Ex Situ Detection Limits of Contamination Metrology on EUV Multilayer Mirrors: A First Step Toward an *In Situ* Metrology Feasibility Assessment

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Rationale

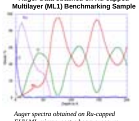
In situ metrology is now being applied to monitor and control a wide range of phenomena associated with crystal growth and semiconductor processing. Optically-based techniques in particular are being used to control stress, engineer alloy compositions, and reduce dislocation densities during epitaxial growth; real-time analysis of post-CMP residue and control of birefringence in CaF_2 crystal production are other notable examples. Given the potential for added process cost, *in situ* metrology is considered only in cases where traditional "post-mortem" analytical characterization fails. Where *in situ* metrology is adopted in a manufacturing environment, the economics of falling yields must clearly justify the cost of process disruption. While it is clear to most that EUV projection optics simply do not last long enough to meet specifications for high volume manufacturing, what is unclear is how costly, disruptive, and effective various candidate metrologies might be for the *in situ* control and monitoring of projection optics contamination. The question is especially relevant given that this is a research area where the failure of current strategies is keenly felt; in other words, some degree of process disruption *might* be acceptable to lengthen the lifetime of the short-lived projection optics.

Accordingly, the overall goal of this work is to understand the minimal amount of information required to monitor / control optics contamination during actual exposures and to determine the maximum amount of allowable process disruption. As a first step toward meeting this goal, candidate technologies are reviewed in this context. Here we investigate the *ex situ* detection limits of "thin" C and oxide layers on multilayer EUV optics samples. Where possible, data from EUV-exposed SEMATECH Ru-capped benchmark optics (ML1) samples are reported. These data serve as the necessary first step towards a feasibility assessment for *in situ* metrology for controlling contamination of projection optics.

Auger Electron Spectroscopy

- Minimum detectable thickness? *submonolayer possible; >1 nm (for O)*
- Sampling area? *3e-19 cc (atoms per cubic centimeter concentration)*
- Sensitivity to bonding arrangement? *no*
- Special sample preparation requirements? *information obtained by depth profiling*
- Chemical specificity? *yes*
- In-line capability? *no*
- Real-time control capability? *no*
- Destructive? *yes*
- Vacuum needed? *yes; sample must be small and compatible with high vacuum*
- Caveats? *cannot detect H or He; non-conducting samples often charge & cannot be analyzed; standards required, high resolution detector needed to separate C and Ru peaks*

Auger Data obtained on Ru-capped Multilayer (ML1) Benchmarking Sample

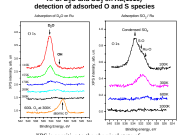


Auger spectra obtained on Ru-capped EUV ML mirror, post-e beam exposure for 40 hours at 5.0 μA/mm^2 and 2E-07 Torr water vapor.

X-ray Photoelectron Spectroscopy

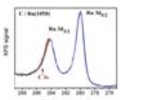
- Minimum detectable thickness? *sub-monolayer detection in general; C is difficult for Ru capped MLs*
- Sampling area? *Small spot ~ 2x2 microns possible for micro-XPS capability*
- Sensitivity to bonding arrangement? *yes*
- Special sample preparation requirements? *yes; UHV and small samples required*
- Chemical specificity? *yes*
- In-line capability? *difficult, but not impossible*
- Real-time control capability? *no*
- Destructive? *not for most measurements*
- Vacuum needed? *yes*
- Caveats? *Ru 3d transition interferes with C detection*

XPS: D_2O and SO_2 on Ru(1010) detection of adsorbed O and S species



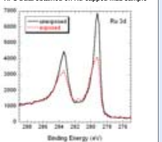
XPS is sensitive to the chemical state of adsorbates, and can distinguish chemisorbed O from OH, and SO_x from O on Ru surfaces

XPS Data obtained on bulk Ru (10-10)



Overlapping of Ru 3d with C 1s for C coverage 0.5 – 1 ML

XPS Data obtained on Ru-capped ML1 sample

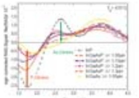


Overlapping of Ru 3d with C 1s for an EUV-exposed ML1 sample, both before (black) and after (red) exposure. Here, the decrease in Ru 3d peak coupled with data obtained at other binding energies for the same sample (where an increase in the oxygen peak was observed for the exposed area)---indicates more RuO_2 after the exposure and less pure Ru.

