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ToF-SIMS and OrbitrapTM-SIMS analyses to unravel the chemistry of thin EUV photoresist layers

Photolithography is a well-established process used for patterning in microelectronic device fabrication [i]. In Extreme Ultra-Violet (EUV) lithography – the most recent lithography technology using photons of 13.5 nm wavelength - research is ongoing regarding the fundamental resist (PR) chemistry active in the different components of chemically amplified resists (CARs), metal oxide resists (MORs), scissioning type resists, molecular resists. In the case of the well-known CAR system, multiple components are involved in its formulation (i.e. polymer, Photo Acid Generator (PAG) and quencher) at various steps of the process. Indeed, many aspects are still not fully understood [ii], with examples including, but not limited to, the distribution of each constituent within the photoresist layer, the specific products generated by the chemical reactions involved, and the proportion of components able to efficiently carry out the reactions (i.e. acid formation, deprotection, etc.). Further research is addressed to the understanding of the underlayer underneath the resist and their relationship/interdependency.

Secondary Ion Mass Spectrometry (SIMS) is a key surface analysis technique in which 1D (depth profiles), 2D (spatial imaging) and 3D (volumetric imaging) distributions of elements and molecules with a solid substrate can be derived [iii]. SIMS operates by directing an energetic ion beam, termed the primary ion beam, at the surface of interest. This induces the emission of surface atoms and molecules, with a small fraction departing in an ionized state. The departing ions, henceforth referred to as secondary ions, are extracted and passed through a mass analyzer such that all elements (H-U), isotopes thereof, as well as molecules can be identified.

When examining organic films, molecular integrity can be retained through the use of a Gas Cluster Ion Beam (GCIB) as this allows for the impact energy per atom (within the impacting molecule) to be reduced to inter-molecular bond energies. And since inter-molecular bond energies are less than intra-molecular bond energies, GCIBs provide a means to non-destructively examine organic molecules and their distributions in 1D, 2D and 3D [iv].

Time of Flight (ToF)-SIMS is one of the most heavily used techniques to study the distribution of organics. This is due to its capability of detecting characteristic molecular peaks of the studied system with a high mass resolving power of ~104, with a lateral resolution of <100 nm [v], with a depth resolution of <5 nm [vi] and all to high sensitivity. However, when studying organic systems such the photoresist layers described, much higher mass resolving power might be needed to avoid any mass interference that would result in incorrect data interpretation. OrbitrapTM mass analyzers [vii] are a recent addition to the SIMS arsenal that allows for even greater mass resolving power (~20× that possible in ToF-SIMS) and the possibility for carrying out Tandem Mass Spectrometry (MS) (also called MS/MS) secondary ion peak verification. The MS/MS capability has been highly successful in the analysis of complex organic materials in mass spectrometry [viii]. This allows for greater confidence in peak assignments, especially when examining large organic molecular secondary ions.

The OrbitrapTM-SIMS analytical methodology has been already successfully applied to a variety of biological systems, especially thanks to the label-free imaging approach and the MS/MS capability, as first reported by Passarelli et al. [ix]. A first demonstration of the need for such an approach in the analysis of photoresist layers has been recently provided by Spampinato et al. [x].

This project aims to the further application of ToF-SIMS and OrbitrapTM-SIMS methodologies (including the use of GCIB and MS/MS capabilities) to unlocking the chemistry involved during the EUV photo exposure on thin photoresist layers when the composition and the processing conditions vary. This study will also give the opportunity to find a clear logic between formulation and performances of such layers.

This work will be done in a collaboration between imec, Belgium (PR group and Materials and Components Analysis department) and National Physical Laboratory (NPL), UK, offering expertise in a multitude of characterization techniques in support of this project. The very close collaboration with the process engineers of imec and its partners warrants direct industrial impact.

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[i] Doering, R.; Nishi, Y. Handbook of Semiconductor manufacturing technology, CRC press, Taylor & Francis Group, Boca Raton, FL, USA, 2008, ISBN-13:978-1-57444-675-3, ISBN-10: 1-57444—675-4.

[ii] Kozawa, T. and Tagawa, S. Radiation Chemistry in Chemically Amplified Resists. Jpn. J. Appl. Phys. 2010, 49, 030001, DOI: 10.1143/JJAP.49.030001.

[iii] van der Heide, P.A.W. Secondary Ion Mass Spectrometry: An Introduction to Principles and Practices, John Wiley & Sons, 2014, ISBN: 978-1-118-48048-9.

[iv] Delcorte, A.; Delmez, V.; Dupont-Gillain, C.; Lauzin, C.; Jefford, H.; Chundak, M.; Poleunis, C.; Moshkunova, K. Large cluster ions: soft local probes and tools for organic and bio surfaces. Phys. Chem. Chem. Phys. 2020, 22, 17427-17447, DOI: 10.1039/D0CP02398A.

[v] Kubicek, M.; Holzlechner, G.; Opitz, A. K.; Larisegger, S.; Hutter, H.; Fleig, J. A novel ToF-SIMS operation mode for sub 100 nm lateral resolution: Application and performance. Appl. Surf. Sci. 2014, 289, 407– 416, DOI: 10.1016/j.apsusc.2013.10.177.

[vi] Shard, A. G.; Havelund, R.; Seah, M. P.; Spencer, S. J.; Gilmore, I. S.; Winograd, N.; Mao, D.; Miyayama, T.; Niehuis, E.; Rading, D.; Moellers, R. Argon Cluster Ion Beams for Organic Depth Profiling: Results from a VAMAS Interlaboratory Study. Anal. Chem. 2012, 84, 7865−7873, DOI: 10.1021/ac301567t.

[vii] Makarov, A. Electrostatic axially harmonic orbital trapping: A high-performance technique of mass analysis. Anal. Chem. 2000, 72 (6), 1156–62, DOI: 10.1021/ac991131p.

[viii] Prasain, J.K. Editor of Tandem Mass Spectrometry – Applications and Principles, InTech, Janeza Trdine 9, 51000 Rijeka, Croatia, 2012, ISBN 978-953-51-0141-3.

[ix] Passarelli, M. K.; Pirkl, A.; Moellers, R.; Grinfeld, D.; Kollmer, F.; Havelund, R.; Newman, C. F.; Marshall, P. S.; Arlinghaus, H.; Alexander M. R.; West, A.; Horning, S.; Niehuis, E.; Makarov, A. Dollery, C. T.; Gilmore, I. S. The 3D OrbiSIMS-label-free metabolic imaging with subcellular lateral resolution and high mass-resolving power. Nat. Methods2017, 14(12):1175-1183, DOI: 10.1038/nmeth.4504.

[x] Spampinato,V.; Franquet, A.; De Simone, D.; Pollentier, I.; Pirkl, A.; Oka, H.; van der Heide, P. SIMS analysis of thin EUV photoresist films, Anal. Chem. 2022, 94, 5, 2408–2415