Spectroscopic Ellipsometry
Room 209 F W - Session EL-TuM

Spectroscopic Ellipsometry Analysis Methods

Moderators: Tino Hofmann, University of North Carolina at Charlotte, **Marcel Junige**, University of Colorado at Boulder

8:00am **EL-TuM-1 Crystal Symmetry and Spectroscopic Ellipsometry*, Gerald Jellison,*** Oak Ridge National Laboratory **INVITED**

Of the known crystals, over 90% are optically anisotropic and therefore birefringent.That is, the complex dielectric function depends on the polarization of the incident light and the orientation of the crystal. The general linear dielectric response for non-magnetic materials is expressed as a complex 3 x 3 symmetric tensor.This tensor can be simplified if the crystal is oriented in the laboratory reference frame, where uniaxial, orthorhombic, and monoclinic crystals require 2, 3, and 4 independent complex elements, respectively.Isotropic materials require only 1 element.Triclinic materials have no symmetry other than translation, so their dielectric tensors have 6 independent elements.

These dielectric functions are best measured by generalized or Mueller matrix ellipsometry [1].If there is no depolarization, then the ellipsometric data can be reduced to the 2 x 2 reduced Jones matrix rho where rho$_{pp}$ = rho$_{pp}$/rho$_{ss}$, rho$_{sp}$ = rho$_{sp}$/rho$_{ss}$ and rho$_{ps}$ = rho$_{ps}$/rho$_{ss}$.For isotropic materials, *rho*$_{pp}$= tan*(psi)*exp*(iDelta)*, where psi and Delta are the standard ellipsometric angles.The cross-polarization terms rho$_{sp}$ and rho$_{ps}$ will be non-zero if the coordinate system of the crystal does not match the coordinate system of the ellipsometer, defined by the plane of incidence.For uniaxial crystals, the cross-polarization terms will be zero if the optic axis is in or perpendicular to the plane of incidence.For orthorhombic and monoclinic crystals, the cross-polarization terms will be zero if a principal axis is perpendicular to the plane of incidence. Even when the cross-polarization terms are non-zero, there are some orientations of the crystal where rho$_{sp}$ and rho$_{ps}$ will be symmetric.If the optic axis of a uniaxial crystal is in the sample surface plane (Theta = 90°), then rho$_{ps}$(phi) = -rho$_{sp}$(phi), rho$_{ps}$(phi) =-rho$_{ps}$(-phi), and rho$_{sp}$(phi)=-rho$_{sp}$(-phi), where the Euler angle phi is the angle of the optic axis with respect to the plane of incidence.

This talk will discuss the symmetry relationships for uniaxial, orthorhombic, and monoclinic crystals and will show spectroscopic generalized ellipsometry data taken from several anisotropic crystals.Example crystals may include: rutile and anatase (TiO_2), ZnO, calcite and aragonite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$,] zinc oxide (ZnO), tin oxide (SnO_2), andparatellurite (a-TeO_2).

[1] G. E. Jellison, Jr., N. J. Podraza, and A. Shan, “Ellipsometry: dielectric functions of anisotropic crystals and symmetry,” *J. Opt. Soc. Am*. A **39**, 2225 (2022).

8:30am **EL-TuM-3 Ellipsometric Reality Check: Are My Results Correct?*, Maxwell Junda,*** Covalent Metrology

Covalent Metrology offers a large range of analytical measurement techniques (150+) and uses these to support scientists and engineers in solving demanding problems across many different industries.There is often tremendous value in combining multiple measurement techniques on a sample to obtain complementary material property information. This provides a fuller understanding of the materials of interest.However, sometimes when spectroscopic ellipsometry (SE) is used in conjunction with other metrology, the corresponding results don’t match.This often opens a Pandora’s Box of questions about the source of the mismatch and which result is “right.”Similarly, even when evaluating ellipsometry results by themselves, the widely varying needs of each application require careful handling of how SE data is modeled and results are interpreted.

As an example, one Covalent customer is fabricating waveguides.Accuracy in our measurements of dimensions and thickness of the waveguide materials is *critically important* since these waveguides are designed to operate at a specific wavelength which defines the required dimensions.Cross sectional transmission electron micrographs (TEM) are also used to measure dimensions which, with surprising frequency, differ from best-fit SE results by a nontrivial margin.As a further complication, using TEM-derived thicknesses as fixed parameters in the SE modeling results in unacceptably poor model fits. This mismatch has necessitated investigation into properties at the interfaces that are detectable by SE, but not TEM.

By contrast, another Covalent customer is using routine SE measurements for process monitoring.Here, the repeatability of SE measurements (i.e. precision) is most important to track the deposition process over time and overall accuracy of the results is secondary.This represents a completely different use-case for ellipsometry where establishing a standardized measurement and modeling methodology for detecting deviations dominates, potentially even over accurate measurement results.

Lastly, specific choices for optical modeling configurations always have tradeoffs between physical realism, sensitivity, and practical utility.Some models are developed to accommodate gross spatial nonuniformities in films on 300mm wafers, whereas others are created to detect weak absorption modes in the infrared when paired with transmittance measurements.Although all are fundamentally based on the information encoded within SE data, the optical models used to obtain final results are unavoidably context-dependent.

8:45am **EL-TuM-4 Spectroscopic Ellipsometry Based on Frequency Division Multiplexing*, Jongkyoon Park,*** KRISS, Republic of Korea

Spectroscopic ellipsometry (SE) is a widely utilized technique in optical metrology, particularly in the semiconductor industry, for its ability to measure thin-film thickness non-destructively and with sub-nanometer precision. Various types of SE have been developed, each type offering unique strengths and limitations, making the selection of an appropriate technique crucial for specific applications. Here, we experimentally and theoretically demonstrate a novel SE technique based on frequency division multiplexing (see Fig. 1), which we call Frequency Division Multiplexing Spectroscopic Ellipsometry (FDM-SE) [1,2].

FDM-SE is a variant of traditional rotating polarizer ellipsometry (RPE) in which the broadband light source is replaced with multiple discrete-wavelength intensity-modulated laser diodes (LDs) (see Fig. 2). This modification enables obtaining the optical properties of materials at multiple wavelengths simultaneously by using a spectrally integrating detector instead of a spectrometer.

In order to assess the performance of FDM-SE method, SiO_2 films on a Si wafer with different film thicknesses were measured by FDM-SE and a commercially available conventional SE instrument. We obtain a difference between the measured thicknesses with both methods of less than 5 Å on average implying that FDM-SE can be used for accurate thickness measurements. Thus, the proposed FDM-SE technique provides a novel alternative SE approach for a variety of optical metrology applications.

9:00am **EL-TuM-5 Advanced Electromagnetic Modeling Techniques for Metamaterial Platforms*, Ufuk Kilic,*** University of Nebraska-Lincoln, USA **INVITED**

Nanostructured metamaterials play a crucial role in cutting-edge applications spanning optoelectronics, quantum information processing, and biomedical technologies [1-3]. Precise characterization of their structural and optical properties is essential for their effective integration into functional systems. The conventional spectroscopic ellipsometry (SE)-based optical characterization faces inherent limitations. SE is largely constrained to far-field analysis and relies on idealized layer-based models, making it insufficient for complex nanostructures with pronounced near-field interactions, strong nonlocal effects, and wavevector-dependent material responses.

