## Emerging Materials
## Room 113-115 - Session EM-MoA
### Laminate, Multicomponent, and Nitride Materials

**Moderators:** Nicholas Strandwitz, Lehigh University, Ji Hye Kim, ISAC Research Inc.

4:00pm **EM-MoA-11 Comparisons Between $TiO_2/Al_2O_3$ Nanolaminates Grown by Thermal and Plasma Enhanced Atomic Layer Deposition: Growth Mechanism and Material Properties***, G Testoni,* Universidade do Vale do Paraíba, Brasil*; **Rodrigo Pessoa**, M Fraga,* Universidade Brasil, Brasil*; N Galvão,* Instituto Tecnológico de Aeronáutica*; W Miyakawa,* Instituto de Estudos Avançados*; H Maciel,* Instituto Tecnológico de Aeronáutica

Nanolaminate coatings can offer significant improvements to traditional single-layer materials. An interesting class of nanolaminate materials is one based on alternatively ordered thin films of transition metal oxides with nanoscale thickness [1]. Using the $TiO_2/Al_2O_3$ nanolaminate concept of our previous work [1], it is possible to obtain at high temperature a 'stable amorphous film' which is very attractive for applications in microelectronics and optics. It is known that amorphous films of certain materials 'crystallize' during the various processing steps (deposition, metallization and lift-off) required for manufacturing a device. This crystallization modifies the fundamental properties of the film, which makes it suitable for the application. Herein, the thermal atomic layer deposition (ALD) and plasma enhanced atomic layer deposition (PEALD) of $TiO_2/Al_2O_3$ nanolaminates on silicon(100) and glass substrates were studied in order to discuss the growth mechanism and material properties of the films. We use the nanolaminate concept where each $TiO_2/Al_2O_3$ nanolaminate incorporates a certain number of $Al_2O_3$ partial-monolayers (between 10 to 90) during 2700 total reaction cycles of $TiO_2$ under temperature of 250ºC [1]. $TiO_2/Al_2O_3$ films were deposited by a TFS-200 ALD system from Beneq. TMA and TTIP were used as metallic precursors, while $H_2O$ or $O_2$ plasma were used as ligand. The growth mechanisms and fundamental properties of the $TiO_2/Al_2O_3$ nanolaminates were inferred from measurements of the film thickness, chemical composition, microstructure and morphology. In addition, some optical and mechanical characteristics were determined and correlated with fundamental properties. Results evidenced that the model proposed for thermal ALD $TiO_2/Al_2O_3$ nanolaminate is valid for PEALD, however it was necessary a higher number of $Al_2O_3$ layers for stop the $TiO_2$ crystallinity. This allows obtaining a nanolaminate with improved properties in comparison with thermal ALD, as for example higher transmittance, lower refractive index (near the value of 3.2 eV), low resistivity, and higher hardness and young modulus. These properties are interesting for sensing application, such as UV detection.

[1] J. Azadmanjiri, C. C. Berndt, J. Wang, A. Kapoor, V. K. Srivastava, C. Wen, J. Mater. Chem. A 2 (2014) 3695–3708

[2] G. E. Testoni, W. Chiappim, R. S. Pessoa, M. A. Fraga, W. Miyakawa, K. K. Sakane, N. K. A. M. Galvão, L. V. Santos, H. S. Maciel. Journal of Physics D: Applied Physics, 49 (2016) 375301.

