Ultrasonic Cure Monitoring of Photoresist During Pre-Exposure Bake Process

Susan L. Morton, F. Levent Degertekin, and B. T. Khuri-Yakub

Edward L. Ginzton Laboratory, Stanford University, Stanford, CA 94305

Abstract - We have developed a sensor to measure the glass transition temperature (T_g) of photoresist during its pre-exposure bake. During prebake, the resist must reach this temperature in order for significant solvent evaporation to occur. To determine T_g we measured the change in phase of a high frequency pulse as it was reflected from the interface between an 8" silicon wafer and a photoresist film. This measurement was performed before and after a prebaked Shipley 1813 resist film was removed from the wafer as well as during the prebake of a subsequent film. The phase change measured when a film of resist was removed from the wafer agreed well with theoretical calculations. The phase change was also monitored during photoresist cure and was found to decrease to a repeatable minimum at about 48 degrees Celsius. We believe that the characteristic temperature that resulted in the phase minimum was the glass transition temperature for the resin/solvent mixture, and that the nonlinear increase in phase that followed this minimum was due to solvent evaporation.

INTRODUCTION

The purpose of the photoresist prebake process is to remove any excess solvent that is initially added to the resist as well as to anneal the polymer film, allowing the resin molecules to relax into their lowest energy state. This thin film of resist is typically on the order of 1-2μm thick, with the change in film thickness during prebake of about 0.5μm.

If the solvent isn't fully evaporated or if the prebake time is too long, then the feature size may not be as small as expected. It is important when heating the resist for prebake that the temperature of the film reach and exceed the glass transition temperature (T_g) in order to facilitate the diffusion of solvent and polymer chains that will anneal the film for prebake [1].

Several techniques are available to measure Tg but none of them have been applied *in situ* for endpoint detection of photoresist softbake [2,3,4,5]. There has been some research in endpoint detection of the prebake process. Metz, et al. (6) performed real-time measurement of resist film thickness on silicon wafers using multi-wavelength reflection interferometry. They determined resist thickness versus spin and bake time. This method was used to monitor non-uniformities for statistical process control.

The technique we describe here monitors not only the effect of thickness change, but also the effect of the change in the elastic properties of the resist as it bakes.

MEASUREMENT PRINCIPLE

The reflection coefficient for a plane wave incident from a medium on a layer was calculated using Equation 1 from classical reflection theory [7].

$$R = \left[\frac{(1 - \frac{z_1}{r_3})\cos k_2 L + j \frac{z_2}{z_3} \sin k_2 L}{(1 + \frac{z_1}{z_3})\cos k_2 L + j \frac{z_2}{z_3} \sin k_2 L} \right] \quad (1)$$

In this equation, z_1 is the acoustic impedance of silicon, z_2 is the acoustic impedance of photoresist, z_3 is the acoustic impedance of air, L is the photoresist thickness, and c_2 is the velocity of sound in photoresist.

Using this equation, we predicted the phase of the reflection coefficient. During prebake, there are changes in the thickness of the resist film, the velocity of the film, and its density. Figure 1 illustrates the effect of prebake on the reflection phase, with the phase of the liquid and solid resist films plotted as a function of frequency. The liquid resist thickness was assumed to be 2.6μm and the solidified thickness 2.2μm. Optimum choice of frequency is necessary to get the maximum sensitivity to resist property changes.
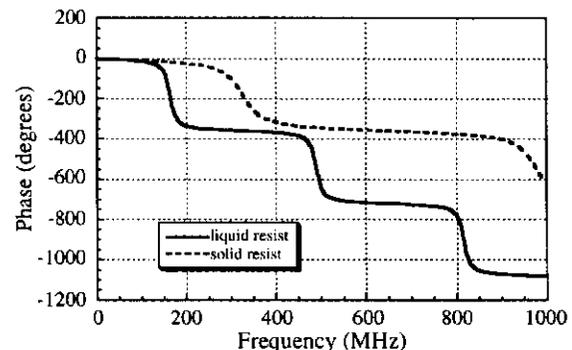

Figure 1: Reflection phase vs. frequency for liquid and solid photoresist (before and after pre-exposure bake, respectively).

