



Evaluation of chemical kinetics in positive photoresists using laser desorption ionization



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ABSTRACT

Positive photoresists are photosensitive materials widely used in lithographic processes in microelectronics and optics for component relief manufacturing. When exposed to ultraviolet radiation, chemical reactions are induced that modify their physical–chemical properties. This work describes a novel technique to determine the kinetic rates of molecular structure changes of the positive AZ series photoresists after exposure to mercury arc lamp radiation. These positive photoresists consist of a photoactive compound (PAC), known as diazonaphthoquinone (DNQ), and a matrix material, which is a thick base resin. This positive AZ series photoresist was chosen because its technical information is well known while presenting potential for many applications. In the present work, we investigate these processes using laser desorption ionization (LDI) by a pulsed ultraviolet laser coupled to a high resolution time-of-flight mass spectrometer (ToF-MS). The LDI-ToF mass spectra present different relative intensities for some of the characteristic negative molecular ions of the positive photoresist after different exposure energies to the mercury arc lamp radiation. For measurement of the chemical kinetic mechanism, LDI-ToF mass spectrometry was used for the first time to obtain the fractional decay rate of the DNQ per unit of exposure radiation intensity. These results provide a novel use of LDI-ToF-MS to study the chemical kinetics of photosensitive materials.

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1. Introduction

A positive photoresist is a photosensitive material which, upon exposure to ultraviolet radiation, undergoes chemical reactions that increase its solubility in alkaline solutions. The radiation absorption properties of the positive photoresist will influence resolution and its process capabilities. The knowledge of the rate (chemical kinetics)

at which these chemical reactions occur permits one to determine the possible technological applications of a specific positive photoresist. After exposure to ultraviolet radiation, a positive photoresist is converted into a relief pattern through a development process, the exposed regions being removed much faster than the unexposed regions. These materials have been widely used in photolithographic processes to manufacture integrated circuits in microelectronics [1–3]. Positive photoresists have also been applied to processes for information storage [4], recording of Bragg gratings in optical fibers, holography [5–9] and holographic memories [10]. The optical absorption mechanism at the microscopic level of the positive photoresist is

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described in terms of three parameters known the Dill ABC parameters. The A parameter is an optical absorption dependent term, the B parameter is an optical absorption independent term and the C parameter provides the optical sensitivity, or the chemical kinetics, of the positive photoresist. These parameters have been traditionally and conveniently determined employing the technique of actinic transmission measurement. However, the actinic transmission technique is limited by positive photoresists that absorb radiation over 300 nm wavelength [12].

In previous work, we have employed the Photon Stimulated Ion Desorption coupled to Time-of-Flight Mass Spectrometry (PSID-ToF-MS) technique to identify molecular structure changes in unexposed AZ-1518 positive photoresist, and to those previously exposed to mercury arc lamp radiation [17,18].

In this work, we employed a high resolution Laser Desorption Ionization Time-of-Flight Mass Spectrometry (LDI-ToF-MS) technique to study, not only the molecular structural changes due to exposure to mercury arc lamp radiation, but also the AZ-1518 photoresist chemical kinetics, defined by its Dill C parameter. It is well known that AZ-1518 photoresist has high absorption in the wavelength range of 310 nm to 440 nm. In the mentioned range of wavelengths there are three major emissions of the mercury arc lamp at 365 nm, 405 nm and 436 nm [12]. In the present experiments, no attempt was made to filter the radiation source so as to replicate what is currently observed in practice. The results were obtained with an accuracy that will allow studies of optical properties and chemical kinetics by using the LDI-ToF technique. This novel technique should be able to be applied to other photoresists, especially those chemically amplified which are difficult to measure employing the actinic transmission methodology, for example those that absorb at 248 or 193 nm [13]. Singly charged negative ion mass spectra for different exposure energies to a typical mercury arc lamp, in the reflectron mode, were obtained for the AZ-1518 photoresist. Changes in the relative quantities of molecular negative ions were monitored as a function of exposure energy. From these data it was possible to obtain the AZ-1518 photoresist Dill C parameter.

2. Theoretical model

The positive photoresist has three main components: a base resin, a photoactive compound (PAC) and a solvent. In the positive photoresist, the PAC acts as an inhibitor before the exposure, decreasing the dissolution rate of the resin in alkaline solutions. The PAC typically represents about 30% of a dried photoresist film [11]. After exposure, photochemical reactions modify the inhibitor facilitating dissolution of the exposed photoresist in alkaline solutions. After exposure of the photoresist to ultraviolet radiation, its absorption coefficient α decreases as a result of decreasing the concentration of the photoactive compound. This can be described in terms of the relative concentration $M(z, t)$ of the remaining photoactive compound, at any depth z and exposure time t , by comparing the photoactive compound concentration before and after exposure. If little

incident radiation is scattered in the photoresist, the absorption constant is

$$\alpha = A M(z, t) + B \quad (1)$$

where, for a certain wavelength, the A parameter describes the absorption by the photoactive compound and B parameter describes the absorption by the other photoresist components [11]. The rate of relative concentration change of the photoactive compound is dependent on the local optical intensity $I(z, t)$, the relative concentration $M(z, t)$ and a measurable optical sensitivity term C, as given by

$$\frac{\partial M}{\partial t} = -I(z, t)M(z, t)C \quad (2)$$

In Eqs. (1) and (2), A, B and C depend upon the photoresist type and exposure wavelength [11]. These constants are referred to as the Dill ABC parameters. The methodology described herein permits determination of the Dill C rate constant by an alternative method with a good degree of correlation and precision using LDI coupled with ToF-MS. In the case where the photoresist is a thin homogeneous film, the intensity of the ultraviolet radiation is not dependent on the exposure time, the solution of Eq. (2) is

$$M(t) = e^{-Ct} \quad (3)$$

or

$$M(E) = e^{-CE} \quad (4)$$

where $It = E$ is the exposure energy E per detector area unit. Therefore, the changes in the relative concentration of the photoactive compound should decrease exponentially as a function of the exposure energy. On a microscopic level, photons are absorbed by an atom or molecule causing an outer electron to be promoted to a higher energy level. This phenomenon is especially important for the photoactive compound since it is the absorption of ultraviolet radiation which leads to the chemical conversion of M to P [12].

$$M(t) \rightarrow P(t) \quad (5)$$

where the relative concentration of the exposure products P is generated by the reaction of M with ultraviolet radiation. The total amount of components in the photoresist should be conserved and therefore

$$\frac{dM}{dt} = -\frac{dP}{dt} \quad (6)$$

or

$$P(E) = 1 - e^{-CE} \quad (7)$$

Thus, the changes in exposure products $P(E)$ should increase as a function of the exposure energy E . Eqs. (4) and (7) provide an important description of the chemical kinetic mechanisms of photoresists.

In some of the most popular positive photoresists, the photoactive compounds are diazonaphthoquinones (DNQ), as is the case of the AZ-1518 photoresist, whose molecular structure is shown in Fig. 1(a). The matrix material of these photoresists is a thick resin called Novolac. Novolac is a methacrylate-based polymer with an epoxy group, and is shown in Fig. 1(b). For the deposition of

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