## Thin Films Division
## Room 102A - Session TF+AS+EL+PS-ThM

### In-situ Characterization and Modeling of Thin Film Processes

**Moderator:** Thomas Riedl, University of Wuppertal

8:00am **TF+AS+EL+PS-ThM-1 Defects in Thin Films: A First Principles Perspective**, ***Douglas Irving***, *J Harris, J Baker, S Washiyama, M Breckenridge,* North Carolina State University*; P Reddy,* Adroit Materials*; R Collazo, Z Sitar,* North Carolina State University **INVITED**

Realization of next-generation power and optoelectronic devices depends on the ability to controllably donor dope thin films of AlN and Al-rich AlGaN. The challenge in donor doping these materials begins with the donor dopant itself, Silicon. While it is a common shallow donor dopant in GaN, it exhibits a deeper ionization level in AlN due to the formation of a DX center near the conduction band minimum. Compensation in both the low and the high doping regime also presents a significant technical challenge to the doping of AlN thin films. In this talk, we explore the mechanisms for compensation in Si-doped AlN in the low and high doping regimes. For this purpose, we have implemented first principles density functional theory calculations with screened hybrid exchange-correlation functionals to determine the properties of individual defects in AlN. The formation energies of each defect are used within a grand canonical equilibrium model to identify the predominant defects as a function of growth conditions. In the low doing regime, important to drift layers in power electronics, we find unintentional impurities and unintentional impurity complexes are often responsible for free carrier compensation. Compensation in films that are doped to higher impurity concentration is found to be related to vacancy-dopant complexes. Possible solutions unique to thin films have also been explored and will be presented. Results from these methods are compared with complementary experimental data that includes below band gap optical absorption and photoluminescence, electrical measurements, dopant implantation, and available SIMS measurements.

8:40am **TF+AS+EL+PS-ThM-3 Advances in Numerical Simulation of SiN ALD**, ***Paul Moroz***, TEL Technology Center, America, LLC

Atomic layer deposition (ALD) includes a fast growing area of applications and could be foreseen as becoming one of the leading semiconductor technologies. In many cases, it allows accurate atomic-scale deposition of films with almost conformal profiles. Here we present new results on the Monte Carlo feature-scale simulations of ALD conducted with a feature-profile simulator, FPS3D [1-5], as well as comparison of obtained simulation results with the corresponding experiments. The ALD processes are often complex, involving large molecules and, to our knowledge, have not been addressed by other feature-profile simulations except FPS3D. The main factor of all of ALD schemes is the cyclic change in flux parameters and in the corresponding surface chemistry, which results in a single monolayer or, most typically, in a fraction of a monolayer of a film deposited after application of a cycle. Here, we consider a case of ALD with two time-steps: (1) dichlorosilane gas and (2) ammonia plasma. The SiN deposition rate in this case is about a half of a monolayer per cycle. A set of surface reactions is considered which emphasize the steric hindrance effect that was found to be an important factor in explaining deposition rates for this ALD process.

References:

[1] P. Moroz, IEEE Trans. on Plasma Science, 39 2804 (2011).

[2] P. Moroz, D. J. Moroz, ECS Transactions, 50 61 (2013).

[3] P. Moroz, D. J. Moroz, J. Physics: CS 550 012030 (2014).

[4] P. Moroz, 15th Int. Conf. on Atomic Layer Deposition, Portland, OR (2015).

[5] P. Moroz, D. J. Moroz, Japan. J. Appl. Phys. **56**, 06HE07 (2017).

9:00am **TF+AS+EL+PS-ThM-4 Diffusion Kinetics Study of Adatom Islands: Activation Energy Barriers Predicted using Data-driven Approaches**, ***ShreeRam Acharya***, *T Rahman,* University of Central Florida

The Self-Learning Kinetic Monte Carlo (SLKMC) method [1] with a pattern recognition [2] and a diffusion path finder scheme enables collection of a large database of diffusion processes including single- and multiple-atoms, and concerted island motion and their energetics. The databases collected from adatom-island (2-8 atoms) diffusion characteristics for a large set of homo- and hetero-epitaxial metallic systems (Cu, Ni, Pd and Ag) are used to extract a set of easily accessible features, geometrical and energetic, using physical insight which are then encoded. Those features along with activation energy barrier are used to train and test linear and non-linear statistical models. A non-linear model developed based on neural network technique predicts the diffusion energy barriers with high correlation with the calculated ones. In this talk, we present the results of kinetics study of these homo or hetero-epitaxial metallic systems some of whose barriers are used for training of the model and are compared to the corresponding quantities obtained from KMC simulation using energy barriers calculated from computationally intensive interatomic interaction potential based approach.

