Electron-induced in EUV Resist Activation

Boris Yakshinskiy, Robert Bartynski, Sylvie Rangan, Senia Katalinic

Dept. of Physics and Astronomy, Rutgers, The State University of New Jersey, Piscataway NJ 08854 USA

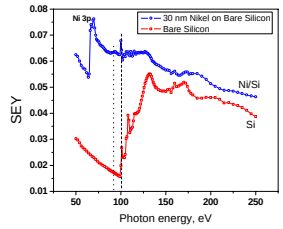
Abstract

We investigate the mechanisms by which EUV photons break chemical bonds and activate EUV resists. Desorption induced by electronic transitions (DIET) processes play important roles in the photoresist activation mechanisms. Secondary electrons are created when the primary EUV-generated photoelectrons excite and release other electrons. Low-energy electrons, i.e. electrons with kinetic energies in the range 0-15 eV, can effectively induce dissociation of organic molecules due to the high dissociation cross sections. The main process is termed Dissociative Electron Attachment (DEA), and is especially effective for molecules containing fluorine atoms, including Photoacid Generators (PAG), which form an integral part of chemically-amplified resists. The electron energy distributions and secondary electron yields (SEY, electrons/photon) of the resist-coated samples were measured at the National Synchrotron Light Source (NSLS). The main results are: the majority of secondary electrons photoemitted under 13.5 EUV photon irradiation by each resist have energies less than 10 eV, and a small fraction have energies up to ~ 20eV. The total SEY depends on photon energy, and is ~ 0.02 at 13.5 nm. These data clearly show that low energy electrons (< 15eV) break bonds in resist molecules, indicating that low energy secondary electrons released by EUV photons may be a primary source of resist activation. The valence and conduction bands of photoresists have been probed using ultra-violet photoemission spectroscopy (He I UPS) and inverse photoemission spectroscopy (IPS), respectively, in the same ultrahigh vacuum chamber. The relationship between measured band gaps, EUV absorbance, and SEYs will be discussed.

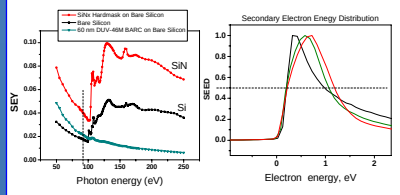
Goals

- Address the extent to which secondary electrons play a role in EUV activation
- Measure secondary electron yield (SEY) and secondary electron energy distribution (SEED) in wavelength range around 13.5 nm
- Measure electron band structure using UPS and IPE techniques

Secondary electron yield (SEY) vs photon energy

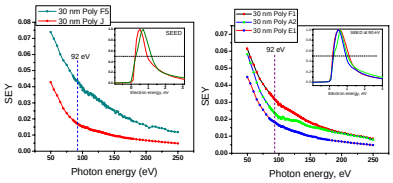


Secondary Electron Yield (SEY) vs photon energy and Secondary Electron Energy Distribution (SEED) for underlayers



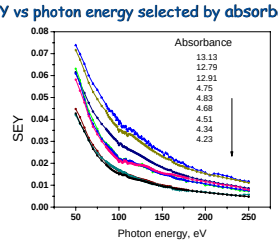
- Photon energy 92 eV (13.5 nm); measured on beamline U5UA of NSLS
- FWHM of SEED qualitatively correlates with SEY for these samples

SEY vs photon energy and SEED



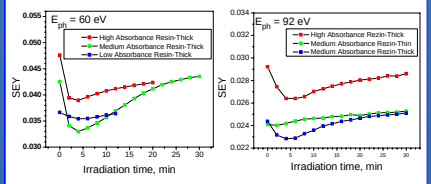
- Photon energy for SEED measurement 92 eV (13.5 nm);
- FWHM of SEED qualitatively correlates with SEY for these samples

