Thin Films Division
Room A124-125 - Session TF+2D+AP+EL+SS-MoA
ALD and CVD: Nucleation, Surface Reactions, Mechanisms, and Kinetics

Moderators: Adrie Mackus, Eindhoven University, Netherlands, Qing Peng, University of Alabama

1:40pm **TF+2D+AP+EL+SS-MoA-1 ALD on Particles: What is Different from Wafers?***, **Ruud van Ommen**,* Delft University of Technology, Netherlands **INVITED**

Advanced materials, often relying on nanostructured particles as building blocks, are crucial in meeting grand challenges in energy and health. Atomic layer deposition (ALD) is an excellent technique to make such nanostructured particles: particles of which the surface is either covered by an ultrathin film or by nanoclusters. Although the underlying mechanisms are similar, there are quite some differences between ALD processing of wafers and ALD processing of particles. This presentation will discuss recent developments and insights in the field of applying ALD to particles, with an emphasis on reactor technology, precursor utilization, operating conditions, and scaling up. I will show that ALD is suited to produce nanostructured particles with very high precision. Moreover, it is scalable such that large amounts of such particles can be produced.

2:20pm **TF+2D+AP+EL+SS-MoA-3 Insights into Particle ALD Peculiarities from In- and Ex-Situ Characterization***, **Benjamin Greenberg**,* American Society for Engineering Education*; J Wollmershauser, B Feygelson,* U.S. Naval Research Laboratory

Particle atomic layer deposition (pALD) is an increasingly popular technique for mass production of core/shell nanoparticles (NPs). In a typical pALD process, NP powders are agitated in a fluidized bed or rotary reactor, and conformal coating of the entire powder surface—often > 100 m^2 in lab-scale reactors—is attempted via prolonged precursor exposures and purges. Over the past 2+ decades there have been many reports of highly encouraging results, including TEM images of NPs individually encapsulated by shells of uniform thickness. Nevertheless, several fundamental questions about pALD mechanisms and behavior remain challenging to answer. For example, how does the pALD growth per cycle (GPC) deviate from the corresponding ALD GPC on a flat substrate, and why? Or more importantly, what conditions are required to maximize the fraction of powder that attains an ideal core/shell structure (individual NP encapsulation) rather than a coated-agglomerate structure in which cores are glued together? In this work, using a commercial rotary pALD reactor to coat various NPs with oxide shells, we employ a wide array of characterization techniques to shed light on these issues and inform process optimization. In situ, we experiment with relatively uncommon techniques such as high-speed video analysis and pyrometry of the agitated NP powder, as well as conventional techniques such as mass spectrometry (RGA). High-speed videos in particular reveal aspects of the process often undiscussed (and sometimes difficult to convey) in the pALD literature, including changes in the powder motion as surface chemistry evolves. Ex situ, we characterize the coated NPs via TEM, XRD, SAXS, XPS, and N_2-adsorption surface area measurements (BET method).

2:40pm **TF+2D+AP+EL+SS-MoA-4 Impact of Medium Energy Ions on HfO2 Nucleation Mechanisms on Si, SiO2,TiN Substrates in PEALD Processes Investigated by In situ Ellipsometry, Optical Emission Spectroscopy, AFM and XPS Analyses***, **Marceline Bonvalot**, S belahcen, A Bsiesy, C Vallée,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

Area Selective Deposition (ASD) processes have recently attracted an increasing technological interest, as a very promising route for the development of bottom-up fabrication processes as an alternative to increasingly expensive thin layer patterning processes in advanced nanoscale devices. However, to achieve a high quality selective deposition, a deep understanding of the very initial stages of growth in Atomic Layer Deposition (ALD) processes is needed. This so-called nucleation step is strongly dependent upon growth conditions in ALD processes, namely pressure and temperature, but also on precursor types and susbtrate surfaces on which growth is carried out.

In this work, we have investigated the nucleation mechanism of HfO_2 with TEMAH precursor by plasma-enhanced ALD carried out in an Oxford FlexAL tool. This tool is equipped with an Atomic Layer Etching (ALE) system from Oxford Instruments, which consists of a continuous tunable bias power set-up applied in the back face of the chuck. When turned on during the plasma step of the PE-ALD cycle, medium energy ions (0 - 100 W) can be extracted from the inductive plasma source toward the sample surface. They may in turn contribute physically and chemically to the growth mechanism, and thus, a careful adjustment of this bias power allows a tuning of the physical properties of the layer under growth.

The nucleation behavior of HfO_2 on 3 types of substrates (H-terminated Si, SiO_2 and TiN) has been followed under applied bias power values between 0 and 100 W, by in situ spectroscopic ellipsometry assisted by Optical Emission Spectroscopy for the identification of plasma active species and desorbed by-products. The samples have then been analysed by means of Atomic Force Microscopy and X-ray Photoelectron Spectroscopy (XPS). Insights into Hf peak intensities allow an estimate of the coverage of HfO2 nuclei formed in the very first (typically 5) cycles of the PE-ALD process. A discussion will be presented on the role of medium energy ions in the observed nucleation mechanism, in view of potential applications to the development of ASD processes.

3:00pm **TF+2D+AP+EL+SS-MoA-5 Controlling the Nucleation of CVD Cobalt Films on SiO_2: Combining an Amido-based Nucleation Promotor with an Amine-based Growth Inhibitor to Afford Atomically-smooth Surfaces***, **Zhejun Zhang**, G Girolami, J Abelson,* University of Illinois at Urbana-Champaign

Cobalt films are of interest for the back-end metallization and transistor contact in microelectronics because cobalt has a greater electromigration resistance and a lower diffusion rate in dielectrics compared with copper. However, few-nanometer thick Co films deposited by CVD on dielectrics are usually non-continuous – they consist of islands with pinholes and significant roughness – which renders them unsuitable for nanoscale device fabrication. A nucleation layer, such as TiN, can be pre-deposited to improve the area density of Co nuclei; this approach eliminates the problem of islanding, but it subtracts cross-sectional area from the plug or line, thus increasing the electrical resistance.

Here, we solve the Co nucleation problem in CVD using a two-pronged approach. First we expose the SiO_2 surface to a tetrakis(dimethylamido)(transition metal) precursor at low temperature. This affords a self-limiting, submonolayer coverage of an intermediate, similar to the behavior of such molecules in ALD processes. The adsorbate layer then enhances the nucleation of cobalt from the $Co_2(CO)_8$ precursor, such that a large area density of nanoscale islands forms with essentially no nucleation delay. Using this approach, the rms surface roughness for a 1.5-nm-thick Co film decreases from 2.5 to 1.0 nm.

Second, we further improve the surface morphology by adding a co-flow of ammonia together with the carbonyl precursor; this serves as a growth inhibitor that reduces the steady-state growth rate of Co films by 50 %. The presence of the inhibitor does not alter the nucleation rate, however, the rms roughness of a 1.5-nm-thick film is further reduced to only 0.4 nm. We suggest that the roughness is due to a better valley-filling at low precursor reaction probability, consistent with the literature. In summary, our approach enables the use of CVD to afford excellent Co films for nanofabrication.

3:20pm **TF+2D+AP+EL+SS-MoA-6 Plasma-assisted Atomic Layer Epitaxy of Indium Aluminum Nitride Studied Using *in situ* Grazing Incidence Small-angle X-ray Scattering***, **Jeffrey M. Woodward**,* ASEE (residing at US Naval Research Laboratory)*; S Rosenberg,* American Society for Engineering Education (residing at US Naval Research Laboratory)*; S Johnson, N Nepal,* U.S. Naval Research Laboratory*; Z Robinson,* SUNY Brockport*; K Ludwig,* Boston University*; C Eddy,* U.S. Naval Research Laboratory

Indium aluminum nitride (InAlN) is an attractive material for power electronic applications. However, conventional methods of epitaxial growth of InAlN are challenged by a large miscibility gap and the significant differences in optimal growth conditions for the constituent aluminum nitride (AlN) and indium nitride (InN) binary compounds. Despite these challenges, the epitaxial growth of InAlN alloys throughout the entire compositional range has been demonstrated using plasma-assisted atomic layer epitaxy (ALEp)[1], a variant of atomic layer deposition in which relatively higher temperatures are utilized. In the ALEp growth of InAlN, the desired alloy compositions are achieved by forming ultra-short period superlattices of alternating InN and AlN layers, referred to as digital alloys (DA). In order to further advance these empirical efforts, significant research is needed to better understand the nucleation and growth kinetics of ALEp DA growth. To this end, we employ *in situ* grazing incidence small angle X-ray scattering (GISAXS) for the real-time study of the evolving

ternary InAlN surfaces as has been done previously for binary InN[2] and AlN[3].

Here we present *in situ* GISAXS studies of ALEp growth of InN, AlN, and a range of InAlN DAs on GaN (0001) substrates, which were performed at Brookhaven National Laboratory's NSLS-II using a custom reactor. The InAlN DAs studied include $In_{0.19}Al_{0.81}N$ (3 AlN cycles and 2 InN cycles per supercycle), $In_{0.5}Al_{0.5}N$ (1 AlN cycle and 3 InN cycles per supercycle), $In_{0.64}Al_{0.36}N$ (1 AlN cycle and 5 InN cycles per supercycle) and $In_{0.83}Al_{0.17}N$ (1 AlN cycle and 14 InN cycles per supercycle). Preliminary analysis of the data suggests that while the pure InN and AlN grew in 3D and 2D modes, respectively, the InAlN growth mode did not follow a simple trend as the nominal composition was tuned from InN to AlN. Instead, select compositions (50% and 83% In) exhibited predominantly 3D growth, while others (19% and 64% In) exhibited 2D growth. We also present complementary ALEp growth studies using a commercial Ultratech/Cambridge Nano Tech Fiji 200 and *ex situ* characterization methods, including high resolution X-ray diffraction, X-ray reflectivity, and atomic force microscopy.

