Modeling of Solvent Evaporation Effects for
Hot Plate Baking of Photoresist

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Abstract

A heat transfer model for hotplate baking is combined with a mass transfer model for solvent diffusion to predict the major effects of photoresist prebaking for photolithography. Solvent diffusivity as a function of solvent concentration and temperature is determined experimentally. The results of the model are a complete time-temperature history of the wafer, final solvent distribution within the resist film, and final resist thickness.

I. Introduction

Hot plate prebaking of conventional positive photoresist is intended to drive off solvent used for spin coating the resist, thereby densifying and stabilizing the film. However, the real impact of this bake step is not felt until development, where solvent content, distribution of solvent within the film, and possible thermal decomposition products as a result of the bake will affect the development rate dramatically. Thus, photoresist prebaking has become one of the most critical, though least understood, steps in the resist process. This paper will present the results of rigorous simulation and experimentation in order to elucidate these effects.

The thermal heat transfer process from heater to hotplate to photoresist has been simulated using rigorous techniques and is described in an accompanying paper [1]. The resulting model includes conduction from the wafer and convection from the top resist surface to simulate the time/temperature profile of the wafer. This model is then combined with a mass transfer model of solvent diffusion to predict the time evolution of solvent content and resist thickness. By comparison with experimental data, solvent diffusivity properties in photoresist are determined and will be presented. The result is a computer model which will predict solvent distribution, thermal history, and resist thickness of a hotplate baked wafer as a function of virtually all important parameters.

The output of this model can contribute to a number of fundamental studies in lithography. Solvent content and distribution will impact development rates and thus this model will serve as the necessary input to such studies. Thermal reactions (such as unwanted decomposition for a conventional photoresist or necessary activation for a chemically amplified resist) can be coupled into the model to provide a kinetic analysis of a real bake, rather than an ideal one. The application of such an analysis to the post-exposure bake step, and especially to chemically amplified resists, is an obvious extension of this work. The use of such a model for kinetic control is also possible.

II. Thermal Model of a Hotplate/Chillplate

A heat transfer model has been developed which provides the temperature-time history of a wafer, initially at a uniform temperature, which is suddenly thermally coupled to a hot or cold chuck [1]. The model includes the ability to model vacuum contact or proximity baking or chilling, and allows for different methods for maintaining the chuck lower surface temperature. This one-dimensional, transient model provides wafer surface temperature time-to-heat (or -chill) as a function of wafer-chuck physical dimensions, thermal properties of air, the wafer, and the chuck, the chuck heating method, the wafer/chuck thermal contact resistance (R_{tc}"), and the convection coefficient of the top surface of the wafer (h_w). The last two parameters in this list are not readily known for any given hotplate or chillplate configuration and thus must be measured. Fortunately, they are easily obtained from a single measurement of the time-temperature history of a wafer.

For example, the temperature-time history of a wafer was measured for a standard hotplate bake of a bare silicon 200 mm wafer on an SVG Series 90 track. The wafer was instrumented with a very small (0.35 mm diameter) thermister at the center calibrated to within 0.01°C of a laboratory standard constant temperature bath. With the vacuum on the chuck turned on, the wafer was placed in contact with the chuck. The temperature of the wafer was sampled every 0.35 seconds to give a complete temperature history of the wafer (Figure 1). A second measurement was also made with the chuck vacuum turned off (i.e., a soft contact bake) to show the difference in thermal contact resistance. By comparing the measured results to the heat transfer model, a thermal contact resistance of 0.00035 m^{2}K/W and a top surface convection coefficient of 10 W/m^{2}K were determined for the vacuum contact case. Further details of this experiment and of the heat transfer model can be found in reference [1].

