Nanostructure Synthesis and Fabrication
Room 113-115 - Session NS-MoA

2D Materials

Moderators: Yo-Sep Min, Konkuk University, John Conley, Jr., Oregon State University

1:30pm **NS-MoA-1 Low-temperature Growth of 2-D SnS Thin Films by Atomic Layer Deposition**, ***In-Hwan Baek***, *J Pyeon,* Korea Institute of Science and Technology, Republic of Korea*; T Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; J Han,* Seoul National University of Science and Technology, Republic of Korea*; C Hwang,* Seoul National University, Republic of Korea*; S Kim,* Korea Institute of Science and Technology, Republic of Korea

Many efforts have been dedicated to 2-D metal chalcogenides because of their characteristic properties which can hardly be expected from bulk materials. A challenging task for implementation of 2-D metal chalcogenides in emerging devices is to synthesize the well-crystallized layer on large area substrates at low temperatures which are compatible with the current fabrication processes for electronic devices are. SnS, a p-type layered semiconductor with high hole mobility, is a promising candidate for the realization of the large-area growth at low temperature because of its low melting point (882^oC). Several techniques such as spray pyrolysis, chemical vapor transport, sulfurization and e-beam evaporation have been introduced to synthesize 2-D SnS thin films. However, There are difficulties in synthesizing phase-pure SnS thin films because tin sulfides exist in various phases such as SnS, Sn_3S_4, Sn_2S_3, and SnS_2.

Here, we demonstrate a successful synthesis of single phase and impurity-free p-type SnS thin films using an ALD technique at low temperatures (< 240^oC). The use of a Sn precursor with an oxidation state of +2, bis(1-dimethylamino-2-methyl-2propoxy)tin(II), enabled the synthesis of single phase SnS(II) thin films at temperatures ranging from 90ºC to 240ºC, which is an exceptionally wide window for an ALD process. The SnS grain size increased with increasing the growth temperature. It was also found out that the SnS van der Waals interlayers were well aligned in parallel to the substrate at 240ºC. Impurities such as carbon, oxygen, and nitrogen were negligibly detected in the SnS(II) films and other phases such as Sn_2S_3 and SnS_2 are not incorporated. Furthermore, we investigated the feasibility of the SnS(II) thin films as a functional material in emerging devices such as thin film transistors and gas sensors.

1:45pm **NS-MoA-2 Atomic Layer Deposition of 2D Semiconductor SnS_2**, ***Miika Mattinen***, *P King, L Khriachtchev, K Meinander,* University of Helsinki, Finland*; J Gibbon, V Dhanak,* University of Liverpool, UK*; J Räisänen, M Ritala, M Leskelä,* University of Helsinki, Finland

Two-dimensional (2D) materials have attracted broad interest due to their unique properties and wide range of applications stemming from their layered crystal structures. In particular, semiconducting 2D materials, such as MoS_2, have been extensively studied for applications including field-effect transistors (FETs), photodetectors, catalysis, energy storage, and sensing. Tin disulfide (SnS_2) has recently emerged as a promising alternative for MoS_2 as a 2D semiconductor. It has an indirect band gap ranging from 2.2 eV in bulk[1] to approximately 2.6 eV in monolayer[2] and it has shown performance comparable to MoS_2 in FET and photodetector applications.[3] Furthermore, SnS_2 appears to have potential for low-temperature processing compared to the dichalcogenides of refractory metals, such as MoS_2.

We have developed a new process for atomic layer deposition of 2D SnS_2 films using tin(IV) acetate and H_2S at 150 °C combined with mild post-deposition annealing at 250 °C in H_2S/N_2 atmosphere. Deposition of continuous, uniform, and conformal ultrathin (2 to 11 monolayers) SnS_2 films is demonstrated for the first time (Supplementary Figure 1). The annealed films exhibit good crystallinity with the expected, layered SnS_2 structure and are very smooth, stoichiometric, and show n-type semiconducting behavior (Supplementary Figure 2). Using the present method, SnS_2 films can be deposited on a range of different substrates.

