Thin Film
Room: 111 - Session TF+AS+NS+SA-ThM

Thin Film: Growth and Characterization, Optical and Synchrotron Characterization I

Moderator: Divine Kumah, North Carolina State University

8:00am **TF+AS+NS+SA-ThM1 Oxynitride Thin Films by Reactive Radiofrequence Magnetron Sputtering - Versatile Materials for Optical Applications**, ***Angelique Bousquet***, *A. Farhaoui, F. Zoubian, C. Taviot-Gueho, J. Cellier, E. Tomasella*, Institut de Chimie de Clermont-Ferrand, France **INVITED**

Transition metal oxynitrides are increasingly studied because of their high versatility. Indeed, by tailoring the material composition, their optical, mechanical or electrical properties are tuned. Among thin film deposition processes, reactive sputtering is particularly attractive for this purpose because of its robustness, its wide using in industry and its high versatility. For several years, our research group at ICCF is specialized in control of reactive sputtering process, especially by plasma analysis using Optical Emission Spectroscopy, to deposit thin films for optical applications.

In this presentation, we will show how by tuning the $Ar/O_2/N_2$ atmosphere during sputtering of elemental target, it is possible to control the film composition in a ternary diagram in metal-rich, oxide, nitride or oxynitride region. The potentiality of this technique will be illustrated by tantalum and silicon oxynitride deposition.

In order to investigate the nature of oxynitride films (Random Bond Model or Random Mixture Model), thin films were characterized by various techniques, such as IR spectroscopy, XPS, XRD/Pair Distribution Function technique and Rutherford Backscattering Spectroscopy. Hence, we obtained an accurate picture of the diversity and the complexity of our material, following the Random Mixture Model, where segregated oxide and nitride phases are randomly distributed at very short scale.

Moreover, the modification of material composition allows controlling their optical properties, characterized by UV-visible spectroscopy and spectroscopic ellipsometry. This latter technique appears as a powerful technique to discriminate metallic, semiconductor and/or insulator contributions into such complex films by using model combining Tauc-Lorentz law and additional Lorentz oscillator. Hence, in a one hand, optical band gap of TaO_xN_y can be changed from 0-4.3 eV. This Eg fine-tuning more particularly in the range of 1.7-2.7 eV is interesting for application in photocalytic water splitting using visible light. In the other hand, the refractive index variation in the 1.56-3.7 range (at 1.96 eV) of $Si_xO_yN_z$ films is used to realized antireflective multilayer system from only one target. Finally, oxynitride films present promising properties for applications in material for Energy.

8:40am **TF+AS+NS+SA-ThM3 Surface Science in The Wild: Using Synchrotron Radiation and Lab Grown Thin Films to Understand The Behavior Of SiC in Accident Tolerant Nuclear Fuels**, ***Jeffery Terry***, Illinois Institute of Technology **INVITED**

Out in the "real world," systems are typically much less clean and much more complex than what is seen in the laboratory. This is often the case in the extreme environment of the core of a nuclear reactors. However, complexity often makes it very difficult to understand the dynamics that are occurring in the "real world" systems. Often our understanding can be greatly improved by using measurements on the "real world" system in combination with fundamental surface science measurements on likely components. We have applied these combinations to study the behavior of irradiated accident tolerant nuclear fuels. Development of new accident tolerant nuclear fuels is important because the explosions at Fukushima were the direct result of interactions between water and the Zr cladding on the fuel. The high temperature chemistry of those interactions led to the production of hydrogen gas which eventually ignited. Our research group has looked at potential claddings such as ZrC, ZrN, and SiC. Specifically, we are using synchrotron radiation techniques to collect data on reactor irradiated materials. We compare the results of those measurements with well controlled laboratory grown systems. The data is then provided to modelers to evaluate the performance of reactor components in extreme environments (temperature, neutron flux, chemistry). This talk will focus on the carbides and nitrides that may be used in accident tolerant, TRISO fuel pellets for application in both conventional and advanced nuclear reactors.

9:20am **TF+AS+NS+SA-ThM5 iTF Modulus Solution with xProbe Applications for Ultra-thin Film Systems (<=10nm)**, ***Anqi Qiu***, *A. Romano*, Hysitron, Inc.

