Modeling Solvent Diffusion in Photoresist

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Abstract

A semi-empirical study into the effects of residual casting solvent on the lithographic properties of photoresist is described. Solvent content of a commercial i-line photoresist after post apply bake has been measured using a quartz crystal microbalance and using radio-labeled solvent with scintillation counting. Analysis of this data has led to a calibrated model of solvent diffusivity as a function of solvent content which can then predict solvent content as a function of depth into the photoresist for a given bake.

I. Introduction

Thermal processing of photoresists (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 [3-7]. 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 intends to establish a lithographic model for the effects of PAB that is based on fundamental and measurable physical properties. 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 purpose of this study is to establish a quantitative relationship between the post apply bake parameters and residual solvent content in novolac-based photoresists. We have employed both radio chemical labeling techniques and quartz crystal microbalance measurements to establish the diffusion coefficient of a common casting solvent in a specific commercial resist formulation. Knowledge of this coefficient and its 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].

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) [6] and liquid scintillation counting of radio-labeled solvent [5].

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 [8]:

$$\Delta f = \frac{-2 f_o^2 \Delta m}{A\sqrt{\boldsymbol{m}_Q \boldsymbol{r}_Q}} \tag{1}$$

where Δf is the frequency change, f_o the resonant frequency of the resonator before this change (nominally 6 MHz), Δm the change in mass, A the piezoelectrically active area (1.04 ± 0.02 cm^2), $\boldsymbol{r}_Q$ the density of the quartz (2.648 g/cm^3), and $\boldsymbol{m}_Q$ the shear modulus of AT-cut quartz (2.947×10^{11} $dyne/cm^2$).

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 change in mass. For our purposes, the adsorption or desorption of solvent from a photoresist film coated on a QCM can be measured as a change in mass of the film.

Experiments were performed by means of an apparatus that is shown in Figure 1 [6]. The photoresist chosen for study was AZ9100 (Clariant Corp., Somerville, NJ), which uses a solvent of propyleneglycol methyl ether acetate (PGMEA) at about 38 wt% solids. Quartz crystals with polished gold electrodes were coated with the resist film by spin coating at 2500 RPM for 30 seconds and hotplate baked at 90°C for 90 seconds, resulting in about 4.5 µm thick films.

The resist coated crystals were inserted into the crystal holder and vacuum was applied until there was no measurable change in the frequency, indicating a stable film. The entire system was maintained at a constant temperature of 50, 70 or 90°C ± 0.3°C 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 the same 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 absorption of solvent by the film was complete (indicated by a constant crystal frequency, typically after about 10 minutes of exposure to the vapor), 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.

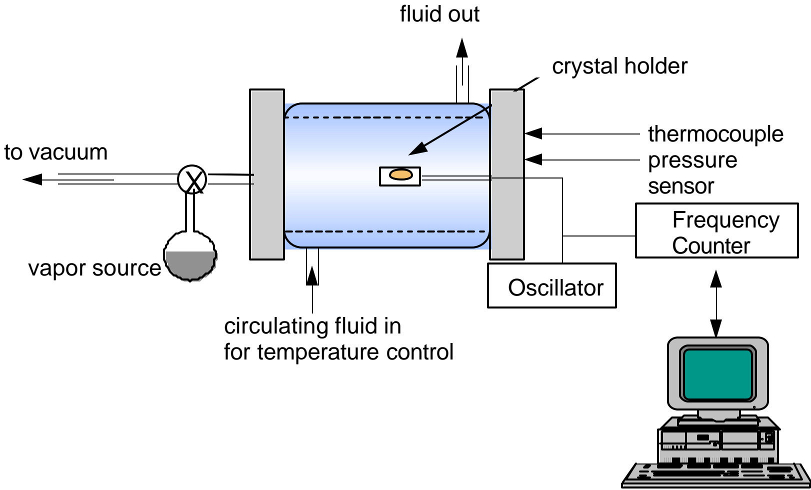

Figure 1. Quartz Crystal Microbalance (QCM) in an environmentally controlled chamber is used to measure the diffusion of solvents in a photoresist film [6].

