# Determination of residual casting solvent concentration gradients in resist films by a "halt development" technique

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The resolution of the microlithography process used to manufacture semiconductor devices is a function of many variables. One interesting and important contributor to resolution is the "surface induction" phenomenon that occurs during development of many photoresist materials. This phenomenon is manifested by a change in dissolution rate as a function of thickness. The top or surface regions of these films dissolve more slowly than the bulk of the film for reasons that are not understood. One popular theory for surface induction is that the variation in rate is caused by a gradient in the concentration of residual casting solvent. However, no study has been performed that directly measured the concentration gradient in residual casting solvent and related that gradient to the extent of surface induction. A "halt development" procedure has been developed that allows isolation and analysis of thin layers (slices) from resist films. The analysis for concentration of residual casting solvent was accomplished by radiolabeling the solvent and analyzing the layers by scintillation counting. The dissolution rate data was acquired by a multiwavelength interferometry technique. Two resists systems were studied, one with a large extent of surface inhibition and one with a nearly constant dissolution rate. Neither formulation has a significant concentration gradient of residual casting solvent over a range of bake temperatures (70-110 °C). Therefore, it can be concluded that concentration gradients in the residual casting solvent alone cannot account for the surface induction observed in this particular resist system. © 2001 American Vacuum Society. [DOI: 10.1116/1.1343096]

#### I. INTRODUCTION

Computer simulation has played an increasingly important role in optimizing the lithographic process and thereby decreasing the size of patterned photoresist features. Several simulator tools can accurately model the aerial image and the corresponding latent image generated in the resist during exposure.<sup>1,2</sup> These models are based on fundamental physical relationships and measurable properties of the photoresist. However, the dissolution of photoresist films is very complex and less well understood. Several studies have provided insight into the effect of photosensitive compound,<sup>3</sup> polymer,<sup>4</sup> casting solvent,<sup>5</sup> developer solution,<sup>6</sup> etc. on the development process, and some theories that describe the dissolution process at a molecular level have been proposed.<sup>7</sup> However, one important aspect of the dissolution process that remains a mystery is the phenomenon of "surface induction."

The term surface induction describes the slower development rate near the surface of a resist film. The plots of the thickness of resist remaining versus time in developer for resist films cast from diglyme [bis(2-<sup>14</sup>C-methoxy ethyl)ether] and propylene glycol methyl ether acetate (PGMEA) are shown in Fig. 1. (The resists are a homemade novolac/ DNQ formulation.) The dissolution rate versus thickness for these two different resists are shown in Fig. 2. When cast from diglyme, films of this resist show little (if any) surface inhibition. However, when PGMEA is used as the casting solvent, there is a noticeable amount of surface inhibition. This dissolution inhibition has a powerful and beneficial influence on the lithographic process and enables manufacturing of reduced integrated circuitry feature sizes.

It has been suggested that surface induction may be explained by the presence of concentration gradients in residual casting solvent (RCS).<sup>5,8</sup> It has been shown that films with lower RCS concentration have lower dissolution rates.<sup>5</sup> It therefore stands to reason that the dissolution rate at the surface of a dried photoresist film should be lower than the bulk rate where the RCS concentration is higher. The nature of casting solvent can also cause variations in the extent of surface induction, and this variation might be explained by the difference in RCS distribution in resists cast from different solvents.9 These RCS gradients in photoresist systems have been measured by others using Fourier-transform infrared methods and cause-effect relationships have been proposed for these gradients and surface induction.<sup>5</sup> However, this relationship has not been supported by direct measurement of solvent concentration gradients and establishment of their relationship to surface induction in photoresist development.

A "halt development" (HD) technique has been developed to test this relationship. This HD technique provides a simple yet powerful method for monitoring the dissolution kinetics of a photoresist while quantitatively separating different layers of the resist film for chemical analysis. The analysis method chosen for detection of trace quantities of RCS was <sup>14</sup>C isotope labeling and liquid scintillation count-

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Fig. 1. Thickness vs time for a novolac resist cast with diglyme and PG-MEA.



