Plasma and Vapor Deposition Processes
Room Town & Country C - Session PP5-TuM

Microfabrication Techniques with Lasers and Plasmas

Moderators: Carles Corbella, National Institute of Standards and Technology (NIST)/ University of Maryland, College Park, USA, **Stephanos Konstantinidis**, University of Mons, Belgium

8:00am **PP5-TuM-1 Synthesis of 2D Transition Metal Dichalcogenides Using Advanced ALD Cycle Schemes***, Ageeth Bol [aabol@umich.edu],* University of Michigan, Ann Arbor, USA **INVITED**

2D materials have been the focus of intense research in the last decade due to their unique physical properties. This presentation will highlight our recent progress on the large-area synthesis of two-dimensional transition metal chalcogenides for nanoelectronics using advanced plasma-enhanced atomic layer deposition cycle schemes. First, I will show how we can use advanced cycle schemes to deposit wafer-scale polycrystalline MoS_2 thin films at very low temperatures down to 100 °C. We have identified the critical role of hydrogen during the plasma step in controlling the composition and properties of molybdenum sulfide films. By increasing the H_2/H_2S ratio or adding an extra hydrogen plasma step to our ALD process, we can deposit pure polycrystalline MoS2 films at temperatures as low as 100 °C. To the best of our knowledge, this represents the lowest temperature for crystalline MoS_2 films prepared by any chemical gas-phase method.[1]

The most dominant methods for preparing MoS_2 via ALD is to alternately expose a substrate to a metalorganic precursor and a hydrogen sulfide (H_2S) or a plasma containing H_2S. H_2S is a corrosive, toxic, and flammable gas that is heavier than air, which makes it hazardous and expensive to store, install, and transport. Alternative sulfur precursors in the solid or liquid phase would be beneficial in terms of cost and safety and would require the installation of no additional hardware for most ALD reactors. In the second half of this contribution, the widely researched ALD process using bis(tert-butylimido)bis(dimethylamino)molybdenum(IV) ($(^tBuN)_2(NMe_2)_2Mo$) and H_2S plasma is compared to a novel ALD process using $(^tBuN)_2(NMe_2)_2Mo$, hydrogen plasma, and di-tert-butyl disulfide (TBDS), which is an inexpensive, liquid-phase sulfur precursor.

8:40am **PP5-TuM-3 Nanocalorimetry for Plasma-Assisted Process Metrology in Semiconductor Microfabrication***, J. Trey Diulus,* National Institute of Standards and Technology (NIST), USA*; **Carles Corbella [carles.corbellaroca@nist.gov],*** National Institute of Standards and Technology (NIST)/ University of Maryland, College Park, USA*; Feng Yi, David LaVan, Berc Kalanyan, Mark McLean,* National Institute of Standards and Technology (NIST), USA*; Lakshmi Ravi Narayan,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park, USA*; William A. Osborn, James E. Maslar, Andrei Kolmakov,* National Institute of Standards and Technology (NIST), USA

New methods to monitor plasma processes in microelectronics industry, such as deposition, etching, and surface modification, require fine control of plasma parameters, basic plasma-surface interactions, and structural/chemical resolution. These challenges can be solved by implementing nanocalorimeter devices, which usually consist of a 100 nm-thin self-sustained silicon nitride membrane with lithographically defined metallic structure as a resistive temperature sensor and heater. The lateral sizes of the sensor can range from micrometer to millimeter scales. The small size/thermal mass, functionalization versatility, and low wafer-scale fabrication cost of nanocalorimeters, enable their facile integration into any reactor chamber to meet specific plasma process requirements. Here, we report on pilot tests of NIST-microfabricated nanocalorimeters aimed to detect reactive radicals generated by hydrogen cold plasma at typical conditions for semiconductor manufacturing (75 W RF, 10-30 Pa). The setup consists of a parallel arrangement of one gold-coated active sensor and a second alumina-coated reference sensor. Au layer serves as a catalyst with known hydrogen recombination coefficient. Hence, the difference in heat of recombination reactions is detected comparatively by activated and reference nanocalorimeters. The inert, reference sensor enables discrimination against the incoming UV-vis radiation, and fluxes of ions and electrons, which constitute the major parasitic signals. The setup was successfully tested, and parameters such as sensitivity in radical detection (5×10^{20} $m^{-2}s^{-1}$) and in radical density (10^{18} m^{-3}), and response time (sub-100 ms), are discussed within the framework of standard plasma diagnostic techniques. In conclusion, fast-scanning nanocalorimetry constitutes a promising platform for plasma process monitoring, whose flexibility enables its possible integration into other optical or electrical metrologies.

