Nanostructure Synthesis and Fabrication
Room 107-109 - Session NS-WeM

Nanostructures III
Moderator: Mike McSwiney, Intel, USA

10:45am **NS-WeM-12 DBD Plasma Assisted Atomic Layer Deposition Alumina Barrier Layer and its Applications**, *H Wei,* Beijing Institute of Graphic Communication, China*; H Guo,* Qilu University of Technology, China*; L Yang, Z Liu,* ***Qiang Chen****,* Beijing Institute of Graphic Communication, China

In this paper, the plasma generated by dielectric barrier discharge (DBD) is utilized to assist atomic layer deposition. We compare the discharge properties in low pressure and atmospheric pressure. By optical emission spectroscope (OES) we find the oxide species in two kinds of plasma are different, the atomic oxygen is the major radicals for oxidization reaction in low pressure condition rather than ozone as the oxidant in atmospheric pressure. With these DBD plasma assisted ALD alumina coatings on polyethylene terephthalate (PET) and polylatic acid (PLA) webs as barrier layers are carried out. The Al O component and the surface morphology in two plasmas are compared. The influence of Al O thickness on barrier, mechanical, optical and degradation properties is investigated. It is obtained that the growth rate of Al O coating are 0.12 and 0.23 nm/cycle respectively in low pressure and atmospheric pressure DBD. For same water vapor transmission rate (WVTR) the alumina thickness is thicker in atmospheric pressure deposition Al_2O_3 than that in low pressure deposition Al_2O_3. Atomic force microscope (AFM) and screening electron microscope (SEM) analysis confirm that alumina deposition in atmospheric assisted ALD is loose, as a result, the moisture permeates the barrier layer at a large magnitude.

11:00am **NS-WeM-13 Sequential Infiltration Synthesis for sub 20 nm Thermal Scanning Probe Lithography Patterns***,* ***Tero Kulmala****, M Spieser,* SwissLitho AG, Switzerland*; B Chan, J de Marneffe,* Imec Vzw, Belgium*; A Knoll,* IBM Research-Zurich, Switzerland

As feature sizes of emerging device concepts in for example nanoelectronics and nanophotonics continuously shrink, a high demand for novel lithography and pattern transfer processes exists. Recently, thermal scanning probe lithography (t-SPL) [1] which relies on the thermal decomposition of thermally sensitive polymer resists, such as polyphthalaldehyde (PPA) has entered the market. Using this technique, single-digit nanometer patterning and pattern transfer [2] as well as superior alignment accuracy [3] and sub-nanometer accurate 3D patterning [4] have been demonstrated. The patterning speed is comparable to high-resolution electron beam lithography [5].

As in all lithographic processes, patterning sub-10 nm features with t-SPL requires use of ultra-thin resist layers which complicates the pattern transfer process. So far, a few nm PVD silicon dioxide layer has been used as a hard mask to enable transferring the PPA patterns into a ~50 nm thick layer of amorphous carbon [6] for further amplification of the shallow t-SPL patterns.

Here, we show how sequential infiltration synthesis (SIS) [7,8] can be used to infiltrate t-SPL patterned PPA with aluminum oxide. We employed a pattern transfer stack consisting of ~10 nm PPA, 6 nm cross-linkable Polystyrene (x-PS) and 13 nm silicon nitride for transferring patterns into silicon. The amount of aluminum oxide infiltration in PPA increases with the number of SIS cycles as verified by energy dispersive spectroscopy carried out in a transmission electron microscope and results in an increase in etching resistance of the material. The resulting patterns were analyzed by atomic force microscopy and cross-section transmission electron microscopy. With an optimized process, patterns with sub-20 nm critical dimension were successfully transferred into Si.

In conclusion, SIS offers an interesting alternative for transferring high resolution patterns written by t-SPL. Furthermore, it eliminates the need for a hard mask layer in the transfer stack, thereby simplifying the process. Moreover, it was shown that such a “soft” transfer stack enhances the resolution of t-SPL patterning to the sub 10 nm range [2].

