A Simple Method for Measurement of Photoacid Generator Photoreaction Kinetics in Formulated, Chemically Amplified Photoresist Films

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A method which utilizes experimental measurement and modeling of photoacid-catalyzed deprotection rates obtained via Fourier transform infrared spectroscopy has been developed for determining photoacid generator (PAG) photoreaction rate constants (i.e., Dill C parameters) in protected polymer matrices. Numerical modeling of deprotection rates as a function of exposure dose and postexposure bake time is used to determine the Dill C parameters for the PAG in the actual resist matrix polymer of interest. This protocol is shown to be a fast, nondestructive, and material-saving technique that can permit measurement of Dill C parameters in reactive polymer matrixes.
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Chemically amplified resists (CARs) are now a critical and enabling technology for the lithography processes used to fabricate modern semiconductor devices. The simplest conventional positive-tone CAR consists of a two-component mixture of a protected polymer matrix and a photoacid generator (PAG).[1] The basic image formation process in a CAR consists of three main steps: patternwise exposure, postexposure baking, and development in an aqueous alkaline solution. Exposure of the CAR to radiation results in the decomposition of the PAG and the generation of a strong photoacid. The photoacid produced in the exposed areas catalyzes a subsequent deprotection reaction that removes the protecting or blocking groups from the matrix polymer during a postexposure bake (PEB), thus rendering the exposed regions of CAR soluble in aqueous alkaline solutions. This differential solubility change created by exposure allows for the formation of the desired relief images in the photoresist during the final development process. Modeling of such chemically amplified resist lithography processes has become an invaluable tool for the semiconductor industry. Such modeling tools are used in a variety of areas such as exposure tool optimization and optical proximity correction. Although the models used to describe the important chemistry and physics occurring in CAR resists are relatively straightforward, accurate parameterization of these models for real resist materials has remained difficult and elusive. The goal of the work described in this paper is to develop methods for the simple and accurate parameterization of the photoacid generation kinetics models which form the basis of the first stage of photoresist response modeling.

The decomposition of a PAG into its photoproducts is generically assumed to be a first-order kinetics process that can be described as shown in Eq. 1.[2] The photoacid generation rate constant of the PAG when exposed to radiation is described by the Dill C parameter

$$[\text{Acid}]_{\text{photo}} = [\text{PAG}]_0(1 - e^{-CE}) \qquad [1]$$

Here $[\text{PAG}]_0$ is the initial loading of the PAG, $[\text{Acid}]_{\text{photo}}$ is the concentration of generated photoacid, E is the exposure dose, and C is the Dill C parameter for the PAG in the resist matrix. This distinction that the Dill C for a PAG is dependent on the polymer photoresist matrix in which it is located is critically important, as energy transfer from the polymer matrix to the PAG is important in many resist material systems.[3,4] Subtle changes in polymer or photoresist composition can dramatically affect the Dill C parameter for the PAG.

