Emerging Materials
Room Evergreen Ballroom & Foyer - Session EM-MoP
Emerging Materials Poster Session

EM-MoP-1 Structure and Magnetism of Electrospun a -Fe_2O_3 Nanofibers SiO_2-Coated by ALD, *F Pantò,* CNR-Istituto di Tecnologie Avanzate per l'Energia (ITAE), Italy*; H Raza,* Humboldt-Universität zu Berlin, Germany*; A Ferretti,* CNR-Istituto di Scienze e Tecnologie Molecolari (ISTM), Italy*; C Triolo,* Università di Messina, Italy*; A Ponti,* CNR-Istituto di Scienze e Tecnologie Molecolari, Italy*; S Patanè,* Università di Messina, Italy*; N Pinna,* Humboldt-Universität zu Berlin, Germany*; **Saveria Santangelo,*** Università Mediterranea, Italy

In the last years, thanks to its appealing properties (high abundance, low-cost, environmental friendliness, good chemical stability, small energy band gap) hematite has attracted considerable attention as a photocatalyst for the H_2 production. Electrospun α-Fe_2O_3 nanofibers (NFs) have been evaluated in other energy related applications potentially benefiting from their high porosity and large surface area and could also be utilized in less common ones, e.g., as a theranostic agent [1]). Besides, magnetism of nanohematite is a current topic in fundamental research. [2] A study focused on the magnetic properties of electrospun α-Fe_2O_3 NFs has shown that the fiber diameter strongly controls the magnetic behaviour [3]. Coating elongated α-Fe_2O_3 nanoparticles (NPs) by silica via sol-gel chemistry allows controlling the saturation magnetisation, remanent magnetisation and coercivity through the thickness of the coating layer [4]. ALD offers the possibility to coat NPs with well-calibrated and conformal thin films, thus in principle enabling the fine-tuning of the magnetic properties. This contribution focuses on SiO_2-coated electrospun a-Fe_2O_3 NFs and their nanostructure. The changes of the magnetic properties, with respect to pristine hematite, due to the SiO_2 coating are discussed as a function of the number of ALD cycles (10–100) and of the sequence of the production steps (i.e. calcination of the electrospun NFs followed by SiO_2-ALD or vice versa). SiO_2-ALD prior to calcination results in fibers formed by smaller α-Fe_2O_3 grains and by a higher structural disorder. Regardless of the sequence of production steps, ALD coating brings about a local rearrangement process in the oxide lattice with gradual surface defects suppression. These structural changes reflect on the magnetic NF properties, especially coercivity and remanence (Morin temperature).

[1] Chem. Mater. 26 (2014) 2105

[2] J. Magn. Magn. Mater. 475 (2019) 611

[3] J. Phys. Chem. C 115 (2011) 17643

[4] *Mater. Lett. 61 (2007) 5268*

EM-MoP-2 Fluidized Bed Molecular Layer Deposition of Ultrathin Poly(ethylene terephthalate) Films on TiO_2 P25 Nanoparticles, ***Damiano La Zara,*** *M Bailey, D Benz,* Delft University of Technology, Netherlands*; M Quayle, G Petersson, S Folestad,* AstraZeneca, Sweden*; J van Ommen,* Delft University of Technology, Netherlands

Molecular layer deposition (MLD) is a vapour phase technique allowing the controlled, layer by layer growth of purely organic thin films on a wide range of substrates. To date, most MLD studies have focused on coating flat substrates, but MLD also holds significant promise for application to particles. In particular, the inherent biocompatibility of organic coatings is of interest to passivate the surface of pigment particles and to tailor the dissolution profile of drug particles. Of the organic coatings produced thus far, polyimide and polyurea coatings predominate, whereas polyester polymerisation chemistry has received considerably less attention. Amongst this class of polymers, Poly(ethylene terephthalate) (PET) is of particular interest due to its widespread industrial usage, thermal stability, and gas and moisture barrier properties stemming from the terephthalate group. The use of conventional deposition reactors operating at vacuum conditions, reported in nearly the entirety of MLD literature, hinders facile and low cost up-scaling. Therefore, the development of processes with better scale-up potential is crucial when aiming for commercial applications, especially when it concerns high-surface area powders.

