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Diffusivity Measurements in Polymers, Part 1:
Lithographic Modeling Results

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Abstract

A first-principles study into the effects of residual casting solvent on the lithographic properties of photoresist has been initiated. Solvent content has been measured using a quartz crystal microbalance and using radio-labeled solvent with scintillation counting. Resists of measured solvent content were then tested for their dissolution properties. Early results have been presented which show the expected strong relationship between solvent content and dissolution rate. Incorporation of these results into lithographic simulation allows the prediction of resist linewidth as a function of post apply bake conditions.

I. Introduction

Thermal processing of resists (post apply bake and post exposure bake) can dramatically influence resist performance in a number of ways. It is well known that residual solvent has a powerful influence on the dissolution rate of thin polymer films [1,2] and that post apply bake (PAB) determines the resist's residual solvent content [3]. However, quantitative determination of the influence of bake conditions on residual solvent, and the impact of solvent on dissolution rate, is still lacking. This study (and the series of four papers that result from it [4-6]) intends to establish a lithographic model for the effects of PAB that is based on fundamental and measurable physical properties rather than empirical fits to experimental data. The availability of such a model would be a valuable tool for both resist designers and lithographic process engineers. The realization of this goal requires an understanding of the influence of many formulation, exposure, and processing variables on resist behavior and performance.

The first purpose of this study is to establish a quantitative relationship between the post apply bake parameters and residual solvent in novolac based photoresists. We have employed both radio chemical labeling techniques and quartz crystal microbalance measurements to establish the diffusion coefficient of common casting solvents in novolac and in resist formulations. Knowledge of these coefficients and their dependence on temperature and concentration allows calculation of the amount of solvent in the film at any point in the process and the distribution of that solvent as a function of depth into the resist [3]. We have also measured dissolution rates as a function of bake conditions, allowing isolation of the influence of residual solvent on the dissolution rate. The effect of residual solvent on resist profiles and linewidth control can then be studied through lithographic simulations.

II. Measuring Solvent Content

Two separate techniques have been used to measure the amount of residual casting solvent in a photoresist: the quartz crystal microbalance (QCM) [5] and liquid scintillation counting of radio-labeled solvent [4].

A. Quartz Crystal Microbalance

The piezoelectric property of crystalline quartz allows this material to be used as an electromechanical transducer and as a highly stable oscillator for frequency control. A quartz crystal oscillator can also be used as a sensing device for measuring the thickness of thin films deposited on the quartz, since a shift in resonant frequency is proportional to the deposited mass. One of the most attractive features of a quartz crystal microbalance (QCM) is that the frequency can be precisely measured to 1 part in 10^{10}, resulting in very precise measurements of the deposited mass. For our purposes, the adsorption or desorption of solvent from a photoresist film coated on a QCM can be measured by measuring the change in mass of the film.

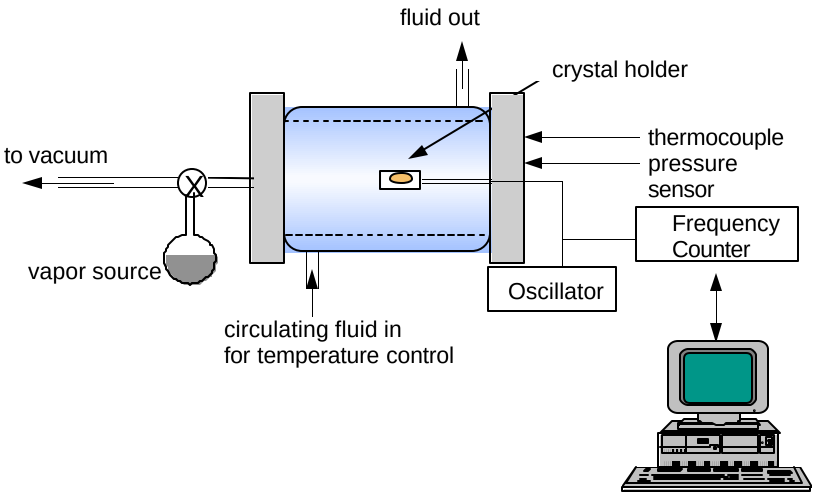

Figure 1. Quartz Crystal Microbalance (QCM) in an environmentally controlled chamber is used to measure the diffusion of solvents in a novolac film [5].