FIG. 2. Rate of development vs thickness for a novolac resist cast with diglyme and PGMEA.

ing (LSC). The LSC method is used extensively in studies of molecular diffusion, and it has been used previously for measuring RCS in a variety of photoresist systems.<sup>10–12</sup> The mass of RCS in the top layer (one tenth) of a 1  $\mu$ m film on a 2 in. wafer is less than 0.05 mg, so gravimetric techniques are challenging. This measurement is further complicated by the variety of other compounds in photoresist samples. The advantages of the LSC method include high sensitivity and no chemical or physical change in the system. The specific advantages of LSC over other conventional methods for RCS measurement in photoresist systems is described in more detail elsewhere.<sup>13</sup>

The dissolution rate of the resist films were measured using a multiwavelength dissolution rate monitor (DRM). The instrument and its operation are described elsewhere.<sup>14</sup> This technique provides accurate information about the absolute thickness of the resist film as a function of development time. The derivative of the thickness versus time curves give rate as a function of time (which can be easily converted to rate versus thickness). This rate was then correlated with the RCS concentration at the thickness that was determined from the LSC data. The combination of these two techniques allowed for the direct measurement of the residual solvent concentration throughout the depth of the resist film. Thus, a quantitative relationship between dissolution rate and the local RCS concentration was established.

#### **II. EXPERIMENT**

#### A. Materials: Resist formulations and radio-tracer preparation

The photoresist systems used for the study were novolac/ diazonaphthoquinone (DNQ) positive resists. The resists were made using cresol novolac (MW=9370, Pd=4.9) from Schenectady International, and a bis-(1-oxo-2diazonaphthoquinone sulfonate) (DNQ) from IBM Corp. The resists consisted of 77 wt % solvent and the DNQ loading was 12 wt % relative to the solids. Two developer solutions were prepared using AZ 300 MIF tetramethly-ammonium hydroxide developer from Clariant Corp. The resists were developed with the first solution, which contained 90% by volume of the AZ 300 MIF and 10% distilled water. The HD cell was then washed with the second solution, of 70% AZ300 MIF and 30% distilled water (by volume). The 70% solution was strong enough to act as a washing solution without causing the developed resist to precipitate, yet it was weak enough not to cause significant resist development.

The <sup>14</sup>C radio-labeling synthesis routes for PGMEA (propylene glycol methyl ether acetate-carbonyl-<sup>14</sup>C) and diglyme have been previously described.<sup>13</sup> A Beckman 1801 liquid scintillation counter was used to measure the activity of each sample. The specific activity of the diglyme and PGMEA based resists were measured to be 8.21 and 9.9  $\mu$ Ci/g, respectively. Scintiverse II from Fisher Scientific Inc. was used as the scintillation cocktail for the developer/resist solution samples. An H-number quenching calibration as defined by Beckman-Coulter, Inc. was performed using a developer/resist solution as the quenching material. The H-number calibration of these aqueous samples has been described in detail previously.<sup>13</sup>

#### B. Film coating and halt development cell description

The resists were spin coated on 2 in. wafers for 40 s using 0.35 ml of resist solution. The spin speed was adjusted to obtain a 1  $\mu$ m resist film for the diglyme resists. The films cast from PGMEA had thicknesses of 1.5  $\mu$ m. The wafers were baked on a Thermolyne hotplate with a vacuum chuck for 90 s at bake temperatures of 70, 90, and 110 °C.

A diagram of the HD cell is shown in Fig. 3. The plastic backing of the HD cell has a recess that holds films coated on 2 in. (in diameter) silicon wafers. A 2 mm Viton<sup>™</sup> gasket rests between the glass plate and the backing. The gasket was designed to provide an inlet for the developer at the top. The tapered area at the bottom of the inlet is designed to allow trapped air to rise into this space and prevent bubble formation over developing resist areas. The gasket covers some of the resist film. Experiments have shown that a negligible amount of resist under the gasket dissolves. The open cell has a total liquid volume of 2.5 ml. This cell volume allows for two 2.5 ml aliquots of aqueous solutions to dissolve and collect the different layers of the resist film. One cell volume of developer was used to dissolve the resist film, and another 2.5 ml volume was used to wash the cell to ensure adequate transfer of resist components into the scintillation vial.



FIG. 3. Halt development cell apparatus (profile and front view).