In this work, we deposit ultrathin PET films on gram-scale batches of TiO_2 P25 nanoparticles (NPs) using terephthaloyl chloride and ethylene glycol as precursors. The MLD process is carried out in an atmospheric-pressure fluidized bed reactor at 150-160 °C for a broad range of growth cycles (i.e., from 5 to 50). Ex-situ diffuse reflectance infrared fourier transform spectroscopy (DRIFTS-FTIR) shows the presence of the characteristic C=O stretch of ester groups in the range 1730-1750 cm^{-1}, thus demonstrating the successful MLD reaction. DRIFTS-FTIR and thermogravimetric analysis (TGA) confirm the self-saturating behaviour of the precursors, and the linear increase in mass with the number of cycles. Moreover, TGA highlights the good thermal stability of the PET films, which are stable up to ~225 °C. Transmission electron microscopy (TEM) enables the visualization of uniform PET films on the surface of TiO_2 NPs. Preliminary TEM observations suggest a low PET growth per cycle (GPC), around 0.03-0.04 nm. This value seems also in agreement with the GPC estimated by the amount of deposited material on TiO_2 NPs measured by TGA as well as with the GPC of PET on SiO_2 wafers measured by spectroscopic ellipsometry. Finally, ultrathin PET films are effective in suppressing the photocatalytic activity of the TiO_2 P25 NPs, without affecting its absorptive properties in the UV-vis spectrum.

EM-MoP-3 Fabrication and Characterization of Organic-Inorganic Hybrid Thin Films, *S Mo,* ***Chu Huong,*** Hanyang University, Republic of Korea

Currently, the next generation of electronic devices requires new materials that have great properties. The straight way to fabricate new materials is the hybridization of existing materials having different properties. The hybrid materials mixed by organic and inorganic components are expected to have combined properties both of inorganic parts, such as stability and high electrical or optical performance and organic parts with great flexibility and functionality. Furthermore, the hybrid materials are expected to have synergic effects which are not shown in just one component.

In this report, we fabricated new types of organic-inorganic hybrid thin films by molecular layer deposition. The hybrid thin films were made by sequential surface reactions of metal alkyls and bifunctional monomers. Diethylzinc and 2,4-hexadiyne-1,6-diol are used as an inorganic precursor and an organic precursor, respectively, in order to fabricate poly(zinc diacetylene). Some methods are used to characterize the microstructure and composition of the hybrid films such as Raman, XPS and TEM analysis. And, the electric and optical properties were analyzed by a TFT fabrication and photoluminescence spectroscopy, respectively. The high performance of TFTs, on/off ratio of over 10^7 and saturation electron mobility of over 10 cm2/V·s. The molecular layer deposition process can proceed under the low-temperature condition that indicates the possible use of hybrid films to flexible devices.

EM-MoP-4 High Performance Encapsulation Polymer-Al_2O_3 Hybrid Thin Layer by Atomic Layer Infiltration, *S Mo,* ***Hong Rho Yoon,*** *J Park, N Long, C Huong,* Hanyang University, Republic of Korea

Encapsulation is an important technology for isolating and protecting air-sensitive materials and is key in the development of new generation flexible electronic devices. Here we report an extremely high performance encapsulation hybrid thin layer prepared by filling the free volume of the polymer with Al2O3 using gas-phase atomic layer infiltration. The high density polymer−inorganic hybrid thin layer shows extremely low gas transmission rate, below the detection limit of the Ca corrosion test (water vapor transmission rate <10^(−7) g/m^(−2) day^(−1)). Furthermore, because of the remarkable nanometer-scale thinness of the complete polymer−inorganic hybrid, it is highly flexible, which makes it useful for encapsulation technology of new generation flexible devices.

EM-MoP-5 ALD of Metal Oxides Fabricated by using $La(NO_3)_3{\cdot}6H_2O$ Oxidant and their Applications, ***In-Sung Park,*** *S Kim, T Lee, S Seong, Y Jung, J Ahn,* Hanyang University, Republic of Korea

The oxide films with high-k including Al_2O_3, HfO_2, and ZrO_2 have been widely applied to dielectric of capacitor devices in fabrication of semiconductor memory. Recently, ALD method has been widely spreading to making the ultra-thin, dense, conformal, and widely-uniform deposition areas in spite of its very low productivity. In ALD process, the selection of oxidant is very important because of the variability of film characteristics such as growth rate, ALD temperature window, crystalline structure, contamination, and dielectric/electrical properties.

