Thin Film Division
Room Oregon Ballroom 203-204 - Session TF-ThP
Thin Film Poster Session

TF-ThP-2 High Heat Resistant Y_2O_3 Film on Quartz Prepared by Ion-Assisted Deposition, ***Naoto Kihara***, *S. Ogawa, K. Kawahara, R. Hayashi, T. Ogawa,* AGC Inc., Japan*; M. Tanimura, H. Okada, M. Ishikawa,* Tsubasa Science Corporation, Japan

Background

Along with the miniaturization of semiconductor devices, equipment using plasma processes such as dry etcher is required to have high plasma durability and low particle generation. Yttrium oxide (Y_2O_3) is used as a passivation film on the surface of the parts which are equipped in the chamber. In recent years, Y_2O_3 films with high heat resistance are required to etch low-volatility or difficult-to-etch materials and developed for new plasma processes. In this study, we focused on the difference of thermal expansion between quartz substrate and Y_2O_3 film, then report that Y_2O_3 film with high heat resistance of 500°C was obtained introducing intermediate layer Y_2O_3-SiO_2

Experiment

In this study, Y_2O_3 and Y_2O_3-SiO_2 films were deposited on quartz substrate using the ion-assisted deposition method (IAD). The Y_2O_3-SiO_2 film which is the intermediate layer was formed by two-source co-evaporation of Y_2O_3 and SiO_2. Plasma resistance was evaluated by measuring the etched depth of the film using a profilometer after etching with CF_4 plasma. For heat resistance, the presence or absence of cracks was evaluated using an optical microscope after annealing in atmospheric environment. In addition, crystallinity and morphology were confirmed by X-ray diffraction measurement (XRD) and scanning electron microscopy (SEM), respectively.

Results and Discussion

On the basis of the XRD analysis results, the obtained Y_2O_3 film crystal structure was a cubic crystal with the (222) orientation as the main peak. In addition, a uniform surface morphology without voids and pores was obtained from surface and cross-sectional SEM observation. The etching rate was 0.009 µm/hr, which was 1/100 of quartz. Moreover, in the heat resistance test results, there were no cracks at 400 °C, and cracks occurred at 500 °C. In the quartz/Y_2O_3-SiO_2/Y_2O_3 stacked film intended to improve heat resistance, there were no cracks at 500 °C, but cracks occurred at 600 °C. Thus, by introducing the intermediate layer, Y2O3 stacked film having heat resistance at 500 °C was obtained. The reason for the improvement on heat resistance is presumed that the thermal expansion coefficient of Y_2O_3-SiO_2 has an intermediate value between quartz (0.5 ppm/°C) and Y_2O_3 (7 ppm/°C), which reduces thermal strain and stress. The detailed mechanism is under analysis.

TF-ThP-3 Improvement of Transparency and Electrical Conductivity of Ti-Doped ZnO Thin Films, ***Naoya Utsu***, *I. Takano,* Kogakuin University, Japan

In recent years, transparent conductive films have been used for touch panels, liquid crystal displays, solar cell electrodes, and other applications. Currently, indium tin oxide (ITO) or other oxide semiconductors are the mainstream materials that combine transparency and electrical conductivity. On the other hand, indium (In) is a rare metal with limited the production area, which limits its stable supply and causes significant price fluctuations. In this study, we focused on zinc oxide (ZnO) with sufficient resources and improved the transparency and electrical conductivity of ZnO by doping titanium (Ti).

The sample substrate was a slid glass with 15 x 10 mm in a size that ultrasonically cleaned with ethanol for 10 minutes. The oxide thin films were deposited by reactive sputtering using the multi-process coating system (BC5146, ULVAC Corp.). The deposition conditions were Zn sputtering input power of 20 W with an Ar gas flow rate of 20 sccm and an O_2 gas flow rate of 5 sccm to obtain a film thickness of 50 nm. At the same time, Ti was doped from 0 to 40 % with calculating from the Ti sputtering rate. For example, in the case of 10 % in the Ti doping, the sputtering rate of Zn is 0.085 nm/s (RF input power 20 W) and that of Ti is 0.0094 nm/s (DC input power 53 W).