Because it is the first step in the image formation process in CARs, a great deal of effort has been devoted to studying the PAG photoreaction process and the measurement of the Dill C parameter for various PAGs. Previous techniques utilized for this measurement include in vitro spectrofluorometric/spectrophotometric techniques,[5] on-wafer spectrofluorometric techniques,[6] and a standard addition technique analogous to acid-base titrations commonly used in chemical analysis.[3,7,8] Despite the general success of these methods in measuring the Dill C, each of these techniques has drawbacks that have limited their widespread application, such as requirements for large amounts of resist material, the need for specialized equipment and chemicals not common in resist processing areas, and extensive experimental time to complete the measurements. Furthermore, for the techniques which require addition of reagents to the resist film before exposure (e.g., on-wafer spectrofluorometric techniques and the standard addition method), the confounding effects of foreign additives such as indicator dyes or base on the PAG photoreaction process are difficult to determine. Because such techniques require the use of additives to the resist before exposure, it is not possible with those techniques to run the proper control experiments that do not include additives to determine their effect on the measurement. More recently, the use of interdigitated electrodes (IDEs) as impedance sensors for determining the Dill C parameter for PAGs in photoresist polymers has been reported as an on-wafer technique that solves many of the problems associated with earlier techniques such as avoiding the use of additives to the resist film.[9,10] However, this technique does require the fabrication of intricate large-area interdigitated electrodes, which is generally only feasible in commercial wafer fabrication facilities and laboratories or in a few select government and university laboratories. In addition, studying PAG photoreaction kinetics in polymer matrices that react at low temperatures in the presence of photoacid, such as polymers possessing very low activation energy protecting groups like tetrahydropyranal ether moieties, can be difficult as the deblocking of the polymer and creation of polar groups result in dielectric constant changes in the polymer that complicate analysis of the capacitance data from the IDE. Therefore, a major goal of our present work in this area is the development of simple techniques for determining the Dill C photoreaction rate constants for PAGs in reactive polymer matrices that do not require the fabrication of special microdevices and which could be applied by a wider number of research groups interested in this area.

Description of Dill C Analysis Technique

The Dill C measurement technique presented in this work is noninvasive, nondestructive, material saving, easy to perform, and requires only basic lithography equipment and an infrared spectroscopy instrument. The two fundamental requirements for measuring the Dill C for a PAG is that one can measure the dose or amount of exposure energy delivered to a resist sample and then also have a

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way to measure the change in concentration of photoacid in the resist resulting from this exposure. Measurement of the exposure dose delivered to a sample is straightforward using calibrated light sources and common energy meters. The major advance of the method reported here is that it uses Fourier transform infrared spectroscopy (FTIR) as a tool to quantitatively measure the deprotection reaction rate of an exposed CAR during the PEB processes which can subsequently be used to calculate the concentration of photoacid in the resist film. To understand this process, a discussion of the reactions and their kinetic descriptions occurring in a CAR film is required.

The deprotection rate of the protected aqueous base soluble comonomer in a CAR can generally be described as the combination of a second-order acid-catalytic, a second-order autocatalytic, and a first-order thermolytic deprotection reaction.[11] Therefore, the rate of such a deprotection process can be described as

$$d[P]/dt = -k_{acid}[Acid]_{photo}[P] - k_{auto}[M][P] - k_{thermo}[P] \quad [2]$$

Here $[P]$ is the concentration of the protected comonomer. k_{acid}, k_{auto}, and k_{thermo} are the rate constants of the photoacid-catalyzed, autocatalytic, and thermolytic deprotection reactions, respectively. $[M]$ is the concentration of acidic molecules originally in the resist polymer formulation or generated via deprotection, such as the hydroxystyrene subunit produced by the deprotection reaction in the resist system reported here which possesses a reasonably acidic proton. In general, under mild PEB conditions (i.e., lower PEB temperature) and in resists possessing high-activation-energy protecting groups (e.g., *t*-butyl ester and butoxycarbonyl groups), the deprotection of the protected groups in the resist polymer caused by autocatalysis and thermolysis is insignificant, and the deprotection rate in the resist is then directly proportional to the amount of photoacid. Using this fact, in conjunction with Eq. 1 and 2, makes it possible to relate the properties of two resist samples processed at the same PEB temperature in terms of their relative deprotection rate, relative photoacid concentrations, and the exposure dose used for each sample in the following manner

$$\frac{d[P]_i/dt}{d[P]_{ref}/dt} \cong \frac{[Acid]_{photo,i}}{[Acid]_{photo,ref}} = \frac{(1 - e^{-CE_i})[P]_i}{(1 - e^{-CE_{ref}})[P]_{ref}} \quad [3]$$

