

Characterization of EUV Outgassing of different Polymer Platforms

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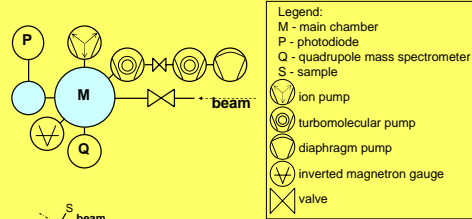
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Abstract

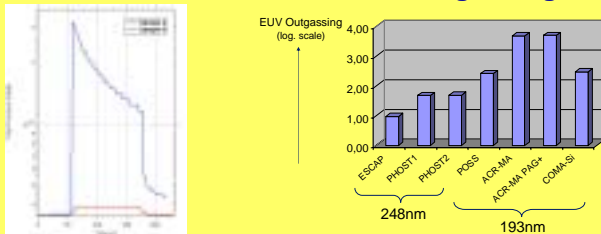
- Corresponding to the ITRS roadmap, EUV Lithography will in the not-too-far future reach the point, where critical resist dimensions are in the same order of magnitude as polymer chains and acid diffusion lengths, while photon energies will largely exceed the bonding energies of all organic molecules.
- The resist interaction with EUV radiation is still not completely understood, especially the impact of secondary electrons on polymer side reactions (radical formation, crosslinking, scissioning,...) which will take place to a higher extent than e. g. at 157nm.
- While these side reactions might lead to a higher outgassing of polymer fragments, and these fragments consecutively will lead to optics and mask reflectivity degradation, EUV outgassing is agreed to be a critical issue for resist development.
- In this paper EUV outgassing is characterized using an online mass spectrometer attached to an exposure vacuum chamber at the Sincrotrone Trieste. The total outgassing and the time dependent outgassing of resist fragments could be characterized for a number of resist polymer platforms, e.g. ESCAP, acrylic, POSS, etc..
- The EUV outgassing results are compared to the data obtained with other exposure wavelengths (157nm and 193nm). Differences that were found are discussed in terms of the applied photon energies. Time dependent scanning of selected mass channels was used to differentiate if an outgassing fragment had its origin from the PAG or from a photolytic or a photochemical reaction of the polymer matrix.
- First attempts are made to correlate the resist outgassing to high dose crosslinking and scissioning behaviour of EUV resists.

EUV Outgassing Setup at Sincrotrone Trieste



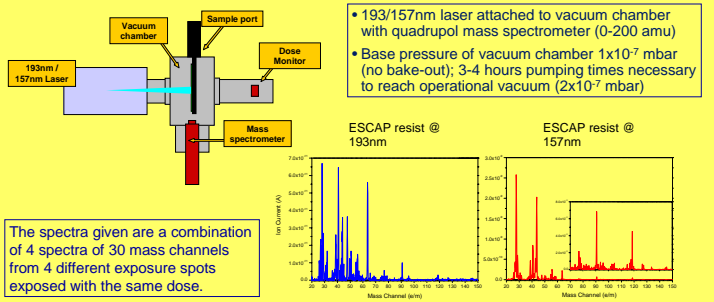
- EUV beam incidence on resist on silicon samples was at an angle of 30°
- quadrupole mass spectrometer was located at 60°, distance from wafer was 15 mm.
- EUV outgassing is sampled at different spots of a coated wafer to allow fast mass spectrometer scanning (10 amu channels per exposure); spot size was 2.5 x 0.5 mm
- mass spectra were reconstructed from several scans at identical dose

Measurement of EUV total outgassing



- Total outgassing was integrated in mbar over a total exposure time of 2 min.
- Total outgassing of different resist samples varied by 3 orders of magnitude; low outgassing resists resulting in 10⁻⁹ mbar sec
- acrylic resist platforms showed highest outgassing; lowest outgassing resist was ESCAP
- 193nm resist platforms show higher outgassing than 248nm resist platforms

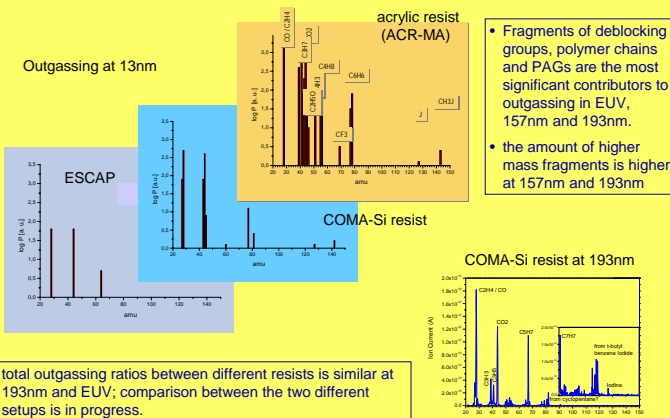
Comparison with other wavelengths



The spectra given are a combination of 4 spectra of 30 mass channels from 4 different exposure spots exposed with the same dose.

