Nanostructure Synthesis and Fabrication
Room 104-106 - Session NS+ALE-TuA

Nanostructures II + ALE

Moderators: Robert Clark, TEL Technology Center, America, LLC, Yong Qin, Institute of Coal Chemistry, Chinese Academy of Sciences

4:00pm **NS+ALE-TuA-11 Atomic Layer Etching and Chemical Vapor Etching of 2D Materials and Metal Oxide Films using MoF_6-H_2O**, ***Anil Mane***, *D Choudhury, S Letourneau, J Elam,* Argonne National Laboratory

To meet the milestones outlined in the semiconductor technology roadmap, precisely controlled layer-by-layer etching processes for metal oxides are required to enable the fabrication of 3D-semiconductor microelectronic devices. In addition, 2D-layered transition metal dichalcogenides (TMDs) with tunable electronic properties exhibit attractive material properties and are under intense investigation as alternatives to silicon. Therefore, integration of 2D-materials with compatible dielectric metal oxide growth as well as etching can pave the way to successful device fabrication. Moreover, both selective material growth and selective etching are required for the cost effective manufacturing of advanced microelectronics.

Here we have developed etching processes using alternating exposures to molybdenum hexafluoride (MoF_6) and H_2O vapor for ALD grown metal oxides and 2D-TMDs. The MoF_6-H_2O precursors offer several advantages including low cost, low processing temperature, and rapid and effective etching spanning the range from continuous etching to atomic layer etching (ALEt).

We have used in-situ quartz crystal microbalance (QCM) and Fourier-transform infrared spectroscopy (FTIR) measurements to monitor the deposition and etching of the metal oxides and 2D-TMDs layers. Next, the etched metal oxides and 2D-TMDs thin films were analyzed by spectroscopic ellipsometry to determine the thickness and refractive index, and the composition was determined by X-ray photoelectron spectroscopy (XPS). These ex-situ measurements confirmed the etching behavior findings from our in-situ studies. Here we will discuss the details of the MoF_6-H_2O based etching chemistry.

4:15pm **NS+ALE-TuA-12 Membranes by Atomic Layer Deposition: Design and Applications**, ***Mikhael Bechelany***, Institut Européen des Membranes, France **INVITED**

Atomic layer deposition (ALD) is a thin film technology that in the past two decades rapidly developed from a niche technology to an established method. It proved to be a key technology for the synthesis of ultrathin film, the surface modification and the fabrication of complex nanostructured materials as well as the membrane tuning. [1]

In this work, we will give an overview about our activities on ALD, from the design of nanomaterials to membrane applications. After a short introduction to ALD, the versatility of the technique for the fabrication of novel nanolaminates thin films [2] and functional nanomaterials [3, 4] will be showed. Selected examples, focused on its use for the engineering of nanostructured functional materials and membranes targeting applications in energy (osmotic energy, biofuel cells and gas separation), environmental ((bio)-sensor and water purification) and health (DNA and proteins sensing) fields [5-9] will be discussed.

[1] **Advanced Materials**, 2012, 24, 1017

[2] **J. Phys. Chem. C**, 2016, 120, 5124–5132

[3] **Nano Energy** 1 (2012) 696

[4] **Nanoscale** 7 (2015) 5794

[5] **Journal of Materials Chemistry A**, 2016, **4**, 6487-6494

[6] **Journal of Materials Chemistry A**, 2016,4, 17686-17693

[7] **Biosensors and Bioelectronics**, 2017, 92, 763–769

[8] **Journal of Materials Chemistry A**, 2014, 2 (48), 20650 – 20658

[9] **ACS Appl. Mater. Interfaces**, 2017, 9, 16669–16678

4:45pm **NS+ALE-TuA-14 Field-effect Transistor using Two-dimensional Electron Gas in ALD Al_2O_3/TiO_2 Ultrathin (<10 nm) Film Heterostructure Interface**, ***Tae Jun Seok***, *Y Liu,* Hanyang University, Republic of Korea; *H Jung, S Kim,* Ajou University, Republic of Korea; *D Kim,* Hanyang University, Republic of Korea; *S Kim, J Jang,* Korea Basic Science Institute, Republic of Korea; *D Cho,* Chonbuk National University, Republic of Korea; *S Lee,* Ajou University, Republic of Korea; *T Park,* Hanyang University, Republic of Korea