In this work, the using of $La(NO_3)_3{\cdot}6H_2O$ catalytic oxidant will be focused to fabricate HfO_2 films for insulator of resistor and dielectric of capacitor. The H_2O oxidant was used to make above films for the comparison. The devices with metal-insulator-metal structure were prepared and their electrical properties were also compared.

HfO_2 films were synthesized by ALD method using $Hf(NCH_3C_2H_5)_4$ precursor and $La(NO_3)_3{\cdot}6H_2O$ solution, which is catalyst and oxidant. The growth rate of HfO_2 film made with $La(NO_3)_3{\cdot}6H_2O$ solution is approximately three times faster than that with H_2O oxidant. The $La(NO_3)_3{\cdot}6H_2O$ solution effectively altered the surface roughness, crystalline status, and resistive switching

properties of HfO_2 films. In spite of the same crystalline structure of both HfO_2 films made with $La(NO_3)_3{\cdot}6H_2O$ and H_2O, the surface roughness of HfO_2 film grown by using $La(NO_3)_3{\cdot}6H_2O$ solution oxidant is smoother than that using H_2O. Moreover, resistive switching characteristics of HfO_2 grown using $La(NO_3)_3{\cdot}6H_2O$ was enhanced not only uniformity of switching parameters but also endurance.

EM-MoP-6 Bringing Higher Etch-resistance to Metal-infiltrated Polymer*, **Norikatsu Sasao**, K Asakawa, S Sugimura,* Toshiba Memory Corporation

Infiltration synthesis is an emerging technology that enables to realize organic-inorganic hybrid materials. The gaseous metal precursors penetrate into polymers followed by oxidation process, which stabilizes the metal derivatives into the polymer-matrix. Up to date, many fundamental studies have been carried out on the infiltration of trimethylaluminum(TMA) into polymethylmethacrylate(PMMA) thin films[1][2]. There has also been reported that TMA is selectively infiltrated to PMMA phase of the phase-separated block copolymer of PMMA and polystyrene, where etch-resistance of infiltrated PMMA is remarkably increased[3].

Although literatures show that TMA readily coordinates onto carbonyl group of the acrylate unit, the density of the resulting aluminum derivatives in PMMA is eliminated to the density of carbonyl groups. By increasing the carbonyl density in the monomeric unit of the polymer, we can expect to have higher aluminum content in the polymer after the infiltration process which could result in higher etch-resistance.

Recently we have synthesized a polymer having two or more carbonyl groups branched on the main-chain to increase carbonyl density compared to PMMA. Evidences show that TMA was infiltrated into the polymer at a higher density compared to that of PMMA and the etch-resistance increased as the aluminum content increased. Our novel strategy shows further pathways for future applications.

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[2]E. C. Dandley, C. D. Needham, P. S. Williams, A. H. Brozena, C J. Oldham and G. N. Parsons, “Temperature-dependent Reaction Between Trimethylaluminum and Poly(methyl methacrylate) during Sequential Vapor Infiltration: Experimental and *abinitio* Analysis,” *J. Mater. Chem. C.*, 2014, 2, 9416

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EM-MoP-7 Magnetic and Electric Properties of Atomic Layer Deposited ZrO_2-based Thin Films*, **Kristjan Kalam**, H Seemen, P Ritslaid, T Jõgiaas, M Rähn, A Kasikov, A Tamm, K Kukli, M Mikkor,* University of Tartu, Estonia*; J Link, R Stern,* National Institute of Chemical Physics and Biophysics, Estonia*; S Dueñas, H Castán,* University of Valladolid

Multiferroic materials of simple stoichiometry may have prospective applications in memory and sensor technologies, especially if they could be produced at low temperatures over large-area substrates by ALD. Tetragonal or cubic sputtered ZrO_2 has found to be ferromagnetic [1], and, when combined with HfO_2 by ALD, behaved as a ferroelectric material [2]. Therefore, it is of interest to investigate if ZrO_2 coupled with another metal oxide would exhibit both ferroelectric and ferromagnetic hysteresis behavior in the same material sample.