III. Mass Transfer Model

Solution to the mass transfer problem is the solution to the standard diffusion equation in one dimension:

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left(D_{AB}\frac{\partial C_A}{\partial x}\right) \qquad (1)$$

where C_A is the concentration 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, L_{fi}. Since the step prior to prebake is spin coating, this solvent distribution would result from the evaporation of solvent during the spin dry step [2]. 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. This is equivalent to saying that the diffusion process is controlled by internal resistance within the film, rather than by external convection effects. This boundary condition is quite reasonable as long as the hotplate is not in a small closed container with limited airflow. In such a case, one could measure the solvent concentration within the air space above the hotplate as a function of time during the bake to generate a measured boundary condition.

The solution of equation (1) 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 solvent concentration. Since the temperature is changing with time during the bake, the diffusivity will be time dependent. 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 (1) must be determined as a part of the solution of equation (1) by an iterative method.

The temperature dependence of the diffusivity can be expressed in a standard Arrhenius form:

$$D_o(T) = A_r \exp(-E_a/RT) \tag{2}$$

where A_r is the Arrhenius coefficient and E_a is the activation energy. The concentration dependence of the diffusivity is less obvious. Several authors have proposed and verified the use of different models for the concentration dependence of a solvent in a polymer. The simplest form is the Fujita-Doolittle equation [3] which can be predicted theoretically using free volume arguments:

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

where α and β are experimentally determined constants and are, in general, temperature dependent. For simplicity, α and β will be assumed independent of temperature here. D_o is the diffusivity of solvent in the limit of zero solvent content in the resist. Other concentration relations are also possible [4], but the Fujita-Doolittle expression will be used in this work.

The diffusion equation can now be solved if the temperature history of the photoresist film is known. One important question remains, however: Does the mass transfer have any effect on the heat transfer? Theoretically, the answer is yes since the evaporation of solvent requires heat transfer (due to the heat of vaporization of the solvent) from the photoresist film and the resulting mass loss reduces the energy stored in the photoresist film. Practically, however, these effects may be negligible. If so, the solution to the heat transfer problem can be carried out independent of the mass transfer solution, simplifying the calculations. Rather than simply make this assumption, we first solved the heat and mass transfer problems simultaneously taking into account the loss of mass and the heat of vaporization of the solvent. The result was as expected: for photoresist thicknesses and properties typical for the semiconductor industry, the mass transfer has a completely negligible impact on the temperature of the photoresist. In fact, the temperature gradient within the resist film is so slight that it is entirely reasonable to say that the photoresist is isothermal at a temperature which is the same as the top surface of the wafer, i.e., $T_f(t) = T_w(0,t)$.

Solution to the diffusion equation results in a calculated mass loss due to solvent evaporation. This mass loss will result in a corresponding photoresist thickness change. Assuming that the film densification is a simple linear function of mass loss and that the temperatures of the bake do not permanently alter the physical structure of the film, the resist thickness will simply be a function of the average mass fraction of solvent in the film (x^{av}) and the densities of the solvent (ρ_s) and dry photoresist (ρ_p). Letting the photoresist film thickness be given by L_f and using a subscript i to designate the initial condition,

$$\frac{L_f}{L_{f\,i}} = \left(\frac{\rho_s - x^{av}(\rho_s - \rho_p)}{\rho_s - x_i^{av}(\rho_s - \rho_p)} \right)\left(\frac{1 - x_i^{av}}{1 - x^{av}} \right) \qquad (4)$$

IV. Experimental Data for Evaluation of the Model

A common method for analyzing the diffusivity characteristics of a solvent in a polymer for drying applications is to experimentally measure the rate at which solvent leaves a known sample over time at some temperature and to compare the results to a theoretical treatment of the problem. This is usually accomplished by drying a rectangular block of the polymer saturated in solvent and weighing the sample continuously as it dries [5,6]. For the case of photoresist drying, the most practical means of performing a similar experiment is to measure resist thickness as a function of baking time. Measurement at different temperatures also provides temperature dependent information about the diffusivity.