Here the subscripts i and ref distinguish the two different resist samples, one exposed to a dose E_i and the other exposed to an arbitrarily chosen reference dose E_{ref}. In practice, a dose array can simply be exposed onto a single resist film and all these exposure dose samples are processed simultaneously under the same conditions. Use of two samples processed at different exposure doses and their relative properties is advantageous in that it avoids the need for knowledge of the exact PAG or protecting group concentrations in the resist. The basic procedure for determination of the Dill C parameter is then simple and straightforward. The initial photoacid profile in the resist film for each dose can be calculated by Eq. 1 with an initially guessed Dill C. The deprotection level of the protected comonomer in the resist polymer is monitored by quantitative FTIR spectroscopy. The deprotection rate for different exposure doses is determined by simply fitting the FTIR data to an appropriate function and calculating the slope of the fitting curve. By choosing one exposure dose as a reference, the relative initial deprotection rate and the corresponding exposure dose can be fitted to the model shown in Eq. 3 by simply iterating and adjusting the Dill C parameter until the error between the calculated relative initial photoacid concentration ratio and the experimentally measured relative initial deprotection rate ratio is minimized. The overall experimental and modeling procedure is illustrated schematically in Fig. 1.

Experimental

The resist samples used in this work were made from a resist solution containing 15.1 wt % partially *tert*-butoxycarbonyl (*t*-BOC) protected poly(*p*-hydroxystyrene) solids (PTBOCST-*co*-PHOST, Mw 12,020, 26% *t*-BOC protected, DuPont Electronic Ma-
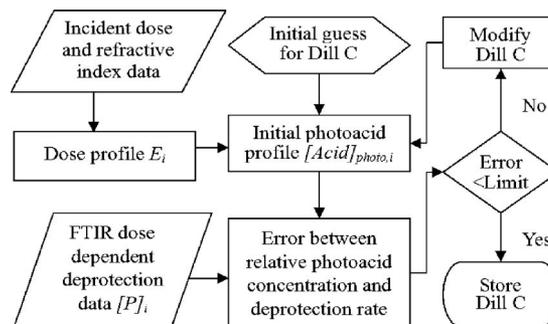

Figure 1. Flowchart of the general procedure developed in this work for determining the Dill C parameter of a chemically amplified resist.

terials), blended with 3.0 wt % triphenylsulfonium triflate PAG (TPS-Tf, Mw 412.15, Sigma Aldrich) in propylene glycol monomethyl ether acetate (PGMEA, Sigma Aldrich). Prime grade silicon wafers were sequentially coated with a 25 nm titanium film and a 250 nm gold film (CVC SC 5000 electron-beam evaporator) and used as the substrates for FTIR reflectance measurements. The resist solution was filtered through 0.2 μm Teflon syringe filters and spin-coated (2500 rpm, 90 s) onto the gold-coated silicon wafers to form resist films with thickness of approximately 580 nm. The films were soft-baked at 80°C for 90 s on a contact hot plate to remove residual casting solvent. Film thicknesses were measured using a variable-angle spectroscopic ellipsometer (V-VASE, J. A. Woollam, Inc.) by fitting the ellipsometry spectra with a Cauchy model for the resist film in the nonabsorbing wavelength range from approximately 500 to 1000 nm. The refractive indexes of the resist film in the deep-ultraviolet (DUV) wavelength region were also then determined from the ellipsometry data. The resist films were exposed using an Oriel Instruments exposure source (model no. 87530-1000, Hg–Xe arc lamp) filtered using a 248 nm bandpass filter (bandwidth ~11 nm at full width at half maximum). The intensity of the lamp source under these was measured to be 1.21 mW/cm² using a Molectron PM3 power probe and EPM2000 energy meter. Reflectance FTIR spectra were collected using an FTIR microscope (IRscope II microscope) connected to a Bruker IFs66vS FTIR/Raman system. Deprotection levels in the resist films were determined by monitoring the intensity of the carbonyl stretching peak associated with the *t*-BOC group (1755 cm⁻¹), while the C–H out-of-plane bending of the para-substituted benzene (827 cm⁻¹)[12] was used as an internal standard for normalization of the collected FTIR data with respect to possible variations in resist film thickness on different samples. Every FTIR measurement was collected from the average of 128 scans. The *t*-BOC carbonyl stretching peak intensity was monitored and assumed to be linearly proportional to the *t*-BOC concentration (i.e., protection ratio) of the polymer resin. The measured peak intensities of the exposed and baked samples were calibrated to the peak intensity of the 26 mol % and 0 mol % protection samples to determine the protection level.

