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°C. 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°C. 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°C. Using anhydrous HF at temperatures >150°C 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°C obtained exceptional selectivity for rapid SiO_2 versus negligible SiN_x spontaneous etching. Similarly, co-adsorbing dimethylamine with HF at 200°C 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.

[2]. J. Steinlechner, et al, *Classical Quantum Gravity* 2015

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.

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