Emerging Materials
Room Hall 3E - Session EM-WeA

Other Emerging Materials

Moderators: Jiyoung Kim, University of Texas at Dallas, **Mato Knez**, CIC nanoGUNE

1:30pm **EM-WeA-1 Atomic-Scale Homogeneous PtRu Alloy Thin Films Prepared by Atomic Layer Modulation (ALM)***, **Yeseul Son**, S. Kim,* Ulsan National Institute of Science and Technology, Republic of Korea*; T. Cheon,* Daegu Gyeongbuk Institute of Science and Technology, Republic of Korea*; S. Kim,* Ulsan National Institute of Science and Technology, Republic of Korea

To create multi-component thin films with ALD, the super-cycle method is commonly used. By adjusting the cycle for each ALD process of each material to be mixed at an appropriate ratio, it is possible to produce a thin film with an arbitrary element ratio. However, the distribution of elements in the depth (thickness) direction is non-uniform or forming nano-laminate structure, and to obtain the composition of the desired ratio, it is necessary to produce a thin film of at least several nm. In this study, to address this problem, a newly proposed atomic layer modulation technology (ALM) [1] was used. ALM technology enables the production of uniform multi-component thin films at the atomic layer level by sequentially exposing multiple precursors within one cycle [Fig. 1]. So, atomic-scale homogeneous alloy films of Pt, which is highly active in hydrogenation reactions and has a bulk resistivity of 10.6 μΩ cm and work function of 4.71 eV, and Ru, which is highly active in oxygenation reactions and has a bulk resistivity of 7.1 μΩ cm and work function of 5.65 eV, was successfully prepared [Fig. 2]. Here, metal-organic precursors, tricarbonyl(trimethylenemethane)ruthenium [Ru(TMM)$(CO)_3$] and dimethyl-(N,N-dimethyl-3-butene-1-amine-N)platinum (C_8H_{19}NPt) were used and a self-limiting growth for each Ru and Pt ALD, was confirmed. By controlling the condition of ALM process, we can prepare ALM PtRu alloy thin films with different compositions and their properties with the composition were systematically analyzed by SIMS, TEM, XPS, XRD, XRR etc. The performance of ALM PtRu alloy film as a wiring material to replace Cu as well as a catalyst for HER (hydrogen evolution reaction) and OER (oxygen evolution reaction) will be presented in the conference.

*Corresponding Author: soohyunsq@unist.ac.kr

[1] Nguyen, C. T., et al., "Atomic Layer Modulation of Multicomponent Thin Films through Combination of Experimental and Theoretical Approaches", Chem. Mater. 2021, 33, 4435−4444.

1:45pm **EM-WeA-2 A New Approach to the Synthesis of Nb@TiO_2 Core-Shell Composite for Oxide Dispersion Strengthened Alloy via Atomic Layer Deposition***, **Ji Young Park**, E. Lee, M. Jeong, J. Byun, B. Hwang, S. Oh, B. Choi,* Seoul National University of Science and Technology, Republic of Korea

More than half of CO_2 emissions in the world come from fossil fuels; therefore, in order to significantly reduce them, it is necessary to develop efficient internal combustion engines. In an attempt to enhance their mechanical properties in extreme conditions, it is required to have high thermal stability and strength as well as high durability and corrosive resistance. Nowadays, many types of research (alloying, surface and heat treatments, etc.) have been conducted to develop eligible refractory materials.

Nano-oxide dispersion strengthened (ODS) refractory alloy has been attracting attention because of its outstanding mechanical reinforcement mechanism. Dispersed oxides enhance the strength by preventing grain growth and recrystallization as well as increasing creep resistance, which allows ODS to be widely applied in extreme fields such as military industries and aerospace. ODS alloys are commonly fabricated by mechanical alloying methods. However, it can draw impurities and cracks in raw powders, which influence on porosity of pellets. In this research, atomic layer deposition (ALD) is applied to synthesize ODS alloy. ALD is one of the most promising technologies in thin film deposition. It is useful to coat conformal thin films even on complex shapes of matrix such as nanorods or powders without mechanical damage. We coat pure Nb powder with TiO_2 thin film by using rotary-reactor type thermal ALD. TiO_2 chosen as the coating layer is non-toxic and chemically stable in high temperatures. In addition, it has superior mechanical strength as well as anti-wear and corrosion properties, thus widely adopted to ODS. TiO_2 is grown by using Titanium tetraisopropoxide (TTIP) precursor and H_2O reactant gas at 200°C. Transmission electron microscopy analysis reveals that TiO_2 is deposited uniformly on the Nb powder and the thin film in pellets is dispersed to be crystallized. Spark plasma sintering method is applied for sintering powders to minimize residual stress and grain coarsening. Thin film analysis including X-ray photoelectron spectroscopy and X-ray diffraction is conducted to understand the physical and chemical properties of the coating layer and its matrix. Grains with grain boundaries in pellets are analyzed via electron backscatter diffraction method. Mechanical properties are investigated by Vickers hardness test and nanoindentation measurement to confirm the TiO_2 dispersion strengthening effect on Nb refractory matrix. This study proposes a new field of ALD. This technology can be further applied to the surface and interface engineering of powder materials for electronic and energy applications.