4:15pm **EM-MoA-12 Texture Control of ALD $PbTiO_3$ and $PbTi_xZr_{1-x}O_3$ Films by Hot Chuck and Rapid Thermal Annealing***, **Nicholas A. Strnad**,* University of Maryland*; D Potrepka, J Pulskamp,* U.S. Army Research Laboratory*; Y Liu, J Jones,* North Carolina State University*; R Phaneuf,* University of Maryland*; R Polcawich,* U.S. Army Research Laboratory

$PbTi_xZr_{1-x}O_3$ (PZT) is a perovskite ferroelectric material that is widely studied for its high dielectric constant and piezoelectric coefficients. Thin-film PZT has found several commercial uses, namely ink-jet print heads, ferroelectric random access memory (FRAM), MEMS gyroscopes, and more recently PZT-MEMS based speakers. Niche technological applications include MEMS resonators, actuators, and transducers. Thin-film PZT is currently deposited by primarily 2-dimensional (2-D) deposition techniques such as sol-gel, sputtering, and MOCVD. Thin-film PZT-based devices could benefit greatly from an atomic layer deposition (ALD) PZT process capable of transitioning traditionally 2-D architectures to 3-dimensional (3-D) architectures utilizing etched high aspect-ratio sidewalls to greatly enhance areal density especially for actuator technologies. The literature on PZT deposited by ALD is sparse and falls short of providing industry with an off-the-shelf solution. Additionally, there is little effort dedicated to controlling the texture of ALD PZT films, which is a desired component for many of the aforementioned technologies. Here we explore several techniques for controlling the texture of ALD PZT by depositing nucleation seed layers. First, we attempt to deposit 1-3nm of ALD grown $TiO_x$ followed by 1-5nm ALD grown $PbO_x$ and anneal in a PZT sputter chamber which has a $PbO_x$ partial pressure. The $PbO_x$ is expected to react with the $TiO_x$ to form $PbTiO_3$ (PTO), but will be self-limited to what can be chemically incorporated because excess lead oxide will boil off the surface with the chuck maintained at 600° C or hotter. Second, we deposit 1-5nm of ALD grown $TiO_x$ and anneal in an RTA that is expected to have a small $PbO_x$ partial pressure due to re-deposition of lead oxide from prior processing of chemical solution deposited PZT films onto a quartz glass liner that is within 1 cm of the wafer surface. Third, as a control we deposit 40nm of PTO by sol-gel with 30% lead excess which crystallizes primarily in the 100/001 orientations following post-deposition anneal. Each of the ALD PZT films are deposited in an amorphous state and later crystallized by rapid thermal anneal in an $O_2$ atmosphere. To further evaluate the contribution of the nucleation layers to the texture, sol-gel PZT films are deposited in the first and second cases to be analyzed alongside the ALD PZT films. The films are characterized primarily by spectroscopic ellipsometry for film thickness, scanning electron microscopy for film thickness and microstructure, x-ray diffraction for phase identification and texture, and for select samples STEM with EDS for detailed structure and chemical analysis.

4:30pm **EM-MoA-13 Optical and Electrical Properties of $Ti_xSi_{(1-x)}O_2$ Films Prepared by ALD***, **Lenka Zajickova**, P Ondracka, D Necas,* Masaryk University, Czech Republic*; M Elias,* CEITEC, Brno University of Technology, Czech Republic*; J Vida,* Masaryk University, Czech Republic*; D Holec,* Montanuniversitat Leoben*; A Goullet,* University of Nantes

The mixed $TiO_2$-$SiO_2$ oxides have multiple possible optical applications with demonstrated use in waveguides, laser mirrors and rugate filters. They are also considered as an alternative dielectric for high-k applications and they attracted considerable attention in the area of photocatalysis because they are more active than pure $TiO_2$. $Ti_xSi_{(1-x)}O_2$ were deposited on Si substrate by plasma enhanced atomic layer deposition using tetrakis(dimethylamido)titanium and tris(dimethylamino)silane precursors for Ti and Si, respectively. The overall stoichiometry of the final thin film was varied by changing the relative number of $TiO_2$ and $SiO_2$ cycles as 1:1, 2:1, 1:2 and 3:1. The chemical bonding in the films was confirmed by X-ray photoelectron spectroscopy (XPS). Optical properties were determined in the wide spectral range from the ellipsometry (NIR-UV spectroscopic ellipsometer J. A. Woollam V-VASE, 0.6-6.4 eV, angles of incidence 60, 65, 70 and 75°) and reflectance (VUV spectrometer McPherson VUVAS 1000, 5.6–10.3 eV, near-normal incidence) measurements. The results on dielectric function and band gap were in good agreement with the density functional theory (DFT) predicted optical properties of amorphous $Ti_xSi_{(1-x)}O_2$ solid solutions. The electrical properties of the films were investigated in the MOS capacitor structures using a wafer probe station and the 4200 Keithley semiconductor parameter analyzer. The mixed oxide dielectric constant is deduced from the C-V curves measured at 1 MHz in accumulation regime whereas the film stability is assessed from the C-V loops recorded by accumulation (A) to inversion (I) and I to A. The dielectric layer insulating characteristics were assessed from the measured leakage current and breakdown voltage.