Such an experiment was performed under the following conditions. Using an MTI FlexiFab wafer track, Shipley SPR510LA photoresist was dynamically dispensed onto a bare 200mm silicon wafer at 1200 rpm, spread for 2 seconds, accelerated at 25 krpm/s to 4000 rpm, and spun for 25 seconds. Exhaust during the spinning was measured to be 4.8 standard linear meters per minute. The wafer was then immediately baked for various times ranging from 5 - 240 sec and temperatures from 70 - 130°C. Exhaust during the bake was 4.0 standard linear meters per minute and the hotplate in this configuration had no cover or enclosure above it. No chill plate was used. The resulting resist thickness was measured by two instruments. A Prometrix FT-500 was used to measure the resist thickness at 49 sites and the average thickness was used in subsequent analysis. However, the Prometrix assumes a constant index of refraction for all measurements. It is known that the index of refraction varies with bake conditions (due to film densification). Thus, a Metricon 2010 Prism Coupler was used to measure the thickness and index of refraction of each sample following the Prometrix measurement. Prometrix measurements were then corrected using the Metricon measured refractive index.

Figure 3 shows a plot of final resist thickness as a function of bake time for three different bake temperatures (a subset of the corrected Prometrix thickness data collected and represented by the symbols in the plot). The model was then used to fit this data by adjusting the unknown parameters in equations (1) and (2) to determine the concentration and temperature dependence of the solvent diffusivity. It is important to note that an actual bake step involves not only baking, but cooling as well. Even though a wafer was baked for a set time, the mass transfer effects of the elevated temperature continue during the cooling step and must be accounted for. In this case, no chill plate was used and the wafer simply cooled while exposed to ambient conditions. To model the complete thermal cycle of the wafer, a combined bake-cool step was simulated where the cool step was considered to be a 240 sec exposure to ambient air conditions, both sides of the wafer exposed.

Figure 3 also shows a fit of the model (curves) to the data. The fit was accomplished in a very simple and straightforward manner. The diffusivity activation energy parameter and Arrhenius coefficient of equation (2) were adjusted to fit two data points: the 60 sec bake at 70 and 110°C. Values for α and β in equation (3) were chosen to be 0.043 and 0.040, respectively, based on values reported in the literature for a similar polymer system [7] and were not adjusted. Thus, although further refinements are possible, Figure 3 shows a reasonable first fit of the model to the data. It should also be noted that the resulting activation energy obtained for this fit is of a quite reasonable magnitude (130 J/mole K). It is quite apparent that the combined heat and mass transfer models very adequately describe the behavior of typical lithographic baking applications. Obviously, adjusting α and β would result in a better fit.

Figure 4 shows an interesting plot of the resist index of refraction data taken from the Metricon tool. The index of refraction, when plotted versus the resulting resist thickness, shows a linear dependence except at the highest temperature. It seems that the optical density of the film follows the physical densification in a linear fashion. This observation also reinforces the earlier assumption that the only mechansim for film densification is simple mass loss.

V. Application of the Model

The goal of hot and chill plate design is to create a piece of equipment which allows for consistent wafer-photoresist characteristics. Having an understanding of how plate features and photoresist properties influence temperature-time histories and final film characteristics is only one part of the design process, but it is the initial and most important part.

Shown in Figure 5 is an example of the time-temperature history and resulting resist thickness versus time that are typical outputs of this model. Zooming in on the first 10 seconds of the bake, Figure 6 shows the variation in temperature, the resulting variation in solvent concentration, their effect on the diffusion coefficient and finally the resist thickness during the initial portion of the bake. The solvent profile within the film at the beginning and end of the bake are shown in Figure 7.

Models are valuable for design activities, especially to establish the feasibility of new approaches and for process performance evaluation. Quantitative descriptions of the temperature-time history and final solvent distribution of a photoresist film are also extremely valuable in assessing the effects of baking on resist performance. Solvent distribution will influence development rate and possibly PEB diffusivity. The time-temperature history of the film will impact possible thermal decomposition of photoresist components and, in the case of PEB of chemically amplified resist will dramatically affect the final linewidths obtained. Of course, the ability to predict the influence of bake parameters on the final resist thickness will allow quantitative evaluation of process errors such as temperature non-uniformities or wafer mishandling.