The HD cell was assembled, and the DRM beam was aligned with the wafer for optimal signal and the DRM data collection was started. The 90% developer solution was added quickly to the cell. (In all experiments, the cell was completely full in less than 2 s.) The resist was allowed to develop for a specified time interval. The stopcock valve was then opened and the contents of the cell flowed into a 20 ml scintillation vial. The cell was then washed with the 70% solution. The solution was held in the cell for 8 s, and the cell was then drained again. The scintillation vial, with  $\sim$ 5 ml of developer/resist solution was sealed. This vial contained the top layer of the resist. The cell was filled again with 90% developer solution, and the remaining resist was dissolved and then transferred into a second scintillation vial for measurement.

This procedure was repeated for different resist films at varying halt times to measure the relative concentration of residual casting solvent throughout the thickness of the resist film. Scintillation cocktail (14.5 ml) was added to both vials, and the solutions were shaken until an emulsion formed. The total volume of sample was less than 8/10 of the total vial volume. This volume of sample did not show any significant amount of vial quenching due to large sample volumes. The samples were counted and the activity was calculated. The ratio of activity in the top layer to that in the total film was convolved with the DRM thickness data to obtain the RCS concentration gradient. The concentration gradient was then correlated with the rate data to establish the relationship between the RCS gradient and surface inhibition.

#### **III. RESULTS AND DISCUSSION**

#### A. Advantages of the halt development technique

The HD cell concept provides several benefits over other methods<sup>5</sup> used for the analysis of concentration gradients in photoresists and the quantitative establishment of the relationship between the gradients and dissolution kinetics. Most important is the ability to simultaneously monitor the dissolution of a film using highly accurate interferometry techniques and to collect dissolved film components for quantitative analysis. The HD cell allows the film to be



FIG. 4. Intensity vs time curves of three regions on the wafer demonstrating uniform film development (including the "halt" region) across the wafer.

interrogated by a light source through a transparent window. The thickness of this film can then be monitored using interference techniques. This monitoring is accomplished simultaneously with the collection of different resist layers dissolving from the film by placing the wafer vertically into the cell and draining the developer solution. This design provides a simple method for quickly removing and collecting the developer solution, in order to halt development quickly and easily.

Another advantage of this method is that the volume of developer can be controlled. The control of the sample size is important for accurate concentration analysis. LSC requires samples to be placed into a liquid scintillation solution (scintillation cocktails) to convert the radiation from the radio nuclide to a light signal for the photomultiplier tube in LSC instruments. Unfortunately, the instruments have sample size limits and the scintillation cocktails have sample loading limitations. Therefore, the control over the sample volume is critical for liquid scintillation counting and this design facilitated minimizing the sample size to volumes compatible with LSC.

The scintillation cocktail used forms an emulsion when the cocktail is mixed with aqueous samples and is cited as being capable of providing accurate counting statistics for aqueous samples with less than 25% loading. This loading limitation was confirmed during LSC instrument calibrations with solutions characteristic of the resist/developer samples expected in the study. The emulsion formation prevents phase separation of the aqueous sample and the cocktail, which causes counting losses due to decreased sample stability.

#### B. Verification of the halt development technique

Experiments with nonlabeled resist formulations were performed to establish the ability of the HD method to quantitatively separate resist layers and prove that one washing was sufficient to remove the developer/resist solution from



FIG. 5. An example of the halted development of a resist film.

the cell. The DRM data was analyzed for each dissolved film. Figure 4 shows the interference intensity signal of the DRM verse time for the three monitoring beams directed at three different areas on the wafer during a halt development experiment. The data become noisy as the cell was drained, washed, and refilled. The data demonstrate that the development rate is uniform across the wafer. Thickness nonuniformities are negligible, and they do not cause unwanted mixing of resist layers. Figure 5 shows an example of the halted development of a resist film. A very small amount of development continues to occur during the halted development period. This plot demonstrates the ability to stop development while the developer solution is changed.

Another set of experiments was conducted to demonstrate that dissolved layers of the film were being separated and that the DRM thickness data could be correlated with the chemical analysis of the dissolved resist samples. These were performed using nonlabeled resist films at different halt times. The relative polymer concentration of the dissolved and remaining portions of the resist film were established by measuring the ultraviolet (UV) absorbance of the solutions with a Hewlett Packard 8452A UV-visible (VIS) spectrophotometer. The novolac solution had a strong and easily iso-



FIG. 6. Feasibility experiment: Relationship between the extent of development measured by the DRM and UV–Vis chemical analysis of the collected effluent developer solution with dissolved resist (novolac cast with diglyme solvent).

lated absorbance at 298 nm. The relative concentration in the top layer of the film was determined by dividing the absorbance (at 298 nm) of the top effluent by the total absorbance (the sum of both effluents). Figure 6 shows a strong linear correlation between the extent of resist dissolved measured by the DRM and the UV absorbance of the developer solution. This strong linear correlation, the slope of one and near zero intercept all indicate successful separation of discrete layers of the resist film.