Reflectance Difference Spectroscopy

- Minimum detectable thickness? *submonolayer*
- Sampling area? *1 um w/ laser source*
- Sensitivity to bonding arrangement? *yes*
- Special sample preparation requirements? *no*
- Chemical specificity? *generally, no*
- In-line capability? *yes*
- Real-time control capability? *yes*
- Destructive? *no*
- Vacuum needed? *no*
- Caveats? *measures anisotropy, hence works only with aligned optically anisotropic materials and structures; however, these anisotropies can be used as basis for in situ semiconductor growth monitors (ternary compound composition, dopant levels, film thickness, growth rate) and for in situ monitoring of stress-induced birefringence for materials like BaF_2 and CaF_2.*

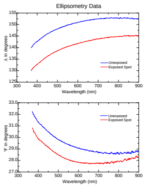
RDS Spectra: An Example From InGaAsP Alloy Growth



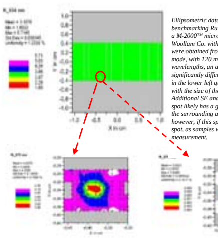
Sign-corrected RDS-spectra for different InGaAsP compositions. The surface response during growth shows the dependence of the RDS signal on changes from the P-rich (2 x 1) reconstruction (typical for InP) to the As-rich (2 x 4) like surface reconstruction (typical for InGaAs) caused by the decreasing P-to-As ratio. This information is used to enable the use of RDS as an situ monitor of the growth of these alloys. (from LayTec GmbH, Applications Note #23, http://www.laytec.de ; figure used with permission.)

Ellipsometry

- Minimum detectable thickness? *submonolayer sensitivity*
- Sampling area? *typically millimeters; for microellipsometry, as small as 20 x 50 um*
- Sensitivity to bonding arrangement? *yes**
- Special sample preparation requirements? *No; but specular surfaces required; optical functions of individual heterostructure layers must be known for modeling*
- Atomic specificity? *Generally no. Only if unique spectral features are generated*
- In-line capability? *yes*
- Real-time control capability? *yes*
- Destructive? *no*
- Vacuum needed? *no; any transparent ambient will do*
- Caveats? **responds to polarizability; many aspects such as surface roughness, voids, contamination layers contribute and therefore may be correlated. Not always possible to distinguish these separately in a post-mortem, model-dependent, static measurement.*



Ellipsometric angles Δ and Ψ illustrating observed differences in optical properties between the exposed (red) and unexposed (blue) spot, featured right. Results of "false data" calculations are consistent with an increased level of oxide on the exposed spot.

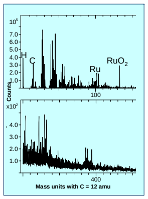


Ellipsometric data obtained on the SEMATECH benchmarking Ru-capped multilayer ML1 sample with a M-2000TM microspot ellipsometer from the J.A. Woollam Co. with mapping capability. Measurements were obtained from 370 nm to 900nm, in mapping mode, with 120 microns between spot locations. At all wavelengths, an approx. 700um by 700 um spot with significantly different optical properties was observed in the lower left quadrant of the sample, consistent with the size of the EUV exposure beam at NIST. Additional SE analysis in the VUV indicated that this spot likely has a greater amount of oxide compared to the surrounding area. It is difficult to determine, however, if this spot corresponds to the EUV exposed spot, as samples were air-exposed prior to measurement.