[1] N. Nepal, V.R. Anderson, J.K. Hite, and C.R. Eddy, Thin Solid Films **589**, 47 (2015)

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[3] V.R. Anderson, N. Nepal, S.D. Johnson, Z.R. Robinson, A. Nath, A.C. Kozen, S.B. Qadri, A. DeMasi, J.K. Hite, K.F. Ludwig, and C.R. Eddy, J. Vac. Sci. Technol. A **35**, 031508 (2017)

4:00pm **TF+2D+AP+EL+SS-MoA-8 Real-time Monitoring of the Surface Chemistry of Atomic Layer Deposition by Ambient Pressure X-ray Photoelectron Spectroscopy**, ***Joachim Schnadt,*** *P Shayesteh,* Lund University, Sweden*; R Tsyshevskiy,* University of Maryland*; G Jean-Jacques, F Bournel,* Sorbonne Université, France*; R Timm,* Lund University, Sweden*; A Head,* Brookhaven National Laboratory*; G D'Acunto, F Rehman, S Chaudhary,* Lund University, Sweden*; R Sánchez-de-Armas,* Uppsala University, Sweden*; F Rochet,* Sorbonne Université, France*; B Brena,* Uppsala University, Sweden*; A Mikkelsen, S Urpelainen, A Troian, S Yngman, J Knudsen,* Lund University, Sweden **INVITED**

Atomic layer deposition (ALD) and chemical vapour deposition (CVD) are very important methods that enable a highly controlled growth of thin films [1]. The surface chemis-try of the underlying processes remains, however, little understood. While idealised reac-tion mechanisms have been developed, they represent postulates rather than models based on the factual identification of surface species and kinetics [2]. New *in situ* and *operando* methods offer the prospect of gaining a much more thorough understanding of the involved molecular and atomic surface processes and (dynamic) structures, which, in turn, means that a much better knowledge basis can be achieved for the future improvement of materials and growth recipes (see, e.g. [3,4]). One such *operando* method, which can be applied to the investigation of ALD and CVD, is synchrotron-based ambient pressure x-ray photoelectron spectroscopy (APXPS). While conventional x-ray photoelectron spectroscopy (XPS) is limited to vacuum pressures of 10^{-5} mbar and below, APXPS can be carried out at realistic pressure. Today, most APXPS machines can operate at pressures up to the 10 mbar regime, which is an ideal match to the pressure regime used in standard ALD reactors.

Here, I will report on our recent efforts to apply density functional theory (DFT)-assisted synchrotron-based APXPS to the ALD/CVD of oxides (TiO_2, SiO_2, and HfO_2) on semiconductor (InAs and Si) and oxide surfaces (TiO_2, RuO_2) [3-5]. I will show that APXPS allows the identification of the surface species occurring during thin film growth and the real-time monitoring of their evolution with a time resolution of down into the millisecond regime. Here, DFT is an important tool for pinpointing the nature of the chemical species and for providing deeper insight in the surface chemical processes. I will also report on our efforts to further improve instrumentation with the goal of achieving a much closer match of the APXPS sample environment with the geometries used in conventional ALD reactors. The development will also open for the use of a wider range of precursors and growth protocols.

[1] V. Miikkulainen et al., J. Appl. Phys. 113 (2013) 021301.

[2] F. Zaera, Coord. Chem. Rev. 257 (2013) 3177.

[3] B. A. Sperling et al. Appl. Spectrosc. 67 (2013) 1003.

[4] K. Devloo-Casier et al., J. Vac. Sci. Technol. 32 (2014) 010801.

[3] S. Chaudhary et al. , J. Phys. Chem. C 119 (2015) 19149.

[4] A. R. Head et al. , J. Phys. Chem. C 120 (2016) 243.

[5] R. Timm et al., Nature Commun. 9 (2018) 412.

4:40pm **TF+2D+AP+EL+SS-MoA-10 Kinetics during TMA-H_2O ALD: The Possible Role of Cooperative Surface Reactions**, ***Brent Sperling,*** *B Kalanyan, J Maslar,* National Institute of Standards and Technology (NIST)

Until recently, the CH_3 groups produced by surface reactions of trimethylaluminum (TMA) during atomic layer deposition were widely believed to always be highly reactive toward H_2O, but *in situ* measurements have shown this is not the case below about 200 °C.[1] At these temperatures, some CH_3 groups react slowly, and a significant amount persists from cycle to cycle under typical growth conditions. Interestingly, these persistent CH_3 groups are not incorporated as carbon impurities. We have observed these CH_3 groups using *in situ* reflection infrared spectroscopy and have confirmed low carbon concentrations in our films using *ex situ* XPS. Furthermore, we have measured the kinetics of the reaction with H_2O and have found them to be well-described by a double-exponential decay function. A simple Monte Carlo simulation that incorporates cooperative effects by clustered surface reactants (as suggested by DFT calculations[2]) reveals that a double-exponential decay of coverage can result even when only one species of reactant is present. Furthermore, the short-range distributions of coverage that result in the simulation differ from purely random ones. This difference implies that measurements sensitive to dipole-dipole interactions when combined with an independent measurement of surface coverage could be used to confirm or disprove the cooperative reaction model.

[1] V. Vandalon and W. M. M. Kessels, *J. Vac. Sci. Techol. A***35** (2017) 05C313

[2] M. Shirazi and S. D. Elliott, *Nanoscale***7** (2015) 6311.

5:00pm **TF+2D+AP+EL+SS-MoA-11 Atomic Layer Deposition of Metal Sulfides: Growth and Surface Chemistry**, ***Xinwei Wang,*** Shenzhen Graduate School, Peking University, China

Atomic layer deposition (ALD) of metal sulfides has recently aroused great interest, and many new sulfide ALD processes have emerged during the past several years. Surface chemistry plays a key role in ALD, but it remains yet to be investigated for many recently developed sulfide ALD processes. In this representation, I will report our study on the growth and surface chemistry of the ALD of nickel, iron, and cobalt sulfides, using various in situ characterization techniques of X-ray photoelectron spectroscopy (XPS), low-energy ion scattering (LEIS), quartz crystal microbalance (QCM), and quadrupole mass spectrometry (QMS). For instance, nickel sulfide (NiS) can be deposited from a Ni amidinate precursor ($Ni(amd)_2$) and H_2S by ALD (*Chem. Mater.* (2016) 28, 1155), but the surface chemistry of this process is found to deviate from the conventional ligand-exchange ALD scheme, and a formation of a nonvolatile acid-base complex from acidic surface sulfhydryl and basic amidine is suggested during the H_2S half-cycle (*J. Phys. Chem. C* (2018) 122, 21514). The initial ALD growth of NiS on a SiO_x surface is also intriguing, as the initial growth mechanism is found to be rather different from that in the later steady film growth. In the initial ALD cycles, the XPS results show a drastic cyclic variation of the signals for the Ni−O bonds, with prominently observable Ni−O signals after each $Ni(amd)_2$ dose but almost negligible after the subsequent H_2S dose. These results suggest that the Ni−O bonds are first formed on the surface in the $Ni(amd)_2$ half-cycles and then mostly converted to NiS in the following H_2S half-cycles. To describe this initial ALD growth process, a reaction-agglomeration mechanistic scheme is proposed (*Chem. Mater.* (2019) 31, 445). Surface thermolysis study of the Ni amidinate precursor further reveals the temperature-dependent behavior of the film growth.

Atomic Scale Processing Focus Topic
Room B130 - Session AP+EL+MS+PS+SS+TF-TuA

Advancing Metrology and Characterization to enable Atomic Layer Processing

Moderators: Eric A. Joseph, IBM Research Division, T.J. Watson Research Center, Jessica Kachian, Intel Corporation

2:20pm **AP+EL+MS+PS+SS+TF-TuA-1 In Situ Ellipsometry Characterization Of Atomic Layer Processes: A Review***, **James Hilfiker**, G Pribil, J VanDerslice,* J.A. Woollam Co., Inc. **INVITED**

Atomic layer processes such as atomic layer deposition (ALD) and atomic layer etch (ALE) provide monolayer-level thin film deposition or etch. Spectroscopic ellipsometry (SE) is ideally suited for the characterization requirements of such very thin layers. In situ SE provides real-time feedback, which is invaluable for establishing new atomic layer processes. In situ SE characterization has been adopted by many researchers due to its versatility. SE measurements are sensitive to deposition or etch at the (sub)monolayer level. The real-time evolution of film thickness provides details on nucleation periods or delays, the growth or etch rates per cycle, and verifies the self-limiting nature of a process. Multiple experiments can be performed within a single run by modifying the process conditions, allowing quick qualification of deposition temperatures, chemical exposure times, plasma influences, and purge times. In this paper, we will review the areas where in situ SE has been applied to both atomic layer deposition and etch.

We will also discuss the applications of in situ SE that benefit from a broad wavelength range. SE is best known for determining film thickness and optical constants. This characterization can be accomplished for many types of materials – dielectrics, semiconductors, organics, and even metals – provided the layer remains semi-transparent. Other material properties affect the optical constants and can be determined via this relationship. In situ SE has been used to estimate the crystal structure, composition, and even conductivity of thin films. We will discuss the advantages and limitations of in situ SE, which in many ways has proven to be an ideal partner for atomic layer processes.

3:00pm **AP+EL+MS+PS+SS+TF-TuA-3 Elucidating the Mechanisms for Atomic Layer Growth through In Situ Studies***, **Jeffrey Elam**,* Argonne National Laboratory **INVITED**

Atomic Layer Deposition (ALD) provides exquisite control over film thickness and composition and yields excellent conformality over large areas and within nanostructures. These desirable attributes derive from self-limiting surface chemistry, and can disappear if the self-limitation is removed. Understanding the surface chemical reactions, i.e. the ALD mechanism, can provide insight into the limits of self-limitation allowing better control, successful scale up, and the invention of new processes. In situ measurements are very effective for elucidating ALD growth mechanisms. In this presentation, I will describe our recent investigations into the growth mechanisms of ALD nanocomposite films comprised of conducting (e.g. W, Mo and Re) and insulating (e.g. Al_2O_3, ZrO_2 and TiO_2) components using in situ measurements. These ALD nanocomposites have applications in particle detection, energy storage, and solar power. We have performed extensive in situ studies using quartz crystal microbalance (QCM), quadrupole mass spectrometry (QMS), Fourier transform infrared (FTIR) absorption spectroscopy, and current-voltage measurements. These measurements reveal unusual ALD chemistry occurring upon transitioning between the ALD processes for the two components. This results in unique reaction products that affect the properties of the films in beneficial ways. The knowledge gained from our in situ studies of the ALD nanocomposite films has helped us to solve problems encountered when we scaled up the ALD processes to large area substrates.

