Nanostructure Synthesis and Fabrication
Room Auditorium - Session NS-WeA2

2D Materials II

Moderators: Suzanne Mohney, Penn State University, Riikka Puurunen, Aalto University, Finland

4:00pm **NS-WeA2-11 Controlled Encapsulation of Monolayer MoS_2 with Ultrathin Aluminum Oxide for Low Resistance Tunnel Contact Formation**, ***Alex Henning***, *S. Levashov, J. Primbs, M. Bissolo, T. Grünleitner, C. Qian, J. Finley, I. Sharp,* Walter Schottky Institute and Physics Department, Technical University of Munich, Germany

Seamless integration of two-dimensional (2D) semiconductors with bulk materials is essential for preserving and exploiting their outstanding optoelectronic properties within functional devices. In this respect, ALD has proven to be a critical tool for the dielectric integration of 2D materials by tailoring substrates and interfaces.[1] A major challenge that prevents harnessing the full potential of 2D materials is to contact mono- and few-layer systems with metals without introducing defects or otherwise impeding interfacial charge transport. Here, we demonstrate the encapsulation and doping of monolayer MoS_2 with van der Waals (vdW) bonded aluminum oxide (AlO_x) and aluminum oxynitride (AlO_xN_y) by ALD. This is accomplished at low substrate temperature (40 °C) *via* sequential exposure to TMA and ozone or TMA and N_2 plasma, respectively. Unique to the field of 2D materials, we utilize *in situ* spectroscopic ellipsometry to assess the effects of adsorbed reactants and film formation on the dielectric function and excitonic properties of a vdW material during ALD, thus allowing optimization of film growth *and* adlayer modulation doping in real-time.

Current-voltage measurements of monolayer MoS_2 field-effect transistors (FETs) reveal that the nanometer-thin AlO_x coating increases the carrier concentration (from 1×10^{12} cm^{-2} to 2×10^{13} cm^{-2}), while it also protects MoS_2 from defect creation during metallization and processing. Complementary Raman spectroscopy and atomic force microscopy characterization reveal the reversibility of modulation doping induced by the AlO_x adlayer. Encapsulated monolayer MoS_2 FETs exhibit a lower contact resistance and an order of magnitude larger maximum drive current, I_{ON}. By alleviating the effects from the contact interfaces, we were able to reliably determine a field-effect room-temperature mobility of ~10 cm^2/Vs for the applied monolayer MoS_2, synthesized by chemical vapor deposition on a large scale (6Carbon Techn.).

Overall, this work demonstrates the scalable and damage-free encapsulation and doping of 2D materials with weakly bonded and ultrathin AlO_x and AlO_xN_y by ALD near room temperature, as well as the fabrication of tunnel contacts, readily compatible with polymer and lift-off processing. Beyond the demonstrated application as a contact interfacial layer, the nanometer-thin conformal coatings are potentially relevant for surface functionalization in chemical sensors and modulation doping of 2D and organic materials implemented in optoelectronic devices.

[1] Grünleitner, T.; Henning*, A.; Bissolo, M.; Kleibert, A.; Vaz, C.A.F.; Stier, A.; Finley, J.J..; Sharp*, I.D.: *Adv. Funct. Mater.* 2022, 2111341.

4:15pm **NS-WeA2-12 Synthesis of Crystalline Tungsten Disulfide Using Atomic Layer Deposition and Post-Deposition Sulfur Annealing**, ***Kamesh Mullapudi***, *R. Addou,* Oregon State University*; C. Dezelah, D. Moser, J. Woodruff, R. Kanjolia,* EMD Performance Materials*; J. Conley Jr.,* Oregon State University

2D transition metal dichalcogenides have attracted interest in recent years for their unique optical and electrical properties. Tungsten disulfide (WS_2)in particular, has gained attention for its applications as channel material for next generation FETs[1] and catalysis.[2] Popular methods such as mechanical exfoliation and chemical vapor deposition have been demonstrated to synthesize crystalline films with grain sizes of up to a few microns and show good electrical properties, but lack scalability and precise layer thickness control, respectively.[3] Atomic layer deposition (ALD) is an ideal technique for achieving highly conformal and uniform films with the layer by layer thickness control needed for these applications, but faces challenges in achieving high crystallinity. Recent work on ALD WS_2 has achieved films with superior electrical properties by improving film crystallinity, either by inducing substrate inhibited growth[4]or by post-deposition annealing.[5] However, growing crystallites of the order of a few microns remains a challenge and new processes are needed.