VI. Conclusions

The work performed here and in the accompanying paper [1] provide a sound theoretical basis for an understanding of heat and mass transfer effects in hot and chill plate baking of photoresist. Future work in this area will include further model development, application of the heat transfer models to hot and chill plate design and analysis; and coupling of the heat and mass transfer models of the photoresist to subsequent models to predict their impact on final resist linewidth. This final effort would include the use of the heat and mass transfer models in the modeling of chemically amplified resists. Further, experimental verification of the models would be improved using in situ monitoring of resist thickness during the bake.

References

1. D. P. DeWitt, T. C. Niemoeller, C. A. Mack, and G. Yetter, "Thermal Design Methodology of Hot and Chill Plates for Photolithography," *Integrated Circuit Metrology, Inspection, and Process Control VIII, Proc.*, SPIE Vol. 2196 (1994).

2. D. E. Bornside, C. W. Macosko, and L. E. Scriven, "Spin Coating: One-Dimensional Model," *Journal of Applied Physics*, Vol. 66, No. 11 (1 Dec 1989) pp. 5185-5193.

3. H. Fujita, A. Kishimoto, and K. Matsumoto, "Concentration and Temperature Dependence of Diffusion Coefficients for Systems Polymethyl Acrylate and n-Alkyl Acetates," *Transactions of the Faraday Society*, Vol. 56 (1960) pp. 424-437.

4. D. E. Bornside, C. W. Macosko and L. E. Scriven, "Spin Coating of a PMMA/Chlorobenzene Solution," *Journal of the Electrochemical Society*, Vol. 138, No. 1 (Jan., 1991) pp. 317-320.

5. D. W. McCall, "Diffusion in Ethylene Polymers. I. Desorption Kinetics for a Thin Slab," *Journal of Polymer Science*, Vol. 26 (1957) pp. 151-164.

6. K. Imre, "A Quick Method for Determining the Diffusion Coefficient for Polymer-Monomer Systems from Desorption Data," *Journal of Polymer Science, Polymer Chemistry Edition*, Vol. 18 (1980) pp. 1647-1650.

7. W. W. Flack, D. S. Snoog, A. T. Bell, and D. W. Hess, "A Mathematical Model for Spin Coating of Polymer Resists," *Journal of Applied Physics*, Vol. 56 No. 4 (15 Aug 1984) pp. 1199-1206.