Reliable measurements of the Elastic Modulus of thin films is particularly challenging due to substrate effect. The prevalent rule of limiting indentation depth to 10% of the coating thickness to avoid the substrate's influence on the mechanical properties is challenging to assure, especially when the film thickness goes below 200nm. The tip radius can be one of the many factors limiting the application of Oliver-Pharr model on the elastic modulus calculation, just as the surface roughness. With the newly developed ultra-low noise **xProbe** transducer combined with the **Intrinsic Thin Film Property Solution from Hysitron**, quantitative mechanical properties from nanoindentation tests on 10nm thin film systems become possible. Here a MEMS based transducer with a noise floor similar to that of a contact mode Atomic Force Microscope (AFM). The linear actuation allows for direct and fully quantitative measurements without the need of modeling, which leads to more precise mechanical properties estimation and higher analysis throughput. By combining the ultra-low noise xProbe transducer and analytical intrinsic thin film solution (Itf), we quantitatively estimate elastic properties of the ultra-thin film systems of 10nm or below.

9:40am **TF+AS+NS+SA-ThM6 Real-time Study of Plasma Enhanced Atomic Layer Epitaxy of InN Films by Synchrotron X-ray Methods**, ***Neeraj Nepal***, *V. Anderson, S.D. Johnson, B. Downey, D. Meyer,* U.S. Naval Research Laboratory, *A. DeMasi, K.F. Ludwig,* Boston University, *C. Eddy*, U.S. Naval Research Laboratory

Atomic layer epitaxy (ALE) is a layer-by-layer materials growth method. Recently, plasma enhanced ALE (PA-ALE) has been used to grow epitaxial III-nitride films at temperatures ≤500°C [1-2]. At these growth temperatures, the ad-atom mobility is low and the growth process is significantly influenced by the nature of the substrate surface. Thus, the mechanisms of nucleation and growth kinetics is very important to understand to improve material quality for technological applications. Synchrotron x-ray characterization is one of the best methods for this study.

The temporal evolution of high quality InN growth on a-plane sapphire at 200-250°C were probed by synchrotron x-rays. The growth was carried out in a thin film growth facility installed at beamline X21 of the National Synchrotron Light Source at Brookhaven National Laboratory and at Cornell High Energy Synchrotron Source, Cornell University. Real-time grazing incidence small angle x-ray scattering (GISAXS) measurements at the x-ray incidence angle of 0.8 degrees show that H_2 plasma cleaning roughens the sapphire substrate surface, but this same surface is recovered completely during subsequent N_2 plasma pretreatment. GISAXS also reveals InN growth steps for each PA-ALE cycle at the optimal growth conditions. During the initial cycles the specular peak broadens and the Yoneda Wing (YW) scattering has a correlated length scale (CLS) of 17.4 nm indicating roughening of the surface during homogenous nucleation. At about 1.3 nm of growth the intensity of YW is increased at the CLS of 10.1 nm indicating a decrease in the surface roughening CLS. Despite this scattering, *ex situ* atomic force microscopy-measured roughness is below instrument sensitivity limits, demonstrating the effectiveness of GISAXS compared to more conventional approaches. *In situ* x-ray reflectivity measurements suggest that the InN growth was self-limited with a growth rate of 0.35 nm/cycle between 200-250°C. Hall measurements show electron sheet carrier density and resistance of $3.5x10^{13}$ cm^{-2} and 3.59 kW/sq, respectively. An electron mobility of 50 $cm^2/V\text{-}s$ is measured for a 5.6 nm thick InN film on a-plane sapphire, which is higher than the reported value of 30 $cm^2/V\text{-}s$ for a 1300 nm thick InN grown by MBE directly on sapphire [3]. *In situ* synchrotron x-ray study of the epitaxial growth kinetics of InN films is one of the most powerful methods to understand nucleation and growth mechanisms to improve material quality and broaden material applications.

References:

[1] Nepal et al., Cryst. Growth and Des. **13**, 1485 (2013).

[2] Nepal et al., Appl. Phys. Lett. **103**, 082110 (2013).

[3] Kuo et al., Diamond & Related Materials **20**, 1188 (2011).