Results and Discussion

Polychromatic DUV intensity profile.— Ultraviolet exposure of a CAR sample on a reflective substrate, such as the gold-coated substrates used in this work, leads to the formation of standing wave intensity profiles in the resist film. The DUV radiation spectrum received by the resist film was calculated by multiplying the emission spectrum of the Hg–Xe arc lamp and the transmission spectrum of the 248 nm bandpass filter used with the lamp. The standing wave intensity profile in the resist film created by such a DUV illumination spectrum in the resist films was calculated using a method described previously by Berger and co-workers.[9] The resulting polychromatic intensity profiles in the unexposed resist film were determined by summing up the properly weighted intensity
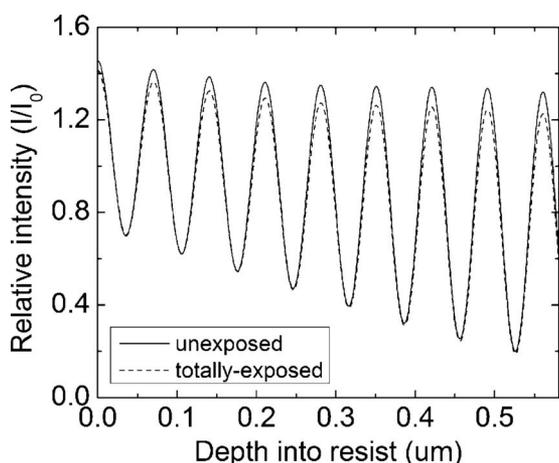
Figure 2. Relative intensity profiles inside resist samples under polychromatic DUV exposure for the *t*-BOC protected PHOST resist material used in this work.

(i.e., by relative spectral intensity) at each wavelength in each spatial position in the film to arrive at the net intensity profile as a function of position in the resist film. These standing wave intensity profiles were then used to determine the exposure doses for each resist film sample for Dill C parameter extraction based on the exposure time and nominal lamp intensity for each sample. The change of the refractive indexes of the resist film during the exposure may change the radiation intensity in the resist film and affect the deposited dose profile due to the change of the PAG structure after photodecomposition or the nonuniformity of the resist film surface among samples measured.[13] Figure 2 shows the calculated polychromatic intensity profiles of both an unexposed film and a resist film exposed to a large dose. The sample exposed to the large dose was calculated for a sample exposed to DUV radiation for 500 s, a dose strong enough to decompose essentially most of the PAG molecules in the resist film. An average 5.36% decrease in the peak intensity in the resist film was observed. Such intensity difference between these two samples showed the maximum exposure dose variations during exposure if the change in DUV refractive index is assumed to be proportional to the PAG decomposition level. The resulting dose variation may affect the determination of Dill C and should be evaluated if one only uses the intensity profile measured from the unexposed sample in calculating the dose and initial photoacid profile.