In EUV only significant signals at 28, 44 and 64 amu detected.

Comparison of outgassing fragments



- Fragments of deblocking groups, polymer chains and PAGs are the most significant contributors to outgassing in EUV, 157nm and 193nm.
- the amount of higher mass fragments is higher at 157nm and 193nm

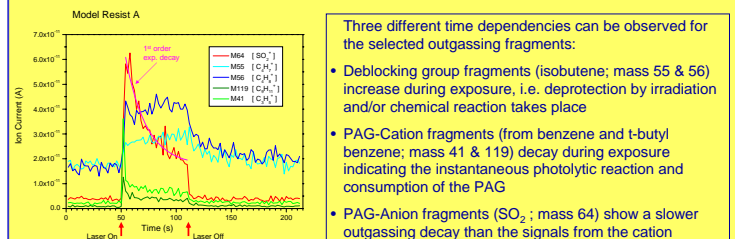
total outgassing ratios between different resists is similar at 193nm and EUV; comparison between the two different setups is in progress.

- The highest outgassing fragments are deblocking group fragments and CO₂
- One order of magnitude less is the outgassing of PAG fragments and polymer chain fragments
- Another order of magnitude less is the outgassing of iodine-containing fragments from the PAG

Summary and Conclusions

- A number of resists has been characterized for their outgassing at 13 nm and compared to data at other wavelengths.
- The total outgassing at EUV varied by 3 orders of magnitude: 193nm resist platforms tend to higher outgassing than 248nm platforms.
- Fragment analysis showed a general trend in steps of order of magnitude: deblocking group fragments > PAG fragments and polymer fragments > Iodine-containing fragments (from PAG).
- The relative outgassing behavior in EUV was similar to 193/157nm.
- time dependent outgassing measurements showed different dependencies for deblocking group fragments, PAG cation fragments and PAG anion fragments.
- scissioning tendency under EUV radiation was correlated to the total outgassing: highest outgassing resists showed high scissioning tendency while resists, that showed crosslinking at higher doses had low outgassing

Time-dependent outgassing



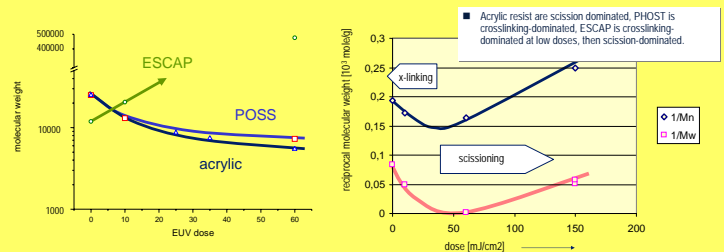
Three different time dependencies can be observed for the selected outgassing fragments:

- Deblocking group fragments (isobutene; mass 55 & 56) increase during exposure, i.e. deprotection by irradiation and/or chemical reaction takes place
- PAG-Cation fragments (from benzene and t-butyl benzene; mass 41 & 119) decay during exposure indicating the instantaneous photolytic reaction and consumption of the PAG
- PAG-Anion fragments (SO₂; mass 64) show a slower outgassing decay than the signals from the cation

Polymer matrix fragments typically increase during exposure time at 193/157nm.

PAG fragments show a sharp outgassing peak followed by a decrease of the signal which is depending on the origin of the observed fragment.

Correlation to Scissioning and Crosslinking



- Acrylic resists show approx. 3 times higher scissioning reaction in EUV than at 157nm
- POSS resists show less scissioning, corresponding to less total outgassing
- ESCAP and PHOST resists show least outgassing and primarily crosslinking
- ESCAP resists show scissioning only at higher EUV doses (> 60 mJ/cm²)

Acknowledgements

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