eindhoven University of Technology, Netherlands; Harm C.M. Knoops, Oxford Instruments Plasma Technology, Netherlands; J de Marneffe, IMEC, Belgium

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