[1] O. Trushin, et al., *Phys. Rev. B***72**, 115401 (2005).

[2] S.I. Shah, et al., *J. Phys.: Condens. Matt.***24**, 354004 (2012).

Work supported in part by MMN-1710306.

9:20am **TF+AS+EL+PS-ThM-5 Using Ellipsometry and XPS to Understand the Degradation of Thin-film Aluminum Mirrors Protected by Ultrathin Fluorides**, *M Linford,* ***Brian I. Johnson***, *R Turley, D Allred,* Brigham Young University

The LUVOIR (Large, UV-optical-IR) telescope is a potential NASA flagship space-based observatory of the 2020's or 30's. It will utilize the largest mirrors ever put into space. The reflective coating for the mirrors will be aluminum, since there is no material with comparable reflectance at shorter wavelengths. However, to achieve high reflectance over the broadest energy range, the top surfaces of such Al mirrors must be protected against the formation of oxide layers that form quickly in air using wide-bandgap fluoride coatings, traditionally about 25 nm of $MgF_2$. Researchers have been endeavoring to use fluorides which are transparent further into the VUV (vacuum ultraviolet) like LiF and $AlF_3$, and to make these barriers more continuous by depositing them on heated surfaces and making the barriers thinner. However, when the barriers are thinner and when materials like LiF are exposed to moist air, degradation of VUV reflectance is observed. Thus, studying fluoride barrier-coated mirrors is vital. We have recently reported on the time dependent growth of apparent aluminum oxide thickness for two Al mirrors protected by ultrathin fluoride layers. These measurements were based on variable-angle, spectroscopic ellipsometric (VASE) measurements. (Allred, Thomas, Willett, Greenburg, & Perry, 2017) (Miles, 2017) . VASE, however, does not provide chemical composition data. An independent analytical technique which is sensitive to surface composition is required. We have undertaken such investigations using X-ray photoelectron spectroscopy (XPS), and now report on correlations between optical properties and XPS for fluoride-coated aluminum mirror test structures.

9:40am **TF+AS+EL+PS-ThM-6 Model for Amorphous Thin Film Formation and Validation**, ***Rahul Basu***, VTU, India

A coupled set of equations describing heat and mass transfer during phase transformation is formulated The model is extended to incorporate surface convective effects. These equations which are non linear due to the moving interface are linearized and decoupled. Effects of various heat transfer parameters are analyzed through small parameter expansions. Solutions obtained via this artifice allow closer examination of surface effects on the boundary layer of the phase transformation. A relation is found for the effect of the glass transition temperature versus the boundary layer thickness for several alloys in various groups of the Periodic Table. Earlier work and results are analyzed in light of the present analysis.

11:00am **TF+AS+EL+PS-ThM-10 2D TMD Monolayer of $MoS_2$ BY ALD and Insight in the Mechanism by Surface Organometallic Chemistry**, ***Elsje Alessandra Quadrelli***, CNRS CPE Lyon, France **INVITED**

*Atomically-thin crystalline domains of $MoS_2$ [1] or $WS_2$ [2] are obtained from an organometallic amorphous deposit obtained by ALD/MLD.*

*This original result with respect to the state of the art has been mechanistically rationalized with in situ and in operando modelling studies on the oxide nanobeads at different annealing temperatures. This contribution will present the surface organometallic method, the characterization of the 2D layers (among which the first in-plane micrographs of ALD-grown $MoS_2$ samples)[1] and the proposed surface coordination chemistry mechanism at hand obtained with model studied on 3D silica beads. These model studies couple in operando infra-red spectroscopy, gas-chromatography detection of the released by-products and atomic composition of the deposit at each cycle, leading to molecular level understanding of the growth process.*

***Acknowledgments*** *: This work was carried out within the framework of the partnership between the C2P2 research unit (UMR 5265 CNRS CPE Lyon University Claude Bernard Lyon 1) and CEA's Directorate of Technological Research (DRT) on the nanochemistry platform installed in CPE Lyon. The authors of the papers below thank CPE Lyon, CNRS, CEA / LETI (Silicon Technology Department and nanocharacterization platform) for the support and the DRF / INAC for the collaboration in the framework of the "2D Factory" project.*

***Ref*** *: [1] Cadot et al.Nanoscale , **2017**, 9, 467. [2] Cadot et al. JSVT A **2017**, 35, 061502 .*

11:40am **TF+AS+EL+PS-ThM-12 A Novel Fourier Transform Ion Trap Mass Spectrometer for Semiconductor Processes***, **Gennady Fedosenko**, H Chung, R Reuter, A Laue, V Derpmann, L Gorkhover, M Aliman, M Antoni,* Carl Zeiss SMT GmbH, Germany

Real-time inline control of process gas compositions with high sensitivity has been of particular importance in recent years in the semiconductor industry and beyond. Commonly quadrupole residual gas analyzers (RGA) are used, together with Optical Emission Spectroscopy (OES) for process control and process development. However, most RGAs are not capable of measuring a whole mass spectrum fast enough to monitor etch or deposition processes of a few seconds. A new process control mass spectrometer, based on Fourier-Transform 3D Quadrupole Ion Trap technology, is more appropriate for real-time inline process monitoring.