Wafer Temperature (°C)
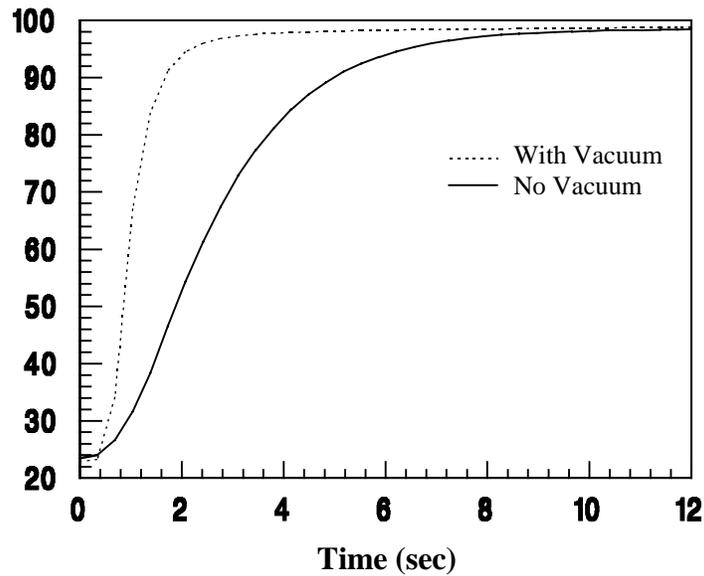
Figure 1. The influence of interface thermal contact resistance on the temperature-time history for a wafer, initially at 23 °C, which is vacuum contact or soft contact heated by a standard SVG 90 hotplate.
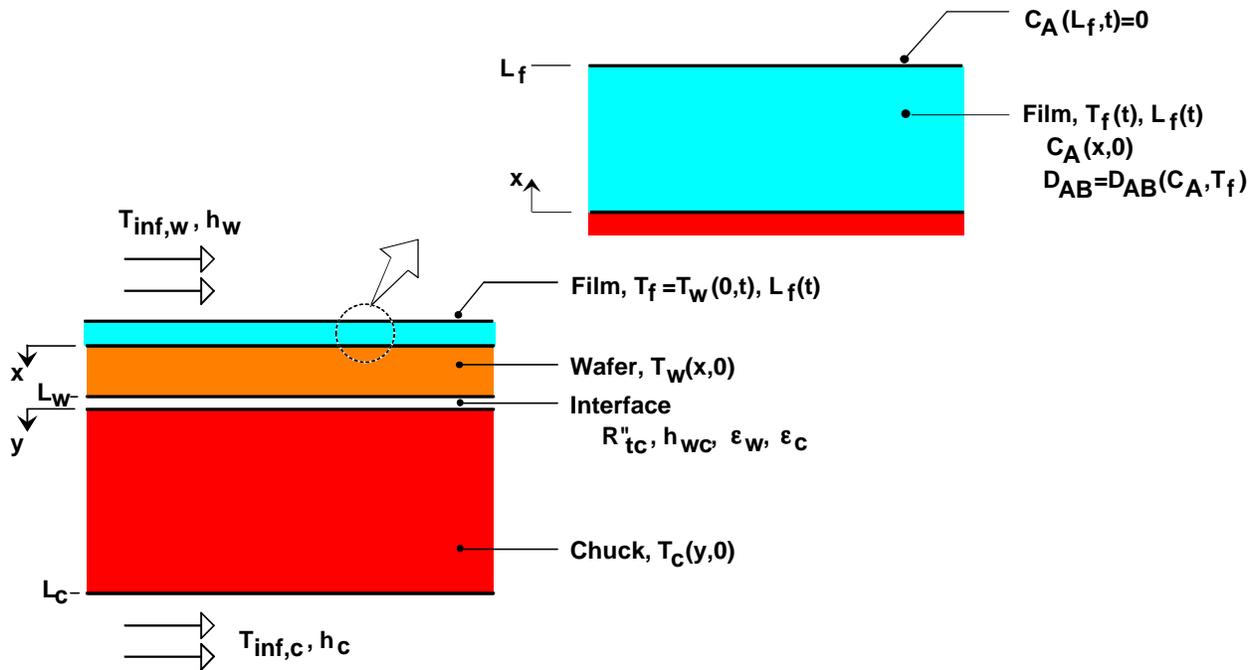
Figure 2. Geometry for heat and mass transfer calculation: a photoresist film on a silicon wafer in contact (or proximity) with a hotplate or chill plate.

Resist Thickness (µm)
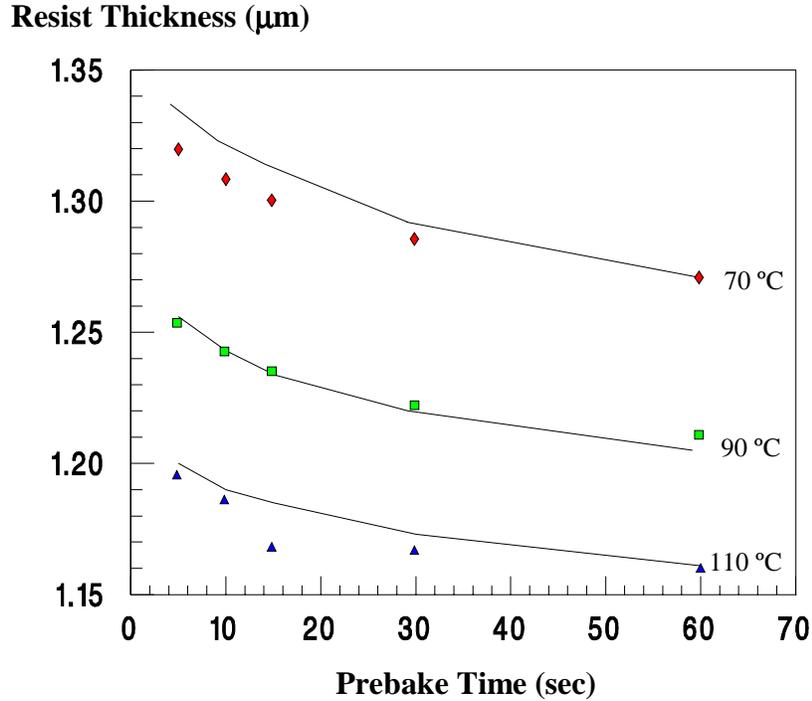
Figure 3. Comparison of experimentally determined (symbols) and model-predicted (curves) photoresist film thickness as a function of hot plate bake time for temperatures 70, 90 and 110 °C. Diffusion temperature coefficients determined by best fit at two selected conditions.