For optical properties, transmittance was measured using a UV-visible spectrophotometer (UV-2550, Shimadzu Corp.). For electrical characteristics, the electrical conductivity was calculated from the resistance value of the deposited sample using a four-point probe (RG-5, NPS Corp.) with a pin spacing of 1.0 mm. Crystal structure analysis was performed by X-ray diffraction (SmartLab, Rigaku Co., Ltd.) at an X-ray incidence angle of 0.4 degrees.

The optimum condition for the transmittance and electrical conductivity was obtained at ZnO doped with Ti of 30 %. The transmittance and electrical conductivity of the film were 95.2 % and 739 S/m, respectively.

TF-ThP-4 Improving Compositional Analysis of Copolymer Thin Films Using a Simple Density Correction, ***Simon Shindler***, *R. Yang,* Cornell University

When synthesizing copolymer thin films, accurate measurements of the polymer composition are essential to understanding and optimizing material properties. Determining the composition of thin films synthesized from the solution phase (e.g. spin coating, or spin casting) is straight forward, since researchers generally know the composition of the polymer before fabricating the film. In polymer vapor deposition of copolymers, the characterization of composition relies instead on techniques like Fourier transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS). While helpful in some applications, chain re-orientation at the polymer-air interface and adventitious carbon often bias XPS data – making it an unreliable tool for standalone film compositional measurement. FTIR transmission spectra are more commonly used to determine composition by comparing peak areas associated with known chemical functionality. This technique uses the Beer-Lambert law to relate composition to absorption and pathlength (film thickness). To obtain composition from this method, it is necessary to measure film thickness (generally using ellipsometry) and assume that all films being analyzed have equal density. For certain chemistries, copolymerization changes the polymer packing, causing density to vary significantly with composition. When uncorrected, the assumption of constant density leads to large errors and non-physical compositions. In the process of collecting film thickness from spectroscopic ellipsometry, the refractive index of the film is also measured. Because the density and refractive index are related through the Lorentz-Lorenz equation, film density is easily estimated. By applying a density correction, we demonstrate significant improvements to the measurement of composition from FTIR at essentially zero cost. Density correction improves the accuracy of compositional analysis using data that is already collected in many labs, making it a simple and cost effective improvement to existing methods.

TF-ThP-5 Theoretical Prediction of Trisilylamine (TSA) Adsorption and Decomposition on Hydrogen-rich Silicon Nitride, ***Tsung-Hsuan Yang***, *T. Wang, G. Hwang,* University of Texas at Austin*; P. Ventzek, J. Zhao,* Tokyo Electron America, Inc.

The reactions of trisilylamine (TSA) precursor on silicon nitride (SiN) thin film in atomic layer deposition (ALD) process was investigated by density functional theory (DFT). A N-rich, H-terminated surface model was used to simulate the surface after NH_3 plasma treatment. Two reaction mechanisms were proposed depending on the abundance of excess hydrogens on the surface: (1) TSA reactions with primary amine ($-NH_2$) and (2) TSA reactions with hydrogenated primary amine ($-NH_3$). The source of excess hydrogen originates from the H radical from the NH_3 plasma which can survive on the SiN surface by being captured by the surface amine groups. Results show that in the first mechanism, the rate-determining step for TSA chemisorption is the TSA-adduct formation step which requires overcoming an energy barrier of 0.67eV predicted by climbing-image nudged elastic band (CI-NEB) method (*i.e.,* $\mathrm{TSA(g)} + \mathrm{-NH_2} \rightarrow \mathrm{-NH\text{-}SiH_3} + \mathrm{(SiH_3)_2NH(g)}$). In the second mechanism, the rate-determining step is the hydrogen transfer step with a much lower energy barrier of 0.34eV (*i.e.,* $\mathrm{TSA(g)} + \mathrm{-NH_3} \rightarrow \bullet\mathrm{SiH_3(g)} + \mathrm{(SiH_3)_2NH(g)} + \mathrm{-NH_2}$).