Evaluation of possible confounding effects on determination of Dill C parameters using this method.— A reaction-diffusion model including all major phenomena, such as acid catalysis, autocatalysis, acid diffusion, acid loss, photoacid generation efficiency, and different initial protection ratio, was built to simulate the possible physical and chemical mechanisms leading to changes in the photoacid and polymer protection level in a CAR during PEB processing. This model was then used to generate simulated deprotection level data sets as a function of exposure and PEB conditions for theoretical resists possessing different resist physiochemical properties (e.g., different levels of photoacid diffusion, different acid catalytic deprotection rates, different autocatalytic deprotection rates, varying levels of photoacid loss, etc.). The generated simulation data with different model parameter settings was then used to test the performance of the simple data analysis model (see Eq. 3) in the face of different levels of photoacid diffusion and various reaction conditions when used to extract Dill C parameters from simulated polymer deprotection data. The resist film for these simulations was represented as a layered set of n slabs with a thickness Δz ($n = 1001$ and $\Delta z = 0.58$ nm). The calculated standing wave profile through the resist depth was assigned to each slab at the correspond-

ing position. The initial photoacid concentration of each slab at a certain exposure dose was generated using Eq. 1 multiplied the photoacid generation efficiency of the PAG, which is defined as the percentage of PAG that actually generates acid when exposed to radiation. The deprotection of the protected polymer subunits was modeled using Eq. 2. Possible loss of photoacid from the film was modeled using a first-order acid loss reaction mechanism to represent possible airborne base contamination or acid volatilization. Fick's second law with a constant diffusion coefficient (see Eq. 4) was employed for calculating diffusion of photoacid between slabs in the resist film due to the photoacid concentration gradients set up by absorption and standing wave effects during exposure of the resist film. A discretized form of Eq. 4 shown in Eq. 5 was implemented for the calculations

$$\frac{\partial [\text{Acid}]_i}{\partial t} = D\nabla^2 [\text{Acid}]_i \qquad [4]$$

$$[\text{Acid}]_i \cong \frac{\Delta z}{\sqrt{2\pi\sigma^2}} \sum_{j=1}^{n} [\text{Acid}]_j e^{-(z_i - z_j)^2/2\sigma^2} \qquad [5]$$

Here $\sigma = \sqrt{2Dt}$ represents the acid diffusion length at a given PEB time t and diffusion coefficient D. The results showed that theoretically a broad range of the acid diffusion (0.0–100.0 nm²/s), acid loss (0.0–0.9 s⁻¹), and acid generation efficiency (10–100%) parameters have no significant effect (<1% Dill C error; Dill C was set as 0.04 cm²/mJ) on the applicability of the method. Low initial polymer protection ratio and high autocatalytic reaction rate may result in significant error to the Dill C extraction method described in this paper. Figure 3 shows the criteria where the autocatalytic reaction due to the combination of these two factors contributes significant deprotection contents and causes an unacceptable error (more than 5% in Dill C parameter; Dill C = 0.04) to this method. In cases where the ratio of the autocatalytic to acid-catalytic rate constants ($k_{\text{auto}}/k_{\text{acid}}$) is below 5.0×10^{-5}, it appears that this simple method is quite robust and insensitive to other material property variations. The partially protected *t*-BOC/PHOST polymer resin used in this work has 26 mol % protection ratio and has been calculated to have $k_{\text{auto}}/k_{\text{acid}}$ equal to 3.02×10^{-7}, according to the reaction rate coefficients provided by previous work.[14] This value is within the parameter space of theoretically less than 1% error in determining the Dill C parameter, as illustrated in Fig. 3. The autocatalytic effect can be prevented in such high-activation-energy systems using moderate bake conditions and does not significantly affect the physical accuracy of this method. The change of refractive index in the resist film due to the photolysis of the PAG may result in variations of the radiation intensity in the film. Simulation data used to test the Dill C extraction method proposed here was generated using an intensity profile calculated using the refractive index of the unexposed film, but as a worst case scenario it was analyzed using the intensity profile calculated from the refractive index of the film exposed to high dose (i.e., when all PAG has undergone photolysis). This exercise showed the extreme case where the maximum intensity profile variation may exist between the conditions used to generate the experimental data and the conditions simulated during data analysis due to PAG photolysis. In this case, however, only a small deviation (~5.0% error in Dill C parameter) was observed. This result suggests that typical variations in the refractive index of a chemically amplified resist sample during exposure also do not likely result in any significant error in the Dill C parameters extracted from experimental data which are analyzed without consideration of such refractive index changes.