[1]Burton et al., *J. Mater. Chem. A*, **2016**, *4*, 1312–1318

[2]Ye et al., *Nano Res.,* **2017**, *10*, 2386-2394

[3]Huang et al., *ACS Nano,* **2014**, *8*, 10743–10755

2:00pm **NS-MoA-3 Wafer-scale Growth of Single Phase SnS_2 Thin Films by Atomic Layer Deposition**, ***Jung Joon Pyeon***, *I Baek,* Korea Institute of Science and Technology, Republic of Korea*; T Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; J Han,* Seoul National University of Science and Technology, Republic of Korea*; C Kang, S Kim,* Korea Institute of Science and Technology, Republic of Korea

Two-dimensional (2-D) metal chalcogenides have received great attention because of their unique characteristics which are not expected from bulk materials. In order to implement the 2-D materials in nanoelecronic devices, it is imperative to develop a facile route for large-area synthesis with precise thickness controllability and excellent uniformity in a temperature range compatible to common fabrication processes for electronics. SnS_2 is great a great candidate material for meeting the above conditions. Because the melting point(T_m) of SnS_2 is 860^oC, lower than that of other 2-D mateirals such as MoS_{-2} and WS_2 (>1000 ^oC). The low meliting point of SnS_2 renders the high crystallized growth below 400^oC that satisfies the device process temperature. In addition, this material has a few hundreds of $cm^2V^{-1}s^{-1}$ and shows a indirect band gap ~ 2.4 eV, lager than that MoS_2 and WS_2. This larger band gap of SnS_2 allows that higher on/off current ratio and lower leakage currents of off state. Also SnS_2 materials is environmental friendly, abundant materials and nontoxic. However, tin sulfides exist various crystal phases such as SnS_2, SnS, and Sn_2S_3. The important point is that the electronic properties of tin sulfides are strongly dependent on the crystal phase. Therfore, it has been challenging to synthesize the pure SnS_2 single phase without the other crystal phase.

Here we demostrated a useful technique to form single phase SnS_2 thin films by Plasma Enhanced Atomic Layer Deposition (PEALD). The SnS_2 thin films were grown by PEALD using unstable 2^+ $Sn(dmamp)_2$ source and H_2S plasma. All the processes were performed below such a low temperature of 300^oC, which is compatible to current fabrication processes for electronic devices. Despite of low temperature, our SnS_2 has van der waals interlayer structure and these films have single phase of n-type SnS_2 without no oher phase. In addition, this method achieved great uniformity over large area (4-inch Si wafer) and excellent step coverage on the 3D structure. Moreover, field effct transtor devices using single phase SnS_2 channel layers were investigated. We expect that this SnS_2 process would provide decisive opportunities for realizing next genenration nano electronic devices.

2:15pm **NS-MoA-4 ALD Tin Sulfide Thin Films and Their Device Applications**, ***Hyeongsu Choi***, *S Shin, J Lee, H Park, N Lee, C Jung, H Cho, H Jeon,* Hanyang University, Republic of Korea

Tin disulfide (SnS_2) and tin monosulfide (SnS), two representative tin sulfide materials, are emerging as two-dimensional (2D) materials after appearances of graphene and black phosphorus. SnS_2, an n-type semiconductor, has hexagonal structure that individual layers consisting of three atomic planes, such as CdI_2. It has been studied, due to the same crystal structure and similar semiconductor characteristics with transition metal dichalcogenides(TMDCs) . In the case of SnS, it has been attracting attention as an absorber layer of solar cell due to its appropriate band gap and absorption coefficient. Recently, SnS is also studied as a 2D material due to orthorhombic double layer structure like black phosphorus. However, very few studies have been done to obtain tin sulfide thin films with current thin film fabrication methods such as chemical vapor deposition (CVD) and atomic layer deposition (ALD).