In this work, we report ALD of WS_2 using bis(t-butylimido)bis(trimethylsilylmethyl)tungsten (WSN-4) and H_2S. 200 cycles of a 1/5/10/0.1/5/10 s WSN-4/soak/N_2/H_2S/soak/N_2 pulse sequence shows film growth at temperatures above 290 °C. Grazing incidence x-ray diffractograms of as-deposited films show a strong peak at 13.9° near the dominant 14.32° (002) peak of 2H polytype of WS_2. While no characteristic Raman signal is seen for as-deposited films, x-ray photoelectron spectroscopy reveals the presence of sulfur-deficient WS_2 at 290 °C with improved film quality at a deposition temperature of 350 °C. Post-deposition elevated temperature anneals in elemental sulfur produce a significant improvement in crystallinity at temperatures as low as 600 °C, with SEM images revealing multi-layered WS_2 pyramids with sizes of up to ~ 1 µm. The presence of WS_2 in sulfur-annealed films is further confirmed by the signature Raman 2LA(M), E^1_{2g} and A_{1g} peaks.

Further details on the ALD process, sulfur annealing, and electrical properties will be presented at the meeting.

1. D. Lin *et al.,* in *2020 IEEE International Electron Devices Meeting (IEDM)* (2020), p. 3.6.1
2. D. Voiry, *et al.,* Nat Mater **12**, 850 (2013).
3. M. Mattinen *et al.,* Adv. Mater. Interfaces **8**, 2001677 (2021).
4. B. Groven, *et al.,* Chem. Mater. **30**, 7648 (2018).
5. H. Yang *et al.,* Research **2021**, (2021).

4:30pm **NS-WeA2-13 In-Situ-Prepared Protective Seed Layer by Plasma ALD on Graphene**, *S. Riazimehr,* Oxford Instruments Plasma Technology, Germany*; A. Esteki,* RWTH Aachen University, Germany*; M. Powell,* Oxford Instruments Plasma Technology, UK*; M. Otto, G. Rinke, Z. Wang,* AMO GmbH, Germany*; A. Omahony,* Oxford Instruments Plasma Technology, UK*; M. Lemme,* RWTH Aachen University, Germany and AMO GmbH, Germany*; R. Sundaram,* Oxford Instruments Plasma Technology, UK*;* ***Harm Knoops***, Oxford Instruments Plasma Technology, Netherlands

In this work, we describe a novel method to deposit high-κ dielectrics on graphene through an in-situ-prepared protective aluminum nitride (AlN) seed-layer. The process is performed in an Oxford Instruments Atomfab™ plasma ALD system.[1] Short and low power remote plasma conditions were used to directly grow a thin layer of AlN on graphene, followed by deposition of high-quality aluminum oxide (Al_2O_3) by remote plasma ALD.

For the development of graphene-based devices, such as transistors, photodetectors, or optical modulators, a deposition of a high-quality dielectric film on graphene is required. However, this deposition is challenging because nucleation on pristine graphene is difficult. While defect-induced nucleation, for example through plasma exposure, improves nucleation, it also decreases the quality of the graphene layer. Recently we reported dielectric deposition using remote plasma ALD, without observable damage, by protecting the graphene by hexagonal boron nitride (hBN).[2] However, using hBN involves additional transfer processes, which may complicate the fabrication and introduce contamination, defects, and wrinkles.

Inspired by this process, we developed a new process using an in-situ deposited AlN seed-layer to protect the graphene effectively, which enables plasma-assisted deposition of Al_2O_3 without damaging the graphene. Raman measurements demonstrate that the wafer encapsulated by PEALD without AlN shows damage to the graphene, while the wafer protected by the AlN seed layer shows negligible damage. This result confirms that a thin layer of AlN provides sufficient protection for the graphene against the O_2 plasma in the subsequent Al_2O_3 deposition step. The N_2 based plasma conditions for the AlN layer were such to allow AlN growth but not lead to observable damage to the graphene. In this contribution, we will furthermore discuss electrical and device properties for this scalable wafer-level production method.

Acknowledgment: This project has received funding from the European Union's Horizon 2020 research and innovation program 2D-EPL (952792) and German BMBF project GIMMIK (03XP0210).

References:

1. Knoops et al., JVST A 39 (6), 2021
2. Canto et al., Adv. Mater. Technol. 6 (11), 2021

4:45pm **NS-WeA2-14 Polycrystalline MoS_2 Thin Films at 100 °C by Plasma-Enhanced Atomic Layer Deposition***, **Miika Mattinen**, M. Verheijen,* Eindhoven University of Technology, The Netherlands*; F. Gity, E. Coleman, R. Duffy,* Tyndall National Institute, University College Cork, Ireland*; E. Kessels,* Eindhoven University of Technology, The Netherlands*; A. Bol,* University of Michigan, Ann Arbor and Eindhoven University of Technology