[1] Ricardo Garcia, Nature Nanotechnology **9**, 577-587 (2014).

[2] Y. K. R. Cho, ACS Nano **11** (2017).

[3] C. Rawlings et al., *ACS Nano***9**, 6188 (2015).

[4] C. Rawlings et al., Scientific Reports **7**, 16502 (2017).

[5] P. Paul et al., *Nanotechnology* **22,** 275306 (2011).

[6] H. Wolf, JVST B (2014).

[7] S. Biswas, US Patent #8,980,418 (2011).

[8] G. N. Parsons, Coordination chemistry reviews **257** (2013).

11:15am **NS-WeM-14 Fabrication of BN Coated Carbon Nanostructures using ALD Based on Polymer Derived Ceramics Route***,* ***Catherine Marichy****,* Univ Lyon, France*; W Hao,* LMI - UMR CNRS/Univ Lyon 5615, France*; C Journet, A Brioude,* LMI - UMR CNRS/Univ Lyon 5615

Development of sustainable energy as well as environment issues are two of the most important current concerns. In particular, applications in corrosive and/or high temperature treatment such as in heterogeneous catalysis need support with excellent thermal stability and chemical inertness. Boron Nitride (BN) seems thus an excellent candidate; however it is an electrical insulator. Carbon nanotubes, despite their excellent electric properties, suffer of instability under reaction condition at high temperature (>300°C) especially, if the targeted reactions are partial oxidations. Deposition of a very thin BN coating appears an elegant approach to prevent the CNT oxidation while preserving its electric properties [1,2] and access to a support allowing for instance heterogeneous catalysis/electrocatalysis even at high temperature (e.g. 400-700°C). Nevertheless, fabrication of such hetero-structures requires a synthetic approach capable of controlling the size and morphology of the desired materials. Atomic Layer Deposition (ALD) has demonstrated to be an effective approach for surface modification and fabrication of carbon based heterostructures.[3] Currently, BN coating of carbon material by ALD has been poorly investigated. Based on polymer derived ceramic chemistry, a novel two-step ALD approach for BN has been recently reported.[4] Due to its low deposition temperature and non-corrosive precursors, it has been successfully use for BN deposition onto various substrates such as inorganic and polymer nanostructures.[5]

Herein coating of various carbon nanostructures is reported using this new ALD process. As inertness of highly graphitic carbon inhibits the initiation of ALD growth, use of amorphous and graphitized carbon substrates allows studying the impacts of the crystalline nature of the substrate on the coating in term of growth and structure. The obtained BN coated carbon materials are characterized by advanced electron microscopy and related techniques. As a function of the degree of graphitization, nucleation delay and impact on the crystalline quality (amorphous, turbostratic, hexagonal phase) of BN films are observed. Finally, potential of such coating to improve the oxidation resistance of carbon material is demonstrated.

1- Liew K.M., Yuan J., *Nanotechnology*, **2011**, 22 (8), 085701.

2- Jing L., Tay R.Y., Li H., Tsang S.H., Huang J., Tan D., Zhang B., Teo E.H.T., Tok A.I.Y, *Nanoscale*, **2016**, 8 (21), 11114.

3- Marichy C., Pinna N., *Coordination Chemistry Reviews*, **2013**, 257, 3232.

4- Hao W., Marichy C., Brioude A., *ChemNanoMat.*, 3, **2017**, 656.

5- Hao W. Marichy C., Journet C., Brioude A., *Enviro. Science Nano.,* 4, **2017**, 2311.