In this talk, to overcome these challenges, we leverage the finite element modeling (FEM) based theoretical characterization, optimization, and verification technique which basically relies on the frequency dependent full-wave electromagnetic solutions of Maxwell's equation [3]. FEM provides a powerful framework for directly visualizing electromagnetic field distributions, incorporating experimental inputs from imaging techniques such as scanning electron microscopy and transmission electron microscopy, and refining optical models through spectroscopic ellipsometry-based dielectric function analysis. By enabling precise modeling of both near- and far-field interactions, as well as capturing nonlocal material responses that go beyond standard effective medium approximations, FEM pushes the boundaries of conventional characterization techniques. This deeper understanding of light-matter interactions is essential for advancing photonic, optical, and quantum materials, enabling next-generation applications.

References:

[1] Carneiro, S. V., et al., *Materials Today Nano* 22 (2023): 100345.

[2] Kilic, U., et al., *Advanced Optical Materials* (2024): 2302767.

[3]Kilic, U., et al., *Nature communications* 15.1 (2024): 3757.

9:30am **EL-TuM-7 Magnetic Field-Controlled Polarized Emissivity in Low-Temperature Spin Systems via the Bloch Formalism***, **Sina Khayam**,* Mechanical and Materials Engineering Department, University of Nebraska-Lincoln, Lincoln, NE 68588*; Viktor Rindert,* NanoLund and Solid State Physics, Lund University, 22100 Lund, Sweden*; Ufuk Kilic,* Electrical and Computer Engineering Department, University of Nebraska-Lincoln, Lincoln, NE 68588*; Mathias Schubert,* NanoLund and Solid State Physics, Lund University, 22100 Lund, Sweden & Electrical and Computer Engineering Department, University of Nebraska-Lincoln, Lincoln, NE 68588

This study investigates how polarized emissivity in spin-based systems can be modulated at low temperatures using the Bloch model, focusing on the role of magnetic fields in tuning their optical response. The emissivity, a key quantity in radiative heat transfer, is strongly influenced by the temperature-dependent distribution of spin states, which in turn is governed by their interaction with magnetic fields. To model this, we use a permeability tensor derived from Bloch's equations for nuclear magnetic moments in magnetically resonant materials [1, 2, 3], combined with a dielectric permittivity tensor. These tensors are incorporated into a 4×4 matrix formalism [4] to compute emissivity and analyze how its polarization properties are affected by magnetic anisotropy. The study also presents a generalized analytical framework for calculating thermal emissivity that accounts for both magnetic and dielectric responses under varying temperature and magnetic field conditions. Model validation is performed using WVASE32TM ellipsometry software, confirming the accuracy of theoretical predictions. Overall, this work provides new insights into magnetically tunable quantum emissivity, with promising implications for next-generation thermal management in quantum and nanoscale technologies.

Spectroscopic Ellipsometry
Room 209 F W - Session EL1-TuA

Spectroscopic Ellipsometry Material Applications

Moderators: David Aspnes, North Carolina State University, **James Hilfiker**, J. A. Woollam Co., Inc.

2:15pm **EL1-TuA-1 Optical Properties of Chromogenic Thiazolothiazole-embedded Polymers***, Nuren Shuchi, Dustin Louisos, Glenn D. Boreman, Tyler Adams, Michael G. Walter,* University of North Carolina at Charlotte*;* ***Tino Hofmann,*** New Jersey Institute of Technology **INVITED**

The growing demand for advanced optical technologies capable of dynamic manipulation of spectral properties through external stimuli has spurred significant interest in chromogenic materials with tunable optical properties. Chromogenic materials that exhibit reversible changes in their optical properties in response to optical stimuli are called photochromic materials [1,2].These materials have been demonstrated to play a significant role in facilitating the development of tunable infrared metasurfaces by leveraging their light-induced changes in optical properties [3]. The development of photochromic materials that exhibit strong and reversible changes in their optical properties in the infrared and visible spectral regions could offer an alternative approach to achieving tunable ir/vis metasurfaces, potentially with advantages in terms of cost, fabrication, or power consumption.Viologens represent an important class of photochromic materials [4]. Their properties can be enhanced by incorporating a thiazolo[5,4-d]thiazole (TTz) fused, conjugated bridge, an approach that has gained growing interest due to its strong fluorescence, solution-processability, and reversible photochromic transitions. Notably, dipyridinium thiazolo[5,4-d]thiazole viologens exhibit high-contrast, rapid, and reversible photochromic changes when integrated into a polymer matrix. Upon exposure to radiation with energy exceeding 2.8 eV, they undergo a color transition from light yellow (TTz^{2+}) to purple (TT^{+}) and then to blue (TTz^{0}) due to two distinct photoinduced single-electron reductions [5]. In this presentation, we report on a parameterized dielectric function of photochromic dipyridinium thiazolo[5,4-d]thiazole embedded in polymer obtained from a quantitative analysis of the polarization-sensitive optical response in the visible and infrared spectral ranges. In addition to discussing the photochromically-induced changes to the optical response we will report on recent results on the infrared imaging contrast obtained for this material as well as interesting temporal responses observed upon photoexcitation. **References:** [1] J. Crano and R.J. Guglielmetti, Organic Photochromic and Thermochromic Compounds Vol. 1 (New York, NY: Kluwer Academic Publishers., 1999). [2] H. Konaka, *et al.*, Inorg. Chem. **42**, 1928-1934 (2003). [3] S. Bang, *et al.*, Micromachines **9**, 560 (2018). [4] Z. Guo, *et al.* , Adv. Opt. Mater. **12**, 2401791 (2024). [5] T.J. Adams, *et al.*, ACS Appl. Opt. Mater. **2**, 704-713 (2024).

2:45pm **EL1-TuA-3 Dielectric Function of Atomic Layer Deposition Grown VO_2 Determined by Spectroscopic Ellipsometry***,* ***Dustin Louisos,*** *Nuren Shuchi, Glenn Boreman,* University of North Carolina at Charlotte*; Tino Hofmann,* New Jersey Institute of Technology

VO_2 is a transition metal oxide that experiences a temperature driven metal insulator transition at 68 °C [1,2], which makes it a promising material for tunable optical and electronic devices [3,4]. Accurate knowledge of its optical constants is critical for design and modeling of devices, however, reported optical constants vary widely depending on deposition method, annealing recipe, and film quality. In this work, the optical properties of VO_2 thin films grown by atomic later deposition are investigated using spectroscopic ellipsometry in the visible and infrared spectral range.

VO_2 films with a nominal thickness of 35 nm were grown on c-plane sapphire substrates using atomic layer deposition [5]. Atomic layer deposition was followed by a post-deposition thermal annealing step for 30 minutes at 400 °C. Spectroscopic ellipsometry measurements were performed from 0.045 to 5.9 eV using the J.A. Woollam IR-VASE and RC2. Spectroscopic ellipsometry measurements were taken on the as-deposited amorphous VO_x, annealed VO_2 at room temperature, and annealed VO_2 at 100 °C.

