Thin Films
Room Makai - Session TF-MoE
Nanostructured Surfaces & Thin Films I

Moderator: Joe Greene, Linköping University, Sweden, University of Illinois at Urbana-Champaign

5:40pm **TF-MoE1 Reducing Losses In Magnetic Thin Films by Surface Patterning**, ***Goran Rasic***, *BV. Vlahovic,* North Carolina Central University, USA; *J. Schwartz,* North Carolina State University, USA

As technology advances the demand for smaller and faster devices with reduced power losses becomes increasingly important. For high-frequency devices, such as antenna and sensors, two loss mechanisms are relevant, electrical and magnetic. Electrical losses are reduced by forming laminate structures and/or choosing materials with high electrical resistivity. Magnetic losses, however, arise from the magnetic hysteresis of the material, and thus are intrinsic. At frequencies above 1 GHz, these losses become immense. To reduce magnetic losses, the hysteresis losses must be reduced without losing desirable magnetic properties; reduced coercivity is needed, while retaining high saturation magnetization.

Textured nickel ferrite ($NiFe_2O_4$) thin films were deposited onto a c-plane sapphire substrate using chemical solution deposition. Surface of the films was patterned with a polydimethylsiloxane (PDMS) stamp using a modified nanoimprint lithography technique. A series of pattern masters with periods ranging from 500 nm to 1500 nm was used for patterning. In addition, samples with different thicknesses were prepared. Atomic force microscopy showed that the pattern was faithfully copied from the pattern masters to the thin films. X-Ray diffraction revealed all samples to be textured single phase inverse spinel nickel ferrite with preferential orientation along the <111> easy axis direction. Magnetic measurements showed the magnetic field response in the patterned samples to be unchanged as compared to plain samples, indicating there was no loss in magnetic properties. Similarly, the patterned samples showed appreciable and consistent saturation magnetization values. The coercivity of all samples showed significant reduction as compared to the plain samples. In addition, two distinct regimes were identified. For the out-of-plane measurements, the coercivity reduction increases with increasing feature size, whereas for the in-plane measurements the opposite is observed. These polar trends for the in-plane and out-of-plane measurements allow us to further fine tune the material for specific applications by not only controlling the feature size but also the orientation of the film with respect to the field. Finally, the origin of the coercivity reduction was shown to be the surface morphology anisotropy by MFM measurements. Magnetic domains were shown to be strongly affected by the surface features and oppositely oriented, reducing magnetostatic energy and leading to coercivity reduction. These results, in combination with the theoretical investigation, confirmed the origin of the coercivity reduction to be a direct consequence of altered surface topography.

6:00pm **TF-MoE2 Orientational Control of Polar Molecules in Macroporous Systems and their Dielectric Properties**, ***Ryosuke Yamamoto***, *N. Kimizuka,* Kyushu University, Japan

Organic ferroelectric materials have been attracting much interest as a new family of memory materials that operate under lower electric field. However to date, most of the reported organic ferroelectric materials are solid and they show dielectric hysteresis only in the presence of high electric field. Accordingly, there is a compelling need for new dielectric materials working at a lower electric field and ambient temperature. In this light, we have focused on supramolecular gels as organic soft dielectric materials. Gelator molecules were dissolved in solvents with large dipole moment such as nitrobenzene by heating and succeeding cooling of the mixture afforded organogels. In the electron microscopes (SEM, TEM) observations, extended nanofibrous aggregates were abundantly observed for the dried gel. In this gel, polar solvent molecules are confined and their molecular motion are expected to be limited since they interact with fibrous gel networks which contain extended hydrogen bonding networks. Thus, the dielectric properties of these supramolecular gels were investigated systematically. The gels showed increase in the magnitude of polarization with distinctive polarization-electric field hysteresis loop, though such hysteresis was not observed for the polar solvents without gelators. In addition, in contrast to the gels formed with polar solvents, gels formed with non-polar solvents didn't show the hysteresis loop. From these findings, confinement of polar solvent molecules in the suramolecular gel fiber networks play an important role to control mobility of solvent molecules, thus leading to orientational polarization.