11:30am **NS-WeM-15 Atomic Layer Deposition of Lead(II) Iodide***,* ***Georgi Popov****, M Mattinen, T Hatanpää, M Vehkamäki, M Kemell, M Ritala, M Leskelä,* University of Helsinki, Finland

Over the years of ALD process development, metal halides have attained the role of classic metal precursors. Lead(II) iodide for instance, was studied as a lead precursor for ALD of PbS.[1] An attempt to deposit these typical precursor compounds might seem as a questionable endeavor at best. However, this is not theoretically impossible, provided that technical challenges, such as the relatively high vapor pressure of the target compound, are addressed. Therefore, it is tempting to explore whether the library of materials that can be deposited by ALD, can be expanded to metal iodides. Our interest in lead(II) iodide has also practical motivation. Lead(II) iodide possesses a two-dimensional structure and a band-gap in the visible range. The material is suitable for photodetectors[2] and lead(II) iodide thin films are an established starting point for preparation of hybrid halide perovskite thin films employed in perovskite solar cells[3].

The ALD process we developed for lead(II) iodide relies on lead(II) bis[bis(trimethylsilyl)amide] as the lead precursor and tin(IV) iodide as the iodine precursor. The process works at low temperatures (< 100°C) and is compatible with a variety of starting surfaces ranging from oxides to metal thin films. We observed saturative film growth with respect to both precursors on substrates selected for detailed study, namely silicon and fluorine doped tin dioxide coated glass. We also noticed a linear relation between the film thickness and the number of deposition cycles. The

process yields crystalline films that show different crystalline textures depending on the nature of the starting surface. We also demonstrate that lead(II) iodide films deposited with this process, when treated with methyl ammonium iodide vapors, convert into a methyl ammonium lead triiodide. Methyl ammonium lead triiodide is a hybrid halide perovskite commonly employed as a light absorber in perovskite solar cells.

(1) M. Leskelä et al.: J. Preparation of Lead Sulfide Thin Films by the Atomic Layer Epitaxy Process, Vacuum 1990, 41, 1457–1459.

(2) W. Zheng et al.: High-Crystalline 2D Layered PbI_2 with Ultrasmooth Surface: Liquid-Phase Synthesis and Application of High-Speed Photon Detection, Advanced Electronic Materials 2016, 2, 1–8.

(3) A. B. Djurišić et al.: Perovskite Solar Cells - An Overview of Critical Issues, Progress in Quantum Electronics 2017, 53, 1–37.

11:45am **NS-WeM-16 Crystalline High-k Dielectric Films on Atmospheric Plasma Treated Graphene by Atomic Layer Deposition***, **Jeong Woo Shin**,* Seoul National University of Science and Technology, Republic of Korea*; M Kang,* Kwangwoon University, Republic of Korea*; S Oh, B Yang, K Seong, H Ahn,* Seoul National University of Science and Technology, Republic of Korea*; T Lee,* Kwangwoon University*; J An,* Seoul National University of Science and Technology, Republic of Korea

Graphene has excellent electrical and mechanical properties such as high carrier mobility (~200,000cm^2/Vs), high surface-to-volume ratio, high flexibility and high mechanical property (Young's modulus: ~0.1TPa). Due to these excellent properties, graphene has been extensively studied for flexible electronics and sensors.

However, the basal plane of graphene is known to be chemically inert because of its strong sp^2 carbon bonding. For the fabrication of graphene-based field-effect transistors (GFETs) with high sensitivity and stability, it is important to deposit thin and uniform dielectric films on the graphene surface. Among various dielectric deposition method, atomic layer deposition (ALD) has the advantage of being able to deposit ultra-thin and uniform films. However, the inertness of the graphene basal plane prevents the facile nucleation of ALD dielectric materials on the graphene surface.

In this paper, we demonstrate the deposition of high-quality ALD dielectric films without additional seed layer on the atmospheric oxygen plasma treated graphene while minimizing the structure and electrical degradation. Optical microscope, raman spectroscopy, water contact angle analysis and X-ray photoelectron spectroscopy show that the atmospheric oxygen plasma treated graphene surface become super-hydrophilic. Also, it is confirmed that the uniform and highly crystalline ALD dielectric films deposited at a relatively low temperature (150℃) on the functionalized graphene surface through the atomic force microscopy, field-emission scanning electron microscope and X-ray diffraction analysis. ALD dielectric films on the plasma-treated graphene result in negative shift in the Dirac voltage and the enhanced air stability.

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