A single-model dielectric function was developed to describe the dielectric function over the entire spectral range. The oscillator model for the as-deposited sample is a sum of four Gaussian oscillators [6] and one Tauc-Lorentz oscillator [7]. The oscillator model for the as-deposited VO_x sample was used to determine the oxygen content, x, using a technique given by [8]. The oxygen content was found to be approximately 2, which has the proper stoichiometry needed to anneal to VO_2. For the annealed sample, the model uses a sum of Lorentz and two Tauc-Lorentz with a Drude term [9] added for the metallic state. For the sample measured in this work, we find a resistivity of 5.71 10^{-4} Ohm·cm which is significantly lower than the resistivity found for films deposited by magnetron sputtering [10] and other atomic layer deposition approaches [11] reported recently.

References

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[2] M. Nazari, et al., Phys. Rev. B **87**, 035142 (2013).

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3:00pm **EL1-TuA-4 Temporal Properties of Photochromic Thiazolothiazole-Embedded Polymer Films***,* ***Nuren Shuchi,*** *Tyler Adams, Naz Tumpa, Dustin Louisos, Glenn Boreman, Michael Walter,* University of North Carolina at Charlotte*; Tino Hofmann,* New Jersey Institute of Technology

Organic photochromic polymers, whose photo-chemical and optical properties can be altered through optical stimulation, are found in diverse applications ranging from tinted lenses and smart windows to memory devices, actuators, tunable filters, and holographic gratings [1-4]. Recently, extended viologens containing the thiazolo[5,4-d]thiazole (TTz) backbone are increasingly attracting interest due to their strong fluorescence, solution-processability and reversible photochromic transition [5]. Especially, dipyridinium thiazolo[5,4-d]thiazole viologen exhibits high-contrast, fast, and reversible photochromic changes. When exposed to radiation with an energy larger than 3.1 eV, it transitions from light yellow (TTz^{2+}) to purple ($TTz^{\cdot+}$) to blue (TTz^{0}) state due to two distinct, photo-induced single electron reductions [5]. The complex dielectric function of a non-photochromic TTz derivative and a photochromic TTz-embedded polymer has been determined previously in the visible and near-infrared spectral range using spectroscopic ellipsometry [6-7].

In this presentation, we will discuss the dynamic optical properties of photochromic thiazolothiazole-embedded polymer films. Attenuated total reflectance ellipsometry was used in order to isolate surfaces exposed to oxygen-rich and oxygen-deficient environments. This facilitates the spatial separation of surface regions based on oxygen exposure and the distinction between surface and bulk contributions to the overall optical response.

Reference

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3:15pm **EL1-TuA-5 Determination of optical properties of ultrathin silane films coated on Silicon substrate by means of Immersion Ellipsometry***,* ***Samira Jafari,*** Brigham Young University*; Blaine Johs,* Film Sense LLC*; Matthew Linford,* Brigham Young University

This study investigates the optical properties of ultrathin silane films deposited on silicon substrates using Immersion Ellipsometry (IE). IE is a very sensitive optical technique and can determine the refractive index (n) of very thin films (< 5 nm) by analyzing ellipsometric data acquired in both air and liquid ambients (water, n=1). The immersion approach enhances the accuracy of very thin film characterization, by decorrelating the film thickness and optical constants. A series of silanes, including chloro octadecyl silane, chloro decyl silane, (heptadecafluoro-1,1,2,2-tetrahydrodecyl) silane, and other silanes were studied, revealing distinct optical characteristics attributable to their varying chemical compositions. Notably, a correlation between refractive index and electronegativity was observed, where lower electronegativity resulted in a lower refractive index, given the film thickness approximation to the molecular length. This demonstrates SIE's ability to decouple optical constants from film thickness in ultrathin films, enabling accurate determination of optical parameters. To complement the optical analysis, X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical composition and bonding states of the deposited silanes, while contact angle goniometry provided insights into the films' surface wettability. This comprehensive approach highlights IE's efficacy in characterizing transparent ultrathin films and underscores its potential for improving control over silane-based coatings in microelectronics, biomedical devices, and optical applications.

Spectroscopic Ellipsometry
Room 209 F W - Session EL2-TuA

Spectroscopic Ellipsometry Novel Methodologies

Moderators: Ufuk Kilic, University of Nebraska - Lincoln, **Mathias Schubert**, University of Nebraska - Lincoln

4:00pm **EL2-TuA-8 In Situ Spectroscopic Ellipsometry Studies of Selective Thermal Dry Etching**, ***Marcel Junige***, *Steven M. George,* University of Colorado Boulder **INVITED**

Thermal dry etching uses gas-phase reactants in a vacuum and physicochemical reactions based on thermal activation, providing isotropic material removal for lateral patterning without line of sight. Thermal dry etching covers atomic layer etching (ALE) and spontaneous etching. ALE is defined by self-limiting reactions, separated by purge steps. These half-reactions modify and sequentially volatilize a thin film surface, thereby removing material digitally one ultra-thin layer per cycle. Conversely, spontaneous etching is characterized by a sustained reaction of a thin film surface with one etchant only, thereby removing a targeted material with a continuous etch rate.

This invited talk reviews exemplary studies of thermal ALE and spontaneous etching, utilizing *in situ* spectroscopic ellipsometry (iSE) to reveal thickness changes, self-limiting behavior, synergy between half-reactions, and selectivity between different materials. An iSE instrument (J.A. Woollam Co.) acquired ellipsometric spectra for 5 s at the end of reactant purge steps. Interference enhancement enabled thickness precision of ±0.01 Å.

Al_2O_3 thermal ALE using sequential hydrogen fluoride (HF)/trimethylaluminum (TMA) exposures exhibited a linear etch per cycle (EPC) at 275℃. After initial fluorination, consecutive HF exposures gave virtually no Al_2O_3 thickness loss. This self-limiting behavior corresponded to ideal ALE synergy because all material removal resulted solely from a favorable interaction of the HF/TMA sequence and no etching occurred by either HF or TMA alone. SiO_2 thermal ALE using sequential TMA/HF exposures likewise exhibited a linear EPC at 275℃. Consecutive HF exposures displayed negligible SiO_2 thickness loss, especially after eliminating H_2O during the fluorination step. This self-limiting behavior revealed near-ideal synergy for SiO_2 ALE.

SiN_x thermal ALE using sequential TMA/HF exposures discovered no ALE synergy because consecutive exposures of HF alone caused predominant SiN_x spontaneous etching. This difference between near-ideal versus no ALE synergy obtained great inherent selectivity between major SiN_x versus minor SiO_2 spontaneous etching using anhydrous HF vapor at 275℃. Using anhydrous HF at temperatures >150℃ also discovered facile spontaneous etching of single-crystalline, poly-crystalline, and amorphous Si films with high selectivity compared to SiO_2 retention.

In contrast, co-adsorbing polar molecules with anhydrous HF had a drastic effect. Co-dosing NH_3+HF at 275℃ obtained exceptional selectivity for rapid SiO_2 versus negligible SiN_x spontaneous etching. Similarly, co-adsorbing dimethylamine with HF at 200℃ enabled substantial SiO_2 spontaneous etching.