A test was performed to determine if one washing was adequate using the radio-labeled resist cast from diglyme. Employing the HD method, a film was coated and developed half way. The top layer, as well as the first and second washings were placed into separate scintillation vials. The amount of radioactivity removed from the HD cell with the first washing was on the order of 5% of the amount of radioactivity removed in the main solution. The amount of radioactivity removed with further 2.5 ml washing solutions was below the background levels of the LSC instrument. Therefore, one washing was adequate.

However, it is possible that solvent molecules diffuse out of the polymer film and into the developer at a rate *faster* than the film develops. Ito and Sherwood have reported a large transport of residual solvent out of resists in a humid environment.<sup>15</sup> They have suggested that water molecules are able to diffuse into and plasticize the resist, allowing solvent molecules to diffuse out of the resist into the surrounding environment. In this case, the surrounding environment is the developer solution. If this type of solvent transport does occur quickly, it would have an appreciable effect on the interpretation of the HD experimental results. In light of this issue, an experiment was devised to quantify the "leaching" of RCS into aqueous developer.

## C. Radio-labeled HD experiments: Leaching of residual casting solvent

The first set of leaching experiments was performed with the radio-labeled diglyme resist. The HD cell was used in the usual manner with one change. Instead of using developer, pure distilled water was poured into the cell initially. The water was allowed to contact the resist for a given time, after which the cell was drained and washed with distilled water. The water did not cause appreciable dissolution of the resist film. The remaining resist was dissolved using the standard developer, and washed with the standard washing solution. The experiment was repeated, allowing the water to contact the resist for various leaching times. The relative amount of solvent that was transported into the water was measured with the liquid scintillation counter. The results of this experiment are shown in Fig. 7.

At long contact times ( $\sim 25$  min) as much as 5% of the residual casting solvent diffuses into the water. Only 1% of the residual solvent diffuses out of the film in 5 min. The halt times used for the RCS experiments are all less than 5 min. A second experiment was conducted with the PGMEA labeled resist (Fig. 7). Less than 2% of the PGMEA leaches out of the resist during 5 min of contact with water. There-



FIG. 7. Relative amount of residual diglyme and PGMEA "leached" out of a novolac resist for varying contact times with water.

fore, the rate of solvent transport into developer is too low to give significantly incorrect RCS gradient results.

# D. Radio-labeled HD experiments: Measuring residual casting solvent distribution

The HD/LSC method was used to determine the RCS concentration gradient in the resist cast from diglyme. Six resist films were spin coated with a 90 °C PAB and developed for various lengths of time. The thickness and RCS concentration was determined in the individual resist layer and RCS concentration was plotted against depth into the film (Fig. 8). Films cast from diglyme dissolve at nearly a constant rate and there is no significant depletion of RCS at the surface of the film (Figs. 1 and 8). It was important to determine if this lack of RCS gradient was a result of the detection method or whether these diglyme cast films do not have a significant RCS gradient. In order to test the sensitivity of the measurement method, the experiment was repeated with films baked at different temperatures (70 and 110 °C) to create films with different degrees of depletion in the surface region. The results of these additional experiments are also shown in Fig. 9. There were not any observable RCS con-



FIG. 8. Measured concentration of residual diglyme casting solvent vs thickness of resist using the HD procedure at bake temperatures of 70, 90, and  $110 \,^{\circ}$ C.



FIG. 9. Measured concentration of residual PGMEA casting solvent vs thickness of resist using HD procedure at bake temperatures of 70 and 110  $^{\circ}\mathrm{C}.$ 

centration gradients in the films. The extent of surface inhibition observed for each bake temperature was the same. The bulk RCS concentration corresponded well with measurements made previously.<sup>13</sup> Therefore, the HD method is capable of accurately measuring both the overall solvent concentrations and the concentration gradients in these developer solutions.