TF-ThP-6 Effects of Surface Morphology on the Phase Coexistence and Evolution in Li_xCoO_2 Films Studied by PEEM, ***Elena Salagre***, Dpto Fisica Materia Condensada, Universidad Autónoma de Madrid, Spain*; E. Fuller,* Sandia National Laboratories*; M. González-Barrio, A. Mascaraque,* Dpto Física de Materiales, Universidad Complutense de Madrid, Spain*; T. Mentes, A. Locatelli,* Elettra-Sincrotrone Trieste, Italy*; I. Takeuchi,* Materials Science and Engineering, Univ. Of Maryland*; A. Talin,* Sandia National Laboratories*; P. Segovia, E. Garcia Michel,* Dpto Física Materia Condensada, Universidad Autónoma de Madrid, IFIMAC, Spain

The cathode material Li_xCoO_2 (LCO) and related intercalation oxides are widely used in lithium-ion batteries and are now being investigated for applications in catalysis and neuromorphic computing[1][2][3], leading to great interest in their surface properties and mechanisms. The ability of LCO to change its composition from stoichiometric $LiCoO_2$ to Li_xCoO_2 is the key feature for most technological applications. This process changes its atomic and electronic structures. Oriented islands and epitaxial thin films of Li_xCoO_2 grown on $SrTiO_3$ (STO) have been studied at the Nanospectroscopy beamline of the Elettra storage ring using photoemission electron microscopy (PEEM) and low energy electron microscopy (LEEM)[4].

Different surface morphologies have been studied during Li deintercalation, including the phase coexistence regime. Stoichiometric LCO islands and films were delithiated in situ under UHV conditions by preferential Ne^+ sputtering followed by thermal treatment. Surface crystallinity and morphology were maintained throughout the experiments. The effects of delithiation on island size, distribution and the surrounding substrate and wetting layer were characterized. A shift in the valence band position towards the Fermi energy marks the IMT and is accompanied by a change in the surface conduction, observed as changes in the charge shift of the PEEM spectra. This has allowed us to relate the Li content to the metallization and therefore emergence and propagation of the IMT.

The spatial resolution of PEEM provides further and more detailed information on phase formation and evolution, as well as nucleation points and domain sizes. We were able to isolate the contribution of the different phases formed in the $0.5<x<1$ region.

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TF-ThP-7 Sorption-Vapor Synthesis of Zr-MOF, UiO-66-NH_2, Sponge Composites*, **Jimmy Nguyen, G. Parsons,* North Carolina State University

Metal-organic frameworks (MOFs) are materials of interest for their high surface area and chemical tuneability. MOF-Fabric, fiber, and sponge composites have been an area of research enhancing materials for applications like catalysis, separation, sensors, and energy storage. In comparison to other support matrices, sponges have greater molecular transport through their macroporous structure. The majority of current approaches for creating MOF-sponge/foam composites require multiple lengthy and resource consuming steps. These approaches often rely on either support pretreatment followed by MOF synthesis or support formation around premade MOF powder. The pretreatment method adds an additional hazardous step using high temperatures or heated acidic solutions. The support formation method requires more uncommon instruments like a high-pressure homogenizer and/or freeze-dryer. Here, a straight forward method for *in-situ* synthesis of a MOF film onto as-received commercially available sponges is reported. Sorption-vapor synthesis first involves the sponge absorbing precursor solution followed by a vapor-driven MOF nucleation and growth phase. The vapor phase exposure serves multiple roles including increasing the mobility of reactants to connect together, promoting crystalline behavior, and creating desired defects in the framework under specific conditions. This sorption-vapor synthesis technique enables the formation of plant fiber sponge@UiO-66-NH_2 composites retaining significant mechanical integrity capable of withstanding compressions. Through exploring different solvent systems, acidic vapors, and metal precursors, the conditions that maintain the most structural integrity was discovered. The conditions using a dimethyl formamide, ethanol, and water solvent system, acetic acid and water modulating vapor, and $ZrCl_4$ led to a crystalline MOF composite with a BET surface area of 114 ± 17 m^2/g.The composite formed via sorption-vapor synthesis was found to be capable of catalyzing the hydrolysis of an organophosphate, dimethyl paraoxon, with a preliminary study exhibiting a half-life of < 20 mins. This work presents insight into a simple vapor driven mechanism for UiO-66-NH_2 film growth onto an as-received, commercial sponge.