To better understand this confinement effect and to generalize the approach, we employed porous polymer films with controlled pore-size as matrixes. Dielectric properties of polar molecules introduced into these porous polymer systems were investigated, which show similar hysteresis. We also found that polar molecules trapped in the different pore-sized polymer films showed distinct phase transition and dielectric behaviors. From these observations, it is suggested that polar molecules in the pores exert interactions with the pore surfaces and accordingly, their orientation is maintained even after cutting off the electric field. Furthermore, this system works at low electric fields. We believe that our approach would provide a new concept to design soft ferroelectrics.

7:00pm **TF-MoE5 Atomic Layer Deposition of Al_2O_3 films on Various Two-Dimensional Materials**, ***Taejin Park***, Samsung Electronics, Republic of Korea; *H.J. Kim, M. Lim, W.S. Ahn, S.H. Choi,* Sungkyunkwan University, Korea, Republic of Korea; *J.B. Kim, J. Uh, B.S. Kim, Y.S. Hwang, H.S. Hong,* Samsung Electronics, Republic of Korea; *S.J. Jeong, S.J. Park,* Samsung Advanced Institute of Technology, Republic of Korea; *Y.S. Kim, H.S. Kim,* Sungkyunkwan University, Korea, Republic of Korea

The atomic layer deposition (ALD) of high-*k* films usually fails on two dimensional (2D) materials due to the absence of dangling bonds on their surface, which only allows physisorption of a precursor that can be easily detached *via* thermal desorption [1].

In this presentation, the surface coverage of the ALD-Al_2O_3 films on various 2D flakes (MoS_2, WS_2, WSe_2, and *h*-BN) was examined as a function of the substrate temperature to extract the adsorption energy (E_{ads}) of a trimethyl-aluminum (TMA) precursor . The film coverage exhibited a strong dependence on the ALD temperature and the 2D substrate. The E_{ads} values of TMA on various 2D material surfaces were experimentally determined using the measured film coverage after 10-cycled ALD at different temperatures. The E_{ads} values were in the range of 0.05-0.26 eV, which corresponded to the values for van der Waals physisorption and could be well explained by different induced dipole polarizability of 2D materials.

[1] H. Liu *et al*., Appl. Phys. Lett. **100**, 152115 (2012).

7:40pm **TF-MoE7 Initial stage Growth Mode of ALD deposited Al2O3 on Tungsten Nano-powder**, ***Kedar Manandhar***, *J.A. Wollmershauser, B.N. Feigelson,* U.S. Naval Research Laboratory, USA

Powders with particle size ≤100 nm typically posses unique physical, chemical, opto-electronic, mechanical and catalytic properties compared to bigger size particle powder and their bulk counterpart and are increasingly being used in commercial systems. However a path to exploit these size specific properties of nano-powders is not always straight forward since they are often in danger of being deteriorated from the environments in which they are intended to be used. To enable these powders to withstand working environments, the surface of powders are commonly engineered via coating with films of thickness varying few monolayer to thousands of monolayers. For many cases a continuous ultrathin shell is desired. In the applications where a continuous ultrathin films is desired, understandings about growth mode, in the early stage of growth is very important since it defines how the material is arranged on the surface.

When it comes to the need of a thin metal-oxide film as protective layer or active surface, aluminum oxide is the material of choice for at least two reasons, (i) ALD chemistry of alumina from trimethylaluminium/ water is well studied (ii) relative easiness of forming a continuous film with alumina. To understand film morphology of alumina in the early stage of growth, we selected tungsten powder as substrate because this substrate/ film material combination eases for core-shell analysis by transmission electron microscopy (TEM) as TEM micrographs show a high contrast between core and shell for easy and more accurate determine of films thickness ranging from ultrathin to thin[1]. Alumina films resulting from 1 to 20 ALD cycles were grown on W-nanopowders with an average particle size of 50 nm using rotary reactor ALD. The results for alumina deposition at ~110 ℃ demonstrated stoichiometric and continuous but non-uniformly thick films in the beginning with varying growth per cycle (GPC) as a function of number of cycles. The as prepared samples were investigated with x-ray photoelectron spectroscopy , scanning and transmission electron microscopy. Film surface morphology and GPC as a function of ALD cycle for early stage growth will be presented and discussed.