In this study, we will present about results of high crystalline tin sulfide thin films deposited by ALD method. High crystalline SnS_2 thin films were obtained by phase transition from the high crystalline SnS thin films. SnS thin films were deposited on Si/SiO_2 substrate with tetrakis(dimethylamino)tin ($Sn[N(CH_3)_2]_4$, TDMASn) and hydrogen sulfide (H_2S) at 170°C, and subsequent H_2S annealing was performed in the tube furnace at 450°C. We then characterized the crystal structures, chemical bonding states, and optical band structures with XRD, XPS, TEM and UPS. In addition, we fabricated the field effect transistors (FETs) with SnS and SnS_2 thin films, and compared their switching device characteristics. Consequently, changes in the crystal structure and chemical state from SnS to SnS_2 were examined by XRD and XPS, respectively. After transition from SnS to SnS_2, the optical bandgap was measured and increased from 1.35 to 2.70 eV, but absorption coefficient decreased from ~10^5 to ~10^4 cm^{-1} at visible region. Transition of electrical characteristic from p-type to n-type were also observed, and highly crystalline orthorhombic and hexagonal layer structures of two tin sulfide thin films were directly shown in the images of high resolution-transmission electron microscopy (HR-TEM). The electrical characteristics of FETs of SnS and SnS_2 thin films showed on-off

current ratios of 8.8 and 2.1 X 10^3 and mobilities of 0.21 and 0.014 cm^2/Vs, respectively. These deference of switching device characteristics will be discussed based on the major carrier concentrations of the SnS and SnS_2 thin films.

2:30pm **NS-MoA-5 Synthesis of 2D MoS_2 and MoS_2-Graphene Heterojunction by Atomic Layer Deposition***, **Youngjun Kim**, D Choi, W Woo, J Lee,* Yonsei University, Republic of Korea*; G Ryu, Z Lee,* Ulsan National Institue of Science and Technology, Republic of Korea*; J Ahn, J Park, H Kim,* Yonsei University, Republic of Korea

The effective synthesis two-dimensional molybdenum disulfides (2D MoS_2) with atomically controlled thickness is essential for their use in electronic devices. In this work, 2D MoS_2 was grown directly on SiO_2 and Graphene using Atomic Layer Deposition (ALD) with MoF_6 and H_2S. We investigated the growth characteristics of the Molybdenum precursor (MoF_6) by Raman spectroscopy and microscopy. By using MoF_6 precursor, 2D MoS_2 synthesized also on the graphene forming MoS_2/graphene heterostructure. The optical microscopy, Raman spectroscopy, photoluminescence (PL), X-ray photoemission spectroscopy (XPS), and transmission electron microscopy (TEM) measurements indicate that the ALD MoS_2 is layered structure with good uniformity, stoichiometry and controlled layer number. Furthermore, we demonstrated the electrical properties of 2D MoS_2 and optical characteristics of MoS_2/Graphene 2D heterostructure. This fabrication process could also provide an opportunity for the production of burgeoning MoS_{-2} and other Transition Metal Dichalcogenides (TMD) for nanoelectronics and optoelectronics.

2:45pm **NS-MoA-6 Atomic Layer Deposition of MoS_2/WS_2 Nanolaminates from bis(tert-butylimido)-bis(dialkylamido) Compounds and 1-Propanethiol***, **Berc Kalanyan**, J Maslar, B Sperling,* National Institute of Standards and Technology*; R Kanjolia,* EMD Performance Materials

Layered two dimensional (2D) transition-metal dichalcogenides (TMDs) are finding use in nanoelectronic and optoelectronic applications due to their thickness dependent optical and electrical properties. Scalable fabrication of TMD-based devices requires deposition routes that can produce continuous and uniform films with sub-nanometer thickness control. Atomic layer deposition (ALD) is a highly promising route for the synthesis of 2D TMDs and heterostructures due to digital thickness control achieved by sequential self-limiting chemistry. Another advantage of ALD is that thickness control and the structural development of the films can be decoupled by separating the deposition and crystallization steps. We take advantage of these process attributes to prepare ALD MoS_2/WS_2 nanolaminates that would be otherwise difficult to grow by conventional chemical vapor deposition approaches. We have recently characterized the self-limiting deposition of MoS_2-containing amorphous films from bis(tert-butylimido)-bis(dialkylamido)Mo and 1-propanethiol. Using the homologous W precursor, we now report on the development of MoS_2/WS_2 nanolaminates, which offer a convenient means to tune the optical and electronic properties of few-layer TMD systems.