TF-ThP-8 Coating the Insides of Capillaries with a Flow-Through Atomic Layer Deposition (ALD) Reactor*, **Jacob Crossman**, J. Pinder, D. Patel,* Brigham Young University*; D. Bell,* RESTEK*; M. Linford,* Brigham Young University

Atomic layer deposition (ALD) is a process by which single or partial atomic or molecular layers are applied sequentially to a substrate. ALD often relies on a series of self-limiting half-reactions, where the number of these reactions applied to a surface is used to control the thickness of a deposited film to atomic dimensions. Ideally, ALD layers are consistent and conformal, which makes it an increasingly useful technique for semiconductor manufacturing. Traditionally, ALD is performed in a vacuum chamber that introduces and pumps away the precursors of the half-reactions. This approach is often effective on planar surfaces. However, it is not a viable method for coating high aspect ratio materials like the interior walls of capillary columns that are 5 meters or longer. To resolve this limitation, we developed a flow-through, atmospheric pressure (AP) ALD reactor that relies on flowing nitrogen rather than diffusion in a vacuum to present a precursor to the substrate surface. Thin film growth with this reactor was confirmed with spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS), chromatography, and transmission electron microscopy (TEM). Indeed, our AP-ALD reactor includes two witness chambers containing planar silicon ‘witness shards’ placed before and after the capillary. The operation of this reactor was demonstrated with the well-known trimethylaluminum-water reaction. Reasonable ALD growth of Al_2O_3 was confirmed by SE of witness shards and TEM of sections of a coated capillary. Little difference in film thickness was observed between witness shards in the two witness chambers and in the capillary itself. A chemical engineering analysis of our system suggested that a ca. 10-fold excess of reagent was present in the capillary, which explains the nearly uniform film growth at both ends of the capillary and in the witness chambers.

TF-ThP-9 Surface studies and molecular beam epitaxy of Kagome Antiferromagnetic Mn_3GaN grown on MgO (001)*, **Ali Abbas**, A. Smith, A. Shrestha,* Ohio University

There have been very few studies of antiperovskite structure Mn_3GaN in general although it was seen in molecular beam epitaxial growth as a second-phase precipitate when growing MnGaN [1]. And so, we grow thin films of Mn_3GaN on MgO (001) substrates using rf N–Plasma MBE. In this abstract, we will discuss the growth recipe and surface study of Mn_3GaN. To take advantage of noncollinear antiferromagnetic thin films in spintronics applications, it is important to study their spin structures using local probes like spin polarized scanning tunnelling microscopy. Initially we start with room temperature scanning tunneling microscopy of MBE–grown Mn_3GaN surfaces and later will progress toward variable low temperature spin–polarized scanning tunnelling microscopy. In our work, Mn_3GaN is deposited at 250 ± 10°C with a Mn: Ga: N flux ratio of 3:1:1. We keep the Ga:N ratio fixed using an RF plasma nitrogen source. The sample surface is continuously monitored throughout the growth using reflection high energy electron diffraction. During growth, the RHEED pattern was observed to be highly streaky, indicating an atomically smooth surface. In addition, we observed half-order fractional streaks (2x pattern) in the [100] direction. The calculated *in–plane* lattice constant based on RHEED is 3.89 ± 0.06 Å. This value is very close to the theoretical lattice constant *a* of Mn_3GaN (3.898 Å) [3] and with the *in–plane* experimental value for sample growth by sputtering (3.896 Å); and in that work, the authors also observed a 2x pattern [2]. We also measure the *out–of–plane* lattice constant using X–ray diffraction. For the major 002 peak, the value calculated is 3.84 ± 0.06 Å which also agrees well with the theoretical value (3.898 Å) [3] and with the experimental reported *c* value (3.881 Å) [2]. Rutherford backscattering confirms a stoichiometry of 3:1:1.

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TF-ThP-10 Improved Interface of Mo/Si Bilayers by Magnetron Sputtering*, **Chao-Te Lee**, W. Chen, H. Chen,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan

The periodic Mo/Si bilayers were deposited on Si substrate by RF magnetron sputtering with cooling system.The effects of substrate temperature on the surface roughness and interface of Mo/Si bilayers were investigated by atomic force microscopy (AFM), and high resolution transmission electron microscopy (HRTEM), The AFM measurements showed the Mo/Si bilayers to have a uniform morphology with a very low surface roughness value under 0.2 nm. It was found that the Mo-on-Si and Si-on-Mo interfaces of Mo/Si bilayers were clearly observed by HRTEM in sputtering without using cooling system. The thickness of Mo-on-Si interface was almost 0.45 nm in the Mo/Si bilayers. However, the thickness of the Si-on-Mo interface was increased with increasing layers of Mo/Si bilayers. It was increased from 0.9 to 1.36 nm. After using cooling system in sputtering, the temperature was 15 ℃, the Mo-on-Si and Si-on-Mo interfaces were all under 0.1 nm.The improved interface of Mo/Si bilayer was attributed the interdiffusion of Mo/Si bilayer was been improved in sputtering by cooling system.