4:20pm **AP+EL+MS+PS+SS+TF-TuA-7 Surface, Interface, or Film: A Discussion of the Metrology of ALD Materials in Semiconductor Applications***, **G. Andrew Antonelli**, N Keller,* Nanometrics **INVITED**

Atomic layer deposition, etching, and interface engineering are enabling technologies for semiconductor manufacturing. These processes have led to an explosion in the use of laboratory techniques such as transmission electron microscopy and the need to bring such instruments closer to or into the fab itself. However, there remains a need for in-line, non-destructive, non-contact metrology capable of quickly characterizing and monitoring these extremely thin films on test structures, on product, or in device as these data are the only meaningful method for monitoring of ultimate device performance. Indeed, in cases such as the use of selective deposition or etching, no test vehicle other than the ultimate product may be relevant. A variety of measurement techniques with a focus on x-ray and optical probes as applied to this class of problems will be reviewed. Examples will be provided on relevant logic such as the Gat-All-Around FET and memory devices such as 3D NAND.

5:00pm **AP+EL+MS+PS+SS+TF-TuA-9 In Line and Ex Situ Metrology and Characterization to Enable Area Selective Deposition***, **Christophe Vallee**, M Bonvalot, B Pelissier, J Tortai, S David, S belahcen, V Pesce, M Jaffal, A Bsiesy,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; R Gassilloud, N Posseme,* CEA-LETI, France*; T Grehl, P Bruner,* IONTOF GmbH, Germany*; A Uedono,* University of Tsukuba, Japan

Innovation in materials, architectures (3D), gap filling technologies, lithography and etch processes are mandatory at every node of CMOS or memory devices. These challenging integration issues can be facilitated by the use of an integration scheme currently being intensively investigated known as area selective deposition (ASD). Criteria for an adequate area selective deposition process are: growth only on specific regions, high throughput compatible with industrial demands, no so-called mushroom profiles into adjacent features as well as no nuclei defectivity on undesired sites. Several routes can be developed to achieve an ASD process with ALD. The one discussed here concerns the deposition/etch approach which takes benefit from an *in situ* etching step inserted in a standard ALD cycle [1]. By incorporation of anisotropic or isotropic etching steps in the ALD process, “surface” selective deposition, as well as topographically selective deposition (TSD) have been obtained [2, 3]. The major current shortcoming of this approach lies in the deep insight which is required regarding elementary atomic-scale reaction mechanisms. Indeed, in the case of an ALD/ALE Area Selective Deposition process, a highly precise control of etching and its selectivity at the atomic scale is needed. Controlling the nature and density of defects induced by etching or passivation steps and understanding their impact on the physical and electrical properties of selectively deposited films are of course also required. Moreover, in order to optimize these processes, an accurate understanding of the underlying reasons why passivation after a low number of ALD cycles, is no more effective. Thus, *in situ* as well as *ex situ* monitoring and metrology are mandatory.

In this presentation, we will discuss how to optimize and understand atomic-scale reaction mechanisms in an ALD/ALE ASD process using combined *in situ* or *ex situ* measurements, such as ellipsometry, XPS, XRR, LEIS, FIB-STEM, and positron annihilation. We will show that when crosslinked, these technics are very effective to perform atomic scale metrology and characterization. As an example, we will discuss F atom localization and density in selectively deposited oxides thanks to a F-based ALE chemistry incorporated in the ALD process. In the case of a topographically selective deposition (TSD) process attempts will be presented to understand ion/surface interactions when low energetic ions are extracted from the plasma of the PEALD reactor both during deposition and plasma-ALE steps.

[1] R. Vallat et al, JVSTA **35** (2017) 01B104

[2] R. Vallat et al, JVSTA **37** (2019) 020918

[3] A. Chacker et al, APL **114** (2019)

5:20pm **AP+EL+MS+PS+SS+TF-TuA-10 Recent Progress in Thin Film Conformality Analysis with Microscopic Lateral High-aspect-ratio Test Structures***, **Riikka Puurunen**,* Aalto University, Finland **INVITED**

Conformal thin films which cover complex 3D shapes with a film of uniform properties (thickness, composition, etc.) are increasingly demanded applications such as semiconductor devices, microelectromechanical systems, energy conversion/storage and catalysis. Atomic layer deposition (ALD) and its counterpart atomic layer etching (ALE) [together known as atomic layer processing (ALP)], are increasing in usage largely thanks to their known conformal character.

A question that needs to be asked in the R&D of 3D applications using conformal ALD/ALE processes is: how conformal is conformal; is the conformality sufficient to meet the specs? In semicon industry, vertical vias and cross-sectional transmission electron microscopy (TEM) are standardly used for conformality analysis. Recently, microscopic lateral high-aspect-ratio (LHAR) test structures have been developed to improve the conformality analytics capabilities. LHAR structures e.g. enable detailed conformality analysis at arbitrarily high aspect ratios (e.g., >5000:1), where no film can coat the 3D structure fully, thereby exposing the saturation

profile characteristic for the process. This, in turn enables the kinetic analysis of the process and e.g. extraction of the sticking coefficients related to the growth reactions.

This invited talk will address recent progress related to the fabrication and the use of microscopic LHAR conformality test structures. After the breakthrough with the first prototypes (PillarHall LHAR1; Gao et al. 2015, Mattinen et al. 2016; reviewed in Cremers et al., 2019), third and fourth generation prototypes have been developed (PillarHall LHAR3 and LHAR4). This work will review the conformality analysis progress enabled by the microscopic LHAR structures and discuss the benefits and challenges of this approach. Recent published progress includes the conformality modelling by Ylilammi et al. (2018) and experimental extraction of sticking coefficient by Arts et al. (2019). In addition, several other ongoing conformality analysis cases will be presented.

References

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Ylilammi, Ylivaara, Puurunen, J. Appl. Phys. 123, 205301 (2018); https://doi.org/10.1063/1.5028178

6:00pm **AP+EL+MS+PS+SS+TF-TuA-12 *In operando*XPS Study on Atomic Layer Etching of Fe and Co Using $Cl_2$and Acetylacetone or Hexafluoroacetylacetone***, Zijian Wang**, O Melton, D Angel, B Yuan, R Opila,* University of Delaware

Etching of transition metals is one of the major challenges in magnetoresistive random-access memory (MRAM) device fabrication. In this work, atomic layer etching of iron and cobalt surfaces with halogen and an organic molecule was studied. We successfully performed etching of Fe and Co thin films via forming volatile metal complexes at low temperature with cyclic sequential reactions of Cl_2 and acetylacetone (acac) or hexafluoroacetylacetone (hfac) . The etching reaction mechanism of acac and hfac reacting with Clorine-modified Fe and Co surfaces was investigated: the surface was first activated with Cl_2 gas, and subsequently, the top layer of chlorinated metal was removed by reaction with a diketone (acac/hfac). The extent of Cl_2 reaction determines the etching rate of the metal. At substrate temperatures lower than 135°C, acac could remove the chlorinated Fe metal layer from Fe surfaces, but not chlorinated Co from Co surfaces. *In-operando* x-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) simulation shows that the reaction of acac or hfac with Chlorinated Fe or Co surfaces is likely following a complex reaction pathway instead of simple diketone substitution for the metal chloride. Diketone decomposition may play an important role in the etching process.

Spectroscopic Ellipsometry Focus Topic
Room A212 - Session EL+AS+EM+TF-WeM

Optical Characterization of Thin Films and Nanostructures

Moderators: Eva Bittrich, Leibniz Institute of Polymer Research Dresden, Tino Hofmann, University of North Carolina at Charlotte

8:00am **EL+AS+EM+TF-WeM-1 Enhanced Strong Near Band Edge Emission from Lanththanide Doped Sputter Deposited ZnO***, C Heng,* Beijing Institutute of Technology, China*; W Xiang, T Wang,* Beijing Institutete of Technology, China*; W Su,* Beijing Instititute of Technology, China*; P Yin,* Beihang University, China*; **Terje G Finstad,*** University of Oslo, Norway

Research on ZnO films and nanostructures have increased steadily in the last decades being motivated by many applications including photonic applications. Incorporation of rare earth (RE) elements for the purpose utilize transition therein for conversion or manipulation of the wavelength spectrum. That was also our original motivation, however we observed the REs also can provide an enhancement of near band gap emission,NBE. This has been observed for Tb, Ce, Yb and Eu. The ZnO films were co-sputtered with RE elements onto Si wafers in an Ar+O_2 ambient yielding oxygen rich films as observed by RBS and XPS. The films were annealed in an N_2 ambient for various temperatures from 600 to 1100 °C. The luminescence behavior was studied emission and excitation spectroscopy as well luminescence decay measurements. Both undoped and RE doped films showed a large increase in emission with increasing annealing temperature, while the increase was largest for the RE doped samples. The crystallinity and microstructure of the films were studied by XPS, SEM, XRD and HRTEM. It is observed that the increase in UV NBE is correlated with crystalline improvements of ZnO. At the temperature for maximum PL emission intensity there is silicate formation due to interaction with the substrate. The maximum occurs for an annealing temperature where not all the ZnO has been consumed in the silicate reaction. This maximum appears to be 1100 °C for the thicker films and 1000 °C for thinner films. For samples having maximum NBE there seem to be random lasing occurring indicated by the intensity dependence of UV PL emission. A hypothesis for the main reason behind the increase in NBE intensity with RE doping is that the RE ions influence the film structure during nucleation early in the deposition process by influencing the mobility of atoms. The initial grain structure will have an affect on the development grain structure for the whole film and an influence on the grain growth. This influences the presence of non-radiative defect centers in the film and the grain surface and grain boundaries. As a side effect, we observe that there is very little transfer of excitation energy to the RE ions. This supports the notion that oxygen deficient centers may be necessary to have efficient energy transfer to RE ions in ZnO. Finally we remark that strong UV light from ZnO films have been sought particularly because they could offer a low temperature production for some application. The present method is still a high temperature method, but it is very simple and can be directly combined with Si technology which can be advantage for certain applications.