Identical experiments were performed using the PGMEA labeled resist baked at temperatures of 70 and 110 °C. One minor difference in the experiment is that the average film thickness was 1.5  $\mu$ m. The resist cast from PGMEA had a much higher viscosity than the diglyme resist and required a much higher spin speed to coat a 1  $\mu$ m film. The higher spin speed also resulted in poor film uniformity. The nature of the HD experiment requires a very uniform film to keep the dissolution uniform across the wafer. The lowest spin speed which would provide uniform coatings resulted in a film thickness of 1.5  $\mu$ m. It has been shown that the RCS overall concentration was the same for 1 and 1.5  $\mu$ m films.<sup>13</sup> Therefore, the RCS gradients of these films with two different thicknesses and the same overall RCS concentration was assumed to be roughly the same. It is expected that the RCS gradient is controlled primarily by the influence of the bake conditions and the solvent-film interactions. It should also be noted that 1  $\mu$ m PGMEA films showed similar dissolution profiles to the 1.5  $\mu$ m films.

No observable RCS gradient was measured for either set of films using the HD method (Fig. 8). (It is assumed that there are no concentration gradients within the thickness segments measured. Other than the surface region of the resist, there is not expected to be any large deviations in residual solvent concentration.) Clearly, the RCS gradient is not the primary cause of surface inhibition. The PGMEA cast resists have surface induction that persists through more than one third of the film thickness (Fig. 1), but the concentration of the RCS is constant throughout the film.

### E. Comparison of HD data with a casting solvent diffusion model

Further evidence against the relationship between RCS distribution and surface induction comes from the correlation



FIG. 10. Measured and simulated concentration of residual PGMEA casting solvent vs thickness of resist for bake temperature of 110 °C. The simulated concentration profile has been integrate to compare with the experiment.

of this HD data with simulation data from a solvent diffusion model by Mack.<sup>16</sup> The RCS distribution for this resist cast from PGMEA was simulated using this model.<sup>17</sup> The calculated distribution was integrated to simulate the data from the HD experiments. Figure 10 shows the simulated distribution, the simulated integral of the distribution, and the HD experimental data. The simulated integral data corresponds well with the measured data. These results show the majority of the RCS gradient exists in the very top layer of the resist, and the HD data confirms the results of the model. This steep concentration gradient produces a fairly smooth curve. This experimental technique does not have the resolution necessary to detect a concentration profile as steep as that predicted.

Figure 11 shows the simulated RCS gradient plotted with the measured dissolution rate versus thickness (also shown in Fig. 2). The residual solvent concentration rises steeply and nearly reaches a bulk concentration within the first 10% of the resist thickness. Conversely, the dissolution rate does not



Fig. 11. Dissolution rate and simulated concentration of residual PGMEA vs thickness of resist for bake temperature of 110  $^{\circ}$ C. The development rate has been normalized.

reach a bulk rate until one half of the film is developed. While the residual solvent may be responsible for slower development rates *very* close to the surface, it cannot be entirely responsible for the change in development rate observed for this particular resist system. Since small changes in RCS have been shown to produce large changes in dissolution rates, all these data together suggest that the presence of RCS gradients alone does not explain surface induction.

#### **IV. CONCLUSIONS**

A technique has been presented which allows for layer by layer analysis of resist films. This technique has been used in conjunction with liquid scintillation to determine the concentration profile of residual casting solvent in a DNQ/novolac resist system cast with PGMEA and diglyme. The experiments show no observable concentration gradient for films cast with either diglyme and PGMEA over a range of bake temperatures from 70-110 °C. The experiments were compared with the solvent diffusion model for resist films by Mack.<sup>16</sup> The measured and simulated concentration profile of residual casting solvent was consistent. Furthermore, the dissolution rate profile of both resists were measured in conjunction with the chemical analysis of RCS distribution, to test the theory that the residual solvent profile was responsible for observed surface induction. The resist cast from diglyme supported the theory — a linear solvent profile and a linear dissolution profile were observed. However, the resist cast from PGMEA showed a linear solvent profile (within the resolution of the experiment), and a very nonlinear dissolution rate profile. For this resist system, another mechanism must be responsible for the observed surface induction. Future work is being performed to explore the mechanism(s) responsible for surface induction.

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