2:00pm **EM-WeA-3 Influence of an Artificial Structure on the Mechanical Properties of Atomic Layer Deposited Al_2O_3 and Ta_2O_5 Composite Thin Films***, **Helle-Mai Piirsoo**, T. Jõgiaas, K. Kukli,* University of Tartu, Estonia

The functionality of nanodevices depends on the mechanical reliability of their components like thin films. It has been shown that atomic layer deposited oxides in a periodic layered architecture possess lower residual tensile stresses [1], higher hardness [2], better wear properties [3] compared to their single constituents. ALD-grown nanocomposite thin films can improve the mechanical resistance of nanodevices.

In this work, amorphous Al_2O_3 and Ta_2O_5 thin films, their nanolaminates and mixtures were atomic layer deposited to thicknesses of ~70 nm. The single constituent layer thickness in multilayers, consisting of equal amounts of Al_2O_3 and Ta_2O_5, was varied from 18 to 1 nm. Trilayers with varying oxide volume fractions were deposited. The films were annealed at 800 °C for 10 min in air.

The amorphous reference Al_2O_3 film was harder compared to reference Ta_2O_5 by ~3 GPa and possessed ~15 GPa higher Young's modulus [4]. The hardness did not vary with the single layer thickness of amorphous nanolaminates, while mixtures were slightly harder compared to the laminates (Fig. 1). The elastic modulus decreased below that of the references in some multilayers (Fig. 2).

Annealing promoted the formation of orthorhombic Ta_2O_5 phase in the reference film [5] and in some composites. The Al_2O_3 film remained amorphous. The single constituent layer thickness had an influence on the hardness in nanolaminates with crystallized Ta_2O_5 layers. Nanolaminates with constituent layer thickness below 12 nm remained X-ray amorphous and softer compared to the crystalline nanolaminates and mixtures (Fig.1). The elastic modulus was modified with annealing for some of the multilayers (Fig.2).

The architecture of the trilayers affected hardness more than the Al_2O_3/Ta_2O_5 volume ratio, while the modulus of elasticity increased with increasing Al_2O_3 content after annealing.

The results show a possibility of engineering the mechanical properties of ALD thin films.

References

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[3] L. Kilpi *et al*. *J. Vac. Sci. Technol. A* 36, 01A122 (2018) https://doi.org/10.1116/1.5003729

[4] H.-M. Piirsoo *et al*. *Coatings* 12, 404 (2022) https://doi.org/10.3390/coatings12030404

[5] H.-M. Piirsoo *et al*. *Materials* 16, 3207 (2023) https://doi.org/10.3390/ma16083207

2:15pm **EM-WeA-4 ALD Young Investigator Award Finalist Talk: Phosphorus-Rich Metal Phosphide Thin Films Using Zintl Ions***, **Jordan Bentley**,* University of Western Ontario, Canada*; B. van Ijzendoorn,* Manchester Metropolitan University, UK*; J. Lomax,* University of Western Ontario, Canada*; M. Bakiro, S. Barry,* Carleton University, Canada*; M. Mehta,* Manchester Metropolitan University, UK*; P. Ragogna,* University of Western Ontario, Canada

Metal phosphide thin films can be prepared by vapour deposition techniques using various metal and phosphorus precursor combinations.[1] The resulting materials have applications in microelectronics, catalysis, and energy storage. For example, transition metal analogues such as FeP, CoP, and NiP, are effective catalysts in hydrogen evolution reactions or as

electrode materials for Li-ion batteries.[2,3]As for main-group metals, group 13 and 14 congeners such as GaP, InP, and GeP possess bandgaps that are amenable to photovoltaic and transistor applications.[4] Metal phosphides usually require organophosphorus or PH_3 as the phosphorus source, but here, we demonstrate that the heptaphosphide cluster (P_7^{3-}) can serve as an effective phosphorus precursor for making thin films by molecular layer deposition.[5] This opens a pathway to phosphorus-rich metal phosphide thin films (MP_2, MP_3, MP_4) which can exhibit superior properties to binary metal phosphides in some cases. [6] We used a specially designed crossflow vapour deposition system and then annealed the films to achieve uniformity. To the best of our knowledge, this is the first time that main group clusters were employed in vapour deposition. This opens up the possibility of creating novel materials with tailored properties at the nanoscale level. Current data supports that $P_7(SiMe_3)_3$ is sufficiently robust up to ~250 ^{o}C as measured by DSC and can be volatilized. A volatilization temperature under 1 torr (T_v) was estimated to be ~130 ^{o}C; isothermal data at 130 ^{o}C and 150 ^{o}C support the linear mass loss of $P_7(SiMe_3)_3$ over 2 hours. We will present details on the precursor, thin film preparation, and analyses such as powder X-ray diffraction, electron dispersive spectroscopy, X-ray photoelectron spectroscopy, atomic force microscopy, and quartz crystal microbalance.