8:20am **EL+AS+EM+TF-WeM-2 Ellipsometry Study of PLD based Temperature Controlled Thin Film Depositions of CdSe on ITO Substrates***, **Flavia Inbanathan,*** Ohio University*; M Ebdah,* King Saud University, Kingdom of Saudi Arabia*; P Kumar,* Gurukula Kangri Vishwavidyalaya, India*; K Dasari,* Texas State University*; R Katiyar,* University of Puerto Rico*; W Jadwisienczak,* Ohio University

Cadmium Selenide(CdSe), a n-type semiconductor with a direct bandgap of 1.73eV has been explored widely for its suitability in various applications including photovoltaics and optoelectronics, because of its optical and electrical properties. The literature presents various deposition methods for CdSe thin films out of which this work is based on pulsed laser deposition(PLD)[1]. The optoelectronic applications of CdSe thin films depend on their structural and electronic properties that depends on deposition and process parameters[2]. The stability of the thin films at various temperatures is an important factor to improve the efficiency and durability of photosensitive devices. The present work aims to fabricate the high quality CdSe thin films using PLD method and affirms the optimal deposition temperature at 250°C as validated by the films surface roughness and ellipsometry studies[3][4]. The effect of different *in-situ* deposition temperature on structural, morphological and optical properties through XRD, AFM, SEM, optical absorption/transmission and ellipsometry spectroscopy have been investigated. CdSe thin films with thickness close to 200nm were deposited on the Indium Tin Oxide (ITO) coated glass substrates at temperatures ranging from 150 to 400°C. The light absorption spectrum analysis of all the CdSe films confirmed well defined direct energy band gap from 2.03 to 1.83eV. The ITO substrate is modelled using a two sub-layers model that consists of 130nm graded ITO on top of a 0.7mm bulk ITO layer, and the experimental ellipsometry spectra agreed very well with the fitting spectra. The ellipsometry study confirmed that CdSe thin films show an increase of 44% in refractive index(*n*) in the violet spectrum, and a constant value in blue-yellow spectral range but with significant changes in red spectrum for increase in temperature upto 350°C; beyond which resulted in constant value, possibly due to the stagnation in the grain growth. The extinction coefficient(*k*) value of CdSe approaches zero in the red spectrum region for 150°C and 300°C temperatures whereas it showed a value of 0.25 and 0.7 for 250°C and 400°C temperatures, respectively. The peaks observed around 650nm and 750nm in ellipsometry spectra are assigned to excitonic transitions. The collected data will be critically analysed in terms of CdSe optical properties engineered for optoelectronic and photovoltaic applications.

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8:40am **EL+AS+EM+TF-WeM-3 The Application of Mueller Matrix Spectroscopic Ellipsometry to Scatterometry Measurement of Feature Dimension and Shape for Integrated Circuit Structures***, **Alain C. Diebold,*** SUNY Polytechnic Institute **INVITED**

One of the most difficult measurement challenges is non-destructively determining the feature dimensions and shape for complicated 3D structures. This presentation will review Mueller Matrix Spectroscopic Ellipsometry based scatterometry which uses the Rigorous Coupled Wave Approximation (RCWA) to solve Maxwell's equations for a model structure and the resulting Mueller Matrix elements are compared to experimental results. Here we use the structures used in GAA transistors fabrication as an example of challenging measurements.(1, 2, 3) In this talk, we present simulations aimed at understanding the sensitivity to changes in feature shape and dimension for the structures used to fabricate GAA transistors. Simulations of the multi-layer fins show a clear sensitivity to fin shape and Si layer thickness which is enhanced by the use of the full Mueller Matrix capability vs traditional spectroscopic ellipsometry. We also discuss experimental measurement of nanowire test structure demonstrating the ability to measure the etching of mutiple sub-surface features. [3]

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9:20am **EL+AS+EM+TF-WeM-5 Optical Constants and Thickness of Ultrathin Thermally Evaporated Iron Films***, **Nick Allen**, D Shah, R Vanfleet, M Linford, R Davis,* Brigham Young University

Carbon nanotube templated microfabrication (CNT-M) is a technique that uses a patterned iron catalyst to grow 3-D structures for device applications. Iron catalyst thickness strongly affects carbon nanotube (CNT) growth heights and the straightness of the CNT-M structures. Atomic force microscopy has been used to directly measure the thicknesses of such iron/iron oxide films, but this technique is slow and not easily scalable. A faster method is ellipsometry, but for very thin films, the optical constants and thickness are not easily separated, thus standard ellipsometry approaches are inadequate. The 2-6 nm thick iron films used as CNT growth catalysts are in this challenging region. The absorptive nature of the iron/iron oxide films adds further difficulty. In this study, a multi-sample ellipsometry analysis using iron films of various thicknesses was performed to obtain the optical constants of thermally evaporated iron. We used

contrast enhancement by incorporating a silicon dioxide layer under the film being analyzed to enhance sensitivity to the optical constants.

9:40am **EL+AS+EM+TF-WeM-6 Birefringent Photonic Crystals for Polarization-discriminatingInfrared Focal Plane Arrays**, ***Marc Lata**, Y Li, S Park, M McLamb, T Hofmann,* University of North Carolina at Charlotte

Infrared optical materials fabricated using direct laser writing have received substantial interest since the emergence

of this technology which is based on the two-photon polymerization of suitable monomers [1, 2]. We have

demonstrated that direct laser writing allows the fabrication of structured surfaces to reduce Fresnel reflection

loss in the infrared spectral range while two-dimensional photonic crystals enable optical filters with high spectral

contrast [3, 4]. In combination with the ability to fabricate large scale arrays of uniform structures, two-photon

polymerization could be a disruptive technology for enhancing focal plane arrays in IR imaging systems.

So far, photonic crystals which provide polarization selectivity have not been used for the pixel-based enhancement

of infrared focal plane arrays. Here we explore the form-birefringence found in photonic crystals composed

of arrays of subwavelength-sized slanted micro wires (Fig. 1) for this purpose. The photonic crystals investigated

here were fabricated in a single fabrication step using direct laser writing of an infrared transparent photoresist.

The lateral dimensions of the photonic crystals are comparable to the pixel size of infrared focal plane arrays which

is on the order of some tens of micrometers [5]. We observe a strong contrast under cross-polarized illumination

in the mid-infrared spectral range at w = 1550 cm-1. Finite-element-based techniques are used to optimized the

geometry of the constituents of the photonic crystals to minimize edge effects. We envision laser direct writing as

a suitable technique for the enhancement of focal plane arrays to enable focal-plane polarimeters for the infrared

spectral range.

11:00am **EL+AS+EM+TF-WeM-10 Relevance of hidden Valleys in the Dequenching of Room-temperature-emitting Ge Layers**, *T Sakamoto, Y Yasutake,* University of Tokyo, Japan; *J Kanasaki,* Osaka City University, Japan; ***Susumu Fukatsu**,* University of Tokyo, Japan

Ge offers a unique advantage of gaining a deeper insight into the intervalley coupling of *hot* electrons [1], which is arguably of importance in the context of controlling the optoelectronic and photonic functionalities [2]. In view of the complicated valley degeneracy in the near-band-edge region, such intervalley coupling of electrons plays a pivotal part even when strain-engineering pseudomorphic Ge-based quantum structures.

The capability of direct-gap emission at room temperature is of considerable practical significance of Ge, for which an added advantage is that emission wavelengths fortuitously fall within the telecom bands. Moreover, Ge is particularly interesting from the device physics point of view as it outperforms many semiconductor allies in the sense that thermal *dequenching* occurs near room-temperature: the emitted light intensity increases with increasing temperature, which is convenient but nevertheless logic-defying.

Such a rather counterintuitive “thermal roll-up”, as opposed to thermal roll-off which is usually more relevant, has been interpreted in terms of two-level electron kinetics assuming local thermal equilibrium; long-lived electrons populating the indirect conduction-band bottom, i.e., L-valleys, are excited up into the direct-gap Γ-valley by absorbing phonons, which seems to fit a fairly standard phenomenological picture reasonably well. To the contrary, this model system fails in the case of Ge layers, the quality of crystallinity of which is compromised because of a low growth temperature. In fact, they only show steady thermal roll-off, viz. *quenching*, without a trace of the anticipated dequenching.

These apparently conflicting observations can be reconciled only by considering another otherwise invisible *hidden* conduction-band valley that comes in between the L andΓ valleys to decouple them. A three-level scheme is naturally invoked thereby. Indeed, it explains not only the missing dequenching but the lost local thermal equilibrium in low-quality layers. As a proof of such a conjecture, an attempt was made to directly capture the *hidden* valleys by means of time- and angle-resolved two-photon photoemission [3]. Preliminary results indicate the relevance of X(Δ)-valleys, which are slightly above the Γ-valley, in the dequenching of room-temperature emission as a result of ultrafast coupling of L-X(Δ)-Γ valleys by phonons taking up large crystal momenta. These are consistent with theory and luminescence study.

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11:20am **EL+AS+EM+TF-WeM-11 Spectroscopic Ellipsometry on Organic Thin Films - From in-situ Bio-sensing to Active Layers for Organic Solar Cells**, ***Eva Bittrich**, P Uhlmann, K Eichhorn,* Leibniz Institute of Polymer Research Dresden, Germany; *M Schubert,* University of Nebraska-Lincoln, Linköping University, Sweden, Leibniz Institute of Polymer Research Dresden, Germany; *M Levichkova, K Walzer,* Heliatek GmbH, Germany **INVITED**

Nanostructured surfaces and thin films of small organic molecules, polymers or hybrid materials are promising interfaces for versatile applications like sensing, water purification, nanoelectronics, energy production and energy storage devices. Ellipsometry, as non-invasive method, is well suited to contribute to the understanding of structure – property – relationships in organic thin films, but can also act as probing technique for hybrid sensing elements. Aspects from our research ranging from switchable responsive polymer brush interfaces for biosensing to thin films of small organic molecules for organic solar cells will be presented. On the one hand, swelling of polymer brushes grafted to slanted columnar thin films of silicon will be visualized by anisotropic optical contrast microscopy, as an example for a new class of hybrid sensing materials with unique sensitivity on the nanoscale. On the other hand the effect of template molecules on the morphology and optical properties of semiconducting thin films will be discussed, emphasizing the correlation of ellipsometric data with structural analysis by grazing incidence wide angle X-ray scattering (GIWAXS).