4:30pm **EL2-TuA-10 Band Filling and Relaxation Effects in Semiconductors Using Ultrafast Spectroscopic Ellipsometry**, ***Carlos Armenta***, New Mexico State University; *Martin Zahradník,* ELI ERIC, Czechia; *Mateusz Rebarz,* ELI ERIC, Poland; *Shirly Espinoza,* ELI ERIC, Colombia; *Carola Amminger,* New Mexico State University, Austria; *Saul Vazquez-Miranda,* ELI ERIC, Mexico; *Jakob Andreasson,* ELI ERIC, Czechia; *Stefan Zollner,* New Mexico State University **INVITED**

We investigate the transient dielectric function (DF) of Germanium at very high electron-hole pair densities using time-resolved spectroscopic ellipsometry. By employing a pump-probe technique, we explore the evolution of the critical points near the L-valley on a femtosecond time scale. Through modeling the DF of the material under different carrier concentrations, we analyze the impact that the photo-induced phenomena, such as phase-filling and many-body effects, have on the material's optical properties.

Pump-probe ellipsometry measurements were conducted on Ge as an ideal prototype for other semiconductors of interest. The time delays range from -10 ps to 1 ns with a minimum step size of 50 fs. Using pump excitation, we probe carrier densities ranging from 10^{19} cm^{-3} up to 10^{20} cm^{-3}. The evolution of the DF over delay time is dictated by the ultrafast dynamics of the photo-excited carriers. Since the critical points (CP) E_1 and $E_1+\Delta_1$ lie inside the energy range of our probe (1.8 to 3 eV), the primary focus of our model is to describe these features as a function of delay times. Due to the two-dimensional nature of these CPs, excitonic effects significantly enhance the absorption in Ge. Furthermore, at high carrier densities, intervalley scattering and band saturation will play a significant role in the optical response of the material. To address these effects, we combined band-filling effects with a 2D excitonic line shape to model the DF. We also simulated the Fermi energies and carrier temperatures governing the measurements using Fermi-Dirac statistics. Our aim is to enhance our understanding of Ge's optical behavior under intense laser excitation. Beyond Ge, these findings offer insights into the ultrafast carrier dynamics and optical responses of other semiconductor materials under high excitation conditions.

5:00pm **EL2-TuA-12 Self-Referencing Photothermal Common-Path Interferometry to Augment Ellipsometry in Low-Loss Membranes**, ***Tanuj Kumar,*** University of Wisconsin - Madison; *Demeng Feng,* University of Wisconsin-Madison; *Merlin Mah, Phyo Lin,* University of Minnesota; *Shenwei Yin, Hongyan Mei, Aakankshya Mishra,* University of Wisconsin - Madison; *Ronald Warzoha,* United States Naval Academy; *Victor Brar,* University of Wisconsin - Madison; *Joseph Talghader,* University of Minnesota; *Mikhail Kats,* University of Wisconsin - Madison

Ellipsometry and direct transmission/reflection FTIR spectrometry are versatile techniques for measuring the optical constants and thicknesses of arbitrary stacks of thin films. The self-referencing nature of ellipsometry allows high sensitivities and low noise, and the parallelized nature of FTIR spectroscopy allows convenient and fast measurements, but these techniques are insufficient to measure extinction coefficients (κ) lower than ~$1x10^{-2}$ in thin samples. When κ cannot be readily measured with ellipsometry and FTIR spectroscopy, it may be interpolated between regions of measurable κ with Kramers-Kronig consistent oscillator models. However, in low-loss regimes, different oscillator models can result in κ differing by orders of magnitude; for example, for UV-visible-NIR ellipsometry on ~200-nm-thick Si_3N_4 membranes, we observed diverging fits for κ at wavelengths longer than ~300 nm using three different oscillator models (Cauchy-Urbach, Tauc-Lorentz, and Cody-Lorentz) that all fit the ellipsometry data.[1]

We propose the use of an additional direct measurement of absorptivity at a low-loss wavelength using self-referencing photothermal common-path interferometry (PCI). PCI is a sensitive absorption-measurement technique wherein a thermal lensing effect caused by absorption of a chopped high-powered pump laser in a sample is observed through the distortion of a co-incident low-powered probe laser. PCI has been previously used to measure losses in materials for LIGO interferometer mirror coatings and other optical components,[2] but conventional PCI does not allow calibration of the measurement of freestanding membranes, and is more suited for supported thin films.[1] Our self-referencing PCI makes use of monolayer graphene deposited on a freestanding membrane to create a high absorptivity reference sample that is similar in photothermal characteristics to the sample being tested, but whose loss can be measured with ellipsometry to allow calibration of the PCI measurement and thus accurately measure the low-loss sample.

We measured the imaginary part of the refractive index, κ, for Si_3N_4 (~$1.9x10^{-7}$) and SiN_x (~$6.8x10^{-5}$) at 1064 nm using self-referencing PCI. Using this data, we have assembled comprehensive optical models of Si_3N_4 and SiN_x from UV-Vis-NIR-MIR ellipsometry and FTIR spectroscopy. More broadly, our approach of merging several different spectroscopic techniques can be translated to other low-loss materials and allows the creation of highly accurate broadband materials datasets for optical simulation and design.

[1]. D.Feng, et al, *arXiv:2404.04449*, 2024.

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5:15pm **EL2-TuA-13 Artificial Intelligence for Ellipsometric Analysis of Liquid Mixtures Using Multi-Bounce ATR-FTIR**, ***Jeremy VanDerslice,*** J.A. Woollam Co.; *Alyssa Mock, Madison Coleman, Mar Diehl, Madison Meaney, Tyler Adams,* Weber State University

Artificial intelligence is emerging as a valuable tool in optical metrology, offering a new avenue for data interpretation in model-based techniques like ellipsometry. Optical models used to describe thin films traditionally measured by ellipsometers often require careful initialization or involve significant computational cost. In these cases, AI methods can assist by providing initial parameter estimates or, in some applications, by replacing the physical model entirely. One such application benefiting from the combination of ellipsometry and predictive data interpretation is the concentration analysis of liquid mixtures using Fourier-transform infrared (FT-IR) ellipsometry in a multi-bounce prism configured for attenuated total reflection (ATR) measurements. In this approach, neural networks learn the nonlinear relationships between ellipsometric measurements and analyte concentrations in these mixtures. This capability is particularly relevant in industries relying on optical techniques for liquid analysis. In the wine and beverage industry, for example, concentrations of ethanol, sugars, phenolic compounds, organic acids, and other analytes are commonly measured using reflection or transmission intensity. While the existing intensity-based methods offer non-destructive analysis, they generally exhibit lower sensitivity to absorption features specific to each analyte compared to polarization-based measurements, which suggests a reduced sensitivity threshold compared to ellipsometry. The use of predictive neural networks, in combination with ellipsometry, enables enhanced determination of analyte concentrations within a liquid mixture without requiring prior expertise in ellipsometry.