Refractive Index
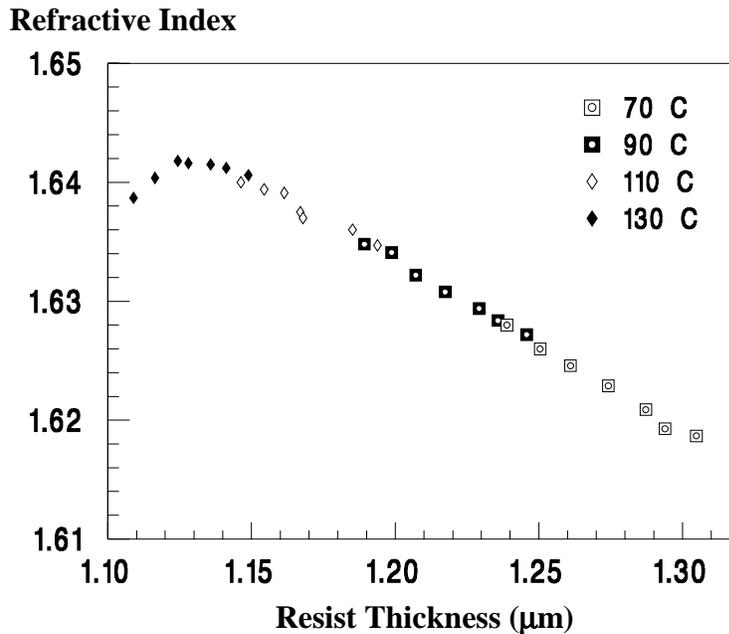
Figure 4. Measured resist index of refraction versus final resist thickness for prebakes of various times and temperatures.

Wafer Temperature (°C)

Time (sec)

Resist Thickness (μm)