1. Manandhar, K., et al., Growth per cycle of alumina atomic layer deposition on nano- and micro-powders. Journal of Vacuum Science & Technology A, 2016. 34(2): p. 021519.

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8:00pm **TF-MoE8 Crystal Growth Simulation of ZnO Thin Film on α-Al_2O_3 Substrate by Molecular Dynamics Simulation**, ***Shunsuke Kawagishi**, J. Xu, Y. Ootani, T. Nishimatsu, Y. Higuchi, N. Ozawa, M. Kubo,* Tohoku University, Japan

A ZnO thin-film semiconductor is used as light emitting devices and quantum hall effect devices because of its broad wide band gap of 3.2 eV and large exciton binding energy of 60 meV. In the previous research, optical properties of the ZnO thin film depend on the crystal orientation and quality [1]. Therefore, in order to obtain the high-quality thin film, it is necessary to understand crystal growth process such as physical vapor deposition. However, it is difficult to observe the crystal growth process at atomic scale by experiments. In this study, to elucidate the crystal growth process of ZnO, we performed crystal growth simulation of a ZnO thin film on an α-Al_2O_3 substrate by our molecular dynamics simulator and analyzed crystal quality of the formed ZnO thin film.

At first, to investigate crystal growth process of the ZnO thin film, we irradiated ZnO molecules on an α-Al_2O_3(0001)substrate at a velocity of 900 m/s at 700, 900, and 1200 K. The ZnO thin films are formed on the substrate at 700, 900, and 1200 K. Next, to evaluate crystal quality of the formed ZnO thin films, we analyzed radial distribution function of the formed thin films. The first and second peaks of the radial distribution function at 1200 K are sharper than those at 700 and 900 K. This indicates that crystallinity of the formed thin film at 1200K is higher than that at 700 and 900 K. Our simulation result is in good agreement with the experimental result in which crystal quality is improved by increasing the substrate temperature [2]. Next, we investigated the atomic behavior in the growth process. At only 1200 K, some of the irradiated ZnO molecules dissociate on the thin film. Then, the Zn and O atoms diffuse into the formed thin film. Finally, 6-membered rings are formed by diffusion of the Zn and O atoms in the formed thin film. This indicates that atomic mobility of the Zn and O atoms on the substrate is promoted due to raising substrate temperature and this high mobility of the Zn and O atoms contributes to the quality of the formed thin film. Thus, we succeeded in crystal growth simulation of a ZnO thin film on an α-Al_2O_3 substrate and found difference in the growth process of the thin film at 700, 900, and 1200 K.

[1] S. Dutta et al., Progress in Materials Science, 54, 89-136 (2009).

[2] A. El-shaer et al., Superlattices and Microstructures, 38, 265-271 (2005).

8:20pm **TF-MoE9 Nucleation and Aggregation of Nanoparticles during Atomic Layer Deposition on High-Surface-Area Substrates**, ***Fabio Grillo**, H. Van Bui,* Delft University of Technology,The Netherlands*; J.R. van Ommen,* Delft University of Technology, The Netherlands