Atomic Scale Processing Mini-Symposium
Room 206 A W - Session AP+AS+EL+EM+PS+TF-ThM

Advancing Atomic Scale Processing through Modeling and Simulation

Moderators: Heeyeop Chae, Sungkyunkwan University (SKKU), **Sagar Udyavara**, Lam Research Corp

8:00am **AP+AS+EL+EM+PS+TF-ThM-1 Multiscale Simulations for Atomic Scale Processing*, Michael Nolan,*** Tyndall Institute, Ireland **INVITED**

In modern semiconductor device fabrication, the dimensions involved require atomic level control over materials deposition and etch. Atomic Level Processing, exemplified by Atomic Layer Deposition (ALD) and thermal atomic layer etch (tALE), is therefore critical deposition and etch of relevant materials. Further scaling and use of complex three-dimensional structures means that Thermal ALE will take centre stage in etching. The key chemistry takes place at surfaces which drives the self-limiting characteristics and other advantages of these atomic level processing approaches. In this presentationt I will discuss how atomistic simulations based on first principles Density Functional Theory, ab initio Molecular Dynamics and kinetic Monte Carlo methods can be used to predict the chemistry of atomic level deposition and etch processes. I will first discuss the key chemistries involved in atomic level processing chemistries and the challenges that we have identified in this exciting area.The first scientific topic is the simulation of plasma enhanced deposition (PE-ALD) of metals, using the example of cobalt for next generation interconnects. This is the first example of an atomistic level study of the full PE-ALD cycle for Co metal and show that the process requires use of ammonia or mixed H2/N2 plasma. Calculated energy barriers for key steps give guidance regarding the temperatures required for the process. We show how substrate pre-treatment can reduce nucleation delay and therefore allow selectivity in deposition of the target film. Finally we show how kinetic Monte Carlo can be used to predict the structure of deposited metal films on different nitride substrates using data from DFT level simulations.The second example is molecular layer deposition of hybrid materials, using alucone as the prototypical example. Comparison of aliphatic with functionalized aromatic molecules allows differences in film properties to be understood. A further application of this involves selective, templated deposition of target films using block co-polymer infiltration where differences in reactivity of a precursor in two polymers promotes selective deposition of the target films. Finally, I present our work on self-limiting thermal atomic layer etching (ALE), highlighting how simulations can (1) predict the window of self-limiting etch (2) unravel the difference between amorphous and crystalline substrates and (3) probe the impact of surface orientation on tALE chemistry, all of which are important for future, selective thermal ALE processing on complex 3D substrates.

8:30am **AP+AS+EL+EM+PS+TF-ThM-3 The Si-Cl2-Ar+ Atomic Layer Etching Window: Fundamental Insights from Molecular Dynamics Simulations and a Reduced Order Model*, Joseph Vella,*** TEL Technology Center, America, LLC, USA*; David Graves,* Department of Chemical and Biological Engineering Princeton University

Plasma assisted atomic-layer etching (ALE) processes are frequently characterized by the ALE window. This is a range of ion energies where the amount of substrate etched remains constant as a function of the ion energy. Silicon (Si) etch by alternating exposure to chlorine gas (Cl_2) and argon ions (Ar^+) is frequently used as a demonstrative example to illustrate concepts of ALE, including the ALE window.[1] Despite this, when examining the literature, properties of the ALE window for this system remain obscure. For example, Kim et al.[2] studied Si-Cl_2-Ar^+ ALE and report that the ALE window should be below 40 eV. On the other hand, Park et al.[3] report the ALE window as being from 70 to 90 eV. Still others report an Ar^+ ion energy of 50 eV as being within the ALE window.[4] In this talk, we aim to resolve these contradictory reports by studying the Si-Cl_2-Ar^+ ALE with classical molecular dynamics (MD) simulations and a reduced order model (ROM).[5] The MD results show that the range of Ar^+ ion energies where the amount of Si etched per cycle (EPC) remains relatively constant is from 15eV to 20 eV, which is very narrow. The EPC in this region is also less than one atomic layer, because atomic Cl sputtering is significant. The results also show that a large ion fluence (roughly 4.2 10^{16} ions/cm^2 for 15 eV ions) is required to remove all Cl from the near surface region, which is a key insight when developing processes that achieve “true ALE”. Using the ROM, parameters can be varied to observe their effect on properties of the ALE window. For example, by increasing the threshold sputtering energy of Si, the width of ALE window can be increased. While this study focuses on the relatively simple Si-Cl_2-Ar^+ system, it is clear learnings from this study can be extended to other systems.

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[2] B. Kim, S. Chung, and S. M. Cho, “Layer-by-later Etching of Cl-adsorbed Silicon Surfaces by Low Energy Ar^+ Ion Irradiation”, Appl. Surf. Sci. 2002, 187, 124-129.

[3] S. Park, K. Min, B. Yoon, D. Lee, and G. Yeom, “Precise Depth Control of Silicon Etching using Chlorine Atomic Layer Etching” Jpn. J. Appl. Phys. 2005, 44, 389-393.

[4] K. J. Kanarik, T. Lill, E. A. Hudson, S. Sriraman, S. Tan, J. Marks, V. Vahedi, and R. A. Gottscho, “Overview of Atomic Layer Etching in the Semiconductor Industry”, J. Vac. Sci. Technol. A, 2015, 33, 020802.

[5] J. R. Vella, Q. Hao, M. A. I. Elgarhy, V. M. Donnelly, and D. B. Graves, “A Transient Site Balance Model for Atomic Layer Etching”, Plasma Sources Sci. Technol., 2024, 33, 075009.

8:45am **AP+AS+EL+EM+PS+TF-ThM-4 Influence of Fluorination and Oxygenation Sources on the Thermal Atomic Layer Etching of MoS2*, Jacob A. Tenorio,*** *Icelene Leong, John D. Hues, Steven M. Hues, Elton Graugnard,* Boise State University

Atomic layer etching (ALE) has emerged as a pivotal technique in the precise fabrication of two-dimensional (2D) materials, particularly molybdenum disulfide (MoS_2), which holds promise in the semiconductor industry due to its high mobility in monolayer form. The ability to precisely etch amorphous and crystalline MoS_2 films provides a pathway for controlling thickness, which is critical to achieving desired electrical and optical properties. Previous studies used MoF_6 and H_2O in thermal ALE of MoS_2. Here, we report studies of alternate sources of fluorination and oxygenation and evaluate their impact on thermal ALE of MoS_2. Oxygen sources include water and ozone, and fluorine sources include HF/Pyridine and MoF_6. Etch rates, uniformity, and surface chemistry post ALE were characterized using spectroscopic ellipsometry, atomic force microscopy, and X-ray photoelectron spectroscopy. Results indicated at ALE of amorphous MoS_2 with HF with either H_2O or O_3 showed no signs of etching at 200 ºC or 250 ºC. Whereas the combination of MoF_6 + O_3 at 250 ºC on amorphous MoS_2 films exhibited an etch rate of 1.6 Å/cycle and a mass loss of 44 ng/cm^2. Further MoF_6 + O_3 etching at 200 ºC showed a mass loss of 19 ng/cm^2, similar to prior reports using MoF_6 + H_2O at 200 ºC. Surface morphology showed little change from etching, but surface oxygen concentration increased. This research further expands the capabilities for atomic layer processing of 2D materials.

9:00am **AP+AS+EL+EM+PS+TF-ThM-5 Insights Into Atomic Layer Etching of Diamond Surfaces*, Jack Draney*,** *Athanassios Panagiotopoulos, David Graves,* Princeton University

Thanks to its nitrogen vacancy color centers, diamond is a candidate for many quantum applications from quantum sensing to quantum computing. Pristine surfaces engineered for each application are required for good device performance. We investigated atomic-scale plasma processing as a method for reaching these pristine diamond surfaces. Our investigation takes the form of combined experiments and molecular dynamics simulations, allowing atomic-scale insights into the effects of argon / oxygen atomic layer etching on diamond surfaces.