TF-ThP-11 Optical Emission Spectroscopy Analysis of Self-limiting AlN Growth Process during Low-Temperature Plasma-Assisted ALD*, **Narmin Ibrahimli**, R. Sultana, I. Saidjafarzoda,* University of Connecticut*; M. Kilinc,* University at Buffalo*; A. Okyay,* OkyayTech*; N. Biyikli,* University of Connecticut

This research aims to present the potential and advantages of implementing optical emission spectroscopy (OES) as a non-invasive technique to investigate and optimize the plasma-assisted atomic layer deposition (ALD) process for AlN thin films. OES enables the identification of species present in the plasma and analysis of the light emitted, rendering it as a crucial tool for evaluating the reactant species delivered to the surface and for gaining unique insights into the surface reaction products and possible mechanisms of the deposition process. The incorporation of time-resolved OES measurements allows for the determination of optimal precursor dosing and plasma exposure times necessary for saturating half-reactions, thereby enhancing the efficiency of the ALD process. Additionally, the versatility of time-resolved OES as a process monitoring tool for plasma-assisted ALD processes on production equipment provides the capability for real-time detection of process faults and monitoring of reactor wall conditions.

AlN thin films were deposited by employing trimethylaluminum (TMA) in combination with various nitrogen plasmas (N2/H2/Ar). The growth experiments were carried out in a hollow-cathode plasma-ALD reactor at 200 °C and 100 W RF plasma power. The light emission during the plasma half-cycle is coupled into a multimode fiber through one of the optical access ports via a collimating lens which feeds a compact spectrometer unit spanning from 300 to 1000 nm with a wavelength resolution of ~2 nm. The spectral data obtained from the AlN deposition procedure was assessed by examining the emission spectrum within the initial few milliseconds of a plasma half-cycle that followed a TMA dose, and contrasting it with the emission spectrum observed towards the end of the same half-cycle, when the plasma had become adequately saturated. The differences in the emission spectra are due to the reactions initiated by plasma species with precursor fragments adsorbed at the surface. At the end of the plasma step, when the surface reactions have saturated, the emission spectrum recorded during the ALD cycle resembles that of a steady-state plasma. The results indicate that time-resolved OES measurements can help determine optimal precursor dosing and plasma exposure times to enhance the efficiency of the ALD process. Future work involves a more detailed investigation of surface ligand-exchange reactions, plasma-surface interactions, and formed reaction byproducts in real-time to gain a deeper insight into the ALD process.

TF-ThP-12 Oblique Angle Deposition on Porous Polymer Films*, S. Bacheller, N. Welchert, **Malancha Gupta**,* University of Southern California

Our group has developed a modified initiated chemical vapor deposition (iCVD) process in which frozen monomer is first captured on a cooled substrate, then polymerization occurs via a free radical polymerization mechanism, and finally the excess monomer is sublimated resulting in a porous polymer film. This talk will discuss applying oblique angle deposition to this modified iCVD process. We will demonstrate that delivering the monomer through an extension at an oblique angle results in porous films with three morphological regions: region 1 consists of porous polymer pillars, region 2 consists of densified pillars, and region 3 consists of dendritic structures. We will discuss the role of the substrate temperature, the extension angle, and the monomer deposition time on the growth process.