Transition metal dichalcogenides (TMDCs), such as MoS_2, are 2-dimensional materials that exhibit vast potential in a variety of applications due to their unique and favorable electronic, optical, and mechanical properties. However, synthesis of uniform, high-quality TMDC films under application-relevant conditions remains a challenge. The most commonly used CVD processes operate at high temperatures that are incompatible with many substrates and applications. For example, typical plastic substrates used for flexible electronics can only withstand temperatures up to about 150 °C.[1] As a result, using ALD to prepare TMDC films is being pursued actively.[2,3]In this contribution, we show deposition of polycrystalline MoS_2 (c-MoS_2) thin films at temperatures down to 100 °C using plasma-enhanced ALD (PEALD). To date, this is the lowest temperature process reported for c-MoS_2 films using any chemical gas-phase method. Building on an existing PEALD process using $Mo(N^tBu)_2(NMe_2)_2$ and mixed $H_2S/H_2/Ar$ plasma as precursors,[4] we have identified H_2 content in the plasma feed gas as a crucial parameter in controlling the composition and properties of MoS_x films. Based on thorough film characterization, we find that adding H_2 in the plasma helps avoid excess S incorporation at low temperatures. The correct stoichiometry, in turn, enables crystallization of MoS_2. By increasing the plasma feed gas H_2 content to 80%, we are able to deposit polycrystalline MoS_2 films at temperatures as low as 100 °C, compared to a minimum temperature of 300 °C without any H_2.We have further demonstrated the generality of the approach by depositing TiS_2 and WS_2 films at lower temperatures than those achieved previously without added H_2.Besides crystallinity, the feed gas H_2 content is found to control growth rate, film morphology, and electrical properties. For example, electrical conductivity can be varied by at least four orders of magnitude. Thus, the PEALD process enables tailoring MoS_x films to meet the requirements of different applications, such as flexible electronics (low-temperature c-MoS_2) and electrocatalysis (a-MoS_x).

1 Yao and Gang, *J. Appl. Phys.* **2020**, 127, 030902
2 Mattinen et al., *Adv. Mater. Interfaces* **2021**, 8, 2001677
3 Kim et al., *Adv. Mater.*, **2021**, 20059074 Sharma et al., *Nanoscale*, **2018**, 10, 8615

5:00pm **NS-WeA2-15 Selectively Decorated Pt Nanoparticle on WS_2 by Atomic Layer Deposition for High-Performance Gas Sensor***, **Dain Shin**,* School of Electrical and Electronic Engineering, Yonsei University, Korea (Republic of)*; T. Nakazawa,* TANAKA Kikinzoku Kogyo K.K., Isehara Technical Center, Japan*; I. Sohn, S. Chung, H. Kim,* School of Electrical and Electronic Engineering, Yonsei University, Korea (Republic of)

Two-dimensional transition metal dichalcogenides (2D TMDCs) have attracted much attention in many research fields owing to their remarkable electrical, chemical, and optical properties. In addition, 2D TMDC-based gas sensor indicates significant gas detection characteristics at room temperature, opposed to the oxide-based sensor which requires external heating for gas detection.[1] Therefore, various 2D TMDC gas sensor studies have been conducted, and as the use of gas sensor expands, performance improvement becomes the challenge of TMDC gas sensors.

Sensing characteristics of 2D TMDC can be enhanced via functionalizing with a noble metal such as Pt, Au, Pd. Among them, Pt is known as a highly effective oxidation catalyst, and Pt nanoparticles (Pt NPs) can make sensing surface more sensitive to gas molecules owing to electronic sensitization and spillover effects.[2] In contrast, as the Pt NPs are difficult to form, atomic layer deposition (ALD) is used to precisely control atomic-scale deposits.

In this study, ALD Pt decorated tungsten disulfide (WS_2) was used as a sensing channel to maximize the response of the gas sensor. Pt NPs preferentially grew at higher surface energy point such as dangling bonds and grain boundaries of WS_2. Then, sensing characteristics of selectively decorated on WS_2 gas sensor was evaluated by various gases. It showed that the NO_2 response extremely increased with the number of ALD cycles. However, when the Pt film was formed at the increased number of cycles, the response decreased due to the loss of the semiconducting property of WS_2. Thus, we could investigate the proper number of cycles for maximizing the sensing response. In addition, it showed that the selectivity of the gas sensor could also be improved by the ALD Pt process.

References

[1] K.Y. Ko, J.G. Song, Y. Kim, T. Choi, S. Shin, C.W. Lee, K. Lee, J. Koo, H. Lee, J. Kim, T. Lee, J. Park, and H. Kim, ACS Nano 10, 9287 (2016).

[2] C. Wang, L. Yin, L. Zhang, D. Xiang, and R. Gao, Sensors 10, 2088 (2010).

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