The extracted Dill C parameter.— Resist films of the partially *t*-BOC protected PHOST were exposed to a range of incident doses from 3.62 to 42.21 mJ/cm² and PEB-baked for times between 0 and 90 s at 55°C. The FTIR reflectance data for each sample were collected and translated into a *t*-BOC protection level as shown in Fig. 4. The deprotection extent was observed to be proportional to the
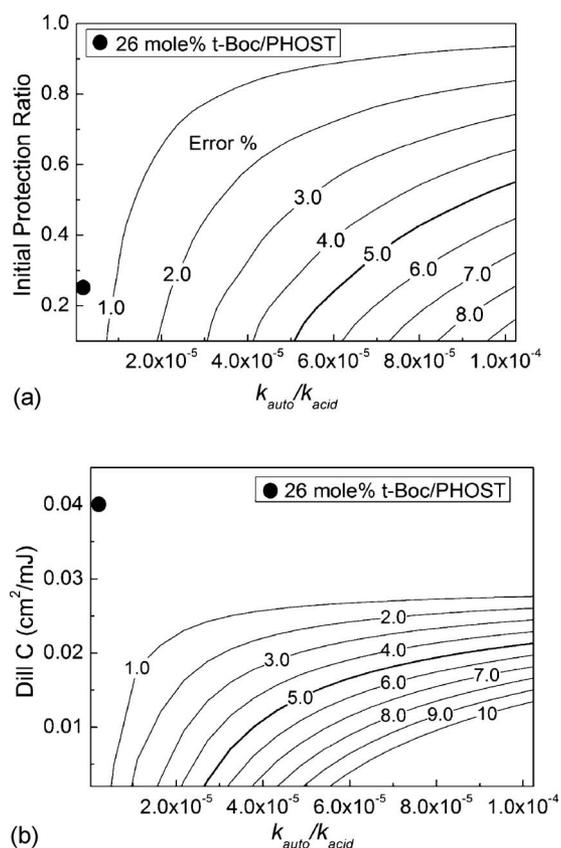
Figure 3. (a) Plot showing the error in the Dill C parameter calculated from the initial deprotection rate data using the method described in this paper as a function of the initial polymer protection ratio and the ratio of the auto-catalytic to acid-catalyzed deprotection rate constants (k_{auto}/k_{acid}) for a PAG with a Dill C value of 0.04. (b) Plot showing the error in the Dill C parameter extracted using the proposed method as a function of Dill C value and k_{auto}/k_{acid} ratio for polymers with a 26% initial protected monomer level. Shown on these plots also are the points corresponding to the *t*-BOC protected PHOST samples used in the experimental work described in this paper, illustrating that there should be less than 1% error in the Dill C values obtained from the method.

dose deposited in the resist film and the photoacid generated. A slight decrease in protection level (>5 mol %) of the samples was observed for all of the samples before PEB baking and is assumed to
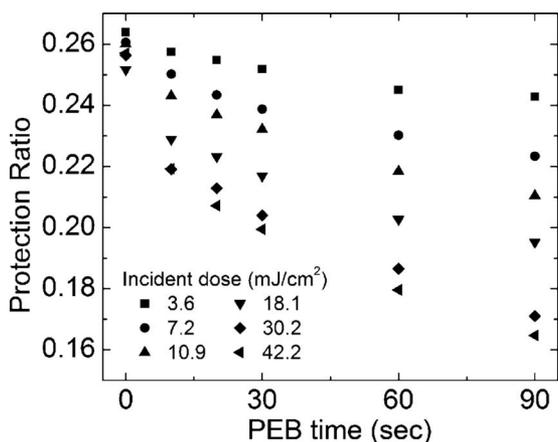