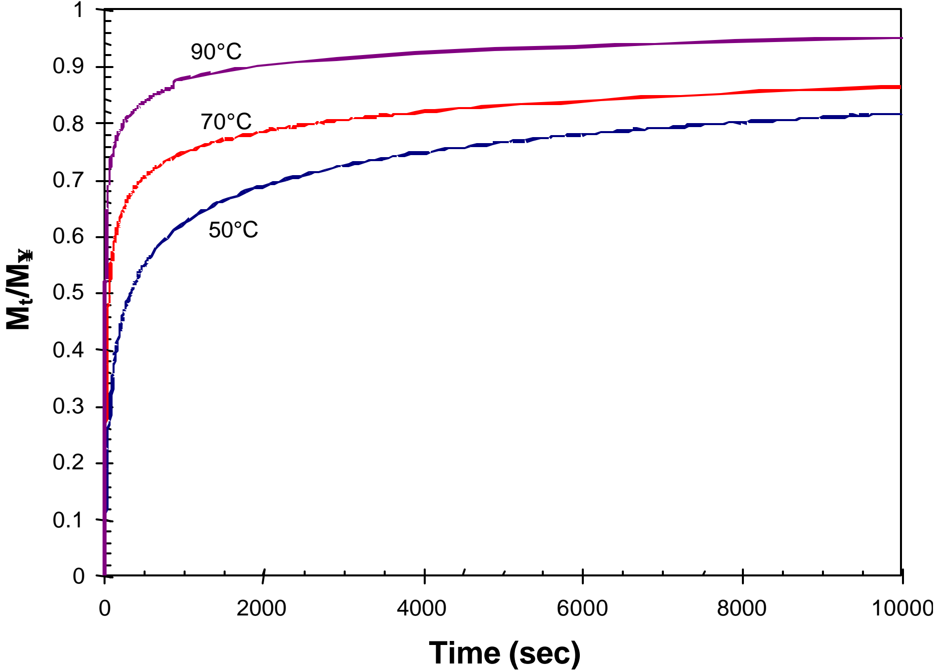

Figure 2. Solvent desorption from an AZ9100 resist film at 50, 70 and 90°C, represented as a fractional weight loss (M_t / M_{∞}).

Figure 2 shows an example of the output produced by this experiment. The mass loss of the film at time t, given by M_t, is shown relative the final mass loss at the end of the experiment, designated as M_{∞}. Although only the first 10,000 seconds (2.78 hours) of data are shown in Figure 2, data collection continued for a total of 14.4 hours at 90ºC, 50.5 hours at 70ºC, and for 65.9 hours at 50ºC. The kinetics of thermal decomposition of the photoactive compound [9] used for this resist are known to produce insignificant amounts of decomposition for the times and temperatures used in this study. Thus, it was assumed that all of the mass loss measured could be attributed to loss of solvent.

B. Liquid Scintillation Counting

The total amount of residual casting solvent in a resist film after post apply bake (PAB) can be measured by scintillation counting of a radio-labeled solvent [5]. This method provides the most direct means of determining solvent content in resist films. For this study, the solvent was radio-labeled with ^{14}C and the radioactivity of the solvent and resist film was analyzed using a Beckman 1801 liquid scintillation counter and Fisher ScintiVerse II scintillation cocktail.

Radio-labeled solvent was first used to calibrate the QCM measurements described above. For each temperature studied, resist laced with the radio-labeled solvent was coated on a quartz crystal and subjected to the desorption experiment in the QCM apparatus. The crystal was then removed and the final weight percent of solvent remaining was determined by liquid scintillation counting. The results are shown in Table 1. Once an absolute value for the final solvent content was determined, the initial solvent content was calculated using the data from Figure 2 and equation (1). In addition, final resist thickness was measured using a reflectance spectrophotometer (using Cauchy coefficients of the refractive index measured for each sample with a spectroscopic ellipsometer). These results are also given in Table 1.

Table 1: Measured final solvent content and film thickness for the data shown in Figure 2.

