Live Session
Room Live - Session LI-WeM1

Wednesday Morning Live Session I: Recent Advances in Thin Films

Moderators: Svitlana Pylypenko, Colorado School of Mines, Angel Yanguas, Argonne National Lab

10:00am **LI-WeM1-1 Welcome and Opening Remarks**, ***Angel Yanguas-Gil,*** Argonne National Lab

Welcome to the AVS 67 Virtual Symposium! We hope you will enjoy the event!

10:05am **LI-WeM1-2 Metalorganic Vapor-Phase Epitaxy of Gallium (Aluminum) Oxide Thin Films and Heterostructures for High Frequency and Power Electronics**, ***Sriram Krishnamoorthy,*** University of California, Santa Barbara; *P. Ranga, A. Bhattacharyya, S. Roy,* Electrical and Computer Engineering, The University of Utah **INVITED**

Beta- Gallium Oxide (β-Ga_2O_3) is an emerging ultra-wide band gap (UWBG) material with the availability of high quality native substrates grown using potentially inexpensive melt-based techniques. In this talk, I will highlight the tremendous progress made by the Gallium Oxide research community in the last few years, in the area of metal-organic vapor phase epitaxy (MOVPE).

In the first part of the talk, I will focus on our group's first demonstration of delta doping and modulation-doped Aluminum Gallium Oxide/ Gallium Oxide heterostructures grown using metal organic vapor-phase epitaxy (MOVPE) towards achieving high electron mobility. Growth of delta-doped (010) β-Ga_2O_3 films is performed by Agnitron Agilis MOVPE reactor with TEGa, O_2 and silane as precursors and argon as carrier gas. Delta doping of β-Ga_2O_3 is achieved by interrupting the growth of β-Ga_2O_3 and supplying silane to the reactor with purge steps before and after the flow of silane. Multiple samples are grown under varying silane flows to study silicon incorporation inβ-Ga_2O_3. CV measurements are used to characterize the sheet charge density and FWHM of the silicon delta sheet. SIMS measurements are used to estimate the concentration of silicon donor atoms in β-Ga_2O_3. Sheet charge density extracted from CV measurements is in the range of 2 x 10^{12} cm^{-2} and 1 x 10^{13} cm^{-2}. Sharp delta doping profiles are achieved by controlling the surface riding of silicon donors. Using a delta-doped β-$(Al_{0.26}Ga_{0.74})_2O_3$ barrier layer, a room temperature electron sheet charge density as high as 1 x 10^{13} cm^{-2} is realized at the β-$(Al_{0.26}Ga_{0.74})_2O_3$/β-$Ga_2O_3$ heterojunction. The electron sheet charge did not exhibit freeze out at 90 K, confirming degenerate behavior. This value is the highest reported degenerate electron density in β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 material system.

In the second part of the talk, I will discuss MOVPE-regrown selective area ohmic contacts with resistance as low as 1 x 10^{-4} ohm cm^2. This is particularly enabled by the large growth temperature window of MOVPE-grown homoepitaxial (010)-oriented Ga_2O_3, resulting in excellent material growth at growth temperatures as low as 600°C. These early results on delta doping, modulation doping and the large growth temperature window for β-Ga_2O_3 homoepitaxy show the potential of the MOVPE technique for achieving high quality UWBG thin film and heterostructures towards applications in high frequency and high power electronics.

10:25am **LI-WeM1-6 Selection Criteria for Small Inhibitor Molecules in Area-Selective Atomic Layer Deposition**, ***Marc Merkx,*** *P. Yu, J. Li,* Eindhoven University of Technology, Netherlands; *D. Hausmann,* Lam Research Corp.; *T. Sandoval,* Universidad Técnica Federico Santa Mariá, Chile; *E. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands **INVITED**

Implementing vapor-phase dosing of small inhibitor molecules in advanced atomic layer deposition (ALD) cycles is currently being considered to enable area-selective ALD. When using small inhibitor molecules, it can be challenging to completely block precursor adsorption, due the inhibitor size and the relatively short vapor-phase exposures. This work aims at providing a framework for the selection of small inhibitor molecules such that area-selective ALD with a high selectivity can be achieved. In previous work, we showed that small inhibitor molecules typically adsorb in a mixture of bonding configurations, and that not all bonding configurations block precursor adsorption equally well.[1]

Inhibitor selection requires consideration of the packing of inhibitors, inhibitor bonding configurations, the inhibitor binding strength, and intermolecular interactions. As a model system, the adsorption of acetic acid ($C_2H_4O_2$), acetylacetone (Hacac, $C_5H_8O_2$), and 2,2,6,6-tetramethyl-3,5-heptanedione (TMHD, $C_{11}H_{20}O_2$) was studied. Infrared (IR) spectroscopy shows that TMHD has the highest efficiency for blocking bis(diethylamino)silane (BDEAS) precursor adsorption. In terms of surface packing, random sequential adsorption (RSA) simulations [2] indicate that TMHD adsorbs in a lower surface density as compared to acetic acid and Hacac, but due to its larger size still covers a larger fraction of the non-growth area. Density functional theory (DFT) calculations reveal that attractive interactions with incoming BDEAS molecules, which cause a loss of selectivity when using Hacac,[1] are less likely to occur when using TMHD due to steric limitations. Correspondingly, IR spectroscopy shows less inhibitor displacement by the BDEAS precursor than for acetic acid and Hacac.