The 3D-Quadrupole Ion Trap mass spectrometer *iTrap*® by ZEISS is installed in a vacuum chamber (~ 120mm x 120mm x 500mm) with a fast switching valve for pulsed gas sample injection (pulse duration ~ 50ms or less). An electron gun is used for ionization of the gas pules. The Ion Trap achieves ion trapping and accumulation by means of a radio frequency applied to the ring electrode of the trap. With the aid of advanced electronic amplifiers and selective ion excitation technique the ion oscillations can be measured electrically by means of the induced current on the cap electrodes without using any separate particle detector. The mass spectrum can be finally obtained in less than one second.

Real-time measurements of the hydrogen plasma cleaning process of Sn contaminated samples were performed with the *iTrap* mass spectrometer. The working pressure of the plasma cleaning process was 0.5 mbar. Decreasing signal of $SnH_4$ and other contaminations from the samples which are directly correlated to the cleaning process were observed with *iTrap*. This result is extremely useful for the process control of plasma processes and inline real-time contaminations control for high-end applications.

Inline measurement at a MOCVD chamber showed that *iTrap* is capable to detect reaction products, contaminations on the wafer holder and dopant memory in real-time. These results demonstrate that *iTrap* is a very sensitive and fast process mass spectrometer suitable for real-time inline process monitoring.

Many etch processes take place in 10 to 30 s process steps. Different processes were examined with e.g. HBr or $BCl_3$ chemistry together with several wafer materials such as Silicon, Hafnium Oxide or Titanium Nitride. The obtained mass spectra show the etch plasma chemistry together with etch reaction products (HfClx, SiClx, etc.). This data gives new insight into the etch processes, which until now were rarely understood on a chemical level. First wafer effects related to the chamber cleaning and pre-coating steps prior to the etch step were also examined.

12:00pm **TF+AS+EL+PS-ThM-13 Realization of Shifts in Threshold Voltage and Subthreshold Swing in Atomic Layer Deposited Zinc Oxide As Channel Layer through *in-situ* Half-Cycle Analysis***, **Harrison Sejoon Kim**, A Lucero, S Kim, J Kim,* University of Texas at Dallas

Thin film process monitoring of atomic layer deposition (ALD) has been adopted as the versatile technique to identify both chemical and physical properties of ALD films. Their *in-situ* characterization technique includes mostly Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, and quartz crystal microbalance analysis. [1–3] However, currently there are no reports on monitoring the results of sub-nm device physics even if we are already in the era of beyond 10 nm node semiconductor processes. Moreover, even if there are a few initial studies, demonstrating *in-situ* electrical characterization with ALD, it requires device packaging, which ultimately limits the flexibility to be further characterized. [4]

In this current work, we have developed an ultra-high vacuum (UHV) cluster tool equipped with thermal processing, plasma surface treatment, thin film deposition, and electrical characterization which can be performed *in-situ* (Figure 1). With this feasibility, we demonstrate the deposition of semiconducting zinc oxide (ZnO) in inverted-coplanar structured thin film transistors (TFT). Diethylzinc (DEZ) and water ($H_2O$) is used as ALD precursors at 100°C. DEZ and $H_2O$ half-cycle analysis is carried out to monitor the interface states of ZnO/dielectric (Figure 2). Initially, 45 ALD cycles of ZnO have shown switching behavior with an on/off ratio of ~$10^2$ in vacuum. Subsequent ALD cycle shifts the threshold voltage ($V_{th}$). $V_{th}$ shifts associated with each ALD cycle are assumed to be attributed to the changes in interface trap density as a result of interface state passivation in ZnO during its growth, especially passivating fixed oxide charges ($Q_{ox}$). To understand interface states of ZnO and the bulk of oxide better, further analysis of shift of subthreshold swing (SS) is demonstrated. Since shifts in SS best represents changes in interface trap density, [5] it is worthwhile to note the changes in SS in metal-oxide-semiconductor transistors.

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[5] P. J. McWhorter *et al*., *Appl. Phys. Lett.48*, 133, **1986**.

# Author Index

## Bold page numbers indicate presenter