9:15am **AP+AS+EL+EM+PS+TF-ThM-6 Benchmarking Large Language Models for Atomic Layer Deposition*, Angel Yanguas-Gil,*** *Matthew T. Dearing, Jeffrey W. Elam, Jessica C. Jones, Sungjoon Kim, Adnan Mohammad, Chi Thang Nguyen, Bratin Sengupta,* Argonne National Laboratory

In this work we introduce an open-ended question benchmark, ALDbench, to evaluate the performance of large language models (LLMs) in the field of atomic layer deposition. Our benchmark comprises questions with a level of difficulty ranging from graduate level to domain expert current with the state of the art in the field. Human experts reviewed the questions along the criteria of difficulty and specificity, and the model responses along four different criteria: overall quality, specificity, relevance, and accuracy. We ran this benchmark on an instance of OpenAI's GPT-4o using an API interface. This allows us to fine tune hyperparameters used by the LLM for text generation in a way that is not possible using conventional chat-based interfaces.

The responses from the model received a composite quality score of 3.7 on a 1 to 5 scale, consistent with a passing grade. However, 36% of the questions received at least one below average score. An in-depth analysis of the responses identified at least five instances of suspected hallucination. We also observed statistically significant correlations between the following question and response evaluation criteria: difficulty of the question and quality of the response, difficulty of the question and relevance of the response, and specificity of the question and the accuracy of the response. Finally, we will address other issues such as reproducibility, impact of hyperparameters on the quality of the response, and possible ways in which the performance of the LLMs can be further improved.

[1] A. Yanguas-Gil et al, J. Vac. Sci. Technol. A 43, 032406 (2025)

9:30am **AP+AS+EL+EM+PS+TF-ThM-7 Developing a "Digital Twin" for Area-Selective Deposition on 3D Nanopatterns***, **Nicholas Carroll**, Gregory Parsons,* North Carolina State University

Area-selective deposition (ASD)—a bottom-up patterning technique that enables precise material deposition on specific regions while preventing deposition elsewhere—has garnered significant attention as an augmentation to lithographic patterning of nanoscale features during semiconductor manufacturing. Some potential applications, such as contact-over-active-gate, will require multiple ASD materials to be deposited in sequence, heightening the challenge of effective process design. Given the vast time and resources required for experimental assessments of process integration, demand is rapidly growing for a "digital twin" (i.e. a software representation of a physical system) of device fabrication sequences. A comprehensive ASD digital twin will require advances in analyzing atomic layer deposition (ALD) reactor design and mechanistic insights into interactions between inhibitor molecules, ALD reactants, and substrate surfaces over time as reactions proceed.

We have recently developed a stochastic lattice model describing metal oxide ASD on planar substrates, including means to visualize the film shape and extent of lateral overgrowth during ASD.[1] Parameters in the model can be adjusted based on steric hindrance during each half-cycle, differences in interfacial energies between the non-growth surface and the growing film, and the preferred molecular bonding orientations. These factors elucidate subtleties in shape evolution during ASD, but results to date have been limited to vertical and lateral growth on 2D surfaces. A functional ASD digital twin must describe ASD on arbitrary 3D nanopatterns and on sub-lithographic feature sizes, including effects of selectivity loss where the selectivity decreases as film thickness increases.

We will present recent efforts in our group to extend the functionality of the stochastic lattice model to describe ASD on 3D substrates, including surfaces with pattern dimensions less than 10 nm. On very small features, for example, the model shows that lateral growth during ASD results in a wide distribution of feature separation distances, even when the growth per cycle is uniform across a growing film surface. We will also discuss intricacies that need to be considered to integrate multiple ASD steps into processes involving more complex "multi-color" substrates where several substrate materials exposed to reactants simultaneously. We believe that such insight will be critical for the realization of a functional digital twin model of atomic-scale processing needed for future semiconductor devices and other advanced manufacturing processes.

(1) Carroll, N. M.; Parsons, G. N. *J. Vac. Sci. Technol. A* **42** (6), 062411 (2024).

9:45am **AP+AS+EL+EM+PS+TF-ThM-8 Activation of C-X Bonds on Transition Metal Surfaces: Insight from DFT Studies***, **Matias Picuntureo**,* Universidad Tecnica Federico Santa Maria, Chile*; Ilker Tezsevin, Marc Merkx,* Eindhoven University of Technology, The Netherlands*; Scott Semproni, Jiun-Ruey Chen,* Intel Corporation*; Adriaan Mackus,* Eindhoven University of Technology, The Netherlands*; Tania Sandoval,* Universidad Tecnica Federico Santa Maria, Chile

Area-selective atomic layer deposition (AS-ALD) represents an advanced bottom-up nanofabrication technique enabling selective material growth on targeted areas of patterned substrates. In advanced semiconductor manufacturing, such as next-generation processes at the back end of line (BEOL), small molecule inhibitors (SMIs) can enable AS-ALD through the selective formation of inhibitor layers on metal surfaces that block deposition.

A recent study by Merkx et al. reported hydrogenolysis and potentially dehydrogenation of aniline on Ru surfaces during AS-ALD, leading to the formation of a carbonaceous layer with enhanced inhibition performance. This highlights the importance of understanding the driving forces behind the surface chemistry of SMIs.

To explore whether similar surface-mediated reactions can occur for other inhibitor–metal combinations, we employ density functional theory (DFT) to investigate the adsorption and dissociation mechanisms of benzene-derived SMIs on Ru(0001), Mo(110), and W(110) surfaces.

To enable a systematic comparison across different molecules and surfaces, our study focuses on radical-mediated dissociation pathways involving the cleavage of functional groups from the aromatic ring. This approach allows us to isolate the effect of the functional group and its interaction with the metal surface in determining the reaction thermodynamics between the molecular and dissociated adsorbed states.

We find that charge transfer to the adsorbed inhibitor modulates its dissociation energy landscape. The resulting radical intermediates are substantially stabilized through coordination with the metal surface. We further explore their subsequent hydrogenation, which transforms these surface-bound radicals into more stable, saturated species. Lastly, we show that the fate of reaction by-products—whether they remain adsorbed or desorb into the gas phase—can significantly impact the overall reaction thermodynamics and shift the equilibrium toward or away from product formation.

The investigation of the reaction pathways explored in this study contributes to the fundamental understanding of molecule–surface interactions during AS-ALD and offers insight that may support future strategies for the rational design of small molecule inhibitors.

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[1] Merkx et al., J. Chem. Phys. 160, 2024.