The model system suggests that using a more bulky inhibitor is beneficial for precursor blocking, as a larger size helps to shield the reactive group of the inhibitor from interacting with the incoming precursor. Overall, both the packing and stability of the inhibitor on the surface need to be as high as possible for effective precursor blocking, where the stability is affected by the bonding of the inhibitor with the surface and potential interactions with incoming precursors. The mechanisms that affect precursor blocking will be discussed within a framework for selecting small inhibitor molecules.

[1] Merkx *et al., Chem. Matter.***32**, 3335 (2020)

[2] Khan *et al., Chem. Matter.***30**, 7603 (2018)

10:45am **LI-WeM1-10 Ligand-Exchange Reactions Using Silane Precursors Containing Different Ligands: Pathways for Selective Thermal Atomic Layer Etching**, ***Ann Lii-Rosales,*** *V. Johnson, A. Cavanagh, S. Sharma, S. George,* University of Colorado Boulder **INVITED**

The ligand-exchange reaction is an effective pathway for thermal atomic layer etching (ALE) of metal oxides. The metal oxide is usually fluorinated by HF to make metal fluoride. Then, the metal fluoride can undergo ligand-exchange reactions with a precursor molecule. Depending on the choice of ligands on the precursor, ligand-exchange can produce stable and volatile etch products. Silanes are important precursors for ligand-exchange with metal fluorides because silicon forms strong Si-F bonds. In addition, silicon can bind to a variety of ligands including CH_3, Cl, H and $N(CH_3)_2$. This study examined ligand-exchange reactions with metal fluorides using various silane precursors such as $SiCl_4$, $SiCl_2(CH_3)_2$ and $SiH(CH_3)_2Cl$. The investigations were performed with *in situ* mass spectrometry experiments to detect the ligand-exchange products and etch species during temperature ramps from 30-520°C.

For the reaction of $SiCl_4$ with SnF_4 powder, $SiCl_4$ was observed to undergo complete F-Cl exchange with SnF_4 powder to produce SiF_4. The F-Cl exchange also produced $SnCl_4$ as the volatile etch species at 150°C. Calculations of the sequential ligand-exchange required to convert SnF_4 to $SnCl_4$ also confirmed the favorability of these reactions. In contrast to $SiCl_4$, $SiCl_2(CH_3)_2$ has both Cl and CH_3 ligands that can be involved in ligand-exchange. The reaction of $SiCl_2(CH_3)_2$ with SnF_4 powder produced $SiF_2(CH_3)_2$, and $SnCl_4$and $SnFCl_3$ as etch species. No CH_3-containing Sn species were observed in the mass spectra indicating the preference of F-Cl ligand-exchange. In addition, $SnCl_4$ etch species did not appear until a much higher temperature of 300°C. This may be attributed to the lower Cl content in $SiCl_2(CH_3)_2$.

$SiH(CH_3)_2Cl$ contains Cl, CH_3 and H ligands that may be involved in ligand-exchange. The mass spectra revealed that $SiF_2(CH_3)_2$ was the ligand-exchange product with SnF_4 powder. $SiF_2(CH_3)_2$ was observed at 150°C and indicates both F-Cl and F-H exchange. In contrast, the SnH_2Cl_2 etch product was not detected until 350°C. HF was monitored throughout the temperature ramp and H_2 was also observed at T > 400°C. These products clearly indicate that H is transferred to the SnF_4 powder. Moreover, *ex situ* XPS measurements of the SnF_4 powders after ligand-exchange revealed the presence of metallic Sn. This indicates that the H on the precursor molecule can serve as a reducing agent. The reactions between silanes with SnF_4 and other metal fluoride powders are revealing the details of the ligand-exchange reactions during thermal ALE. These details can lead to pathways for selective thermal ALE by varying the temperature and ligands on the precursor molecule.

11:15am **LI-WeM1-16 Superconformal Trench Filling With $Hf_{1-X}V_XB_2$ Using Two-Precursor Chemical Vapor Deposition**, ***Kinsey Canova,*** *Z. Zhang, G. Girolami, J. Abelson,* University of Illinois at Urbana Champaign **INVITED**

Seamless filling of deep recessed features is an ongoing challenge in the fabrication of advanced microelectronic devices.We demonstrate a new CVD method that affords superconformal films (i.e., faster growth deeper

in the feature) based on the use of two precursor molecules with sharply contrasting adsorption and reaction properties.One precursor adsorbs strongly but reacts relatively slowly; the other precursor adsorbs less strongly but reacts more rapidly. The strongly adsorbing precursor inhibits the overall growth rate, but it is progressively consumed along the trench sidewalls.Consequently, the inhibition effect diminishes and fast growth from the second precursor affords an increase in growth rate with trench depth.The resulting thickness profile is superconformal (V-shaped), which leads to seamless fill.We show that the needed adsorption and reaction kinetics exist using $V(N(CH_3)_2)_4$ as the inhibiting precursor and $Hf(BH_4)_4$ as the second precursor; together, these afford films of the refractory metallic ceramic $Hf_{1-x}V_xB_2$. Under practical growth conditions, we obtain seam-free filling up to a depth-to-width (aspect) ratio of 10.