There will also be a phase change in the reflected signal as the wafer changes temperature. During prebake, the wafer temperature typically increases from room temperature to 90 C. The relation from which we can calculate the one-way phase change for a given temperature change is given in Equation 2. It has been shown experimentally for silicon that this relationship is

linear within the temperature range of the bake[8]. Here, d is the thickness of the silicon wafer, f is the frequency, $v(T)$ is the bulk velocity in silicon at temperature T, T_0 is room temperature, 25C, and k_v is the temperature sensitivity coefficient of the wave velocity. We used this relation to remove the effects of temperature on the measurements. The calculated change is then multiplied by two to compensate for wave travel to and from the interface.

$$\Delta\varphi(T) = 2\pi f d \left[\frac{1}{v(T_0)(1 - k_v(T - T_0))} - \frac{1}{v(T_0)} \right] \quad (2)$$

EXPERIMENTAL SETUP

In order to determine the changes in the photoresist film during the prebake process, we apply a high voltage pulse across the zinc oxide piezoelectric transducer that is resonant at 260 MHz. As shown in Figure 2, longitudinal waves excited by the transducer are coupled into the silicon wafer and its coatings by direct contact of the sapphire buffer rod to the wafer. These waves are reflected from the silicon/photoresist interface. The transducer serves as the receiver for the reflected signal which is continuously monitored during prebake. We digitized the signal using an HP 54520A digital oscilloscope at 1G sample/sec. An anti-aliasing filter at 450 MHz was used. For each waveform obtained, the wafer temperature was measured using a thermocouple.
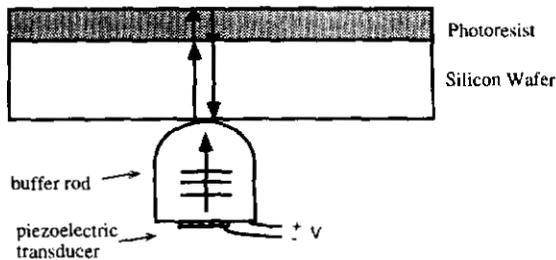

Figure 2: Illustration of sensor technology (not to scale).

Ultrasonic Phase Measurement

In order to measure the change in phase of the reflected ultrasound signal, A sample waveform of the first three reflection signals is shown in Figure 3. The waveform phase was determined by subtracting the phases of the first two reflection signals shown at 40ns and 220ns. Subtracting the phases of the two signals allowed us to remove the effects of the buffer rod from the measurement. Data was collected at a repetition rate of 3 seconds and the phase calculated using MATLAB® software.
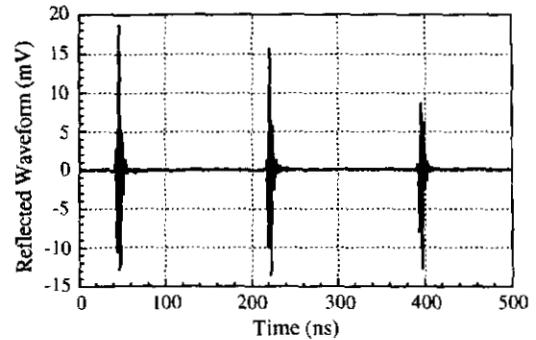

Figure 3: Sample reflected waveform used for phase calculation. The first three reflections from the silicon/photoresist interface are shown here.

EXPERIMENTAL RESULTS

In this section, we present the results of phase measurement during photoresist removal and photoresist softbake. We first measured the overall change in phase when the resist was removed from the wafer and then the change in phase that occurred while the resist was being prebaked.

Phase Change During Photoresist Removal

To evaluate the sensitivity of the phase measurement, we determined the change in phase of the reflected signal as a layer of photoresist was removed with acetone. The expected results for this change in resist thickness were calculated from theory, giving an expected phase change of about 50 degrees at the measurement frequency of 260 MHz.

A clean 8" silicon wafer was spin-coated with a 2.4μm layer of Shipley 1813 resist and prebaked for 90 seconds on a hotplate at 90C. The wafer was placed on top of the transducer and two quartz support pins. We monitored the reflected ultrasound signal for about 1-2 minutes prior to removing the resist in order to obtain the measurement noise level. The noise was about 0.2 degrees peak to peak with a standard deviation of 0.07 degrees. Then, we applied acetone to the wafer to remove the resist layer, and continued to monitor the signal until the phase stabilized. We repeated this experiment at other points on the same wafer.