11:00am **AP+AS+EL+EM+PS+TF-ThM-13 Descriptor-driven analysis of inhibitors for AS-ALD processes***, Joost F. W. Maas, Marc J. M. Merkx,* Eindhoven University of Technology, Netherlands*; Matías Picuntureo, Lucas Lodeiro,* Universidad Tecnica Federico Santa Maria, Chile*; Adriaan J. M. Mackus,* Eindhoven University of Technology, Netherlands*; **Tania E. Sandoval**,* Universidad Tecnica Federico Santa Maria, Chile

Area selective atomic layer deposition (AS-ALD) is a bottom-up technique that can address some of the challenges that limit the nanofabrication of complex structures, which require patterning and alignment at the atomic scale. Currently, one of the most robust strategies to carry out AS-ALD is with the use of small molecule inhibitors (SMIs), that selectively adsorb and inhibit the non-growth surface (NGS) and prevent precursor adsorption. These SMIs range from a variety of functionalities and structures depending on the target NGS, and their selection is based on specific criteria, such as reactivity, volatility, and safety.[1,2]

Currently, the library of tested inhibitor molecules is very limited, therefore finding the best candidate for a given surface is challenging. Using computational tools can significantly accelerate the expansion of this library through high-throughput screening and recent advances in machine learning. In the case of the use of descriptors,[3] the goal is to correlate the performance of the SMIs e.g., measured in terms of their stability, as adsorption energy, with the dependence on materials or molecular properties. The derived correlations can serve to establish general guidelines for SMI selection, expanding the analysis to other molecules not included in the initial study. This approach has proven to be very successful in reducing computational costs in other fields, such as heterogeneous catalysis and drug discovery.

In this presentation, we provide an overview of the dependency between a list of descriptors and the adsorption energies of SMIs candidates on a variety of relevant NGS, such as oxides, nitrides, and metals. We explore descriptors based on the molecular properties, such as electronegativity, electrophilicity, and orbital energy, as well as descriptors based on the electronic structure of the material, such as d-band center. Results indicate a with strong correlation with the adsorption energy (E_{ads}) and electronegativity of the core-atom on the adsorption of oxides and nitrides, as well as the d-band center on the adsorption on metal surfaces. Moreover, our data highlights the differences in reactivity across surfaces and the challenges in surface passivation across surfaces with similar surface sites. Overall, this study provides important insights into the use of descriptor-driven analysis in the selection of the right SMI candidates for the advancement of ASD processes.

[1] A. Mameli and A. Teplyakov *Acc. Chem. Res.* 2023, 56, 2084−2095.

[2] P. Yu, et al. *Appl. Surf. Sci.* 2024, 665, 160141.

[3] C. Chen, et al. *J. Phys. Chem. C* 2025, 129, 13, 6245–6253.

11:15am **AP+AS+EL+EM+PS+TF-ThM-14 Understanding Plasma-Induced Bonding and Composition Changes in SiCN ALD via kMC–DFT Modeling***, **Ting-Ya Wang**,* University of Texas at Austin*; Hu Li, Peter Ventzek,* Tokyo Electron America*; Gyeong Hwang,* University of Texas at Austin*; Jianping Zhao,* Tokyo Electron America

Plasma-enhanced atomic layer deposition (PEALD) enables low-temperature processing of silicon carbonitride (SiCN), a critical low-k material for advanced interconnects. However, energetic plasma species—including both ions and radicals—can significantly influence surface reactions, film composition, and structural evolution, ultimately affecting material properties such as dielectric constant and mechanical strength. A comprehensive understanding of these species-specific effects is essential for process optimization.

Integrating kinetic Monte Carlo (kMC) with density functional theory (DFT) offers a powerful approach for simulating ALD. However, a key challenge in kMC lies in the need for a predefined list of permissible events. Traditionally, researchers manually compile a set of reactions deemed most significant. Yet, the vast number of possible events on a surface, combined with the importance of rare events in ALD, raises concerns about the authenticity and completeness of outcomes derived from manually curated reaction lists.

To address this, we developed an atomistic, off-lattice, three-dimensional simulator that integrates kMC with DFT. We employed a strategic approach to construct a comprehensive event list, capturing a broad spectrum of potential surface reactions. This year, we expand our study in four key directions: (1) comparison of ion- and radical-driven reaction pathways to delineate their distinct roles in modifying surface chemistry; (2) evaluation of different plasma chemistries (e.g., N_2 vs. NH_3) to understand how reactive species impact film stoichiometry and termination; (3) simulation of multi-cycle growth to track the evolution of defects and compositional shifts; and (4) simulation predictions against experimental data such as XPS and IR spectra.

Our findings reveal a synergistic interplay between ions and radicals in shaping the formation of Si–N, Si–C, and C–N bonding networks. The simulation platform enables insights into plasma–surface interactions, offering a predictive framework for optimizing SiCN PEALD processes.

11:30am **AP+AS+EL+EM+PS+TF-ThM-15 Understanding SiCN Film Oxidation Mechanism Through Density Functional Theory***, **Tsung-Hsuan Yang**, Hu Li, Jianping Zhao, Peter Ventzek,* Tokyo Electron America

Low dielectric constant (low-k) spacers are essential components in advanced microelectronic devices for mitigating parasitic capacitance and crosstalk, leading to enhanced device performance. Among low-k materials, silicon carbon nitride (SiCN) is widely used for its tunability in dielectric constant, leakage current and chemical robustness. However, the long-term stability of SiCN films is often compromised by atmospheric moisture, leading to the formation of silicon oxide. To address this issue, we utilize density functional theory (DFT) to elucidate the fundamental oxidation mechanisms of SiN and SiC components by H_2O. Reaction rates were estimated with a combination of transition state theory and Arrhenius equation, enabling prediction of oxidation rates under various processing conditions. Additionally, H_2O diffusion within SiCN films was modeled, demonstrating a direct correlation between film density and oxidation kinetics. More importantly, the findings in this work can be applied in depositing SiOCN film as the oxidation mechanisms are predicted to be similar with other oxidation agents. Knowledge of these oxidation mechanisms enables precise control of the SiOCN film deposition process, facilitating component tunability.

11:45am **AP+AS+EL+EM+PS+TF-ThM-16 From Bulk Titanium Nitride to Small Molecule Inhibitors: a DFT Study Aiming Towards Area-Selective Atomic Layer Deposition***, **Lucas Lodeiro**,* Universidad Tecnica Federico Santa Maria, Chile*; Marc J. M. Merkx,* Eindhoven University of Technology, The Netherlands*; Dennis M. Hausmann, Rachel A. Nye de Castro,* LAM Research*; Adriaan J. M. Mackus,* Eindhoven University of Technology, The Netherlands*; Tania E. Sandoval,* Universidad Tecnica Federico Santa Maria, Chile

Titanium Nitride (TiN) is a hard and inert ceramic used as a protective coating, and in microelectronics for its metallic behavior. TiN thin films improve devices performance as conductive connection and diffusion barrier, and can be further functionalized to promote specific applications. Atomic Layer Deposition (ALD) enables precise TiN film deposition, with temperature controlling crystal growth facet. However, achieving area-selective ALD (AS-ALD) on TiN is challenging, because the lack of information of surface groups present in deposited TiN, requiring reliable surface models to search for solutions for precursor selectivity and inhibition with Small Molecule Inhibitors (SMIs) at atomic scale.

This study uses Density Functional Theory (DFT) to examine TiN surface properties, crystal facets, and surface chemistry. It also explores the adsorption of various organic and inorganic precursor (Al, Si, Ti-based) and SMI (aryl, aldehyde, and nitrogen-based) molecules on TiN with the aim of studying their potential for AS-ALD processes with TiN as growth or non-growth area.