TF-ThP-13 Fabrication and Characterizations of Aluminum Doped Cadmium Oxide (CdO:Al) Thin Film using Sol-Gel Spin-Coating Method*, M. Syed, **Krastin Harvey**,* LeMoyne Owen College*; M. Syeda, J. Sultana,* University of Memphis

Aluminum-doped cadmium oxide (CdO:Al) thin films are deposited on silica substrates by the sol–gel spin-coating method as a function of spin coater's rpm (revolution per minute). Cadmium acetate dihydrate and Aluminum nitrate have been taken as the precursor material and a source of Al-dopant respectively. CdO:Al thin films are characterized by x-ray diffraction (XRD), Fourier Transform Infrared (FT/IR), Field emission scanning electron microscopy (FE-SEM) and SEM-EDX. XRD result indicates the highest crystallinity at 6000 rpm with a crystallite size of 31.845 nm, cubic phase formation, and strain of ~1.6 X10-2. FE-SEM/SEM/EDX shows the well-faceted homogeneous surface structure at 6000 rpm having the average particle size of 130.05 nm. FT/IR confirms the presence of CdO:Al in the film with the peak position shifting to higher wavenumbers.

Keywords: Cadmium oxide, Thin Film, SEM, Crystallinity, Sol–gel process

TF-ThP-14 Structural and Electronic Impact on Various Substrates of TiO_2 Thin Film Using Sol-Gel Spin Coating Method*, **Moniruzzaman Syed**, T. Crosby, M. Frierson, J. Muhammad,* LeMoyne Owen College*; M. Syeda, J. Sultana, M. Azim,* University of Memphis, USA

Titanium dioxide (TiO_2) thin film has been deposited on glass and silica substrates by using Sol-Gel spin coating method. The effect of annealing temperature on the structure, surface morphology, optical and electrical properties of these films are characterized by Raman, XRD, FT/IR, UVvis and four-point-probes measurements. XRD confirms the anatase phase of TiO_2. Maximum crystal sizes are found to be ~31 nm on silica and ~23 nm on glass substrates at 500^{o}C respectively. Electrical resistivity decreased with increasing annealing temperature having the higher value on glass substrates observed.

TF-ThP-15 Thin Film Transformations with Spinodal Mechanisms*, **Rahul Basu**,* JNTU, India

The topic of nucleation and growth in thin films traditionally has relied on the free energy barrier concept. In the present approach the growth of secondary phases is examined using a Moving Boundary analysis with heat transfer balances. The coupling of other components is not neglected. The possibility of spinodal breakup occurs within a miscibility gap and involves additional terms in the diffusion equation. These 4th order terms are modeled appropriately and included in the dominant Fickian diffusion model. The thin film approximation is used with a perturbation expansion.

Although the spinodal model required two or more component alloys in a miscibility gap, the differential equations do not exclude a general one component model. It is shown that the onset of a nucleation regime is predictable from the MBP heat transfer analysis without the explicit use of Free Energy variables.

TF-ThP-16 Optical Coating with High Hardness for MIR Optics Deposited by HIPIMS Deposition Technique*, **Bo-Huei Liao**,* Taiwan Instrument Research Institutes, Taiwan

In this research, silicon nitride and silicon oxynitride multilayers are deposited by high power impulse magnetron sputtering. In order to increase the adhesion of theAR coating, plasma treatments in a rf discharge of Ar and O_2 are used to activate and clean the Ge substrate. Besides, Al_2O_3 films are also deposited as the adhesion layer before the multilayers AR coating. The average transmittance from 3000 to 5000 nm was larger than 93.2%.The Mohs hardness scale was also larger than 8.

TF-ThP-17 Thermal Atomic Layer Deposition of Er2O3 Films from a Volatile, Thermally Stable Enaminolate Precursor*, **Chamod Dharmadasa**, C. Winter, N. Jayakodiarachchi,* Wayne State University*; P. Evans, R. Liu,* University of Wisconsin - Madison