We have studied, for instance, ZrO_2-Fe_2O_3 [3], ZrO_2-HfO_2 [4] and ZrO_2-Co_2O_3 [5] mixed layers or nanolaminates grown by ALD from $ZrCl_4$, $FeCp_2$, $HfCl_4$, $Co(acac)_3$, H_2O and/or O_3 mostly at 300 ^oC. The composition of the films could be controlled by varying the ratio of constituent metal oxide cycles. Structural evaluation revealed dominantly tetragonal or cubic ZrO_2. All oxides, as deposited, exhibited magnetization-field behavior characteristic of that in ferromagnetic materials. Most of the films in as-deposited states also showed certain remnant charge polarization in their charge-field dependences. The behavior could be strongly influenced by the charge transport and interfacial charge trapping. Certain ferroelectric component contributing to the polarization could not be neglected, although the charging was probably overwhelmed by leakage currents. Nonetheless, in some films, in particular ZrO_2-HfO_2, hysteresis loops implying both ferromagnetic and ferroelectric components in the materials could be observed. In this presentation, performance of different oxides as potential multiferroic host materials will be comparatively discussed.

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[2] S. L. Weeks *et al*. ACS Appl. Mater. Interfaces, 9(15), 13440 (2017).

[3] K. Kalam *et al*., Beilstein J. Nanotech. 9 (2018) 119.

[4] K. Kalam, et al, ECS J. Solid State Sci. Technol. 7.9 (2018): N117-N122.

[5] K. Kalam, et al., Thin Solid Films 669 (2019) 294-300.

EM-MoP-8 Vapor Phase Infiltration as a New Approach in the Fabrication of Advanced Hybrid Thermoelectric Materials*, **Jaime DuMont**, M Knez,* CIC nanoGUNE, Spain

Hybrid organic-inorganic materials are rising stars in the field of thermoelectrics (TE), whose principal aim is to salvage the rejected heat of energy conversion processes by directly converting waste heat into electricity. With two-thirds of the 160 TWh required for global power consumption lost to the environment each year, the development of flexible, non-toxic, inexpensive and scalable TE materials would be of great economic and environmental interest. Realizing this ambition will require a new approach that can break away from the rare, toxic and expensive materials that have dominated the field until now.

This next generation of hybrid TE materials will require a synthesis strategy which 1) functions at temperatures low enough to not destructively act on the polymer 2) can tune the electrical and thermal conductivity of the hybrid material for optimal TE performance 3) maintain a strong chemical binding between the organic and inorganic components for long term stability and operational efficiency and 4) can be easily scaled for large-area applications. Vapor phase infiltration (VPI) is a technique primed to meet these requirements. In this work we will survey VPI processes of various transition metal compounds as a tool for the top-down fabrication of metal-poly(3-hexyl)thiophene (P3HT) hybrids as promising candidates for advanced TE materials. By monitoring the electrical conductivity and thermopower of these novel hybrid materials, we will show how the VPI process can be used to generate and optimize a new set of thermoelectric materials.

EM-MoP-9 Low-temperature Atomic Layer Deposition of Aluminum Oxide on Polymeric Powder Feedstocks for Improved Powder Rheology*, **John Miller**, C Gillespie, J Chesser,* Lawrence Livermore National Laboratory*; A Scheppe,* United States Air Force Academy*; A Nelson, N Teslich, A Lange, S Elhadj, R Reeves,* Lawrence Livermore National Laboratory

Some organic materials of interest in the additive manufacturing industry require inkjet/colloid based processes to avoid degrading the properties of the material of interest. Some of these organic feedstocks are cohesive in nature and tend to form agglomerates in suspensions, making them undesirable for use in additive manufacturing printing processes. Atomic Layer Deposition (ALD) can be used as a technique used to change the surface property of the material without changing the property of the bulk material of interest. ALD sequentially pumps reactive precursors into and out of a reactor vessel, which react on the surface of a desired substrate to form films with sub-nm level control. This paper studies the reduced temperature ALD deposition of aluminum oxide on polyimide/Si reference flats and melamine and nylon organic powder feedstocks for coating quality and its effect on the powder rheology and cohesivity. The result is a mixed amorphous phase aluminum oxide-hydroxide coating that is both highly uniform and conformal on the powder’s surface. Alumina coatings on the nylon powders did not produce a significant change in the flow properties of the powder, due to the initial low cohesivity of nylon. The melamine however experienced significant improvements to flowability due to a reduction in cohesivity of the melamine feedstocks from the surface coating. Results show that thin coatings of 20 nm or less on these feedstocks can remarkably improve their surface chemistry for use in additive manufacturing processes.