12:00pm **EL+AS+EM+TF-WeM-13 Optical Dielectric Function of Si(bzimpy)2 – A Hexacoordinate Silicon Pincer Complex Determined by Spectroscopic Ellipsometry**, ***Yanzeng Li**, M Kocherga, S Park, M Lata, M McLamb, G Boreman, T Schmedake, T Hofmann,* University of North Carolina at Charlotte

Tang and VanSlyke demonstrated light emission from the first practical electroluminescent device based on a double-organic-layer structure of tris(8-hydroxyquinoline)aluminum, Alq_3, and a diamine film in the late 80's. Since then, organic light emitting diodes (OLED) based on metal chelates such as Alq3 have been widely studied. Despite the widespread use of Alq_3, there has been a broad search for new materials with improved properties, in particular, with respect to their chemical and electrochemical stability. We have recently reported on the successful synthesis of a neutral, hexacoordinate silicon-based fluorescent complex $Si(bzimpy)_2$. Our results indicate that $Si(bzimpy)_2$ exhibits inherent advantages such as the tunability of the luminescence in the visible spectrum, greater thermal stability, and high charge mobility that is comparable to that of Alq_3. Despite the successful synthesis and encouraging electroluminescence at 560 nm the complex dielectric function of the water stable complex has not been reported yet. Here we present spectroscopic ellipsometry data which were obtained from a Si(bzimpy)2 thin-film in the spectral range from 300~nm to 1900~nm. A parameterized model dielectric function composed of a Tauc-Lorentz and Gaussian oscillators is employed to analyze the experimental ellipsometry data. We find a good agreement between the critical point energies observed experimentally and our density functional theory calculations reported recently.

Spectroscopic Ellipsometry Focus Topic
Room A212 - Session EL+EM-WeA

Spectroscopic Ellipsometry: Novel Applications and Theoretical Approaches

Moderators: Vanya Darakchieva, Linkoping University, Sweden, Nikolas Podraza, University of Toledo

2:20pm **EL+EM-WeA-1 Optical Hall Effect in the Multi-valley Semiconductor Te-doped GaSb*, Farzin Abadizaman*,** *C Emminger,* New Mexico State University*; S Knight,* University of Nebraska-Lincoln*; M Schubert,* University of Nebraska-Lincoln, Linköping University, Sweden, Leibniz Institute of Polymer Research Dresden, Germany*; S Zollner,* New Mexico State University

The authors conducted optical Hall effect (OHE) measurements on Te-doped GaSb (n-type) at room temperature in the far-infrared between 30 cm^{-1} and 700 cm^{-1} at magnetic fields of ±7 T and 0 T. The measurements were performed at an angle of incidence of 45̊ and a resolution of 2 cm^{-1}. The complex dielectric functions and Mueller Matrix (MM) elements were determined from spectroscopic ellipsometry at 0 T in the range of 300 cm^{-1} to 8000 cm^{-1} using an FTIR-VASE ellipsometer and from 30 cm^{-1} to 700 cm^{-1} using the FIR ellipsometer. Using a sum of a Lorentzian oscillator and two Drude terms, the experimental data at zero magnetic field were modeled. From the Lorentzian term, we found the transverse optical (TO) phonon energy at 226 cm^{-1} and the longitudinal optical (LO) phonon energy at 237 cm^{-1}.

Although GaSb is a direct band gap semiconductor, a calculation of the electron concentration indicates that at T = 300 K and a total electron density below 10^{18} cm^{-3}, the majority of carriers are located at the L-valley (67%) while the Γ-valley contains only 33% of the carriers. This implies that in the absence of the magnetic field, two Drude terms are needed to model the data. The surfaces of constant energy at the L-point in the Brillouin zone form eight half-ellipsoids at L, which are characterized by their anisotropic masses. However, due to the symmetry, the valleys at this point are two by two equivalent, which leads to the total number of four valleys. In the absence of a magnetic field, the contribution of all eight half-ellipsoids in the L-valley is reduced to only one Drude term, where the effective mass is the harmonic average of the transverse and longitudinal masses. As the magnetic field is turned on, each ellipsoid contributes to the anisotropic dielectric tensor, which, depending on the effective mass tensor, contributes differently to the total dielectric tensor. Therefore, in the presence of a magnetic field, the data is modeled by the sum of a Lorentzian, a Drude tensor at the Γ-valley and four Drude tensors at the L-valley.

2:40pm **EL+EM-WeA-2 Study of the Temperature-dependent Optical Constants of Noble Metals based on High Temperature Spectroscopic Ellipsometry*, Jiamin Liu*,** *H Jiang, S Liu,* Huazhong University of Science and Technology, China

Noble metals have been widely used in thermo-plasmonics field, such as thermo- photovoltaics, heat-assisted magnetic recording and photothermal therapy, thus studying the temperature-dependent optical constants of these metals are crucial for both understanding the temperature effects on optical properties and providing essential data for the plasmonic simulations.

In this work, a high temperature spectroscopic ellipsometry covering the spectral range of 200-1000nm has been built, which is able to measure the ellipsometric parameters of samples when temperature is varying from 300K to 1200K. The noble metallic samples are heated at a mixing atmosphere of 5% H_2 and 95% Ar to avoid the possible thermal oxidation. An oscillator- parametrization regression method based on the Drude-dual-TaucLorentz-Lorentz model and the B-spline model has been proposed to determine the optical constants and the roughness of the heated noble metals. Both the optical constants and the electronics parameters of noble metals heated below 900K have a temperature-dependency similar to the recently reported results. Taking the gold film as an example, the DC resistivity is increasing from 2.273×10^{-6} to $2.414\times10^{-6}\Omega\cdot cm$ with the temperature increasing from 300K to 800K, while the electron relaxation time is decreasing from 20.787 to 9.021fs. Additionally, it has been noticed the first absorption peak near 2.7eV first increases and then decreases, while the second absorption peak near 3.7eV shows the opposite characteristics with the temperature increasing from 300K to 800K. Besides, the optical constants of Au film heated above 900K has some similarities to that of SnTe, which might be caused by the combined effect from the possible formation of Au-Si binary phase and the possible transition of vertical columnar grains to granular grains.

3:00pm **EL+EM-WeA-3 Optical Monitor for the Attitude Tracking using Polarimetry*, Song Zhang*,** *H Gu, H Jiang, S Liu,* Huazhong University of Science and Technology, China

The attitude angles are important parameters describing the motion of the object. In the fields of precision manufacturing, robotics control, navigation of the aircraft, the accurate and real-time measurements of the attitude angles (yaw angle, pitch angle and roll angle) are very important. Due the advantages of non-contact, low cost, non-destructive and high precision, the optical methods have been popular used for measuring the attitude of the object.

In our work, we present a novel optical monitor for the attitude tracking. The proposed method utilizes the principle that polarized light incident in different directions into the birefringent crystals can produce different phase modulations. Then, the attitude angle of the object attached with a birefringent crystal can be obtained by measuring the phase change. The optical monitor is based on the division-of-amplitude polarimetry with a time resolution of several nanoseconds, which is capable of monitoring the changes in all the attitude angles simultaneously. In order to verify the correctness and the performance of the optical monitor, we performed real-time measurement experiments on the attitude angles of a zero-order quarter-wave plate and a multi-order half-wave plate. The roll angle is continuously changed within the range of 0 ~ 360°, while the pitch angle and yaw angle are varied within ±7° and ±40° respectively. The results show that not only the attitude angles, but also the angular velocities and the accelerations of the roll angle, can be extracted, and the errors of all attitude angles is less than 0.5°.

3:20pm **EL+EM-WeA-4 New Progress on the Channeled Spectroscopic Ellipsometry and its Applications*, Gai Chin,*** ULVAC Inc., Japan

This presentation describes a novel method for the spectroscopic measurement of the state of polarization of light. A pair of thick birefringent retarders is incorporated into the spectroscopic polarimeter, so the generated channeled spectrum is composed of three quasi-cosinusoidal components carrying the information about the state of polarization of the light that is being measured. Fourier inversion of the channeled spectrum provides the significant parameters for determination of the spectrally resolved Stokes parameters of light. No mechanical movable components for polarization control or active devices for polarization modulation are used, and all the Stokes parameters can be determined at once from only the single spectrum.

The channeled spectroscopic ellipsometry is a snapshot method for the spectrally-resolved polarization analysis. A pair of high-order retarders are utilized to generate a channeled spectrum carrying information about the wavelength-dependent multiple parameters of polarization of light. This method has a feature that it requires no mechanical or active components for polarization-control, such as a rotating compensator and electro-optic modulator.

This novel spectroscopic ellipsometry can measure the thickness and optical constants of thin films at a dramatically fast speed. Its data acquisition time is as short as 10ms. It does not require any active components for polarization-control, such as a rotating compensator or an electro-optical modulator.

It created great opportunities for new applications of the spectroscopic ellipsometry in which the compactness, the simplicity and the rapid response are extremely important. It can be integrated into the deposition tool and successfully measured thin films in-situ and ex-situ. Obviously, those from PVD, CVD and ALD are some promising applications for this novel spectroscopic ellipsometry.

This presentation describes our new progress on some key technologies for enhancing the performance of this channeled spectroscopic ellipsometry by system configuration, data analysis and other creative efforts on developing a series of new high-speed spectroscopic ellipsometers. Some novel applications will be also introduced, such as the PVD, CVD, ALD, EUV, OLED, MEMS and some excellent measurement data of thin films from the semiconductor, flat panel display and other industries.