Atomic layer deposition (ALD) is proving to be an attractive technique for depositing nanoparticles (NPs) in a controlled fashion. By relying on self-limiting surface reactions, ALD lends itself to the decoration of high-surface-area substrates with NPs for various applications such as enhanced catalysts and batteries. However, the mechanisms underlying the nucleation and growth of NPs during ALD are still poorly understood. Understanding the evolution of the particle size distribution of NPs during ALD is essential for fabricating supported NPs with predictable morphology and functionality. ALD growth is generally explained in terms of self-limited layer-by-layer growth, and although such picture applies to the deposition of a variety of metal oxides, especially at low temperature, it does not apply to the nucleation and growth of metal NPs. In fact, the evolution of the particle size distribution (PSD) of NPs is governed by kinetic processes such as surface diffusion, aggregation and coalescence. Here, we study the evolution of the PSD of Pt and Pd NPs deposited in time scales relevant to thermal ALD based on oxidative chemistries on high-surface-area substrates. To unravel the relevant processes underlying the evolution of the shape of the PSD, we devise a kinetic model based on the Smoluchowski equation that incorporates the generation of adatoms on both the substrate and the pre-existing NPs due to surface reactions, surface diffusion, adatom capture and NP aggregation. In doing so, we show that, during the first cycles, NP growth proceeds mostly due to NP diffusion and coalescence. The evolution of the PSD during dedicated sintering experiments of the ALD-grown NPs suggests that NPs aggregation takes place mostly during the oxygen exposure. In fact, the oxygen exposure not only regenerates the active surface for the subsequent precursor exposure but also mediates the metal-support interaction. Finally, we show that by varying the deposition temperature, while adjusting the exposure times to retain saturation conditions, the determining mechanism for NPs growth shifts from accretion due single-atom capture, at low temperatures (T<100 °C), to NPs diffusion and coalescence at high temperatures (T>150 °C). The insights obtained in this study open up new avenues to the rational design of novel composite materials based on supported metals NPs.

8:40pm **TF-MoE10 Tight-Binding Quantum Chemical Molecular Dynamics Simulation on Water Lubrication Mechanism of Silicon Nitride**, ***Jun Chida**, N. Takahashi, Y. Wang, Y. Ootani, T. Nishimatsu, Y. Higuchi, N. Ozawa, K. Adachi, M. Kubo,* Tohoku University, Japan

Silicon nitride (Si_3N_4) is used as a low friction material under water lubrication. It is suggested that the low friction is caused by the SiO_2・n(H_2O) (silica gel) layer generated by chemical reactions between the Si_3N_4 and the water at a friction interface [1]. Thus, the understanding of formation mechanisms of the silica gel is required to improve the friction properties. However, it is difficult to directly observe the chemical reaction dynamics at atomic scale by experiments. In this work, we investigated the formation mechanism of the silica gel by our tight-binding quantum chemical molecule dynamics simulator [2].

We performed the sliding simulation of Si_3N_4 under water lubrication. The simulation model consists of two amorphous Si_3N_4 substrates and H_2O molecules. The top of the upper substrate was slid by 100 m/s with a load of 3 GPa. The Si atoms and the N atoms on the surfaces were terminated by OH groups and H atoms, respectively.

First, we employed the flat substrate model. During the friction simulation, an H atom of a Si-OH bond on the Si_3N_4 surface transferred to a nearby N atom. Then, the O atom of the Si-O bond approached another Si atom in the surface, and a Si-O-Si bond was generated. The Si-OH groups changed to the Si-O-Si groups at the friction interface. This process leads to the formation of Si-O-Si bond network which is the main component of the silica gel.

Next, in order to reveal the influence of surface roughness on the formation mechanism of the silica gel, we employed the Si_3N_4 substrates with a rough surface. During the friction simulation, the Si-O-Si bonds were generated on the surface of the convex parts, as observed in the simulation with the flat substrates. When the two convex parts collided, the chemical bonds were generated between the two substrates. Then, the convex part of the lower substrate combined with the upper substrate was scraped off. H_2O molecules dissociated and adsorbed on a newly generated surface to saturate the dangling bonds. Finally, the flat Si-O-Si chain was formed on the surface. This result indicates that the collision of the convex parts leads to the formation of the flat Si-O-Si bond network.

In this work, we found that the Si-O-Si network, which is the main component of silica gel, is generated at the friction interface of Si_3N_4 by the chemical reaction of the Si-OH groups and the collision of the convex parts. Remarkably, the flat Si-O-Si network was formed after the scraping the convex parts.

[1] M. Chen et al., Tribol. Lett. 11 (2001) 23.

[2] K. Hayashi, M. Kubo et al., *J. Phys. Chem. C*, 115, 22981-22986 (2011).

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