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2:30pm **EM-WeA-5 Improved Crystallinity and Polarity Determination of Gallium Nitride on Si (111) Using Atomic Layer Annealing**, *S. Yun,* ***Ping-Che Lee,*** University of California San Diego*; A. Mcleod,* University of California at San Diego*; J. Spiegelman,* RASIRC*; A. Kummel,* University of California at San Diego

The crystallinity and polarity of III-V semiconductors are critical for the passivation layers on microLED, the formation of 2D electron gasses in high electron mobility transistors, and for templating growth of piezoelectric materials. The atomic layer annealing (ALA) was reported to improve the crystallinity of the III-V compounds (aluminum nitride) at low temperatures as compared to the conventional thermal ALD. In ALA, a pulse of ion bombardment is added to each ALD cycle to ensure polycrystalline film formation at low temperature. Polycrystalline GaN has been deposited by ALA at low temperatures even on amorphous substrates, but polarity was not reported.

Figure 1a and 1b show the process parameter switching diagram for the GaN thermal ALD and GaN ALA processes, respectively. For GaN, tris(dimethylamido)gallium(III) (Strem Chemicals) and N_2H_4 (Rasirc) were used as precursors. The chemical compositions of GaN ALDs/Si were estimated by *in-situ* AES as shown in Figure 1c. Lower O contents (below 3.3 at. %) and higher N/Ga atomic ratio were observed in the ALA GaN on Si (111) as compared to the thermal ALD GaN film (4.6 at. %). Figure 1d shows that the intensity of GaN (002) XRD pattern in thermal ALD GaN on Si was greatly improved in the GaN stacks (GaN thermal ALD/ALA/Si) with an ALA GaN buffer layer.

Figure 2a and 2b shows the HAADF-STEM images of GaN ALDs/Si demonstrate highly ordered 3 nm × 5 nm ALD GaN layers. The circles of bright regions and the center of dark regions represent Ga atoms and tunnel points (empty element), respectively. The GaN polarity could be determined by drawing triangles connecting adjacent three tunnel points without the interruption of Ga. Using this method, upward triangles were obtained in the Figure 2a, suggesting the formation of N-polar GaN layers during the ALA GaN process on Si. Conversely, downward triangles from the STEM image of thermal ALD GaN/ALA/Si (Figure 2b) suggested Ga-polar GaN during GaN thermal ALD process. The inset figures show the top-view SEM image of selectively wet-etched (30 min, 20 wt.% KOH(aq)) GaN films. The etched surface on the ALA GaN (inset of Figure 2a) indicated N-polar GaN surface. The inset SEM image in Figure 2b shows a nearly unchanged GaN surface in thermal ALD GaN/ALA/Si is consistent with the Ga-polar GaN surface. These observations are in good agreement with the HAADF-STEM images.

The data is consistent with being able to control the polarity of GaN by switching between thermal ALD and ALA. The ion bombardment in ALA promotes N-polar GaN while thermal ALD promotes metal polar GaN. This allows the facile formation of both electron and hole gas layers between ALA and ALD GaN.

2:45pm **EM-WeA-6 Self-limiting Epitaxy of GaN and InN Films on Sapphire Substrates**, *S. Allaby, N. Ibrahimli, F. Bayansal, H. Saleh, B. Willis,* ***Necmi BIYIKLI,*** University of Connecticut

Research efforts on low-temperature (T < 300 ℃) synthesis of crystalline III-Nitride thin films using plasma-assisted ALD utilized various reactor configurations featuring different plasma sources. While our early GaN growth experiments using quartz-based ICP sources resulted in nanocrystalline/amorphous films with elevated oxygen impurities, shifting to oxide-free stainless-steel based hollow-cathode plasma (HCP) sources revealed highly (002) oriented polycrystalline GaN films on Si(100) and sapphire substrates. In this work, we share our experimental findings on the self-limiting growth of GaN and InN films on sapphire substrates using HCP-ALD at 200 ℃ substrate temperature, revealing (002) oriented hexagonal monocrystalline layers.