4:20pm **EL+EM-WeA-7 The Physics of Low Symmetry Metal Oxides: Applications of Ellipsometry***, **Alyssa Mock**,* U.S. Naval Research Laboratory*; S Knight, M Hilfiker,* University of Nebraska-Lincoln*; V Darakchieva, A Papamichail,* Linkoping University, Sweden*; R Korlacki,* University of Nebraska-Lincoln*; M Tadjer,* U.S. Naval Research Laboratory*; Z Galazka, G Wagner,* Leibniz-Institut für Kristallzüchtung, Germany*; N Blumenschein,* North Carolina State University*; A Kuramata,* Novel Crystal Technology, Inc., Japan*; K Goto, H Murakami, Y Kumagai,* Tokyo University of Agriculture and Technology, Japan*; M Higashiwaki,* National Institute of Information and Communications Technology, Japan*; A Mauze, Y Zhang, J Speck,* University of California Santa Barbara*; M Schubert,* University of Nebraska-Lincoln, Linköping University, Sweden, Leibniz Institute of Polymer Research Dresden, Germany **INVITED**

We discuss the analysis of the dielectric function tensor for monoclinic metal oxides obtained from generalized spectroscopic ellipsometry. We investigate the potential high-power device material gallium oxide and derive dispersions of transverse, longitudinal and plasmon coupled modes [M. Schubert *et al*., Phys. Rev. B 93, 125209 (1-18) (2016); Editors' Suggestion] and the band-to-band transitions and excitons along with their eigenvectors [A. Mock *et al*., Phys. Rev. B 96, 245205 (1-12) (2017)]. Additionally, we show that this technique can fully explain the unusual ordering of optical phonon mode pairs which is observed in beta-Ga2O3 [M. Schubert, A. Mock et al. Phys. Rev. B 99, 041201(R) (2019)] as well as their dependency on free charge carrier concentrations. [M. Schubert, A. Mock et al. Appl. Phys. Lett. 114, 102102 (2019) – Editor's Pick]. We apply this technique also for the identification of transverse and longitudinal phonons in scintillator material cadmium tungstate [A. Mock *et al*., Phys. Rev. B 95, 165202 (1-15) (2017)], and then further extend our methodology for analysis of the dielectric and inverse dielectric tensor for transverse and longitudinal phonon mode dispersion characterization in high-power laser material yttrium orthosilicate [A. Mock *et al*., Phys. Rev. B, 97 165203 (1-17) (2018)].

We apply our technique to investigate the effective electron mass tensor using optical Hall effect measurements [S. Knight, A. Mock *et al*., Appl. Phys. Lett. 112, 012103 (2018); Editors' Pick], the temperature dependence of band-to-band transitions energies [A. Mock *et al*., Appl. Phys. Lett. 112, 041905 (2018)], and the effects of aluminum alloying concentration onto the band-to-band transition energies [M. Hilfiker, A. Mock *et al.* Appl. Phys. Lett. (Under Review)]. We further apply our technique to epitaxial layers of beta-phase gallium oxide and discuss the relationship between the X-ray diffraction measured strains with respect to the optically determined shifts in transverse optical phonon modes as compared to the bulk material. Understanding of the stress and strain relationship to properties in monoclinic materials will help facilitate better control of material properties for engineering next generation power devices based on beta-Ga2O3.

5:00pm **EL+EM-WeA-9 Terahertz Dielectric Anisotropy in Randomly Distributed, Spatially Coherent Polymethacrylate Microwire Arrays Fabricated by Stereolithography***, **Serang Park**,* University of North Carolina at Charlotte*; Y Li,* University Of North Carolina at Charlotte*; S Lee,* Harris Corp.*; S Schöche, C Herzinger,* J.A. Woollam Co., Inc.*; T Hofmann,* University Of North Carolina at Charlotte

Fabricating terahertz (THz) optical components with tailored dielectric properties including scalable anisotropies via additive manufacturing is drawing substantial interest as it potentially offers a rapid, low-cost pathway for THz optical system development. Metamaterials composed of slanted columnar structures have been reported to exhibit anisotropic behaviors at THz frequencies, which may allow the design of novel optical components including filters and sensors for the THz frequency range. Here, we report on the anisotropic THz-optical response of stereolithographically fabricated polymethacrylate slanted columnar layers. The samples are composed of randomly distributed, spatially coherent polymethacrylate wires with a diameter of 100 µm and a length of 700 µm, which are tilted by 45° with respect to the surface normal of the substrate. Generalized spectroscopic ellipsometry is employed to obtain Mueller matrix spectra of these samples in the range from 210 to 350 GHz. A simple biaxial (orthorhombic) layer homogenization approach is used to analyze the THz Mueller matrix data obtained at different azimuthal orientations. Our observations confirm that randomly distributed, spatially coherent polymethacrylate wire arrays exhibit a strong anisotropic response. In conclusion, stereolithographic fabrication is introduced as an effective tool for fabricating metamaterials with anisotropic THz-optical properties.

5:20pm **EL+EM-WeA-10 Ultrafast Dynamics of Ge, InP and Si Proved by Time-Resolved Ellipsometry***, **Shirly Espinoza**, S Richter, M Rebarz,* Institute of Physics, Academy of Sciences of the Czech Republic, Czechia*; O Herrfurth, R Schmidt,* Universität Leipzig, Felix-Bloch-Institut für Festkörperphysik, Germany*; J Andreasson,* Institute of Physics, Academy of Sciences of the Czech Republic, Czechia*; S Zollner,* New Mexico State University

Recent developments in time-resolved ellipsometry allow us to study the ultrafast behavior of single crystals of undoped Ge, InP and Si at room temperature after carriers have been excited by an ultrashort laser pulse of 1.55 eV. Information about the dynamic processes such as scattering mechanisms of the hot charge carriers and electron-phonon coupling was obtained.

With a resolution of 120 fs, and a time scale from femtoseconds to nanoseconds, the observed changes are bigger in Ge than in the other materials. Our results are in agreement with theoretical and experimental work done some years ago on the dynamics of germanium studied by time-resolved ellipsometry [1,2]. The result of our experiments could go deeper into the details of the dynamics thanks to the development of the time-resolved experimental setup using state of the art technology in the fields of ultrafast lasers, electronics, and optics.

Our current spectral range is from 1.7 to 3.5 eV. The generated carrier density is on the order of 10^{20} cm^{-3}, which allows us to compare the results with published data on doped materials [3].

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5:40pm **EL+EM-WeA-11 Optical Properties of Organic-Inorganic Lead Halide Perovskite Thin Films for Photovoltaics***, **Biwas Subedi**, M Junda, K Ghimire, N Podraza,* University of Toledo

Organic-inorganic lead halide perovskite based photovoltaics (PV) exhibit high initial efficiency, can be solution processed with potentially low material costs, and material band gaps can be tuned by composition. Unfortunately, these perovskites exhibit degradation upon exposure to atmosphere, light, and heat. Spectroscopic ellipsometry over the near infrared to ultraviolet range (0.73-5.9 eV) has been applied to characterize the complex optical response of solution processed ABX_3 (*A*: methylammonium—MA, formamidinium—FA, Cs; *B*: Pb, Sn; *X*: I, Br, Cl) perovskite thin films of different compositions. A parametric optical property model has been developed which includes contributions from electronic transitions above the band gap, the direct band gap, an exponentially decaying Urbach tail, and sub-gap absorption due to defect states. Using this model, above gap critical points, band gap energies, and sub-gap absorption are compared primarily as functions of *A*- and *B*-cation compositions for thin films. In situ, real time spectroscopic ellipsometry (RTSE) of perovskite films undergoing degradation induced by controlled relative humidity is used to track optical properties changes, particularly with respect to sub-gap absorption, and morphology changes occurring at the substrate / film and film / ambient interfaces. These optical property and morphology changes are tracked by RTSE for perovskite thin films of different compositions. Optical properties characterized by spectroscopic ellipsometry are used as input for external quantum efficiency (EQE) simulations of perovskite based PV devices. Comparisons between simulated and measured EQE spectra are used to identify differences in perovskite characteristics arising from the complete solar cell device fabrication process.

6:00pm **EL+EM-WeA-12 Optical Constants of Ni at 300 K from 0.03 to 6.0 eV***, **Stefan Zollner**, F Abadizaman,* New Mexico State University

The optical constants of single-crystalline, polycrystalline, and thin films of Ni from 0.06 to 6 eV are determined from spectroscopic ellipsometry at an angle of incidence of 70̊. The experimental data are analyzed using three alternative methods. In the first method, the dielectric function is written as a sum of Lorentz and Drude oscillators. The second method writes the dielectric function as a product of these oscillators (Kukharskii product). In the third method, a Drude model with frequency dependent scattering rate

and plasma frequency is used. We used two Drude terms in the sum model to account for d- and s-electrons. The plasma frequencies were found to be 11.9 eV and 4.86 eV for d- and s-electrons, respectively, leading to a DC conductivity of about 80,000 (1/Ωcm) at 300 K, compared to the electrical DC conductivity of 143,000 (1/Ωcm) reported previously. Furthermore, the model reveals a very large free-electron contribution to the optical constants of Ni, which disproves earlier claims about their insignificance. We also employ graphical techniques to find the plasma frequencies and free-electron scattering rates, which agree well with the parameters found from the first and the second methods.

To prepare clean samples and reduce the thickness of the overlayers, the samples were maintained in ultrahigh vacuum at a temperature of 750 K for 6 hours and then cooled down overnight. A surface roughness thickness of 1-3 nm was found using atomic force microscopy and x-ray reflectivity.

Spectroscopic Ellipsometry Focus Topic
Room A215 - Session EL-ThA

Spectroscopic Ellipsometry Late New Session
Moderator: Tino Hofmann, University of North Carolina at Charlotte

5:00pm **EL-ThA-9 Far-infrared Dielectric Functions of $Hg_{1-x}Cd_xSe$ Thin Films Determined via Ellipsometry and Reflectivity**, ***Frank Peiris***, *J Lyons,* Kenyon College; *G Brill,* U.S. Army Research Laboratory

The dielectric functions of molecular beam epitaxy-grown $Hg_{1-x}Cd_xSe$ thin films were determined using a combination of ellipsometry and reflectivity. While we have reported the dielectric functions for this alloy system above 400 cm^{-1}, in the present study, by incorporating reflectivity measurements, we are able to recover the dielectric functions in a much wider spectral region (i.e., 85 cm^{-1} and 50,000 cm^{-1}). Initially, spectroscopic ellipsometry, performed between 400 cm^{-1} and 8000 cm^{-1}, determined the dielectric function and the thickness of $Hg_{1-x}Cd_xSe$ films. Ellipsometry results were then used to model the reflectivity data, which allowed us to obtain the absolute reflectance values and to map the dielectric function from the reflectivity spectra, obtained between 85 cm^{-1} and 8,000 cm^{-1}. By representing the dielectric function as a collection of classical oscillators, we were able to recover the details of absorption due to free electrons, phonons, and band electrons in the $Hg_{1-x}Cd_xSe$ alloy system. Specifically, our models find two transverse phonon modes for $Hg_{1-x}Cd_xSe$, where the HgSe-like mode blue-shifts and the CdTe-like mode red-shifts with increasing Cd concentration.