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EM-MoP-10 Atomic Layer Deposition of Molybdenum Oxide Carbide and Molybdenum Carbide Films*, **Michael D. Overbeek**, C Winter,* Wayne State University

The atomic layer deposition (ALD) of Mo(O,C) and MoC films is described using $MoCl_5$ and the co-reactants oxalic acid or formic acid. Self-limited ALD growth was demonstrated at 350 °C for $MoCl_5$ and oxalic acid, however, the growth rate decreased at long $MoCl_5$ doses, consistent with etching. The growth rate of the $MoCl_5$ and oxalic acid process was 0.18 Å/cycle within an ALD window of 325-400 °C. The resistivities of the films decreased with increasing deposition temperature and was 366 μΩ cm for an 18 nm thick film grown at 400 °C. A plot of thickness versus number of cycles was linear with no nucleation delay. X-ray diffraction of the as-deposited films was consistent with nanocrystalline Mo(O,C). Atomic force microscopy of 18 nm thick films grown with $MoCl_5$ and oxalic acid in the

ALD window gave RMS roughnesses of 0.49-0.56 nm, indicating very smooth surfaces. X-ray photoelectron spectroscopy (XPS) showed Mo, O, and C in the films, with low levels of other elements. The films obtained using $MoCl_5$ and oxalic acid are thus Mo(O,C). Formic acid was also used with $MoCl_5$ as a co-reactant, since oxalic acid decomposes thermally at high temperatures to formic acid and CO_2. A plot of growth rate versus pulse length showed self-limited growth at 400 °C, but a plot of growth rate versus deposition temperature did not show an ALD window between 400-450 °C. Films grown with formic acid at 400 and 450 °C with thicknesses of 28.5 and 48.1 nm, respectively, showed RMS roughnesses between 0.55 and 0.88 nm. XPS of a film grown using $MoCl_5$ and formic acid at 450 °C showed a composition of MoC, with low oxygen and chlorine levels. The resistivity of a 48 nm thick MoC film grown at 450 °C with 1000 cycles was 177 μΩ cm.

EM-MoP-11 Solid Phase Epitaxy of ALD-Grown $PrAlO_3$ Films*, Navoda Jayakodiarachchi*, *W Waduge,* Wayne State University*; Y Chen, P Zuo, T Kuech, S Babcock, P Evans,* University of Wisconsin-Madison*; C Winter,* Wayne State University

An atomic layer deposition (ALD) process is reported for the growth of PrAlO3 thin films using tris(isopropylcyclopentadienyl)praseodymium (Pr(C5H4iPr)3), trimethylaluminum (AlMe3), and water. Pr(C5H4iPr)3 was chosen as a precursor because of its good volatility, high thermal stability, and high reactivity with water. Pr(C5H4iPr)3 was first evaluated as a precursor for the formation of Pr2O3 films using water as the co-reactant. Self-limited growth was demonstrated for pulse lengths of ≥3 s, with a growth rate of ~0.85 Å/cycle. An ALD window was observed between 275 and 350 °C, and the as-deposited Pr2O3 films were crystalline. The ALD growth PrAlO3 films was examined next on Si(100) and SiO2 substrates. Self-limited growth was demonstrated for Pr(C5H4iPr)3), AlMe3, and water at 300 °C using a 1:1 ratio of Pr(C5H4iPr)3) and AlMe3 pulses. An ALD window was observed from 275 to 325 °C with a growth rate of ~1.7 Å/cycle. The increase in film thickness as a function of the number of cycles at 300 °C was linear and showed a small nucleation delay. The as-deposited PrAlO3 films were amorphous, had smooth surfaces, and contained <0.5% carbon and chlorine, as analyzed by grazing incidence wide-angle X-ray scattering, X-ray reflectivity and atomic force microscopy, and X-ray photoelectron spectroscopy, respectively. The films grown with a 1:1 ratio of Pr(C5H4iPr)3) and AlMe3 pulses were slightly aluminum-rich (Pr:Al ~1.2-1.4) by electron probe microanalysis. As deposited PrAlO3 films grown on single crystal (100) SrTiO3 substrates at 300 °C were amorphous and annealing at 800 °C for 3 h resulted in fully crystallized PrAlO3 films. The crystallized PrAlO3 films were highly (001)-orientedwith a small population of polycrystalline grains with other orientations. The PrAlO3 00L and SrTiO3 00L reflections appeared on the same rod of reciprocal space, further indicating that the amorphous PrAlO3 film transforms into an epitaxial layer. The rocking curve width of the PrAlO3 (001) reflection was 9°. By contrast, PrAlO3 films deposited on Si(100) substrates with native SiO2 remained amorphous after annealing at 1000 °C for 8 h. The difference in the crystallization between PrAlO3 layers deposited on crystalline SrTiO3 and amorphous native SiO2 substrates indicates that PrAlO3 on SrTiO3 crystallized by solid phase epitaxy, in which the nucleation and orientation of the crystallized layer is set by the substrate.

