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Photoresists comparative analysis using soft X-ray synchrotron radiation and time-of-flight mass spectrometry

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ABSTRACT

Positive photoresists are widely used in lithographic process for the fabrication of relief components. When exposed to UV radiation they suffer chemical reactions modifying their chemical and physical properties. Aiming to follow molecular modifications among two different photoresists unexposed and previously exposed to ultraviolet light we have employed spectroscopic techniques coupled with mass spectrometry in the study of the AZ-1518 and AZ-4620 photoresists. The photon stimulated ion desorption (PSID) technique following the *S K-edge* NEXAFS spectrum was employed at the brazilian synchrotron light source (LNLS), during single-bunch operation and using time-of-flight mass spectrometry (TOF-MS) for ion analysis. NEXAFS and PSID mass spectra on both AZ-1518 and AZ-4620 photoresists (unexposed and exposed) were obtained and relative desorption ion yield curves determined for the main fragments as a function of the photon energy. They present marked different PSID spectra. Fragments related to the photochemical decomposition of the AZ-1518 photoresist could be clearly identified differently from the AZ-4620. Studies on the hardness of both photoresists were performed using O_2 plasma reactive ion etching (RIE) technique, analyzed by scanning electron microscopy (SEM) and used to explain different desorption yields in the PSID spectra. These results show that the PSID technique is adequate to investigate structural changes in molecular level in different unexposed and exposed photoresists, which is crucial for improving our knowledge about the breakup process.

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1. Introduction

Positive photoresists are widely used in lithographic process in microelectronics, where they are used as masks to transfer geometric patterns by manufactures of the integrated circuits and also in optics, used to construct periodic structures with diffractive optics properties [1]. The most popular positive photoresist is composed of the photoactive compound (PAC) denominated diazonaphthoquinone (DNQ) and the matrix material, a thick resin called novolak. Fig. 1(a) and (b) shows, respectively, the chemical structures of the AZ-1518 and AZ-4620 photoresists, two important kinds of DNQ photoresists, which are studied in this work. The novolak, for which structure is shown in Fig. 2, is a phenol–formaldehyde condensation polymer of moderate molecular weight, used to supply a mechanical support for the photoresist, being very strong to chemical attacks. In unexposed areas the novolak and DNQ films are essentially invariable during the development process.

The chemical processes suffered by the photoactive compound when exposed to the UV light are shown in Fig. 3. The nitrogen molecule is weakly bonded and is

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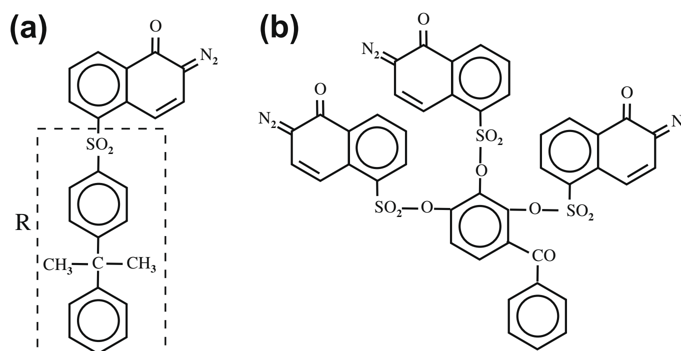

Fig. 1. (a) Diazonaphthoquinone (DNQ)-AZ-1518 chemical structure; (b) diazonaphthoquinone (DNQ)-AZ-4620 chemical structure.

liberated of the aromatic ring, turning the unoccupied orbital highly reagent. To stabilize the structure, one of the carbon atoms moves outside of the ring (ring contraction) and the oxygen atom is then covalently bonded to it. This process is denominated Wolff rearrangement and the resulting molecule is a ketene [2]. In the presence of water, a final rearrangement occurs in which a double bond of the external carbon is changed by a single bond with an OH group, giving as final product a carboxylic acid. The ketene can form cross-links with the novolak if insufficient water is present, which is not desired. As part of a systematic spectroscopic study on positive photoresists using synchrotron radiation and electron beam, we have recently employed the photon stimulated ion desorption (PSID) [3] and the electron stimulated ion desorption (ESID) techniques in the study of the AZ-1518. These studies were extended to the AZ-4620 photoresist with the aim of getting inside into the degradation mechanisms induced by UV photons in this material as well as to compare with those obtained previously for the AZ-1518 photoresist. In this work, near-edge X-ray absorption fine structure (NEXAFS) and PSID mass spectra are presented as a function of the photon energy for the AZ-1518 and AZ-4620 photoresists, unexposed and previously exposed to UV light. The AZ-1518 and AZ-4620 photoresists possess different PSID

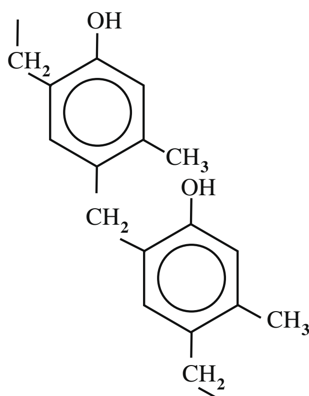

Fig. 2. Meta-cresol novolak chemical structure.

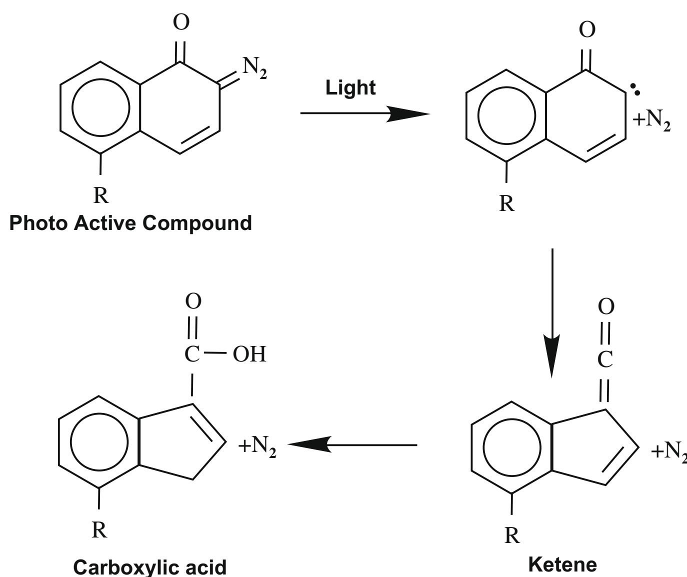

Fig. 3. Photodisintegration of the photoactive compound and subsequent reactions.

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