We deposited thin films using $(N^tBu)_2(NMe_2)_2M$ and 1-propanethiol, where M=(Mo,W), at wafer temperatures of 300°C to 400°C on SiO_2/Si substrates. As-deposited and sulfur annealed films were evaluated using spectroscopic ellipsometry, grazing incidence X-ray diffraction (GIXRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and cross-sectional transmission electron microscopy (TEM). As-grown films were an amorphous matrix of metal sulfides mixed with unreacted ligands, evident as carbon and nitrogen impurities as measured by XPS. As-deposited films were annealed to produce 2H-MoS_2 and 2H-WS_2 under a sulfur atmosphere, which also removed residual ligands. Nanolaminates were prepared by alternating the injections of the two metal precursors at a fixed Mo:W ratio to achieve different film compositions. The overall Mo:W ratio in the film was found to follow the pulsing ratio of the two metal precursors. Upon annealing at 850°C, we obtained films that exhibit Raman modes associated with 2H-MoS_2 and 2H-WS_2, suggesting that distinct phases, rather than a solid solution, were favored. Relative changes in the overall Mo:W composition were also maintained in the annealed films, indicating that final material properties in TMDs could be controlled by implementing ALD nanolaminates. We will also discuss the implications of film incubation during laminate cycling and subsequent effects on film chemistry.

3:00pm **NS-MoA-7 Wafer-scale MoS_2 Monolayer Grown on SiO_2/Si Substrate by Modified Atomic Layer Deposition***, **Dae Hyun Kim**, D Kim, T Seok, H Jin, T Park,* Hanyang University, Republic of Korea

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) have gained great attention due to its potential applications in electronic and optical devices. Among the 2D-TMDCs family, MoS_2 monolayer has been extensively studied due to high carrier mobility over 200 $cm^2v^{-1}s^{-1}$and flexibility. The electronic band structure is transformed from indirect (~1.2 eV) to direct (~1.9 eV) with decreasing the thickness of MoS_2 from bulk to mono layer (0.6 nm), that is suitable for electronic and optical applications. However, most of studies on 2D MoS_2 have utilized small flakes prepared by mechanical exfoliation and chemical vapor deposition with a transfer technique onto SiO_2 substrate due to the difficulty of direct growth of uniform MoS_2 monolayer on SiO_2 substrate.

In this study, an uniform MoS_2 monolayer was grown directly on 4-in. SiO_2/Si substrate by modified atomic layer deposition technique with extremely-precise thickness controllability and uniformity, which were confirmed by various tools such as Raman shift, photoluminance (PL) mapping and atomic force microscopy. The detailed experimental results will be presented.

3:15pm **NS-MoA-8 X-ray Absorption Spectroscopy of Amorphous and Layered ALD Molybdenum Sulfide Films Prepared using MoF_6 and H_2S***, **Steven Letourneau**,* Boise State University*; M Young,* Argonne National Laboratory*; N Bedford,* National Institute of Standards and Technology*; Y Ren, A Yanguas-Gil, A Mane, J Elam,* Argonne National Laboratory*; E Graugnard,* Boise State University

Atomic layer deposition of molybdenum disulfide has recently been demonstrated using various chemistries. Many of these ALD processes, when performed at low temperatures, yield amorphous films and require annealing to obtain layered MoS_2. Raman spectroscopy is one of the most widely used characterization techniques for 2D materials, but these amorphous structures typically do not show the in-plane and out-of-plane vibrational modes of a layered structure. Characterizing these amorphous films is difficult, but crucial if ALD is to succeed in making monolayer or few layer MoS_2. In this work, we use X-ray absorption spectroscopy (XAS) and pair distribution function (PDF) measurements to investigate the as-deposited structure of ALD MoS_2 films prepared using MoF_6 and H_2S at 200°C. Model fits of the extended X-ray absorption fine structure (EXAFS) regime were used to infer the local coordination around the Mo atom centers. While the Mo-S coordination in ALD MoS_2 films seems to fit well with MoS_2 reference structures, the Mo-Mo coordination number was much lower than expected. In addition, PDF measurements performed to examine the bonding pairs suggested small clusters of trigonally prismatic MoS_2 with polysulfides forming between the sulfur atoms. Annealing these films at 400°C in H_2S yielded layered MoS_2, which was confirmed by transmission electron microscopy and X-ray photoelectron spectroscopy, suggesting that thin, layered MoS_2 films are possible using MoF_6 and H_2S.

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