Secondary Ion Mass Spectrometry ToF SIMS

- Minimum detectable thickness? *sub-monolayer detection in general; time of flight configuration gives surface sensitivity*
- Sampling area? *~100nm spot size*
- Sensitivity to bonding arrangement? *no*
- Special sample preparation requirements? *yes; UHV and small samples required*
- Chemical specificity? *yes, but no sensitivity to bonding arrangement*
- In-line capability? *difficult, but not impossible*
- Real-time control capability? *no*
- Destructive? *yes*
- Vacuum needed? *yes*
- Caveats? *some ion sources leave deposits; cross contamination a serious issue if not using a dedicated instrument; spectra can be complex to interpret*

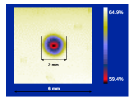
TOF SIMS Data Obtained on a Ru-capped Multilayer (ML1) Sample



Reflectometry

- Minimum detectable thickness? *~monolayer*
- Sampling area? *1 um w/ laser source*
- Sensitivity to bonding arrangement? *for spectral measurements, as ellipsometry*
- Special sample preparation requirements? *no; but specular surfaces required*
- Atomic specificity? *as ellipsometry*
- In-line capability? *yes*
- Real-time control capability? *yes*
- Destructive? *no*
- Vacuum needed? *not for wavelengths longer than VUV; VUV requires N_2 purging; EUV reflectivity requires UHV*
- Caveats? *very difficult to do accurately; accuracy limited by source-intensity and detector-sensitivity variations, affected by macroscopic roughness (scattering)*

2D EUV Reflectivity Map of Ru-capped ML1 Sample

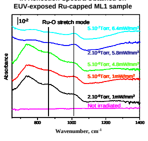


2D EUV reflectance map of the SEMATECH benchmarking Ru-capped multilayer ML1 sample, showing differences in reflectance between areas of the sample exposed to electron beam irradiation in the presence of accelerated water vapor pressures(59.4%) vs. unexposed regions (64.9%).

FTIR

- Minimum detectable thickness? *possible to detect monolayers , though confidence is greater for layers > 100Å (for hydrocarbons)*
- Sampling area? *100 um^2 (round spot)*
- Sensitivity to bonding arrangement? *yes*
- Special sample preparation requirements? *no*
- Chemical specificity? *yes; better detection on heavy metal (e.g., on Au)*
- In-line capability? *yes for FTIR; not easily with micro FTIR*
- Real-time control capability? *yes for FTIR; not easily with micro FTIR*
- Destructive? *no*
- Vacuum needed? *no*
- Caveats? *ATR (Attenuated Total Reflection) FTIR can characterize surface films on special internally reflecting samples, like a Ge crystal with beveled edges. Though monolayer sensitivity can be achieved, the special sample prep requirements render this technique unsuitable for real-time control purposes.*

IR Reflection Spectra Obtained on EUV-exposed Ru-capped ML1 sample

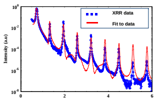


Infrared (IR) reflection spectra for the SEMATECH benchmarking Ru-capped multilayer mirror ML1 exposed to EUV radiation. Each spectrum corresponds to a different spot that saw different water pressures and irradiation power. The spectra are all difference spectra, referenced to a non-irradiated spot. As with the ellipsometric mapping, it is difficult to draw definitive conclusions, as the samples were air-exposed for several months prior to measurement.

X-ray Reflectivity

- Minimum detectable thickness? *>2.5 nm*
- Sampling area? *tens of μm² area possible with micro-focus x-ray source*
- Sensitivity to bonding arrangement? *no*
- Special sample preparation requirements? *no*
- Chemical specificity? *no*
- In-line capability? *possible*
- Real-time control capability? *possible but very expensive to develop*
- Destructive? *no*
- Vacuum needed? *no*
- Caveats? *impinging x-ray beam is spread in one direction over a large area on the sample due to geometry requirements (grazing incidence); a micro-focus x-ray source is required. Minimum detectable thickness of the capping layer is dependent on the period thickness of the ML.*

XRR Data Obtained on a Ru-capped Multilayer (ML1) Mirror Sample

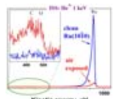


XRR data obtained on a Ru-capped multilayer (ML1) benchmarking sample, in an "as deposited" state. From these data (blue) and fit to the data (red) one obtains period thickness, individual layer thicknesses, and interface roughness / interdiffusion—as well as the ratio of Si to Mo in the ML. In principle one can also fit the density of each material and the function of the compositional variation at the interface.