4:45pm **EM-MoA-14 Concerted Coating and Reduction for the Fabrication of Magnetic $Fe_3O_4/TiO_2$ Core-shell Nanoparticles***, **Sarai Garcia**, A López-Ortega, A Chuvilin, M Knez,* CIC nanoGUNE, Spain

Composite nanoscale materials are under intense investigation, opting for merging the functionalities of the constituting materials. $Fe_2O_3$-$TiO_2$ core-shell nanoparticles (NPs) are among the intensely investigated composite NPs for their application potential in a broad variety of fields, such as, sensing, selective separation, biomedicine, or photocatalysis [1,2]. The combination of a titanium dioxide ($TiO_2$) shell and a magnetic iron oxide core can provide added value to the composite by tuning the biocompatibility, stability and/or photocatalytic properties through the $TiO_2$ shell and at the same time, the possibility to use the materials for hyperthermia, imaging or controlled positioning through magnetic fields [3].

In this work, $Fe_2O_3$ nanoparticles are coated with $TiO_2$ and concertedly turned magnetite $Fe_3O_4$-$TiO_2$ core-shell NPs through atomic layer deposition (ALD) at moderate temperatures (Figure 1). The generated coatings prevent agglomeration of the nanoparticles and re-oxidation to γ-$Fe_2O_3$ even at high temperatures, allowing for the use of post-process annealing and thus crystallization of the amorphous $TiO_2$ to anatase. The occurring reduction of $Fe_2O_3$ to $Fe_3O_4$ is a function of the applied precursor and the processing temperature. This presentation will detail on our process and the characterization of the materials by means of X-ray diffraction (XRD), magnetometry, Energy Dispersive X-Ray analysis (EDX) and electron microscopy.

[1] M. Stefan *et al.*, "Synthesis and characterization of $Fe_3O_4$-$TiO_2$ core-shell nanoparticles," *J. Appl. Phys.*, vol. 116, no. 11, 2014.

[2] W. Wu, X. Xiao, S. Zhang, F. Ren, and C. Jiang, "Facile method to synthesize magnetic iron oxides/$TiO_2$ hybrid nanoparticles and their photodegradation application of methylene blue," *Nanoscale Res. Lett.*, vol. 6, pp. 1–15, 2011.

[3] S. Exhibit, C. Strobel, R. Herrmann, A. A. Torrano, and I. Hilger, "Biocompatibility of titanium dioxide nanoparticles for diagnostic and therapeutic purposes in personalized nanomedicine," pp. 1–17, 2013.

5:00pm **EM-MoA-15 Aluminum Nitride – From Amorphous to Highly Oriented Hexagonal Thin Films***, Z Chen, M Bosund, I Tuoriniemi, V Malinen, Z Zhu,* ***Emma Salmi****, K Härkönen,* Beneq Oy, Finland

Aluminum nitride (AlN) has a wide band gap, good thermal and chemical stability, thermal conductivity and interesting electro-acoustic properties. It is used in several applications, of which many depend on the crystalline structure of the material. Barrier, passivation and dielectric layers benefit from amorphous structures [1]. However, highly oriented crystalline films are needed for instance in optoelectronic and surface acoustic wave devices [2].