Experiments were performed by means of an apparatus that is shown in Figure 1 [5]. The phenolic novolac resin to be studied (M_n = 1900, M_w = 9400) was dissolved in various casting solvents to 22.5 wt.% solids. The solvents that were investigated included: propyleneglycol methyl ether acetate (PGMEA), ethyl lactate, 2-methoxyethyl ether (diglyme), and 2-ethoxyethyl acetate (cellosolve acetate). Quartz crystals with polished gold electrodes (6 MHz nominal resonant frequency) were coated with a novolac film by spin coating at 2500 RPM for 30 seconds and hotplate baked at 90 °C for 90 seconds, resulting in about 1 μm thick films.

The resist coated crystals were inserted into the crystal holder and vacuum was applied until there was no change in the frequency, indicating a dry film. The entire system was maintained at a constant temperature by circulating a water/ethylene glycol mixture through the double-walled sample chamber and the water lines that lead to the crystal holder. The portion of the apparatus that was not heated by the circulating fluid was maintained at a constant temperature through the use of heating tape and insulation. Solvent, which is maintained at a constant temperature by another heating bath, was then introduced into the chamber, and solvent uptake was observed by monitoring the decrease in crystal frequency, indicating an increase in mass. Once the adsorption of solvent by the film was complete, the solvent supply was closed, the system evacuated and a desorption run was carried out. Thus, the measured output for the desorption experiment was the mass of the film as a function of time, giving a direct measurement of the amount of solvent diffusing out of the film.

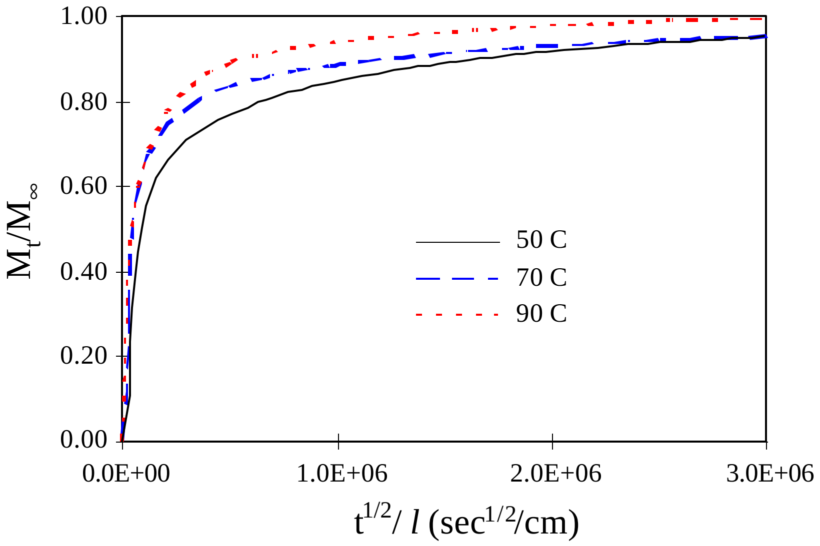

Figure 2. Diglyme desorption from a novolac film at 50, 70 and 90°C, represented as a fractional weight loss ($M_t/M_{¥}$). The time scale is normalized by *l*, the resist thickness.

Figure 2 shows an example of the output produced by this experiment. Initial analysis of this data suggestions a strong concentration dependence to the diffusion coefficient [5]. Further work on the data analysis, as well as measurements of resist films rather than pure novolac, is ongoing.

B. Liquid Scintillation Counting

The total amount of residual casting solvent in a resist film after post apply bake (PAB) can measured by scintillation counting of a radio-labeled solvent [4]. This method provides the most direct means of determining solvent content in resist films. For this study, four identical diazonaphthoquinone-novolac resist formulations were prepared with different radio-labeled casting solvents: cellosolve acetate, diglyme, PGMEA, and ethyl lactate. The DNQ loading for each resist was 12 wt.% of the solids, and the solvent content for each resist solution was 77 wt.%. The solvents were radio-labeled with ^{14}C and the radioactivity of each solvent and resist film was analyzed using a Beckman 1801 liquid scintillation counter and Fisher ScintiVerse II scintillation cocktail.

The resist solutions were spin coated on 4 inch silicon wafers, varying the spin speed for each baking temperature and casting solvent to produce film thicknesses close to 1µm. Six different baking times were used at each hotplate PAB temperature of 70°C, 90°C, and 110°C. Exactly 2 minutes after finishing the PAB, the film was dissolved with 5 mL of non-radio-labeled casting solvent and then 14 mL of scintillation cocktail. During this 2 minute delay period the films were cooled for 15 seconds, the thickness was measured, and the coated wafer was weighed.