Low Energy Ion Scattering

- Minimum detectable thickness? *fraction of a monolayer—LEIS measures mainly the top monolayer*
- Sampling area? *several mm²*
- Sensitivity to bonding arrangement? *no*
- Special sample preparation requirements? *UHV; conducting samples preferred*
- Chemical specificity? *yes*
- In-line capability? *probably not*
- Real-time control capability? *probably not*
- Destructive? *yes– He+ ions sputter low mass surface atoms*
- Vacuum needed? *UHV required*
- Caveats? *greatest sensitivity to higher mass atoms*

Detection of carbon on Ru surface

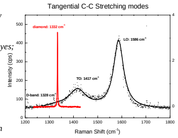


He^+ ion scattering – efficient tool for C and O detection on surface

Raman Spectroscopy

- Minimum detectable thickness? *a few hundred Å*
- Sampling area? *0.5 microns*
- Sensitivity to bonding arrangement? *yes; detects non-polar bonds. E.g., for C, can distinguish between diamond or graphitic bonding*
- Special sample preparation requirements? *no*
- Chemical specificity?*yes*
- In-line capability? *yes*
- Real-time control capability? *unknown*
- Destructive? *no*
- Vacuum needed? *no*
- Caveats? *does not detect IR active bonds; only Raman active modes*

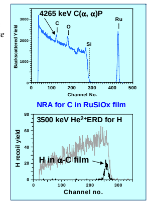
Tangential C-C Stretching modes



Raman scattering is highly sensitive to both the C bonding arrangement (sp^2, sp^3) and geometry, illustrated here with spectra collected from diamond (red) and single-walled carbon nanotubes (black). Whereas a single degenerate phonon mode is expected for diamond, a splitting of the G-band into the longitudinal- and transverse-optic modes occurs for 2D-graphene rolled into a tube. The feature near 1328 cm^{-1} is due to disordered graphite and a breaking of the Raman selection rules involving momentum conservation.

Backscattering Methods Elastic Recoil Detection of Light Elements

- Minimum detectable thickness? *ERD for Hydrogen can detect 10 to 20Å in a hydrocarbon layer (adventitious H makes it difficult to separate signal from noise for thinner films); tens of Å for C (e.g., 30 Å possible; 10 Å lower limit) using Carbon resonance analysis/ Nuclear resonance analysis (NRA)*
- Sampling area? *on the order of mms (e.g., 2mm x 1mm)*
- Sensitivity to bonding arrangement? *no*
- Special sample preparation requirements? *no*
- Chemical specificity?*no*
- In-line capability? *no*
- Real-time control capability? *no*
- Destructive? *Yes (piece is cleaved); however, chamber can be modified to fit whole wafer*
- Vacuum needed? *yes, order of 10E-06 Torr*
- Caveats? *requires a small sample*



Conclusions & Outlook

To assess the feasibility of *in situ* metrology, we need to answer 4 basic questions:

1. What are we trying to measure, to what sensitivity do we need to measure it, and how fast does it happen?
2. How do we insure that work on *in situ* metrology options is of use to EUV exposure tool suppliers?
3. What are the various metrology options? What kind of information can be obtained from these options? How disruptive / invasive would these options be in the PO Box of an EUVL tool?
4. What is the upper limit, in terms of cost, that could be tolerated for any *in situ* optics metrology?

This work focused upon question #3.

<u>What we have learned thus far:</u>

•Optical techniques rather than electron / ion beam-based techniques have real-time control capability because of their non-destructive nature

•Among suitable candidates, those that yield the most detailed information may also be the most expensive to develop for real-time use (e.g., FTIR and Raman vs. reflectometry)

<u>Next steps:</u>

•Understand cap layer surface chemistry and the role of back ground chamber contaminants (to answer question #1)

•Understand cost of ownership / extent of process disruption for each of the candidate techniques; narrow options (question #3)

•Weigh information obtained with cost of process disruption (#2, #4)

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