Temperature (ºC)	Initial Solvent (wt%)	Final Solvent (wt%)	Final Thickness (microns)
50	38.3 ± 1.0	16.7 ± 0.3	4.80 ± 0.02
70	37.3 ± 1.0	12.8 ± 0.3	4.80 ± 0.02
90	36.0 ± 0.8	9.0 ± 0.3	4.46 ± 0.02

In a second experiment, resist solutions were spin coated on 4 inch silicon wafers, varying the spin speed for each baking temperature to produce film thicknesses close to 4.5µm. Several different baking times were used at each hotplate PAB temperature of 90°C, 105°C, and 115°C ± 0.5°C (the recommended PAB temperatures for this resist are between 105 and 115°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 shows the results of this experiment.

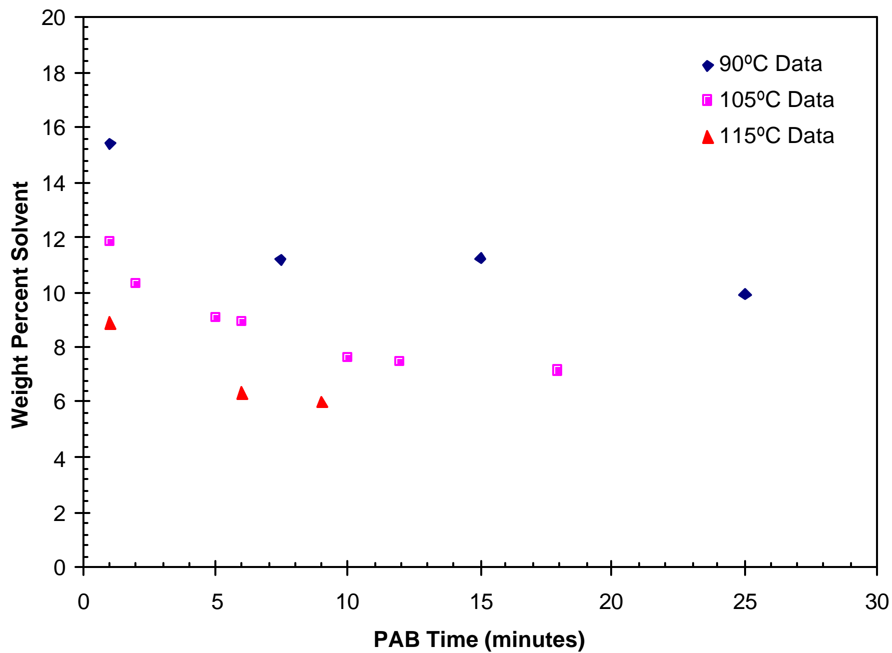

Figure 3. Measured weight percent solvent in resist (coated on a silicon wafer) after post apply bake as a function of PAB time and temperature.

III. Solvent Diffusion Model

One can predict the solvent content in the resist after a post apply bake by solving the standard diffusion equation in one dimension:

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(D_{AB}\frac{\partial C_A}{\partial x}\right) \tag{2}$$

where C_A is the concentration (weight fraction) of solvent (component A) and D_{AB} is the diffusivity of solvent in photoresist (component B). Solving this equation requires a number of things: two boundary conditions, one initial condition, and a knowledge of the diffusivity as a function of position and time.

The initial condition is the initial solvent distribution within the film, $C_A(x,0)$ and, implicitly, the initial film thickness. When fitting the QCM desorption experimental data, the initial condition is simply a uniform solvent concentration using values from Table 1. The two boundary conditions are at the top and bottom surface of the photoresist film. The boundary at the wafer surface is assumed to be impermeable, giving a boundary condition of no diffusion into the wafer. The boundary condition at the top of the wafer will depend on the diffusion of evaporated solvent in the atmosphere above the wafer. In general, one can assume that the diffusivity of solvent in air is significantly higher than in resist. Thus, if the volume of air above the wafer (or the air flow rate) is sufficiently large, solvent which escapes the resist surface will immediately dissipate into the environment, leaving an atmospheric solvent concentration at the top of the photoresist film of zero. For the desorption experiments carried out in a vacuum, this assumption is certainly true. This is equivalent to saying that the diffusion process is controlled by internal resistance within the film, rather than by the rate of evaporation. This boundary condition is quite reasonable as long as the sample is not in a small closed container with limited airflow.