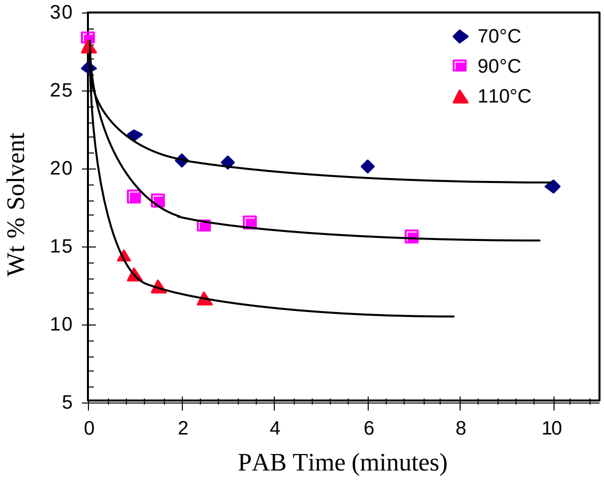

Figure 3. Measured weight percent solvent after PAB for the PGMEA solvent resist as a function of PAB time and temperature.

Figure 3 shows an example of the results for PGMEA solvent based resist [4]. Careful analysis of this recent data to extract diffusion properties is ongoing.

III. Dissolution Rates

Since a direct measurement of solvent content for a model resist material has been accurately obtained using liquid scintillation counting, dissolution rate measurements on the same resist can yield a correlation of rate to solvent content. Using the PGMEA based resist, dissolution rate as a function of exposure dose was measured using the Perkin-Elmer DRM with 90 second PABs of 70, 80 and 90°C. These rates were then analyzed with the ProDRM software to extract rate versus relative photoactive compound concentration and fit to the Mack dissolution model [7]. ABC parameters and resist refractive index were also measured at each temperature and used in the analysis [4].

Figure 4 shows the final results of the analyzed DRM data. Three interesting trends can be observed. First, the “spread” of the data, i.e., the goodness of fit to the model, improves as the bake temperature is increased. Apparently, the higher solvent content resist film produces less consistent dissolution rate data, possibly with less uniformity. The second and most pronounced trend is the reduction in R_{max} (and consequently, the entire dissolution rate curve) with decreasing solvent content. And finally, the dissolution selectivity parameter n (which is proportional to resist contrast) increases slightly with higher PAB temperature. It is unclear, however, how reliable this trend is given the small observed increase. More data should be taken to confirm this result.

The main affect of decreasing solvent content seems to be the decrease in the overall dissolution rate. Table I shows the fitted R_{max} and n as a function of solvent content (measured and estimated from the data in Figure 3). R_{max} is essentially linear, decreasing about 8 nm/s for every 1% decrease in solvent content for this resist system.

Temperature (°C)	wt.% Solvent	R_{max} (nm/s)	n	Simulated CD (0.5μm l/s)	Simulated CD (0.6μm l/s)	Simulated CD (0.8μm l/s)
70	21.1 (est.)	104.3	1.71	0.415	0.528	0.725
80	19.5 (est.)	90.3	1.77	0.500	0.600	0.800
90	17.8	78.9	1.96	0.725	0.766	0.957

Table 1. R_{max} and n values fitted to the measured dissolution rate data as a function PAB temperature (and thus, solvent content). Also shown are simulated linewidth values for these cases.

IV. Simulation Results

PROLITH/2 was used to estimate the impact of the changing dissolution properties with PAB temperature on resist linewidth. Line/space patterns from 0.5 to 0.8 μm were simulated for a generic 0.5NA *i*-line stepper in 1μm of resist with properties to match the PGMEA resist used in this study. The simulated process was adjusted to give the nominal linewidth at the 80°C PAB conditions. The results show a very dramatic change in linewidth as a function of PAB temperature. For this low contrast resist, even the relatively small changes in R_{max} and n produce very noticeable effects.

For the purposes of this study, no surface inhibition was assumed. The collected dissolution rate data did not show significant surface inhibition, but the resolution of the measurements was not optimized to collect this surface data. Modeling of solvent evaporation during PAB [8] predicts a decrease in the solvent content near the surface. Thus, the bulk dissolution data above would imply that PAB for this system would also create surface inhibition. Further work on this subject is needed.

V. Conclusions

A first-principles study into the effect of residual casting solvent on the lithographic properties of photoresist has been initiated [4-6]. Early results have been presented which show the expected strong relationship between solvent content and dissolution rate. The ultimate goal of this effort is to couple heat and mass transfer modeling of solvent desorption during PAB [8] with a model for dissolution rate as a function of solvent content. These early results indicate that this goal is attainable with continued data collection and further analysis.

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