9:00am **PP5-TuM-4 Pulsed Laser Deposition for Energy Materials***, Thomas Lippert [thomas.lippert@psi.ch],* Paul Scherrer Institute, Switzerland **INVITED**

One of the material systems which we study are oxynitrides that are applied as photoanodes in photo-electrochemical water splitting. Shortcomings of this material class are a fast decay in activity over the first few electrochemical cycles and a decay on the long term. While the long-term decay is possibly related to a degradation of the material, i.e., a loss of nitrogen, the fast decay is not really understood, and therefore also no approach can be envisioned how to overcome this problem. We studied the fast decay of the material (and first approaches how to prevent this) by using thin films as model system. We could detect a surface modification, i.e., a change in density, by NR in the range of 3 nm, while XAS was utilized to analyze changes in oxidation state (order) for the different elements. A change of oxidation state of the A cation was detected, while the B cation (here for $LaTiO_xN_y$), which is normally assumed to be the active site, undergoes local disordering. This surface modification reduces the overall water splitting activity, but we could identify a co-catalyst, which supresses these modifications. We could also identify critical steps in the water splitting mechanisms, where during surface modifications the formation of NO_x competes with the oxygen evolution. Without highly defined, high quality PLD films it would have not been possible to utilize the large facilities, and therefore to identify (mitigate) the origins of activity decay of these oxynitrides for water splitting.

Fundamental understanding material properties and reactions of energy materials can often be very well studied by large facility techniques, e.g., at synchrotrons or neutron sources, as unique information can be obtained in this way. A number of these methods require the application of well-defined samples, controlling crystallinity, roughness to interface quality. These requirements can often be fulfilled by thin films. We apply pulsed laser deposition (PLD) to create these thin films to utilize complementary techniques, ranging from neutron reflectometry (NR) to grazing incidence X-ray absorption spectroscopy (GIXAS).

9:40am **PP5-TuM-6 Synergies Between Laser Technology and Thin Films for Advanced Functionalities***, Sylvain Le Coultre [sylvain.lecoultre@bfh.ch],* BFH-ALPS, Switzerland

In our ALPS Institute, laser technology and thin-film deposition are combined with the objective to unlock novel functionalities in nanofabrication. As a first example, by leveraging precise and partial laser ablation within multilayer systems, we achieve high-resolution decorative effects with nanometric precision. Laser structuring on thin-film materials enables tuning of material properties, as seen on carbon allotropes. Additionally, laser processing can be employed to generate nanoparticles by ablating a target, which can then be embedded in coatings to form nanocomposites with enhanced mechanical, optical, or catalytic properties. This presentation will explore a few specific applications and case studies that highlight the advantages of integrating laser processing with thin-film technologies.

10:00am **PP5-TuM-7 Sputtering onto Liquids : From Nanoparticle Suspensions to Functional Polymer Composites***, Stephanos Konstantinidis [stephanos.konstantinidis@umons.ac.be],* *France - Emmanuelle Bol, Valentine Jauquet, Jeremy Odent, Anastasiya Sergievskaya,* University of Mons, Belgium

Magnetron sputter deposition of metal atoms onto vacuum compatible liquids allows producing colloidal solutions of small metal nanoparticles (NPs) without any additional reducing or stabilizing reagents [1]. This presentation aims at presenting the results during which the process parameters were varied to study how the properties of the as-formed metal NPs are impacted. Parameters such as pressure, sputter power, and sputtering regime, e.g., DC or HiPIMS, were varied as well as the characteristics of the host liquid chemistry and viscosity. To monitor in space and time the behaviour of the NPs inside the liquid, in situ UV-Vis absorption spectrophotometry was implemented [2]. The temperature of the liquid was measured as well.

Our data show that the formation of a cloud of particles underneath the oil surface is usually observed while films form in the case of high viscosity liquids [3]. The effect of sputtering time and power, argon pressure, type of sputtering plasma (dcMS vs HiPIMS) were also studied taking castor oil, a vegetable liquid, as substrate. In this case, few - nm - in - diameter Au-NPs have a higher stability in the oil than Ag-NPs but secondary growth processes take place. Interestingly, HiPIMS promotes the formation of NPs

larger than those obtained in dcMS mode [4]. Most recent experiments highllight the possibility of elaborating hydrogel / nanoparticle composites in a two step process by choosing an appropriate polymerizable host liquid [5]. Preliminary measures confirm that the as-obtained Ag-NPs / hydrogel composite can be used to detect mercury cations in aqueous solutions through color change.

Our data highlight that sputtering onto liquid allows for the synthesis of a few nm in diameter NPs but the plasma and liquid parameters matter. Ultimately, by chooseing carefully the liquid host, it is possible to elaborate polymer / NP functional composites.

[1] A. Sergievskaya, A. Chauvin, S. Konstantinidis. *Beilstein J. Nanotechnol.* 13 (2022) 10–53.

[2] S. Konstantinidis, F.- E. Bol, G. Savorianakis, P. Umek, P., A. Sergievskaya, Instr. Sci. Technol. *52*(2), 125–137. https://doi.org/10.1080/10739149.2023.2223627

[3] A. Sergievskaya, R. Absyl, A. Chauvin, K. Yusenko, J. Veselý, T. Godfroid, S. Konstantinidis, Phys. Chem. Chem. Phys. 25 (2023), 2803–2809.

[4] A. Sergievskaya, A. O'Reilly, H. Alem, J. De Winter, D. Cornil, J. Cornil, S. Konstantinidis, Front. Nanotechnol. 3 (2021) 57.

[5] V. Jauquet, Master Thesis, University of Mons (June 2023).

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