Lanthanide oxide films have many applications in optics, catalysis, and semiconductor devices. Er_2O_3 films have useful properties that arise from its high dielectric constant, a large band gap energy, high refractive index, and thermodynamic stability at high temperatures. These properties have led to the investigation of Er_2O_3 films for possible inclusion in CMOS devices, antireflective and protective coatings on solar cells, and passivation layers for III-V semiconductors. Er_2O_3 films have been grown by many techniques, including PVD, CVD, and ALD. ALD is an important technique, since it gives Angstrom-level thickness control and can afford 100% conformal coverage in high aspect ratio features. ALD precursors reported to date for Er_2O_3 films have problems that include low reactivity toward water as a co-reactant, oxidation of substrates when ozone is used as the co-reactant, and variable thermal stabilities. Recently, we described a series of volatile and thermally stable lanthanide(III) complexes that contain enaminolate ligands.[1] We report here detailed synthetic studies of the $Er(L^1)_3$ precursor complex, its ALD precursor properties, and its use in the ALD of Er_2O_3 films using water as the co-reactant. Depending upon the reaction conditions during precursor synthesis the compounds $Er(L^1)_3$, $Er(L^1)_3(L^1H)$, or $K[Er(L^1)_4]$ can be isolated. The reaction conditions can be selected to provide high yields of $Er(L^1)_3$. The volatility and thermal stability characteristics of $Er(L^1)_3$ are favorable for use as precursors for Er_2O_3 and other rare-earth oxides. An ALD window in the growth of Er_2O_3 films using $Er(L^1)_3$ with water as the co-reactant was observed from 150 to 250 °C, with a growth rate of 0.25 Å/cycle. The films were characterized by electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and atomic force microscopy. Advantages of $Er(L^1)_3$ include its simple synthesis, good volatility and high thermal stability, and high reactivity with water to afford Er_2O_3 films. This class of new ALD precursors has the potential to enable more widespread use of the favorable properties of rare-earth oxide compounds and can be expanded to multi-component complex oxides containing rare earths.

TF-ThP-18 Highly Sensitive and Stable pH Sensor Electrodes of TiN Fabricated using HiPIMS with Kick*, **Lucas Mougeot**, S. Stagon, J. Aceros,* University of North Florida

Titanium nitride deposition-sputtered sensors have been shown to function as sensitive pH sensors. The electrical conductivity and inertness of TiN advocates for this functionality. Literature has shown results only for DC-sputtered TiN pH sensors, however. This research identifies and analyzes the differences between DC-sputtered TiN sensors and those fabricated with HiPIMS and HiPIMS with Kick. The methods differ in their power source. Note that DC-sputtering involves a DC power signal. HiPIMS stands for High Power Impulse Magnetron Sputtering and uses a square wave power signal. HiPIMS with Kick also requires a square wave, but involves a short pulse before relaxing to the equilibrium voltage. For all sputtering methods, the power input to the titanium target averages at 250W. Additionally, the initial chamber pressures are all 10^-6 torr. Some settings differ to achieve consistent deposition rates between the techniques, such as the working pressure (3-5 mtorr). To create the sensors, TiN is deposited onto a ceramic screen-printed electrode (with gold metallic ink). There are four leads: active, counter, reference, and signal. The active and signal leads connect to the active electrode. The counter and reference leads connect to their own respective electrodes. TiN is deposited onto the active electrode. The reference electrode is composed of Ag/AgCl. In aqueous environments, a potential difference forms between the active and reference electrodes. This voltage is used to determine the pH of the solution. To compare the sensors, measured properties include sensitivity, hysteresis, response time, and drift. To measure sensitivity, the Nernst equation is employed to determine the linear relationship between voltage and pH. The slope of this graph directly relates with sensitivity, with steeper slopes denoting higher sensitivity (and vice versa). To measure hysteresis, the sensor measures a sequence of pH buffer solutions in time-contained steps (i.e. a pH sequence 4, 7, 10, 7, 4 limited to 240 seconds each). The voltage difference that exists between a first-stage measurement and a second-stage measurement of the same solution denotes hysteresis. For measuring response time and drift, the sensor is placed into a solution for a duration of time. Response time is the duration that exists between the initial exposure to the solution and the point when the output is first within 0.1 pH of the true value. Drift is longitudinal. Measured over the course of hours, drift is the output decay rate from the sensor's initial steady state. The Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) are used characterize the TiN depositions. The SEM characterizes the topographic features of the depositions. The AFM characterizes the film thickness.