Recently, two-dimensional electron gas (2DEG) has attracted great attention due to the observation of 2DEG at various heteroepitaxial perovskite oxide interfaces. Typically, epitaxial $LaAlO_3$/single-crystal $SrTiO_3$ (LAO/STO) heterostructure shows high density of electrons (~10^{13}-10^{14} cm^{-2}) confined at the oxide interface, where the density is about ~100 times higher than those of a typical semiconductor interface (~10^{11}-10^{12} cm^{-2}). Despite its high electrical performance, process schemes are not suitable for practical device applications because of their high cost in the production of the oxide single crystal and epitaxial layer. Although the formation of 2DEG using γ-Al_2O_3 and amorphous LAO with Al_2O_3 over-layers on STO substrate was demonstrated recently, single crystalline STO substrates are still required. Therefore, 2DEG at an oxide interface has not been realized *via* a mass-production compatible thin film deposition process, in contrast to 2DEG at the semiconductor interfaces.

In this work, we demonstrate a realization of 2DEG at the interface in an extremely thin film (< ~10 nm) heterostructure comprised of two binary oxide stacks of Al_2O_3/TiO_2 *via* atomic layer deposition (ALD) on a SiO_2/Si substrate without using an oxide single crystal or epitaxial substrate. The Al_2O_3/TiO_2 heterostructure was composed of a few nm-thick amorphous Al_2O_3 over-layer and poly-crystalline anatase-TiO_2 bottom layer. We achieved high electron density (~10^{13}-10^{14} cm^{-2}) and mobility (~4 $cm^2/V{\cdot}s$) in the 2DEG at the interface of ultrathin Al_2O_3/TIO_2 heterostructures, comparable to those obtained from epitaxial oxide heterostructures. More importantly, we demonstrate a new type of field-effect transistors (FETs) using Al_2O_3/TIO_2 heterostructures with a high on-current (I_{on}, > 12 A/m), high on/off current ratio (I_{on}/I_{off} > ~10^8), low off current (I_{off}, ~10^{-8} A/m), and low sub-threshold swing (SS, ~100 mV/dec.), which outperforms the oxide heterostructure-based FETs reported so far. Ultrathin (< ~7 nm) TiO_2 bottom layer in the proposed Al_2O_3/TiO_2 heterostructure prone to be fully depleted, allows an extremely low I_{off}, high I_{on}/I_{off} ratio and low SS with maintaining high I_{on} *via* 2DEG channel with a high carrier density at the interface. The proposed new-type devices would provide a great opportunity for practical applications and mass-production of 2DEG devices, allowing a multi-level three-dimensional (3D) integration scheme. The detailed experimental results including new materials systems will be presented.

5:00pm **NS+ALE-TuA-15 Increased WS_2 Crystal Grain Size by Controlling the Nucleation Behavior during Plasma Enhanced Atomic Layer Deposition**, ***Benjamin Groven***, *A Nalin Mehta,* KU Leuven, Belgium; *H Bender, J Meersschaut, T Nuytten, T Conard, A Franquet, W Vandervorst, M Heyns, M Caymax, I Radu, A Delabie,* IMEC, Belgium

Two-dimensional (2D) transition metal dichalcogenides such as molybdenum and tungsten disulfide (MoS_2, WS_2) emerge as semi-conducting three-atom-thick layers that are widely applicable, for example as the complement of Si in ultra-scaled nanoelectronic devices at the back-end-of-line (BEOL) [1]. To exploit the potential of 2D layers in BEOL structures, they need to be grown using manufacturable deposition techniques in a highly crystalline structure with control over the orientation of the basal plane at low deposition temperatures (< 450°C).

When grown by atomic layer deposition (ALD) for atomistic growth control and compatibility with temperature sensitive structures, the crystallinity and structure of 2D materials is determined by the nucleation mechanisms, which are currently not yet understood. In our earlier work, polycrystalline WS_2 with well-controlled composition (S/W ratio ~2) and 2D structure was grown by PEALD from WF_6, H_2 plasma and H_2S on Al_2O_3 at 300°C [2]. The WS_2 layers suffered from a nanocrystalline grain structure (< 20 nm).