5:20pm **EL-ThA-10 Tunable Giant Circular Dichroism in Spatially-coherent Si-Au/Ag Nano-plasmonic Chiral Heterostructures**, ***Ufuk Kilic***, *M Hilfiker,* University of Nebraska-Lincoln; *R Feder,* The Fraunhofer Institute for Microstructure of Materials and Systems (IMWS), Germany; *R Korlacki, E Schubert, C Argyropoulos, M Schubert,* University of Nebraska-Lincoln

The differential absorption of left-and right-handed circularly polarized light so-called circular dichroism (CD) has recently gained enormous interest in optics, chemistry, pharmacology and biotechnology fields. [1] Particularly, the subwavelength scale periodic arrangement of nano-plasmonic structures is predicted to be a facile enhancement method of CD response and offers a great potential for chiral opto-electronics. [2,3]

In this study, by using the ultra-high vacuum, electron beam evaporated glancing angle deposition system, we successfully fabricated optically active, spatially coherent, and highly porous chiral hetero-structures (CHS).

Subsequent and repeated depositions of silicon (Si) and gold (Au)/silver (Ag) lead to nanometer-dimension sub-chiral segments which enables to tailor the circular dichroism induced by size, shape and material choice.

The incorporation of transmission mode Mueller matrix spectroscopic ellipsometry technique with finite element modeling(FEM) provides an excellent framework for optical characterization of this new type plasmonic metamaterials within the spectral range from 0.6 eV to 4.5 eV. We systematically studied the influence of geometrical parameters (such as handedness of the structure (left or right), pitch size, minor and major radius of fabricated CHS, and also number of turns) on CD phenomenon.

Interestingly, Au/Ag sub-chiral segments in CHS result in the emergence of multiple plasmonic modes which can be tunable depending on the Au/Ag-Si ratio in a single turn. In addition, the effects of both azimuthal rotation and angle of incidence on CD are also investigated as a part of this study. According to the FEM calculations, as compared with Si chiral structures, we observed a significant enhancement in the circular dichroism of Si-Au/Ag CHS which can be attributed to plasmonic resonance effect [2]. We also calculated Kuhn's dis-symmetry (g) factor ($g \approx (A_+ - A_-)/(A_+ + A_-)$, where A_-, A_+ are the absorbance coefficients for left and right circularly polarized light, respectively), which is useful for quantitative comparisons of chiro-optical properties of different structures. Unlike the other studies [4,5] which employs periodic nanostructures made up of single type material, we observed a very pronounced g-factor in our fabricated CHSs around 3-4 eV range.

References:

[1] de Dios, Carolina, et al. Optics Express 27.15, 21142-21152, (2019).

[2] Kneer, Luisa M., et al., ACS nano 12.9 :9110-9115(2018).

[3] Hentschel, Mario, et al., Science advances3.5, e1602735, (2017).

[4] Schulz, Matthias, et al., Nature communications 9.1, 2413, (2018).

[5] Lee, Hye-Eun, et al., Nature 556.7701, 360, (2018).

5:40pm **EL-ThA-11 Numerical Ellipsometry: Methods for Selecting Measurements and Techniques for Advanced Analysis Applied to β - Gallium Oxide**, ***Frank Urban,*** Florida International University; *D Barton,* retired; *M Schubert,* University of Nebraska-Lincoln

Ellipsometry is an optical technique through which properties of materials may be determined from measurements of light reflecting from or transmitting through a sample. Usually the measurements require data processing and a key issue is determining which measurements to make. Previously two of us (Urban and Barton)[1] have addressed this for orthorhombic, anisotropic films on substrates and here we treat the case of reflection from a single anisotropic, monoclinic β-Ga_2O_3 crystal which is non-depolarizing and has a smooth, flat surface. Prior work on Ga_2O_3 by one author (Schubert)[2] used a very large dataset containing measurements at each wavenumber for three angles of incidence and 5 azimuth angles for each of 2 crystal orientations. Step 1 in that process was to determine the best-fit permittivity tensor, ε, using Levenberg-Marquardt least squares regression. Here we present methods to determine practically the same ε using a substantially reduced subset of the same data. We exclude measurements which are less useful due to large instrument-reported estimated experimental errors (σ), noise (low intensity), and mathematical insensitivity to the desired solutions. From 10 to 30 numerical solutions to the model equations are found at each wavenumber using the reduced data set as these allow an analysis of measurement accuracy. Solutions are found using each crystal independently. The number of measurements is reduced by a factor of 25 or so depending on the options selected with further reductions expected in future works. Examples using two β-Ga_2O_3 crystals, (010) and (-201) are presented.

1. F.K. Urban III and D. Barton, Thin Solid Films, 663, pp 116-1251, (2018)

2. M. Schubert, R. Korlacki, S. Knight, T. Hofmann, S. Schöche, V. Darakchieva, E. Janzén, B. Monemar, D. Gogova, Q.-T. Thieu et al., Phys.Rev.B 93, 125209 (2016).

Thin Films Division
Room A124-125 - Session TF+AS+EL+PS+RA-ThA

Characterization of Thin Film Processes and Properties
Moderators: Richard Vanfleet, Brigham Young University, Virginia Wheeler, U.S. Naval Research Laboratory

2:20pm **TF+AS+EL+PS+RA-ThA-1 Phase Separation in III-V Semiconductor Thin Films**, ***Mark Twigg***, *N Mahadik, N Kotulak, S Tomasulo, M Yakes,* U.S. Naval Research Laboratory **INVITED**

Phase separation in III-V semiconductor alloys remains a problem that limits the performance of electronic materials. As the first stage in a comprehensive program addressing this issue, we have begun investigating an alloy system in which only the group III elements differ: InGaAs. Lattice-matched InGaAs alloy films were deposited at three temperatures (400, 450, and 500C) by molecular beam epitaxy on a (001) InP substrate.

According to kinetic instability theory, the critical temperature for spinodal phase separation in InGaAs is 814C, a temperature well above the growth temperatures used in this study [1,2]. Dark-field (DF) cross-sectional transmission electron microscopy (XTEM), using the composition sensitive g=002 reflection, was used to determine the amplitude of composition modulations averaged over the thickness of the XTEM sample. The amplitude of composition modulation was found to decrease with increasing growth temperature, yielding values of 0.6, 0.4, and 0.3 atomic percent for the growth temperatures 400, 450, and 500C, respectively, a trend in accord with kinetic instability theory. X-ray reflectivity and 2-dimensional small angle x-ray measurements also indicate that the 400C growth shows significantly greater phase separation than the 450 and 500C growths. Atom probe tomography indicates that the amplitude of composition modulation for the 400C growth is approximately 1 atomic percent, a value that compares favorably with the 0.6 atomic percent measured by DF XTEM.

The range of wavelengths for lateral composition modulation is found to extend from approximately 3 to 30 nm. According to the literature, such wavelengths have been found to depend on growth temperature for a number of III-V semiconductor alloys, in agreement with predictions based on surface diffusion. Measurements of the composition modulation wavelength as a function of temperature have been performed by analyzing DF XTEM images recorded using the g=220 diffraction vector, from XTEM samples with the glue line along the rapidly-diffusing [110]

direction. Fast Fourier Transform (FFT) power spectra recorded from each image allowed the dominant composition modulation wavelengths to be determined. Analyzing these wavelengths as a function of temperature yields the same activation energy (0.55 eV) as that found in surface diffusion measurements for In adatoms on the (001) InGaAs surface [3]; thereby confirming the role of surface diffusion in phase separation driven composition modulations.

[1] F. Glas, Phys. Rev.B, 62, 7393 (2000).

[2] I. P. Ipatova, V. G. Malyshkin, and V. A. Shchukin, J. Appl. Phys. 7198 (1993).

[3] Stevens et al., J. Appl. Phys. 121, 195302 (2017).

3:00pm **TF+AS+EL+PS+RA-ThA-3 In-Situ Spectroscopic Monitoring of Methylamine-Induced Hybrid Perovskite Phase Transitions**, ***Jonathan Meyers***[1], *L Serafin, J Cahoon,* University of North Carolina at Chapel Hill

Lead halide perovskites have shown remarkable promise for use in thin film optoelectronic devices such as photodetectors, light-emitting diodes, and solar cells. Methods for casting thin films of perovskite have been extensively studied, and great improvements have been made in an effort to improve device efficiency and stability. A few reports have suggested some benefits to processing or post-processing techniques in a methylamine (MA) atmosphere, including healing grain boundary defects to create pinhole free films with grains on the order of tens of microns and improving crystallinity. The process can be observed spectroscopically as the MA induces a reversible phase change which bleaches the dark perovskite film. In this work, we perform the MA-treatment in a vacuum reactor while monitoring in-situ the UV-visible spectral response correlated with temperature and MA partial pressure. Clear evidence is found for the existence of a solid intermediate phase in transitioning from $MAPbI_3$(s) to $MAPbI_3$*xMA(l) and back again. We construct a phase diagram and demonstrate that the critical partial pressure of the phase transition changes from 10 to 500 torr between 25 and 120 °C. By tuning the kinetics of film crystallization, compact films with domains up to 80 µm can be produced.