11:00am **TF+AS+NS+SA-ThM10 Nucleation and Growth of Few-Layer ALD Films on Various Substrates Studied by Low Energy Ion Scattering (LEIS)**, ***Malcolm Hathaway***, Harvard University, *T. Grehl, P. Bruener,* ION-TOF GmbH, Germany, *M. Fartmann,* Tascon GmbH, Germany, *H. Brongersma*, ION-TOF GmbH, Germany

Atomic Layer Deposition has found applications in many semiconductor processes due to its several unique characteristics, including high purity, conformality, pin-hole-free character, and atomic level thickness

controllability. It is these last two characteristics which are of particular interest in this present work. The thickness control of ALD films is precise down to the angstrom level, even when depositing layers as thin as a few atomic layers. Ideally, in layers only a few angstroms thick, the ALD process produces material which is completely continuous and free of pin-holes. One of the challenges of characterizing ALD processes is the difficulty of directly measuring such thin films and confirming their continuous nature.

Low Energy Ion Scattering (LEIS) spectroscopy is uniquely suited to exploring these questions, due to its extreme surface sensitivity, easy quantification and its ability to yield additional information about the sub-surface composition. Using LEIS, analytical questions like layer closure, surface composition, diffusion processes, or growth modes can be addressed. In this work, we explore the limits of this technique to characterize few-layer ALD films on a variety of substrates, to confirm the capabilities of LEIS in this arena, and to shed new light on the nature of few-layer ALD films.

In the LEIS process, a noble gas ion beam of (1 -10 keV) is directed at the sample, and the fraction of backscattered ions is measured as a function of kinetic energy. Two main mechanisms determine the spectral response: Firstly, scattering in the first monolayer of atoms creates elemental peaks, allowing quantitative determination of the elemental composition of the outermost atomic layer. The intensity of these peaks is directly proportional to the surface coverage. Secondly, scattering processes below the surface (with the ion penetrating the surface, scattering at deeper layers and returning to the surface before leaving it) provide information about sub-surface layers, sometimes as deep as 10 nm, in a non-destructive way. As the additional energy loss is proportional to penetration depth, these data can be evaluated to determine the layer sequence, layer composition and layer thickness in a single measurement and in addition to the top layer composition.

In this study a number of oxide films (e. g. HfO_2, AL_2O_3) on Si and other substrates like glassy carbon are evaluated. We apply LEIS among other techniques to characterize the films, especially in the early phases of film growth. Using the unique information from LEIS, conclusions on the nucleation behavior and growth are drawn.

11:20am **TF+AS+NS+SA-ThM11 $Ni_{1-x}Pt_xSi$ Film Characterization for sub-32 nm CMOS Fabrication**, ***Suraj Patil***, *R. Rai, S. Beasor, L. Zhou*, GLOBALFOUNDRIES, NY, USA

Aggressive scaling of CMOS devices demands silicide engineering for high performance in the sub-32nm technology node and beyond. Ni-silicide can satisfy many of the integration challenges but it is limited by morphological stability at elevated temperatures. On the other hand, incorporating Pt into Ni-silicide forms a more robust nickel platinum silicide ($Ni_{1-x}Pt_xSi$) and improves morphological stability. Advantages of Pt incorporation include extension of the temperature range over which the NiSi exists, delay in the agglomeration of NiSi phase, suppression of the high resistive $NiSi_2$ phase formation and retardation of the Ni diffusion at the interface and grain boundaries which could lead to encroachment or piping. This work discusses three important aspects of $Ni_{1-x}Pt_xSi$ formation: (1) understanding NiPt diffusion with two step RTA anneals – formation (RTA1) and transition (RTA2), which is very important for thickness uniformity across structures with varying CDs, encroachment control, device performance and yield; (2) understanding NiSi phase formation for thermal stability, and (3) understanding Pt distribution in the final film with low RTA1 temperatures. For this study $Ni_{1-x}Pt_xSi$ samples were fabricated from a simple n-$Si/Ni_{0.85}Pt_{0.15}$/TiN stacks, annealed at range of RTA1 temperatures from RTA-20°C to RTA+30°C for 20s followed by a standard RTA2 anneal for 30s. Characterization of final $Ni_{1-x}Pt_xSi$ films obtained at different RTAs based on XRD phase identification and XPS analysis will be presented. Pt distribution in the final silicide films will be discussed.