In this work the aim was to deposit AlN films with varying crystallinities to separately address the needs of different application areas. TMA and $AlCl_3$ were utilized as the metal precursors, while $NH_3$ or $NH_3$ plasma were used as the nitrogen source. The deposition temperatures were varied from 220 to 550°C.

PEALD AlN films were deposited at 220°C from TMA and $NH_3$ plasma in a Beneq TFS 200 ALD reactor. On a 200 mm wafer a uniformity of 1.7% was achieved. The films were amorphous and had a refractive index of 1.88.

Thermal ALD process from TMA and $NH_3$ was studied at 350–475°C with a Beneq P400 batch ALD reactor. Significant effect of the pulsing sequence on the growth characteristics and film properties was observed. With the optimized process at 350°C, a GPC of 1.37 Å/c and refractive index of 2.10 were measured. The bulk oxygen and carbon contents were 1.0 and 0.4 at.%. The films were polycrystalline with randomly oriented hexagonal structure, and the degree of crystallinity was increased with increasing deposition temperature (Figure 1).

The Beneq P400 batch ALD reactor is equipped for studying ALD processes at high temperatures. This enabled us to increase the temperature range of the thermal ALD $AlCl_3$–$NH_3$ process from the previously reported 500 up to 550°C [3,4]. Significant improvement on the film quality was observed with increasing deposition temperature. The GPC and refractive index increased from 0.67 to 0.76 Å/c and 1.99 to 2.06. Simultaneously the bulk oxygen and chloride impurity contents decreased from 3.2 to 2.5 and 1.8 to 0.7 at.%. Furthermore, these results were achieved with a uniformity of 2.5% on a batch set-up with a planar surface area of 20 000 $cm^2$. All the films were polycrystalline with highly oriented hexagonal [001] structure as the only observed peak was (002) (Figure 2).

[1] M. Bosund et al., Appl. Surf. Sci. 256 (2010) 7434-7437.

[2] G.F. Iriarte at al., Mater. Res. Bulletin 45 (2010) 1039-1045.

[3] K.-E. Elers et al, J. De Phys. IV France 5 (1995) C5-1021–C5-1027.

[4] V. Rontu, J. Vac. Sci. Technol. A 36 (2018) 021508.

5:15pm **EM-MoA-16 Purely Thermal Deposition of Polycrystalline Gallium Nitride Films at 400$^o$C***,* ***Sourish Banerjee****, S Dutta, A Aarnink, J Schmitz, D Gravesteijn, A Kovalgin,* University of Twente, Netherlands

In the field of III-V semiconductor materials, research is focused mostly on epitaxially grown films. Developing their polycrystalline counterparts (e.g., polycrystalline gallium nitride or poly-GaN) may lead to their more widespread adoption in application areas, such as in microelectronics and lighting. Unlike traditional epitaxy, atomic layer deposition (ALD) of poly-GaN films allows for less stringent growth requirements such as reduced temperatures, atomic-level thickness control and direct growth on a variety of substrates without the need of buffer layers.

The majority of reports on low temperature deposition of poly-GaN from trimethylgallium (TMG) and ammonia ($NH_3$) precursors mention an additional means of activation (e.g., plasma) to dissociate $NH_3$. This is done to increase the chemical activity of ammonia (by forming radicals) with the TMG-chemisorbed surface. However, in this work, we have used a different (radical-free) chemistry to deposit GaN films by a purely thermal route; i.e., without plasma or other radical-production means. Such a deposition approach can be beneficial, for example, in industrial-scale batch-type reactors where uniform radical delivery is a challenge.