EM-MoP-12 Homogenous Distribution of Dopants in ALD Films: Tin-Doped Zinc Oxide (ZTO) Case Study*, Triratna Muneshwar*, *D Barlage, K Cadien,* University of Alberta, Canada

ALD is a well-established thin film deposition technique where the material growth stems from the stacking of partial atomic monolayer in each surface reaction step. Being a bottom-up approach, doping of ALD could be readily achieved from introduction of dopant species during growth. For example, the most common approach for deposition of B-doped AO oxide growth, is to periodically deposit oxides AO with n_1 cycles and BO with n_2 cycles (super-cycle: n_1·AO + n_2·BO). Although the relative A/B content is precisely controlled with n_1 and n_2, the resulting multilayered structure would have a non-homogeneous dopant-B distribution (hence may require additional processing steps like annealing, ion bombardment, etc.). To overcome this limitation we demonstrate a method for homogeneously doped ALD films with BAOBAO… pulsing sequence. We show that the choice of dopant precursor, process parameter and also the sequence (ABO… or BOA…) are critical in controlling dopant concentration. As example we report our early results on tin-doped zinc oxide (ZTO) ALD films grown at 50 °C substrate temperature using tetraallyltin (TASn), diethyl zinc (DEZ), and a remote ICP O-plasma. We show that the pulsing sequence Sn/Zn/O gives a better control over Sn-content in ZTO films. With increasing Sn-content, measured room temperature electrical resistivity (ρ^{ele}) of as-grown ZTO films (each ~24 nm thick) was found to systematically decrease from 450 Ω-cm for ZnO, to 19.72 Ω-cm, 5.7×10^{-1} Ω-cm, and 2.8×10^{-2} Ω-cm for samples ZTO#1, ZTO#2 and ZTO#3 respectively.

EM-MoP-13 Uniform, Thermal ALD of Al_2O_3 and ZnO on Zirconia Particles*, Dhruv Shah*, *D Patel, J O'Tani, M Linford,* Brigham Young University

The technical literature contains relatively little on the topic of atomic layer deposition (ALD) on particles. Here we report thermal ALD of thin films of alumina and zinc oxide on zirconia powder substrates from trimethylaluminum and water, and diethylzinc and water, respectively. Very similar growth was obtained when ozone was substituted for water in these depositions. Depositions were optimized by varying the dose and purge times for the precursors with an aim to obtain uniform film thickness and growth per cycle (GPC). X-ray photoelectron spectroscopy (XPS) clearly showed an increase in surface aluminum and zinc with increasing numbers of ALD cycles. Transmission electron microscopy (TEM) showed uniform film growth and particle coverage. Film thicknesses were also measured on planar witness shards by spectroscopic ellipsometry (SE). Ultimately, up to 10 nm films of alumina and zinc oxide were grown on zirconia particles via 100 ALD cycles.