Time (sec)
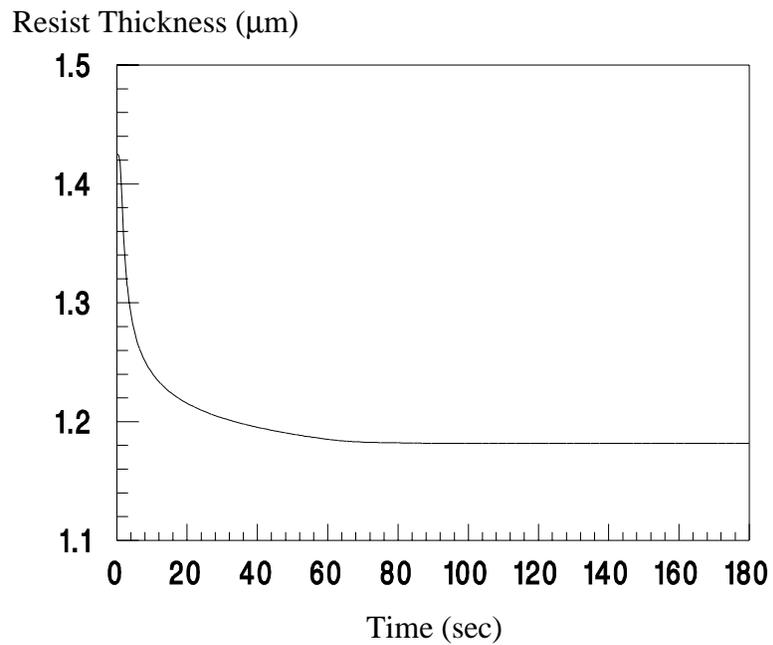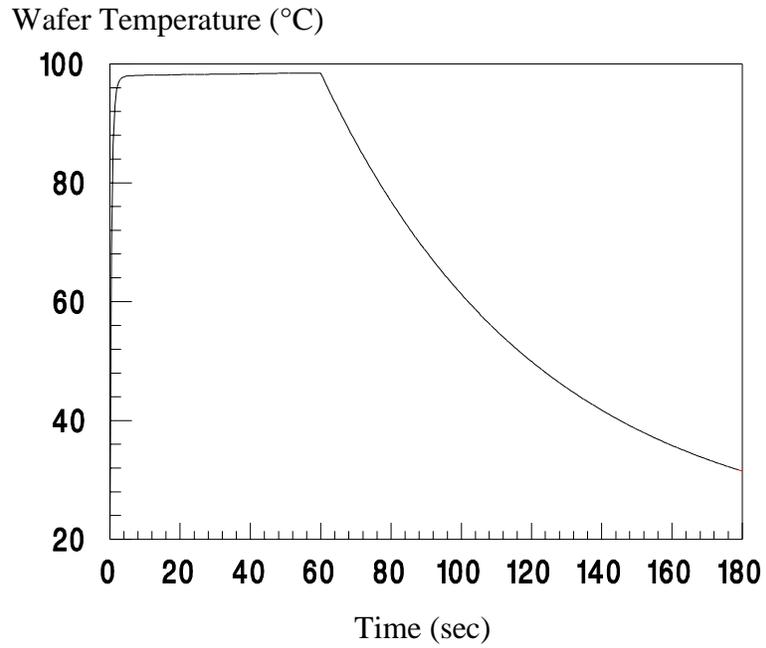
Figure 5.   Modeled temperature variation and resulting resist thickness for a 60 sec, 100 ℃ hotplate bake followed by air cooling.
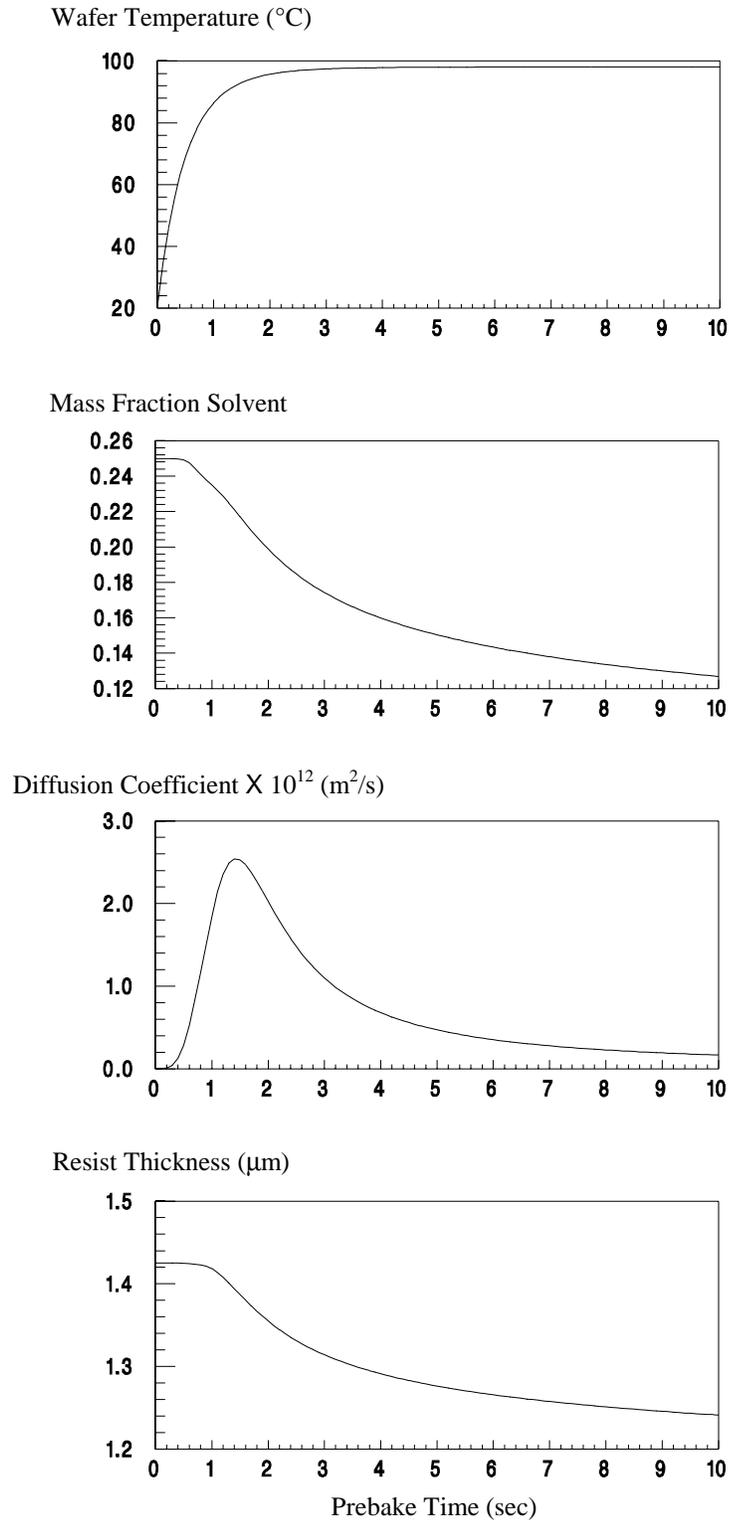
Figure 6. Modeled temperature variation and resulting resist thickness for the first 10 seconds of a 100 ºC hotplate bake. The mass fraction of solvent and the diffusion coefficient are shown for the middle of the resist film.