We have utilized the strong adduct-forming chemistry of the Lewis-acid TMG and the Lewis-base $NH_3$ on the growth surface (Fig. 1). At the deposition temperature of 400$^o$C the TMG-$NH_3$ adduct dissociates into a Ga-$NH_2$-Ga linkage, thereby forming the first monolayer of GaN in a self-limiting fashion. Due to the reversible nature of this adduct formation, at optimal gas-pressure conditions, alternate pulses of TMG and $NH_3$ with in-between purges result in the efficient film growth. This pressure-dependency of adduct formation is revealed by in-situ monitoring the growth with spectroscopic ellipsometry (SE), which shows a strong dependence of the growth per cycle (GPC) with the $NH_3$ partial pressure (Fig. 2). Using this approach, we obtained GPC values as high as 0,045 nm/cycle.

The efficient removal of all methyl groups of TMG during GaN deposition in the adduct-assisted mechanism is revealed from the low carbon content (1 at. %) in the films, as obtained from depth profiled X-ray photoelectron spectroscopy (Fig. 3). The cross-section scanning electron microscope (SEM) image (Fig. 4) shows a 23-nm GaN film deposited on aluminium nitride (AlN). Grazing-angle X-ray diffraction (GIXRD) spectrum (Fig. 5) reveals that the GaN film is polycrystalline and has a wurtzitic structure.

In our presentation, the purely thermal radical-free deposition of poly-GaN films will be detailed: focussing on the growth mechanism, determining the ALD window, and presenting several film properties.

5:30pm **EM-MoA-17 ABC-type pulsing for group 13 nitrides***, P Rouf,* ***Henrik Pedersen****,* Linköping University, Sweden

The group 13 nitrides (13-Ns) are essential electronic device materials for present and future technologies. Thin film deposition of AlN and GaN are well explored by CVD at relatively high temperatures (800-1000°C). The high temperature aids epitaxial growth and ligand removal, rendering high crystalline quality films with low impurity levels. As 13-N CVD almost exclusively uses the trimethyl complexes of the group 13 metals, carbon is a major impurity with concentrations in the $10^{17}$ $cm^{-3}$ range.

ALD is less explored for the 13-Ns but would open to topographically more advanced 13-N structures, higher control when depositing multilayer superlattice 13-N structures and possibly low deposition temperatures. A major challenge for ALD is the limitation in deposition temperature set, mainly by the thermal stability of the monolayers formed by the surface chemical reactions in the ALD cycle. The thermal stability of the group 13 precursors also limits the deposition temperature; $AlMe_3$ decomposes at about 330°C and previous studies have shown that the carbon content in the films increases rapidly when deposition temperature starts to approach the decomposition temperature [1]. The lower temperatures used in ALD compared to CVD hampers the crystalline quality and the removal of ligands leading to an increase in impurity levels, mainly carbon and oxygen, to the several atomic percentage levels.

Here we discuss the possibility to use the time-resolved precursor supply in ALD with an additional pulse between the precursor pulses, i.e. an ABC-type pulsing, to decrease impurities and increase crystalline quality. To improve the crystalline quality, we intentionally move out of the ALD temperature window and did time-resolved CVD of 13-Ns at 480°C, allowing thermal decomposition of the $13Me_3$ precursors. We then introduced a pulse of $H_2$ or $N_2$ gas or $H_2$-, $N_2$- or Ar plasma as B-pulse between the $13Me_3$ (A-pulse) and $NH_3$ (C-pulse) to study how it can aid the removal of ligands, as probed by the impurity levels in the deposited films. XPS measurements shows that the carbon content in AlN can be reduced from about 3 at. % to below 1 at. % (which is on the detection limit of XPS) by a $H_2$ gas or $H_2$ plasma as the B-pulse. $H_2$ gas as B-pulse also increases the GIXRD peak intensity, which is likely an effect of a higher crystalline quality, and the growth per cycle. Initial results do not show any improvement on the carbon content for $N_2$ plasmas as B-pulse in AlN deposition.

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[1] H. Van Bui et al. ECS J. Sol. Stat. Sci. Technol. 2014, 3, P101-P106.

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