The solution of equation (2) can now be performed if the diffusivity of the solvent in the photoresist is known. Unfortunately, this solution is complicated by two very important factors: the diffusivity is a strong function of temperature and of solvent concentration. The concentration dependence of diffusivity results from the densification of the resist film: as solvent evaporates, the film becomes more dense, reducing the diffusivity of the solvent. Since the solvent concentration is time and position dependent, the diffusivity in equation (2) must be determined as a part of the solution of equation (2) by an iterative method.

The proper concentration dependence of the diffusivity is not obvious. Several authors have proposed and verified the use of different models for the concentration dependence of a solvent in a polymer. One of the simpler forms is the Fujita-Doolittle equation [3] which can be predicted theoretically using free volume arguments:

$$D_{AB} = D_o \exp\left(\frac{\alpha C_A}{1 + \beta C_A} \right) \tag{3}$$

where α and β are experimentally determined constants and are, in general, temperature dependent. D_o is the diffusivity of solvent in the limit of zero solvent content in the resist (the "dry" diffusivity). Other concentration relations are also possible, but the Fujita-Doolittle expression appears to be the simplest form that adequately describes the data presented above. Although the terms α and β can be directly related to physically important properties of the polymer/solvent system, for simplicity they are treated as fitting variables here.

The temperature dependence of the dry diffusivity will be assumed to follow a standard Arrhenius form:

$$D_o(T) = A_r \exp(-E_a/RT) \tag{4}$$

where A_r is the Arrhenius coefficient and E_a is the activation energy. The temperature dependence of the α and β terms will be discussed below.

IV. Matching Model to Experiment

The solution to the diffusion equation (2) using the diffusivity given by equation (3) was fit to the data presented in Figure 2 by finding the unknown diffusivity parameters D_o, α, and β. Some general observations can be made about the results. It is straightforward to find several different sets of parameters that fit any one set of data over a limited range of time (for example, the first one hundred seconds or the 500 - 2000 second range or the long-time data). The challenge is to find a set of diffusion coefficients that fit well over all time ranges simultaneously. It was found that this kind of match was obtained with only with a highly non-linear concentration dependence to the diffusivity. Figures 4 and 5 show a typical result using α = 325 and β = 8.

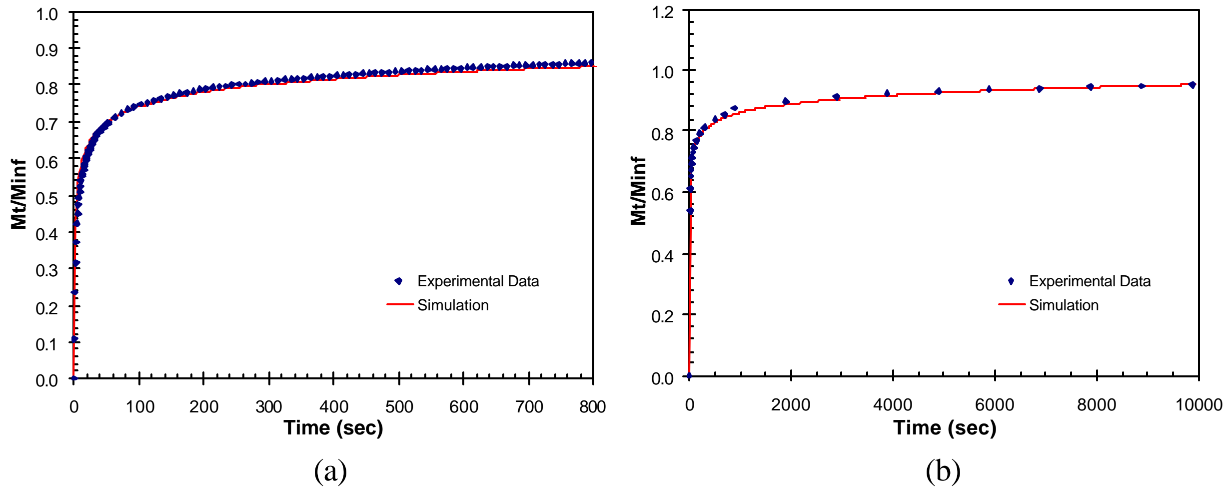

Figure 4. Best fit of the 90ºC microbalance data using α = 325, β = 8.0, and $D_o = 5.3\text{x}10^{-6}$ nm^2/s shown on (a) moderate and (b) long time scales.