Mass Fraction of Solvent
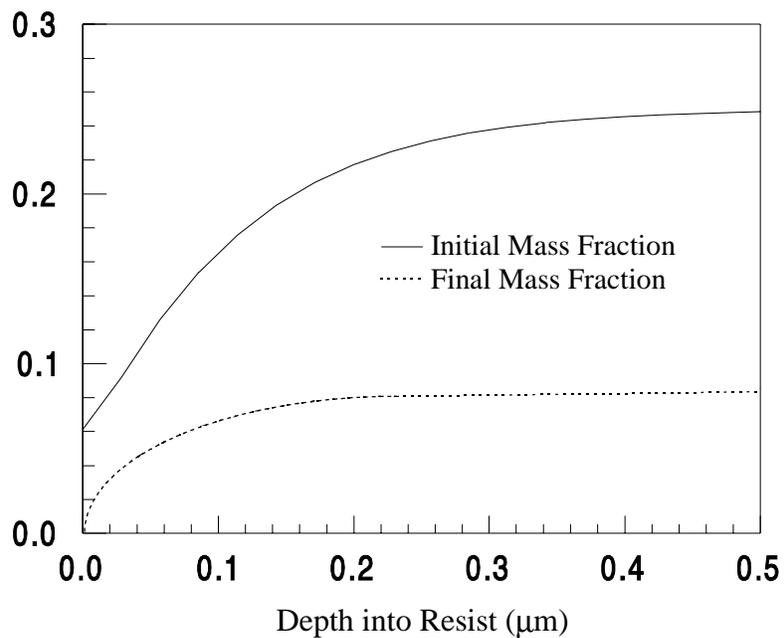
Figure 7.   Beginning with an assumed initial mass fraction of solvent distribution, the final distribution shows the effect of evaporation as predicted by the mass and heat transfer model.