3:20pm **TF+AS+EL+PS+RA-ThA-4 Angle-Resolved HAXPES Analysis of Al_xO_y and Cu_xO_y Layers formed by Metal Salt Diffusion into a poly 2-vinylpyridine (P2vP) Polymer Layer**, ***Pierre Mani,*** Universidad Autonoma de Ciudad Juarez, México; *M Snelgrove,* Dublin City University, Ireland; *P Rueff,* Synchrotron SOLEIL, France; *R Lundy,* Trinity College Dublin, Ireland; *J Bogan, R O´Connor,* Dublin City University, Ireland; *J Enríquez,* Universidad Autonoma de Ciudad Juarez, México; *M Morris,* Trinity College Dublin, Ireland; *G Hughes,* Dublin City University, Ireland

This work is motivated by the desire to develop a semiconductor device patterning technology based on precursor infiltration into block copolymer materials. Developing an understanding of the preferential infiltration of metal precursors into one of the polymer blocks is of critical importance to advance this patterning approach. In this study, metal salts were used as a means to diffuse metal ions into poly 2-vinylpyridine (P2VP) polymer brush layers (~4 nm), which had been deposited by spin coating onto silicon substrates. Thin P2VP films infused with aluminum nitrate and copper nitrate by a wet chemical process were analyzed with angle resolved hard x-ray photoelectron spectroscopy (AR HAXPES). This photoemission based technique gives a lot information about a variety of core levels.[1] The large sampling depth of HAXPES measurements (20-30nm) enabled details of the chemical composition of the thin film to be characterized and subsequent angle-resolved HAXPES measurements offered a robust analysis of the interfaces and discrete layers that are present in the films. These measurements displayed evidence of bonding interactions between the elements in the polymer film and the infiltrated salts, which assists in developing an understanding of the infiltration process which needs to be optimized for device fabrication applications.[2]

[1] P. G. Mani-Gonzalez, M. O. Vazquez-Lepe, F. Espinosa-Magaña, and A. Herrera-Gomez J. Vac. Sci. Technol., A 31, 010601 (2013).

[2] C. Cummins and M. A. Morris. Using block copolymers as infiltration sites for development of future nanoelectronic devices: Achievements, barriers, and opportunities. Microelectron Eng., 195:74–85, 2018.

4:00pm **TF+AS+EL+PS+RA-ThA-6 Obtaining Smooth Surfaces and Measuring Surface Roughness**, ***Steven M. George,*** University of Colorado at Boulder **INVITED**

Smooth surfaces are important in many areas including friction, adhesion, optics and film growth. Smooth surfaces can be obtained from rough surfaces using chemical mechanical polishing (CMP). Rough surfaces can also be smoothed using atomic layer deposition (ALD) if the conformal ALD film thickness is comparable with the lateral length scale of the roughness. In addition, rough surfaces can be smoothed using isotropic thermal atomic layer etching (ALE) if the ALE etch depth is comparable with the width of the surface asperities. Quantifying the degree of surface roughness after CMP, ALD or ALE is challenging. Surface roughness can be obtained using atomic force microscope (AFM) or x-ray reflectivity (XRR) measurements. However, the AFM and XRR techniques do not always agree. Some of the inconsistencies are attributed to the different lateral length scales for the AFM and XRR measurements. Using both AFM and XRR to characterize surface roughness is recommended for reliable measurements. In addition, XRR measurements for surface roughness should include both specular and diffuse off-specular scattering.

4:40pm **TF+AS+EL+PS+RA-ThA-8 Characterizing Ultra-thin Layer Growth and Area Selective Deposition using High Resolution Low Energy Ion Scattering (LEIS)**, ***Thomas Grehl,*** IONTOF GmbH, Germany; *P Brüner,* ION-TOF GmbH, Germany; *V Pesce, B Pelissier, R Gassilloud, C Vallée,* Laboratoire des Technologies de la Microélectronique (LTM), France

When depositing ultra thin films of only very few nm of thickness, the characterization of the early stages of film growth is crucial for the quality of the film. For example, the initial thickness distribution before layer closure, created by the nucleation mechanism, will often remain after the film is complete. To analyze these early stages of growth requires very surface sensitive analytical techniques with good detection limits.

Specifically for area selective deposition, the demand for characterization increases even further. The deposition processes get more complex, involving atomic layer or plasma etching to remove nucleation on blocked areas. This also requires means of characterization, determining the effects of etching steps on the film being created, possible contamination and the level of success of the blocking.

One technique specifically suited for this application is Low Energy Ion Scattering (LEIS). By scattering noble gas ions from the surface of the sample, the mass of the atoms in the outer atomic layer is determined non-destructively. Due to specific charge exchange processes, the peaks in the scattering spectrum correspond only to the outer atomic layer, making LEIS the most surface sensitive technique to determine the elemental composition of a surface.

In addition, information from deeper layers is available in two ways: First of all, features in the spectrum contain information about the first few nm of the sample – especially for heavier elements, the in-depth distribution can be determined non-destructively. For more complex systems or light elements, sputter depth profiling can be applied as well.

In this presentation, we will illustrate the main features of LEIS on ALD films. The main part will be on an area selective deposition (ASD) process for Ta_2O_5 films on TiN or Si. Here, plasma-enhanced ALD (PE-ALD) and various plasma or ALE like etching processes, all using fluorine-containing compounds, are used to develop a super-cycle scheme for ASD. We show the effect of the different etching methods and use sputter depth profiling to determine the distribution of F – a light element not accessible to non-destructive depth profiling in LEIS. An important result is the distribution of F close to the surface, in the bulk of the film, or at the interface.

Besides this, some further sample systems will be used to highlight the use of LEIS for ultra-thin film characterization.

5:00pm **TF+AS+EL+PS+RA-ThA-9 Real-Time Monitoring of Aluminum Oxidation Through Wide Band Gap MgF_2 Layers for Protection of Space Mirrors**, *B Johnson, T Avval, G Hodges, K Membreno, D Allred,* ***Matthew Linford,*** Brigham Young University

Because of its extraordinary and broad reflectivity, aluminum is the only logical candidate for advanced space mirrors that operate deep into the UV. However, aluminum oxidizes rapidly in the air, and even a small amount of oxide (as little as a nanometer) can have a noticeable, detrimental impact on its reflectivity at short wavelengths. Thin films of wide band gap materials like MgF_2 have previously been used to protect aluminum surfaces. Here we report the first real-time, spectroscopic ellipsometry (SE) study of aluminum oxidation as a function of MgF_2 over layer thickness, which ranged from 0 – 6 nm. SE data analysis was performed vis-à-vis a multilayer optical model that included a thick silicon nitride layer. The optical constants for evaporated aluminum were initially determined using a multi-sample analysis (MSA) of SE data from MgF_2 protected and bare Al surfaces. Two models were then considered for analyzing the real-time data obtained from Al/MgF_2 stacks. The first used

[1] **National Student Award Finalist**

the optical constants of aluminum obtained in the MSA with two adjustable parameters: the thicknesses of the aluminum and aluminum oxide layers. The thicknesses obtained from this model showed the expected trends (increasing Al_2O_3 layer thickness and decreasing Al layer thickness with time), but some of the Al_2O_3 thicknesses were unphysical (negative). Because the optical constants of very thin metals films depend strongly on their structures and deposition conditions, a second, more advanced model was employed that fit the optical constants for Al, and also the Al and Al_2O_3 thicknesses, for each data set. In particular, the Al and Al_2O_3 thicknesses and optical constants of Al were determined in an MSA for each of 50 evenly spaced analyses in each four-hour dynamic run performed. The resulting optical constants for Al were then fixed for that sample and the thicknesses of the Al and Al_2O_3 layers were determined. While the first and second models yielded similar Al and Al_2O_3 thickness vs. time trends, the film thicknesses obtained in this manner were more physically reasonable. Thicker MgF_2 layers slow the oxidation rate of aluminum. The results from this work should prove useful in protecting space mirrors prior to launch. Detailed surface/material analysis by X-ray photoelectron spectroscopy will also be shown, as well as more advanced SE modeling.

5:20pm **TF+AS+EL+PS+RA-ThA-10 Visualization of Ultrafast Charge Motion in Thin Films via THz Emission Spectroscopy***, **Aaron Lindenberg**,* Stanford University **INVITED**

We describe a method for probing ultrafast time-dependent currents in thin films and heterostructures by recording the associated emitted electromagnetic fields. This detection scheme offers direct sensitivity to the flow of charges at the atomic-scale and enables a real-time probe for investigating ultrafast charge transfer processes at molecular interfaces. Applied to transition metal dichalcogenide heterostructures having a staggered (Type-II) band alignment, we observe a burst of electromagnetic radiation at terahertz frequencies following above gap excitation. The emitted electric field transients encode information about the charge transfer within the heterostructure. The polarity of the emitted field reflects the direction of the charge transfer and the polarity is reversed as the order of the bilayer within the heterostructure is altered. We find that the charge transfer proceeds at an ultrafast rate (~100 fs) indicating a remarkable efficiency for the charge separation across these atomic-scale bilayers.

We will also describe initial experiments and coupled theoretical efforts probing charge separation and ultrafast photovoltaic responses in multiferroic BFO periodic domain structures. We show that charge separation occurs dominantly at the domain walls and provide a quantitative estimate of the efficiency of this process.

Spectroscopic Ellipsometry Focus Topic
Room Union Station AB - Session EL-ThP

Spectroscopic Ellipsometry Focus Topic Poster Session
Moderator: Tino Hofmann, University of North Carolina at Charlotte

EL-ThP-1 Teaching Ellipsometry to Undergraduates*, John Woollam,*
University of Nebraska-Lincoln

Ellipsometry is taught at universities at different levels. This class is a beginning course at the undergraduate level for students who have not had classes in optics or solid-state physics. We use Fujiwara's *Spectroscopic Ellipsometry*[1], Collett's *Field Guide to Polarization*[2], and other sources for basic theory. We have simple in-class experiments to demonstrate basic concepts. The most unique aspect of our class is the use of a 1960s Gaertner model L119 manual null ellipsometer. The instrument is ideal to demonstrate alignment of light source, rotation axis of instrument, and sample to rotation axis of instrument. In addition, students "calibrate" Ps and As, the azimuth offset positions of the polarizer and analyzer. They learn practical aspects of polarizers, retarders, and multiple reflections from optical elements. They measure P- and S-reflectance vs. angle of incidence and compare to predictions by Fresnel equations.

Students measure polarization state of light by null ellipsometry, rotating analyzer ellipsometry (by hand!), and Stokes parameter methods. They compare results of all three methods and explain sources of systematic and random errors. They are then shown how modern ellipsometry instruments drastically reduce both types of errors. The course generally has 6 to 8 students, making laboratory aspects practical and educational. The combination of classroom demonstrations, theory, and hands-on experiments is both fun and an effective learning process.

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2. E. Collett, *Field Guide to Polarization* (SPIE Press, Bellingham, Washington, 2005).

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