One important aspect of this modeling effort extends beyond just fitting the experimental data for bulk solvent content as a function of bake conditions. By default, the solution of the diffusion

equation also provides solvent content as a function of position within the resist. Figure 6 shows an example of this important capability.

The next challenge was to determine the temperature sensitivity of each parameter. As a first guess, we assumed that α and β are not temperature dependent. Under this assumption, a reasonable fit of all data for the 50, 70, and 90ºC temperatures was obtained with α = 201, β = 4.0, and D_o = 9.7×10^{-8}, 1.2×10^{-6}, and 2.0×10^{-4} nm^2/s, respectively. The fit is shown in Figure 7. Certainly the fits are not as good as when α and β are optimized for each data set. Also, the resulting D_o values are not well described by the Arrhenius relationship of equation (4). It seems clear that better results could be obtained if α and β were also allowed to vary with temperature. Work to determine this dependence is ongoing.

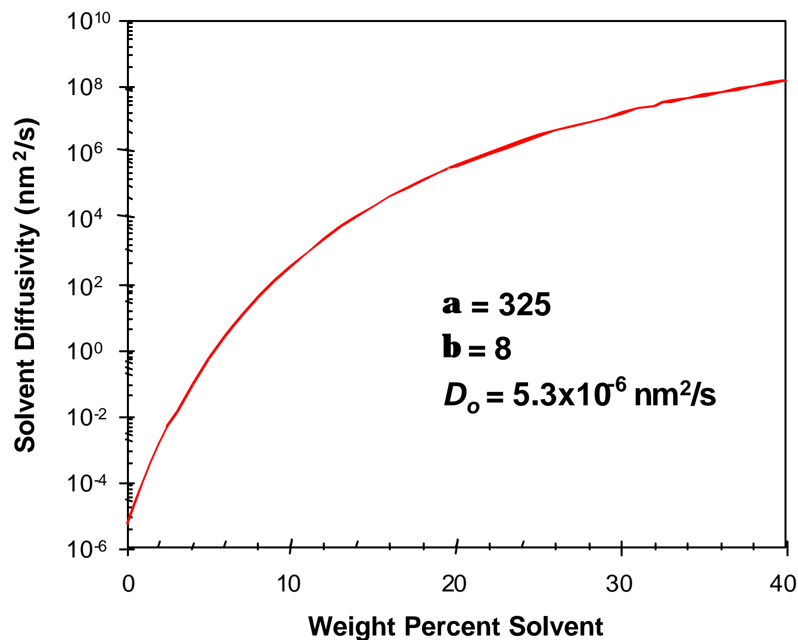

Figure 5. Solvent diffusivity variation according to the Fujita-Doolittle model for the best fit parameters of Figure 4.