In this work, we show that the WS_2 crystal grain size can be increased from ~20 nm to beyond 200 nm by lowering the nucleation density. The latter is achieved by using a starting surface with a lower reactivity towards the PEALD precursors (i.e., thermally grown SiO_2), and by enhancing the mobility of the adsorbed species at higher deposition temperature (< 450°C) and reactor pressure (Figure 1).

By analyzing the morphology of the WS_2 crystals, we derive a qualitative model for the nucleation behavior of WS_2 during the PEALD process. The SiO_2 starting surface is less reactive to the PEALD precursors compared to

Al_2O_3 starting surfaces, which results in growth inhibition on SiO_2. The PEALD precursors preferentially adsorb on the existing WS_2 nuclei. In combination with enhanced surface diffusion of the adsorbed species across both the SiO_2 starting surface as well as the growing WS_2 nuclei, lateral growth from WS_2 crystal edges is promoted which maximizes the WS_2 crystal grain size and develops a strong (0002) texture.

This work demonstrates how insight in the nucleation behavior of 2D materials can be used to increase the crystal grain size and control the basal plane orientation during ALD. A better understanding of these nucleation mechanisms is crucial to advance the field of ALD of 2D materials.

[1] 47th IEEE European Solid-State Device Research Conference (ESSDERC) **2017**, pp. 212–215. T. Schram, et al.

[2] *Chem. Mater.* **2017**, 29 (7), 2927–2938. B. Groven, et al.

5:15pm **NS+ALE-TuA-16 Controlling Material Properties of Nanostructured WS_2 during Plasma ALD for Improved Electrochemical Performance**, ***Shashank Balasubramanyam***, *L Wu, V Vandalon, M Verheijen, E Kessels, J Hofmann, A Bol,* Eindhoven University of Technology, Netherlands

Transition metal dichalcogenides like WS_2 are promising candidates for sustainable production of H_2 through electrochemical hydrogen evolution reaction (HER), when engineered into nanostructures with exposed reactive edge sites. Controlling the various parameters during the plasma exposure step of plasma-enhanced ALD (PEALD) allows tailoring of material properties which can influence the HER performance. In this work, we demonstrate a novel approach to maximize the density of reactive edge sites in nanostructured WS_2 by tuning the composition of co-reactant gas mixture during the plasma exposure step of PEALD.

H_2S+Ar and H_2 diluted H_2S+Ar were used as co-reactant gas mixtures for tuning the plasma composition during PEALD of WS_2. The addition of the strong reducing agent H_2 to the H_2S+Ar plasma gas mixture can significantly influence the WS_2 growth behaviour and resulting material properties. The H_2S+Ar plasma yielded a GPC of 0.8Å while the H_2S+Ar+H_2 plasma increased GPC to 1.4Å for the same metalorganic precursor bis(tertbutylimido)-bis(dimethylamido)-tungsten, at a low temperature of 300°C. Transmission electron microscopy (TEM) studies revealed the growth of WS_2 'nanoflakes' when using H_2S+Ar plasma, while H_2S+Ar+H_2 plasma resulted in the growth of WS_2 'fins'. The nanoflakes comprised of closely packed basal planes with their edges predominantly terminating on the top surface, while the fins appeared to have higher surface area and were observed to taper out on the top surface. Rutherford backscattering spectroscopy studies indicated an excess S content for nanoflakes (S:W=2.2), while a S deficiency was observed for fins (S:W=1.9). In line with TEM studies, X-ray diffraction measurements showed differences in preferential orientation of crystals for nanoflakes and fins.

The HER performance of WS_2 nanoflakes was significantly better than of WS_2 fins. To reach a current density of 10mA/cm^2, a relatively lower overpotential of ~390mV was sufficient for the nanoflakes while a significantly higher overpotential of ~460mV was required for the fins. In line with HER results, copper underpotential depositions on the respective nanostructures revealed a three-fold increase in the amount of reactive edge sites for nanoflakes when compared with fins. In order t o further enhance the HER performance, catalytically superior WS_2 nanoflakes were grown on top of high surface-area WS_2 fins. This WS_2 stack yielded the best HER performance in our work (overpotential of ~365mV). To summarize, we demonstrate how PEALD can be used as a new approach to nanoengineer and enhance the HER performance of WS_2 by maximizing the density of reactive edge sites at low temperature.

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