Our findings on crystal facets align with experimental data, showing the (001) facet is the most stable, followed by the (111) facet, which is observed at high deposition temperature.[1] The reactivity and functionalization strategies of these surfaces differ significantly. The (001) surface shows low reactivity (especially with H_2O, NH_3, and H_2), resulting in bare surface sites.[2] Conversely, the (111) surface is reactive and can undergo hydrogenation, altering its electronic properties.

The differences in electronic surface properties significantly affect surface chemistry and the adsorption mechanism of the different molecules. The (001) surface exhibits metallic behavior, with strong interactions with various functional groups (for example, -1.8 eV for Benzaldehyde, BA), similar to copper surfaces.[3] In contrast, adsorption on the (111) surface is weaker and mainly dispersive (-0.8 eV for BA), highlighting the importance of the TiN film facet. Experimental findings show enhanced inhibition of BA and higher selectivity for low temperature deposited TiN, which could indicate the presence of the (001) surface, and a more stable inhibitor adsorption.

The key findings of this study offer valuable insights into surface reactivity and electronic properties to use TiN in AS-ALD process. Ultimately, this work aims to provide insights into controlling TiN deposition at the nanoscale, opening avenues for advanced microfabrication and surface engineering applications.

[1] Met. Mater. Int. 2001, 7, 621–625.

[2] J. Phys. Chem. C 2013, 117, 38, 19442–19453.

[3] Chem. Mater. 2025, 37, 1, 139–152.

12:00pm **AP+AS+EL+EM+PS+TF-ThM-17 Trimethylaluminum Reactivity on SiO_2 Surfaces at Cryogenic Temperatures – Implications for Al_2O_3 ALD***, **Leonhard Winter**, Ravi Ranjan, Francisco Zaera,* University of California, Riverside

The atomic layer deposition (ALD) of aluminum oxide films on solid substrates using trimethylaluminum (TMA) and water is often considered a prototypical ALD process. Several investigations have attempted to understand the mechanistic details of this deposition by following the corresponding steps *in situ* under reaction conditions. To gain a more fundamental understanding, we have set out to study this system following a UHV surface-science approach, slowing down the reaction, decreasing the gas exposures and substrate temperature, and following the progress of the reactions using surface science techniques. We chose to study this chemistry on SiO_2 films grown *in situ* onto a Ta support because SiO_2 is one of the most common substrates in the microelectronics industry.

We investigated the adsorption and reaction of TMA with SiO_2 by using X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD). We found that TMA starts to react with the SiO_2 surface at ≈110 K, i.e. below the cryogenic temperatures required for multilayer condensation. This low-temperature chemistry appears to be complex, as multiple reaction pathways can be deduced from analysis of the TPD data. In addition to the expected product methane, we observed the formation of ethylene and heavier fragments, probably also containing Al. The complex behavior of TMA on SiO_2 is not limited to low temperatures, as the loss of alkyl groups continues over several hundred kelvins upon heating of the sample. Isothermal adsorption experiments show that at room temperature the TMA uptake is self-limiting with an initial sticking coefficient that is approximately 4-5 times smaller than at cryogenic temperatures, where multilayer growth occurs. To model ALD-type growth, we alternately dosed TMA and water at 200 K and followed the chemical composition of the surface with XPS. The results are in agreement with the expected ALD behavior, which shows that ALD growth is possible at these extremely low temperatures for the TMA/water system. The two precursors were also co-dosed in a CVD-type deposition, which results in the growth of multilayer films of aluminum oxide on the SiO_2 substrate. Surprisingly, the growth was observed to proceed faster at 200 K than at room temperature, which we explain by a kinetic effect of prolonged residence times of the precursors at lower surface temperatures.

Spectroscopic Ellipsometry
Room Ballroom BC - Session EL-ThP

Spectroscopic Ellipsometry Poster Session

EL-ThP-1 ATR-Ellipsometry Using a Custom Liquid Cell*, Madison Coleman,* *Mar Diehl, Madison Meaney, Tyler Adams,* Weber State University*; Jeremy VanDerslice,* J.A. Woollam Co., Inc.*; Alyssa Mock,* Weber State University

A custom multi-bounce, prism-based liquid cell has been developed for use with infrared ellipsometry to enable quantitative analysis of liquids and the species dissolved within them. Traditional optical methods for liquid-phase analysis often rely on attenuated total reflection (ATR), where changes in signal intensity are caused by absorption via interaction between the evanescent wave and the liquid sample. In contrast, this approach leverages ellipsometric polarization measurements, capturing the reflected light’s amplitude ratio (Ψ) and phase difference (Δ). These measurements probe molecular vibrations in the fingerprint region, enabling analysis of the chemical composition of liquids.

Conventional optical measurement schemes are limited in the IR spectrum for liquid applications due to strong absorption, particularly in water-based systems. The ATR measurement technique addresses this limitation by coupling light into a prism and probing the sample with the evanescent wave produced by total internal reflections. Our new method combinesthe traditional ATR concept with ellipsometric detection. Multiple internal reflections within a high-index prism produce evanescent waves that repeatedly interact with the liquid sample. The repeated interactions with the liquid enhance sensitivity to small constituent fractions of species within the liquid. By capturing both the intensity and the polarization changes, this configuration extends the sensitivity of ellipsometric measurements to liquid environments.

The prism is housed in a custom-built sealed liquid cell and cut to provide a 45° angle of incidence. Submerged length wise in the liquid, the prism supports multiple internal reflections, with each reflection generating an evanescent field that probes the sample. Our results demonstrate the potential of ellipsometric ATR for concentration-based analysis of complex liquids, with future applications in quality control for the food, beverage, and water industries.

EL-ThP-2 Engineering the Optimal Filter: Quantitative Assessment of Linear and Nonlinear Noise-Reducing Filters in Spectroscopy*, **David Aspnes,*** North Carolina State University*; Long Le,* Vietnam Academy of Science and Technology, Viet Nam*; Young Kim,* Kyung Hee University, Republic of Korea

The objective of any noise-reduction filter is to preserve information and eliminate noise, both to the maximum extent possible.Up to now filters have been assessed by trial-and-error.Here, we report a cost function that quantifies the action of a filter on information and noise in a spectrum, that is, on distortion and leakage, respectively.For linear filters, which act by direct-space (DS) convolution or (equivalently) by selective attenuation of reciprocal-space (RS) Fourier coefficients, the expression is exact.Consequently, optimal parameters for any linear filter operating on any spectrum can now be determined unambiguously.We find that the best practical linear filter is the Gauss-Hermite filter introduced by Hoffman and co-workers in 2002 [1].

Nonlinear filters operate differently, retaining low-order Fourier coefficients exactly up to the white-noise cutoff and replacing those in the white-noise region with model-independent most-probable analytic extrapolations.With distortion nominally eliminated and noise input limited to retained coefficients, these should outperform any linear filter.However, the only known example, the corrected-maximum-entropy(CME) approach [2], can be used only with positive-definite spectra consisting of superpositions of Lorentzian absorption lines.Here, we report a forward-prediction approach with performance equivalent to the CME, but one that is based on physical principles and is completely general.Examples dealing with spectroscopic-ellipsometric and other types of data, for instance X-ray photoelectron and Auger electron spectra, will be presented.

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