We model the kinetics based on the dependence of the film growth rate and composition *x* on the local pressure (flux) of each precursor, with ballistic transport of precursor between surfaces within the trench.The model uses a Langmuirian framework in which precursors compete for available adsorption sites and adsorbates have different reaction rates.The model shows that there is a limiting aspect ratio for a given set of kinetic coefficients.Here, the growth of $Hf_{1-x}V_xB_2$ facilitates comparisons with the model because the film composition varies with depth; this compositional change reflects the changes in the surface coverage and reaction rate of each precursor as the gas phase composition changes with depth.In future work, it will be desirable to use two precursors that afford the same film, so that the resulting composition will be uniform within the trench.We will suggest precursor combinations that are good candidates for superconformal trench filling with other technologically-relevant materials.

11:35am **LI-WeM1-20 Pyroelectric Heat Detection for *In Situ* Measurement of ALD Reaction Heat*, Ashley R. Bielinski, E. Sprague-Klein, B. Phelan, A. Martinson,*** Argonne National Laboratory **INVITED**

Atomic layer deposition (ALD) is used to deposit a wide range of materials for both academic and industrial applications, yet experimental resolution of the kinetics, thermodynamics, and mechanisms for even the most well-studied ALD half-reactions remains insufficient to test computational models.*In situ* measurements of the heat generated by ALD half-reactions could provide new insight into the complex chemical processes at play during ALD. ALD reactions have been observed to cause >10°C temperature changes on high surface area substrates like nanoparticles or metal organic frameworks, but the relatively small temperature changes (<0.1°C) predicted for planar substrates are much more difficult to accurately measure.Additionally, many reactions exhibit kinetics that are on the same order as or faster than the 10ms to 1s sampling times of *in situ* measurement techniques commonly used for ALD such as mass spectrometry, ellipsometry, or quartz crystal microgravimetry.

We present a pyroelectric calorimeter with thermal and temporal resolution down to 0.1 $\mu J/cm^2$ and 50 ns.This probe enables the time-resolved measurement of individual ALD half-cycles, enabling comparison to first-principles computational predictions.The calorimeter hardware was designed and optimized for operation under ALD conditions.Laser calibration was combined with a mathematical model of the transient thermal and electrical response to provide quantitative measurements of heat generation rates.Trimethylaluminum (TMA) was reacted with a planar, hydroxylated ALD-alumina surface to produce 96 $\mu J/cm^2$ over a reaction time of ~30 ms.Relative to other in situ measurement techniques, calibrated pyroelectric calorimetry offers a faster and more sensitive probe of ALD reactions.In addition to kinetic and thermodynamic measurements of steady state growth reactions, this technique may also provide the necessary precision to study the complexities and far sub-monolayer growth during nucleation or selective deposition.

This material is based upon work supported by Laboratory Directed Research and Development (LDRD) funding from Argonne National Laboratory, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC02-06CH11357

11:55am **LI-WeM1-24 pH Sensor Tattoo*, Katrin Unger, A. Coclite, F. Greco,*** Graz University of Technology, Austria **INVITED**

Temporary tattoo-based body sensors have gained high attention in the expanding field of tracking physiological biomarkers, such as the pH level of sweat. Because of its ultra-conformal adhesion towards the skin while providing excellent water vapor transmission, temporary tattoo sensors can react already at minimal sweat production but can also cope with large amounts of sweat. Within the presented work, a skin pH sensor tattoo is presented, made of a temporary tattoo paper, screen printed polymer electrodes and a pH responsive hydrogel. While so far tattoo papers have been functionalized only by solution-based methods, within this study for the first time a vapor-based coating routine, named initiated chemical vapor deposition, was utilized to deliver a smart hydrogel. The resulting sensor tattoo can be easily transferred on the skin and shows an outstanding conformability to the topography of the epidermis. The measured morphology properties of the layers demonstrate excellent process controllability of the desired electrode width, hydrogel thickness and shielded areas. The pH responsive hydrogel exhibits a reversible pH responsive swelling of 24% to 37%, in respect to the dry state, at pH 4 and pH 6, respectively. With impedance spectroscopy the phase shift at 1000 Hz is identified as an excellent pH-related parameter of the sensor, which can only be ascribed to the presence of the hydrogel layer. The sensor can be triggered and read out also by a cheap and light-weight Arduino setup, verifying the applicability as a wearable sensor device.

12:15pm **LI-WeM1-28 Closing Remarks and Thank You's*, Svitlana Pylypenko,*** Colorado School of Mines

Thank you for attending today's session! Please note that our afternoon sessions begin at 12:50 pm EDT. Remember to check out the AVS 67 On Demand Sessions which are available in the mobile app and online scheduler.

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