EM-MoP-14 Composition Control of Ge-Sb-Te Film by Supercycles of ALD GeSb and ALD Sb Followed by Tellurization Annealing*, Yewon Kim*, *J Lee,* Sejong University, Republic of Korea*; S Baik,* Hankyong National University, Republic of Korea*; W Koh,* UP Chemical Co., Ltd., Republic of Korea*; W Lee,* Sejong University, Republic of Korea

Phase change random-access memory (PCRAM) is getting attention as storage class memory (SCM) which is can fill the performance and cost gap between DRAM and NAND flash. Ge-Sb-Te (GST) compounds have been extensively studied due to their fast switching speed and high data retention. The GST thin films were prepared by physical vapor deposition, chemical vapor deposition and atomic layer deposition (ALD) techniques. As the mushroom structure changes to confined cell structure because of thermal interference, ALD technique is needed in order to deposit a thin film in a nano-size hole. Conventional ALD GST film was prepared with ALD GeTe and ALD Sb2Te3 supercycle. This method is complicated and deposited as amorphous during deposition, resulting in void formation during repeated PCRAM operation. In previous work, we prepared GST film by tellurization of ALD Ge-Sb. This process simplifies the supercycle ALD GST process and can form a crystalline GST thin film. Also, the incorporation of Te improves the gap fill characteristic by expanding the volume. Tellurization of the ALD Ge-Sb film could control the composition of Te by the tellurization temperature or the number of cycles, however it cannot control the composition ratio of Ge to Sb. Since the switching speed and durability of the phase change memory cell depend on the composition of the GST film, a method of controlling the composition ratio of Ge and Sb in the GST film is also required. In the present work, GST films with different compositions were prepared by ALD super-cycle process consisting of ALD Ge-Sb and ALD Sb. The composition ratio of Ge to Sb was controlled by changing the ratio of the sub-cycles. The temperature window and growth rate of ALD Ge-Sb and ALD Sb were investigated to determine the temperature and sub-cycle ratios of the super-cycle process. Ge-Sb films of different compositions were prepared by ALD super-cycle processes and then annealed in a tellurium atmosphere. The composition and phase transition temperature of the GST thin films were examined before and after the tellurium annealing. The phase transition temperature was tunable by controlling the subcycle ratio or tellurization conditions. Step coverage and gap filling characteristics were also investigated.

EM-MoP-15 Study on The Crystallinity and The Dielectric Constant of $Zr_xGe_{1-x}O_2$ Films using Mixed Zr - Ge Precursor by Atomic Layer Deposition ., *Ju Young Jeong*, *Y Han, H Sohn,* Yonsei University, Korea*; H Noh, H Park,* SK Hynix Inc

Scaling of Dynamic Random Access Memory(DRAM) requires high k dielectric materials for data storage capacitor. ZrO_2 is favorite material for storage capacitors becasue of large band gap, low leakage current, good thermal stability. Dielectric constant of ZrO_2 depends on the crystal structure (monoclinic =19.7, cubic = 36.8, tetragonal=46.6). It was reported that doping of ZrO_2 with elements such as Mg, Ca, Y, La, and Ge enhances tetragonal phase of ZrO_2. In general, such elements are incorporated in ZrO_2 using laminated growth structure.

In this study, Ge-doped $ZrO\text{-}_2$ films were fabricated using mixed Zr-Ge precursor ($CpZr[N(CH_3)_2$

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Park, J: EM-MoP-4, 1
Patanè, S: EM-MoP-1, 1
Patel, D: EM-MoP-13, 3
Petersson, G: EM-MoP-2, 1
Pinna, N: EM-MoP-1, 1
Ponti, A: EM-MoP-1, 1
— Q —
Quayle, M: EM-MoP-2, 1
— R —
Rähn, M: EM-MoP-7, 2
Raza, H: EM-MoP-1, 1
Reeves, R: EM-MoP-9, 2
Ritslaid, P: EM-MoP-7, 2
— S —
Santangelo, S: EM-MoP-1, **1**
Sasao, N: EM-MoP-6, **2**
Scheppe, A: EM-MoP-9, 2
Seemen, H: EM-MoP-7, 2
Seong, S: EM-MoP-5, 1
Shah, D: EM-MoP-13, **3**
Sohn, H: EM-MoP-15, 3
Stern, R: EM-MoP-7, 2
Sugimura, S: EM-MoP-6, 2
— T —
Tamm, A: EM-MoP-7, 2
Teslich, N: EM-MoP-9, 2
Triolo, C: EM-MoP-1, 1
— V —
van Ommen, J: EM-MoP-2, 1
— W —
Waduge, W: EM-MoP-11, 3
Winter, C: EM-MoP-10, 2; EM-MoP-11, 3
— Y —
Yoon, H: EM-MoP-4, **1**
— Z —
Zuo, P: EM-MoP-11, 3