The films were deposited using conventional metal-alkyl precursors (triethylgallium, trimethylindium) and various nitrogen plasmas (N_2/H_2, N_2-only, N_2/Ar, and N_2/H_2/Ar) as metal precursor and nitrogen co-reactant, respectively. Growth experiments have been performed at 200 ℃ substrate temperature and a mild 100 W rf-power. *In-situ* Ar-plasma annealing cycles were also employed and tested for the binary III-nitride films to observe its impact on the surface crystallization process. *In-situ* ellipsometry was employed to monitor the surface ligand-exchange reactions and plasma surface interactions, in real-time. *Ex-situ* spectroscopic ellipsometry measurements revealed the film thickness variation, growth-per-cycle (GPC), and optical properties of the III-nitride films.

When compared to reference films grown on Si(100) substrates, growth-per-cycle (GPC) values obtained for III-nitride films on c-plane sapphire substrates showed a notable increase. Grazing-incidence XRD (GIXRD) measurements revealed single-phase hexagonal polycrystalline GaN and InN films on Si(100) substrates while GaN/sapphire and InN/sapphire film samples exhibited substantially weaker crystal peaks or no peaks at all. XRD ($\theta - 2\theta$) scans displayed strong (002) peaks for both nitride films grown on sapphire substrates, confirming the monocrystalline epitaxial character of the synthesized GaN/sapphire and InN/sapphire samples. The impact of plasma gas mixture and Ar-plasma annealing process revealed different results for GaN versus InN films. While H_2-containing plasmas are optimal for GaN, InN prefers H_2-free plasma gas mixtures. Also, Ar-plasma annealing improved GaN film properties while degrading InN film quality.

3:00pm **EM-WeA-7 Epitaxial Rare-Earth Orthoferrites by Atomic Layer Deposition**, ***Linn Rykkje,*** *H. Sønsteby, O. Nilsen,* University of Oslo, Norway

Rare earth orthoferrites ($RFeO_3$, *R* = lanthanide) are a class of materials whose optical and multiferroic properties demonstrate a rich landscape of functionalities. While their ferroelectric and -magnetic behavior are interesting in themselves, it is the potential for magnetoelectrically coupled behavior that make them fascinating candidates for applications in photoferroics [1][2], photocathodes [3]**,** spintronics [4][5], gas sensing [6], and memory storage [1], among others.

The number of studies on orthoferrites has seen a rise in tandem with a growing awareness of their potential, but much of their fundamental behavior remains to be elucidated. Compared to more renowned multiferroics, like $BiFeO_3$, the rare earth orthoferrites are practically unexplored, despite exhibiting very similar characteristics.

A particularly interesting member to study is $NdFeO_3$, which, based on first principles calculations, is located near a multiphase boundary and could exhibit a giant polarization in a phase reminiscent of $BiFeO_3$[7][8].

To achieve such giant polarization, it would be necessary to impose significant compressive strain or apply chemical pressure (through the choice of rare earth) - both of which are highly compatible with the control leveraged by ALD as shown in our previous work. A second pathway towards functionalization is via A- or B-site substitution – which is also attainable by ALD.

The work presented here demonstrates a viable ALD synthesis route for $NdFeO_3$ thin films with tunable chemical composition and crystallinity

achieved after annealing. The growth of the binary oxide layers (Nd_2O_3 and Fe_2O_3) on surfaces terminated by each other has been thoroughly investigated using quart crystal microbalance (QCM) and found to differ significantly. This is surprising given the similarity of the cation precursors used.

While the thin films have not been electrically conductive or any polarization tested at the time of writing, we believe that our approach will shed light on the structure-property relations of an elusive group of materials that are candidates for new functionality in a range of applications. We present characteristics of the ALD-process(es), as well as initial results on structural integrity and functionality.

For references, see Supplemental Document.

3:15pm **EM-WeA-8 Area Selectivity and Crystallographic Orientation of ZIF-8 Films Deposited by Molecular Layer Deposition***, **Jorid Smets**, V. Rubio-Giménez,* KU Leuven, Belgium*; S. Armini,* IMEC Belgium*; R. Ameloot,* KU Leuven, Belgium

Integrating metal-organic frameworks (MOFs) into microfabrication processing requires highly controlled vapor-phase deposition techniques. This study presents a vapor-phase method that enables crystallographic control and direct area-selective deposition of zeolitic imidazolate framework 8 (ZIF-8). The deposition process involves a two-step ZIF-8 molecular layer deposition (MLD), during which an amorphous precursor layer is initially deposited through consecutive self-saturating reactions of diethyl zinc, water, and 2-methylimidazole. Subsequently, a linker post-treatment step promotes crystallization. The use of substrates functionalized with self-assembled monolayers (SAMs) with different head moieties allows tuning the degree of crystalline orientation in the resulting MOF layers. Additionally, the functional groups of the SAMs influence the mobility of the ZIF-8 building blocks on the surface, enabling control over the surface coverage through area-dependent surface diffusion. By exploiting this phenomenon, we successfully achieved direct area-selective deposition of ZIF-8, which can facilitate the integration of MOFs into microelectronics.

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