11:40am **TF+AS+NS+SA-ThM12 Growth of β-Tungsten Films Towards a Giant Spin Hall Effect Logic Device**, ***Avyaya Narasimham***, University at Albany-SUNY, *R.J. Matyi*, State University of New York, *A. Green*, University at Albany-SUNY, *A.C. Diebold, V. LaBella*, State University of New York

Spin-orbit coupling in metastable β-W generates spin transfer torques strong enough to flip magnetic moment of an adjacent magnetic layer. In a MTJ stack these torques can be used to switch between high and low resistive states. This technique can be used in designing efficient magnetic memory and non-volatile spin logic devices. Deposition conditions selective to β- W need to be understood for the large scale fabrication of such devices. The transition from β to α phase of Tungsten is strongly governed by thickness of W layer, base pressure and oxygen availability for example, above 5 nm β film relaxes and forms an α phase. Resistivity measurements as well as x-ray photoelectron spectroscopy and x-ray diffraction and reflectivity analysis are performed to determine the phase and thickness of tungsten films. We show that β phase is influenced by ultrathin thermal oxide of Si layer and the amount of oxygen flow during the growth. These results demonstrate a reliable technique to fabricate β W films up to 20 nm on bare Si and silicon dioxide, while providing insight to growing it anywhere in the device stack.

12:00pm **TF+AS+NS+SA-ThM13 Aluminum Nitride Grown by Atomic Layer Epitaxy Characterized with Real-Time Grazing Incidence Small Angle X-ray Scattering**, ***Virginia Anderson***, *N. Nepal, S.D. Johnson*, US Naval Research Laboratory, *A. DeMasi*, Boston University, *J.K. Hite*, US Naval Research Laboratory, *K.F. Ludwig*, Boston University, *C.R. Eddy, Jr*, US Naval Research Laboratory

Aluminum nitride, gallium nitride, and indium nitride have desirable qualities for many semiconductor applications, and have recently been studied intensely.[1] Because of their direct, tunable band gaps and capacity for high current density they are attractive for photovoltaics and high power transistors. The current methods of depositing high-quality III-nitride films, are metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). The temperatures for the depositions make ternaries challenging. Indium nitride, for example, is difficult to mix with aluminum nitride, as typical MOCVD temperatures for AlN and for InN are 1000°C and 450°C respectively. Aluminum nitride deposition with atomic layer epitaxy (ALE) is currently being explored by some groups as a fabrication friendly technique for thin films at lower temperatures.[2]

Crystalline AlN deposited with plasma assisted ALE (PA-ALE) in a Fiji reactor from Ultratech/Cambridge Nanotech at 500°C currently has lower material purity than the AlN deposited by MBE and MOCVD, and understanding the film deposition mechanism in order to improve quality is the subject of ongoing research.[3] There is a need for a better understanding about the film evolution during nucleation. Grazing incidence small angle x-ray scattering (GISAXS) is sensitive to changing surface features and can be conducted at a wide range of pressures, making it useful for real time monitoring of deposition.[4]

AlN deposited by PA-ALE was grown using trimethylaluminum and hydrogen/nitrogen plasma pulses in a custom reactor at the Brookhaven National Synchrotron Light Source and the Cornell High Energy Synchrotron Source. In both instances, GISAXS was used to examine surface changes during the deposition.

GISAXS information collected during AlN growth at nominally 400°C, 450°C, and 500°C suggested that temperature influenced nucleation, with changes in roughening behavior observed. Post-growth examination of the AlN films with x-ray photoelectron spectroscopy and atomic force microscopy gave important information on the final film elemental composition and morphology. The GISAXS data also show that the surface continued to evolve during the cooling after growth completion while still in the reactor. This information only adds to the necessity of *in situ* growth monitoring to fully understand the mechanisms involved in the ALE growth process.

References:

[1] M. Mori et al., *Appl. Phys. Express* **5** 082301 (2012)

[2] M. Bosund et al., *Appl. Surf. Sci.* **17** 7827 (2011)

[3] N. Nepal et al., *Appl. Phys. Lett.* **103** 0 82110 (2013)

[4] K. Devloo-Casier et al., *Appl Phys. Lett.* **98** 231905 (2011)

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