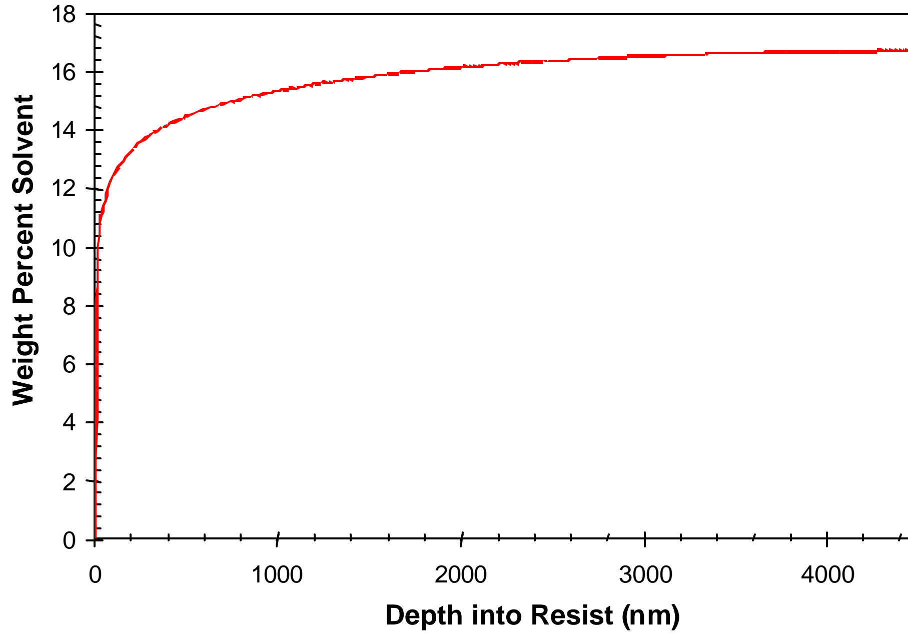

Figure 6. Simulation result corresponding to the parameters of Figure 4 showing the variation of solvent content with depth into the resist at the end of a 200 second, 90°C bake.

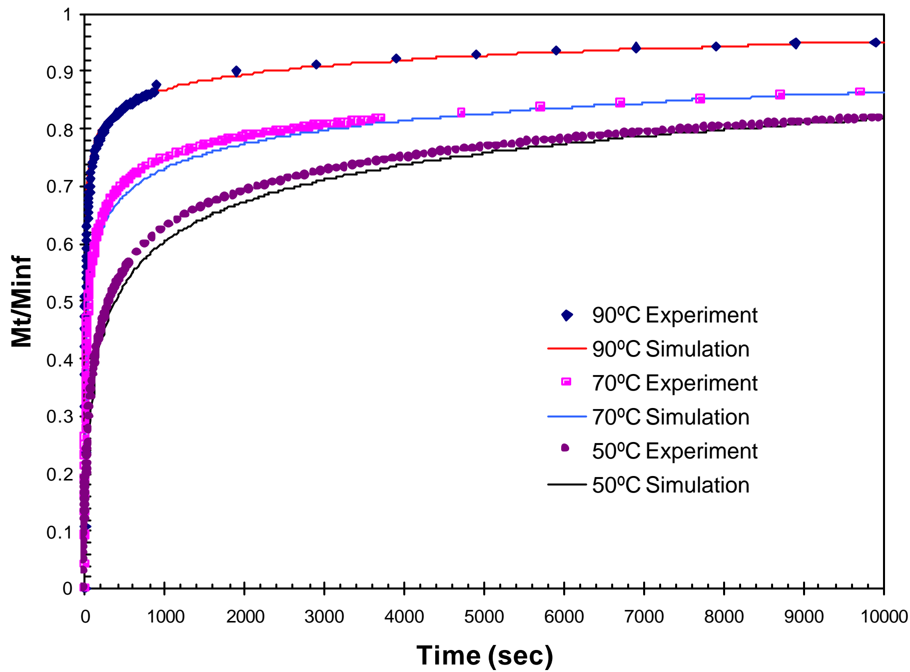

Figure 7. Best fit of the model to the microbalance data assuming α and β do not vary with temperature.

V. Conclusions

The diffusion of solvent during post apply bake is a highly non-linear process where the diffusivity of solvent through the resist varies exponentially with concentration of solvent. The Fujita-Doolittle equation was found to describe this concentration dependency well by fitting a solution of the diffusion equation to experimental microbalance data calibrated with liquid scintillation counting. Unfortunately, the temperature dependence of the diffusivity was more complicated than originally assumed and requires further investigation. In particular, the temperature dependence of α and β will be investigated using first-principle arguments. Also, future work will include measurement of the diffusion behavior for the same material coated to a thinner film thickness, QCM experiments at higher temperatures, and correlation of the QCM data to the wafer data of Figure 3.

The ultimate goal of this effort is to couple heat and mass transfer modeling of solvent removal during PAB [3] 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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