SEY vs photon energy selected by absorbance

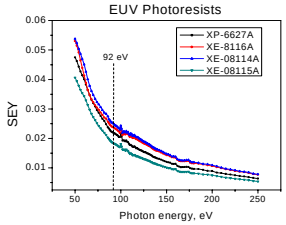


Measured on Beamline U3C of NSLS

Evolution of SEY during irradiation

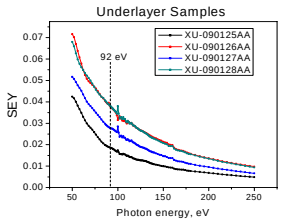


Secondary electron yield for the resists vs photon energy



This set of samples is measured by XPS, UPS and IPE techniques

SEY vs photon energy for the underlayers

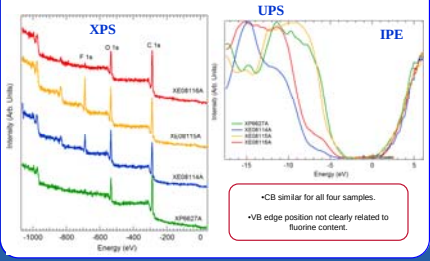


This set of samples is measured by XPS, UPS and IPE techniques

Parameters of the resists for UPS-IPS study

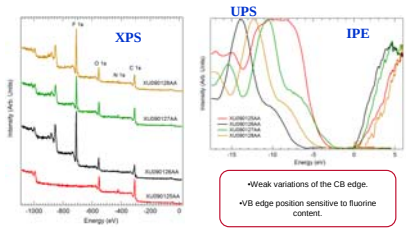
Sample	Gap	SEY	Abs.
XP6627A	3.4	0.0220	4.35
XE08114A	5.3	0.0249	4.82
XE08115A	3.8	0.0182	5.06
XE081016A	4.8	0.0236	4.90
XU090125AA	4.7	0.0175	3.92
XU090126AA	7.3	0.0336	6.59
XU090127AA	4.1	0.0275	5.47
XU090128AA	6.6	0.0336	5.52

Measurement of photoresist samples



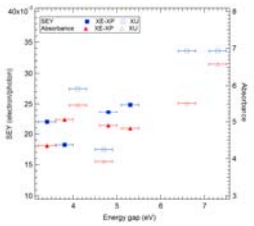
- CB similar for all four samples.
- VB edge position not clearly related to fluorine content.

Measurement of underlayer samples

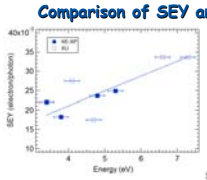


- Weak variations of the CB edge.
- VB edge position sensitive to fluorine content.

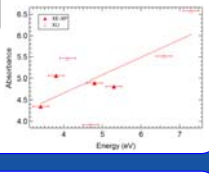
SEY and Absorbance vs Energy gap



Comparison of SEY and Absorbance vs Gap



Linear relation between SEY and gap:
y= 0.00558 + 0.00108 x



Linear relation between absorbance and gap:
y= 3.012 + 0.41335 x

Summary

- We provide benchmark data for secondary electron yield – key parameter for photoresist bond breaking.
- We provide novel benchmark data for electron band structure using UPS – IPE techniques.
- We show the correlation of the resist composition, absorbance and SEY with the band gap (i.e., HOMO-LUMO gap).
- Analysis of these data together with the controlled film thickness and PAG concentration information provide new insights into the physics of resist activation.

Mechanism of the anion desorption

- The threshold energy for the H^- anion yield is around 6 eV. The peak at 9 eV is due to dissociative electron attachment (DEA):

$$e^- + R \rightarrow R^- \rightarrow [R\text{-}H] + H^-$$

- At energies > 14 eV, H^- occurs by dipolar dissociation (DD):

$$e^- + R \rightarrow R^+ + e^- \rightarrow [R\text{-}H]^+ + H^- + e^-$$

- The threshold energy for the F^- anion yield lies at ~10 eV, and the DEA peak is found around 12.7 eV. Desorption of F^- ion via DD process occurs above 17 eV.

Mechanism of the bond breaking

- **Most initial excitations by 92 eV photons lead to production of ~80 eV primary electrons inside the film. These electrons can create excited atoms and molecules, radicals, ions, and secondary electrons with a most probable energy below ~10 eV. LEEs have thermalization distances on the order of 1-10 nm.**
- **In all cases, low energy electrons break C-H and C-F bonds in the resist polymer. Threshold for H^- desorption (breaking of C-H bonds) is lower than threshold for F^- desorption (breaking of C-F) bonds.**
- **Other bonds may be broken at energies < 6eV (e.g., C-C bonds) that do not lead to desorption of charged fragments.**
- **The valence band features change with irradiation time, as expected for changes in electronic structure for an "exposed" resist.**

Discussion

- **Secondary electrons emitted from resists have very low energies <10 eV; electron-stimulated desorption of anions by such LEEs can provide quantitative data concerning bond-breaking in EUV resists.**
- **Similar bond-breaking events are generated extensively in the bulk of the resists by the LE secondaries released by primary EUV photons in nanolithographic processes.**
- **Next step could be SEY and ESD experiments on "neat" polymers and PAGs.**
- **Future experiments could involve SEY measurements from resist films (a few nm to ~10 nm) of controlled thickness on Si or Si-adsorbate-covered substrates.**

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