

Photoresist analysis with synchrotron radiation and electron impact using time-of-flight mass spectrometry

Bruno Gabriel A. L. Borges¹ (PG), Roberto R. Pinho² (PQ), Carlos R. A. Lima² (PQ), Maria Luiza Rocco^{1,*} (PQ). *luiza@iq.ufrj.br

¹ Instituto de Química, Universidade Federal do Rio de Janeiro, 21941-909, Rio de Janeiro, RJ, Brazil

² Departamento de Física-ICE, Universidade Federal de Juiz de Fora, 36036-330, Juiz de Fora, MG, Brazil

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Introduction

Positive photoresists are widely used in lithographic process in microelectronics and in optics for the fabrication of relief components. In microelectronics, they are used as masks to transfer geometric patterns by manufactures of the integrated circuits. In optics, the photoresists are used to construct periodic structures with diffractive optics properties. The positive photoresists react in such a way that regions exposed to ultraviolet light dissolve more rapidly during the development process. The most popular positive photoresist is composed of the photoactive compound (PAC) denominated diazonaphthoquinone (DNQ) and the matrix material that is a thick resin called novolak. The novolak is a phenoleformaldehyde condensation polymer of moderate molecular weight, which is used to supply a mechanical support for the photoresist, being very strong to chemical attacks. In unexposed areas the novolak þ DNQ films are essentially invariable during the development process.

With the aim of identifying molecular modifications in positive photoresists unexposed and previously exposed to ultraviolet light the electron (ESID) and photon (PSID) stimulated ion desorption techniques coupled to time-of-flight mass spectrometry were employed in the study of the AZ-1518 photoresist. Mass spectra were obtained for different energies of the electron beam and at the S 1s edge^{1,2} showing specific changes related to the photochemical decomposition of the photoresist, which reinforces the applicability of these techniques to investigate and characterize structural changes in photosensitive materials.

Results and Discussion

Data acquisition was performed at the Laboratório de Química de Superfícies do IQ-UFRJ and at the Brazilian Synchrotron Light Source (LNLS), during a single-bunch operation mode of the storage ring and using time-of-flight mass spectrometry (TOF-MS) for ion analysis. ESID and PSID mass spectra on both photoresists (unexposed and exposed) were obtained for variable energy electrons and following the S K-shell photoexcitation. Desorption ion yield curves have been determined for the main fragments as a function of the energy. The AZ-1518

photoresists presented different mass spectra, showing characteristic fragments. Most of the analyzed ions showed larger relative yields for the exposed photoresist. Fragments related to the photochemical decomposition of the photoresist could be clearly identified. These results showed that the ESID and PSID techniques are adequate to investigate structural changes in molecular level in unexposed and exposed photoresists.

Conclusions

Electron and photon stimulated ion desorption together with TOF mass spectrometry have been performed on unexposed and exposed to UV light photoresists. Most of the analyzed ions showed larger relative yields for the exposed photoresist. Desorption ion yield curves do not show any significant photon energy dependence, which suggests that the ions desorb mainly through the indirect XESD (X-ray induced electron stimulated desorption) mechanism. The photochemical decomposition by UV exposure of the AZ-1518 photoresist could be clearly identified by ESID and PSID demonstrating the feasibility of the use of these techniques to characterize and investigate structural changes in photoresists.

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