Figure 4. Raw data showing the *t*-BOC protection ratio of the films subjected to different exposure doses and PEB times.
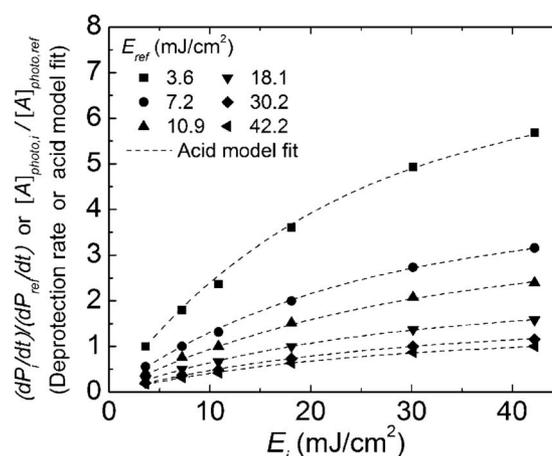

Figure 5. Plot showing the (dashed lines) predicted initial deprotection rates using Eq. 3 and (solid symbols) experimentally measured initial deprotection rates as a function of exposure dose. The predicted initial deprotection rates shown are for a best fit case where the extracted Dill C = 0.0409.

be due to the room-temperature deprotection of the polymer in the presence of a strong photoacid while the samples were being exposed. The initial deprotection rates for different exposure doses were obtained by calculating the first derivative of the fitting curves at time zero. The model fitting results of Eq. 3 to the calculated initial deprotection rates are shown in Fig. 5. Each fitting curve, as well as the corresponding Dill C parameter, was calculated by taking one of the exposure doses as a reference dose and its initial deprotection rate as the reference deprotection rate. The average Dill C value extracted from two repeated experimental FTIR deprotection data sets was 0.0409 cm²/mJ (±0.0023, 95% confidence level), which is well within the range of literature for reported Dill C values (0.037–0.055 cm²/mJ) for this PAG in similar matrices as determined by other methods.[3,7] Therefore, both the sensitivity analysis and the demonstrated ability of the method to extract a reasonable and self-consistent Dill C value for an experimental resist formulation show that this technique is both experimentally simple and accurate for PAGs in high-activation-energy resist systems. The method described here, however, is valid only for resists which show negligible autocatalytic deprotection under the experimental conditions.

Conclusions

The development of a method for extracting Dill C parameters for PAGs in protected polymer chemically amplified resist matrices using quantitative FTIR measurement of polymer deprotection rates has been reported. In this method, the PEB baking time dependent deprotection extent of the polymer matrix is measured by FTIR spectroscopy and translated into the protection level of the resist film as a function of exposure and baking conditions. The deprotection rate as a function of exposure dose and PEB time is then calculated from the slope of a first-order exponential decay curve fit to the protection ratio data. The Dill C parameter is extracted by fitting the relative initial photoacid concentrations to the calculated relative deprotection rates for two resist samples exposed to different doses. Examination of the sensitivity of this method to confounding variables done by performing Dill C parameter extractions on simulated deprotection rate data sets showed insignificantly small effects (±5% error) caused by acid diffusion during PEB, acid loss during PEB, acid generation efficiency, and small variations in the refractive index of the resist film during exposure. However, it was found that resists which display significant autocatalytic deprotection cannot be reliably analyzed using this simple method. This method was demonstrated to successfully yield a Dill C parameter of 0.0409 cm²/mJ for a high-activation-energy resist, consisting of

triphenylsulfonium triflate in partially *t*-BOC protected PHOST, that is consistent with other reported values for similar resist systems determined using other methods. More advanced methods for using quantitative FTIR measurement of deprotection rates to extract Dill C parameters for resist systems which can deal with low-activation-energy resist systems and systems which in general exhibit autocatalytic deprotection during PEB are being developed and will be reported in the near future.

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