TF-ThP-19 Temperature Dependent Thermal Conductivity Measurements of Thin Oxide Films Via Steady State Thermoreflectance*, J. Gaskins, D. Olson, T. Bates, P. Hopkins,* Laser Thermal*; **Ron Fisher**,* Laser Thermal, USA

Continued dimensional scaling of materials in integrated circuits have resulted in major challenge in power dissipation and thermal management. These characteristic length scale reductions at all tiers of devices lead to temperature increases which accelerates the degradation of performance and reliability of very large scale integration. As technology nodes push to the <5 nm length scale, these thermal problems become more pronounced due to metal interconnect scaling resulting in reduced thermal conductivities, interfacial thermal resistances, and novel ultra-low-k amorphous dielectric layers that have intrinsically low thermal conductivities. Accurate understanding of these thermal properties will help guide the upcoming generations of interconnect and transistor technologies. Using Steady State Thermoreflectance in Fiber Optics (SSTR-F), we measure the thermal conductivity of a series of oxide thin films on silicon wafers. Prior to SSTR-F measurement, we coat the samples with a thin (~80 nm) film of Al to serve as an opto-thermal transducer. In practice, due to the steady state nature of the SSTR-F measurements, we are minimally sensitive to the thermal mass of the Al (heat capacity and thickness) as compared to TDTR or FDTR, which is a typical major source of uncertainty in TDTR and FDTR. We report on the thermal conductivity of oxide films with thicknesses of 98, 229, 287, 431, and 867 nm. For the thinnest three samples, SSTR-F measures the thermal resistance of the oxide layer in addition to the ITR at each adjacent oxide layer interface (Al/oxide and oxide/Si). Thus, we measure the thermal conductivity by fitting the thermal resistance of this thickness skew as a function of thickness and fit a series thermal resistor model to these data to determine the thermal conductivity of these amorphous oxide films. This approach yields a the thermal conductivity of 0.96 +/- 0.04 W/m/K. For the thickest two oxide samples, the thermal resistance is dominated by that of the oxide, and thus we report on direct measurements of the thermal conductivity of these films by dividing the thickness of the films by the measured thermal resistance and also come to a thermal conductivity of 0.96 +/- 0.04 W/m/K. The uncertainties in our measured values are calculated from spot to spot variation and propagation of uncertainty in the assumed parameters in our analysis. These SSTR-measured values agree well with prior measurements of the thermal conductivity of amorphous thin film dielectrics on silicon using TDTR that have been reported previously.

TF-ThP-20 Investigation on Atomic Layer Deposition Assisted Growth of Metal Organic Frameworksfilms and Their Sensing Performance*, **Zhe Zhao**,* Fudan University, China

Weak interactions, non-uniformity and powdery assemblies limited the wide application of metal organic frameworks (MOFs) in devices[1, 2]. We report a new strategy for area-selective assembly of MOF particles to prepare a thin film with the assistance of atomic layer deposition (ALD)[3-5].The mechanism of this strategy is utilizing ALD pretreatment to induce the growth ofhydroxy double salt (HDS) nanosheets on substrates, and the HDS nanosheets are then chemicallyconverted into a MOF structure[6]. Self-assembled hierarchically porous MOF films such as ZIF-67 (Co), ZIF-8 (Zn), Ni-MOF (Ni), PCN-333 (Fe), MIL-53 (Fe), etc. were formed on both flat and complex three-dimensional (3D) substrates at a combination of gas and liquid fabrication approaches, and can be precisely patterned by photolithography[7-10]. We demonstrate that the MOF film obtained possesses excellent electrochemical activity and can be applied in biosensor for ultra-high sensitivity and a low limit of detectiontowards glucose, lactic acid and dopamine[5-7]. This strategy is promising to prepare MOF film-based on-chip devices with advanced functions.

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TF-ThP-21 Vapor Phase Infiltration of Metal-Organic Framework for Electrocatalysis*, **Fan Yang**, M. Cao, H. ren, R. Chen,* Huazhong University of Science and Technology, China

Abstract: Metal-organic frameworks (MOFs) with well-defined structures and uniformly arranged tunable pore sizes, large surface area attract lots of attentions for a wide range of application including catalysis, sensing and etc. Intrinsic MOFs, however, often suffers from low conductivity, reactivity, selectivity and etc. Vapor phase infiltration (VPI), as a gas-phase method modified from atomic layer deposition, assures an accurately infiltrated deposition of materials into porous materials like MOFs, due to the self-limiting characteristic. In our work, VPI were applied for MOFs as post-modification at organic ligands and metal nodes, respectively. Due to the modification accuracy both in position and amount altering the MOFs coordination environment, excellent electrochemical CO_2 reduction reactivity of modified MOFs were obtained, showing promising reactivity and selectivity, comparing to pristine MOFs. The VPI strategy gives great implications for the precise and accurate construction of MOFs coordination environment.

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