Figure 4 shows the reflected high frequency signal from the silicon/resist interface before and after the resist was removed from the wafer.
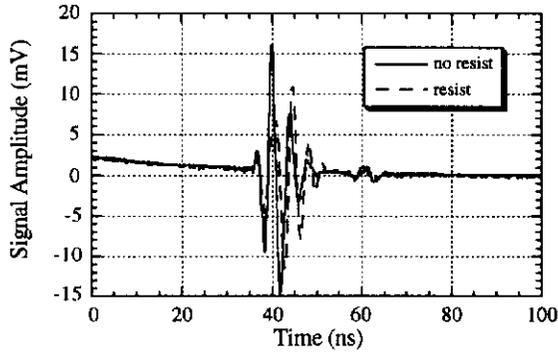
Figure 4: Reflected ultrasound signal before and after photoresist removal.

Figure 5 shows the measured phase change vs. time at 260 MHz. We measured a 48 degree change in phase when the resist was removed, agreeing well with theory. The experiment was repeated on another part of the wafer with similar results plotted on the same graph in Figure 5. The variations in phase directly following removal were attributed to temperature changes associated with solvent evaporation and a second acetone application in Region 2.

Phase Change During Resist Prebake

Next, we measured the phase change during resist prebake to look for a significant and repeatable trend in the results that could be used to determine the state of cure at a given time. The expected change in phase during the bake is a steady increase due to decreasing thickness and increasing density. The actual value of phase change depends on the starting and ending point conditions of the film, including thickness, density, and velocity. This excludes the slowing effects of wafer heating, which is expected to be linear from Equation 2, as well as the changes in the elastic properties of the resist due to its softening.
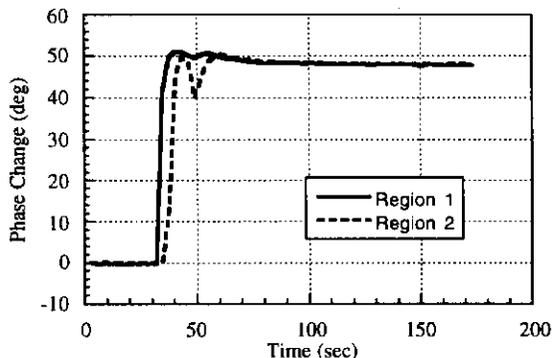
We cleaned an 8" wafer and measured the increase in phase as the bare wafer was heating. In this way, we obtained the slope of the linear relationship between phase and temperature. This was later used to remove the temperature effects from the total phase change during cure. Next, we coated a wafer with 1813 resist at a spin speed of 3000 rpm. We immediately placed the coated wafer on the setup and turned on a heating lamp to begin the prebake. We obtained the reflected waveforms and temperature data once every 3 seconds for about 200 seconds, well beyond the usual bake time of 90 seconds. The total phase change vs. time and temperature was calculated and the temperature effects subtracted using the slope determined in the first part of the experiment.

The measured phase vs. time of cure is plotted in Figure 6, both with and without the temperature effect. The phase is plotted at 280 MHz since the measurement sensitivity was highest at this point. There is an initial decrease in phase followed by a rapid increase which eventually levels off. We believe that the initial decrease in phase is due to a the film softening during heating. Also, the rapid increase in phase that follows the minimum is likely due to the onset of solvent evaporation. This occurs after the resist has softened, allowing for the diffusion of solvent molecules that facilitates evaporation.

Figure 7 shows the change in phase again, this time plotted against temperature. There is a repeatable phase minimum occurring at about 48 C. We believe that the temperature of this minimum represents the characteristic glass transition temperature of the resin/solvent mixture. This is important because it indicates the point at which significant evaporation and polymer relaxation occur and, therefore, the point at which significant prebaking begins. It also can provide us with a temperature calibration point that can be used in determining the temperature profile of a given prebake cycle. The temperature uniformity is known to affect the final critical dimension (CD) of a feature that is being processed. For both Figures 6 and 7, the final thickness of the resist after prebake was 2μm.

Figure 5: Experimental phase change during resist removal at two points on the wafer.
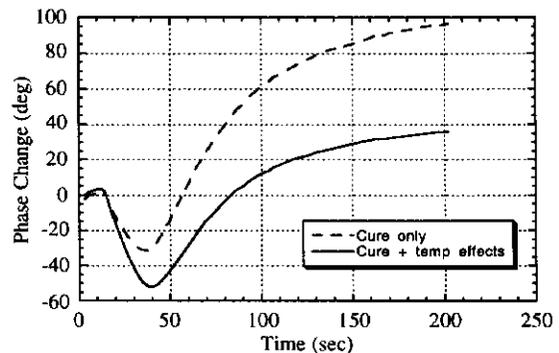

Figure 6: Phase change vs. time of cure at 280 MHz, with temperature effects (solid line) and after temperature effects have been inverted out (dashed line).
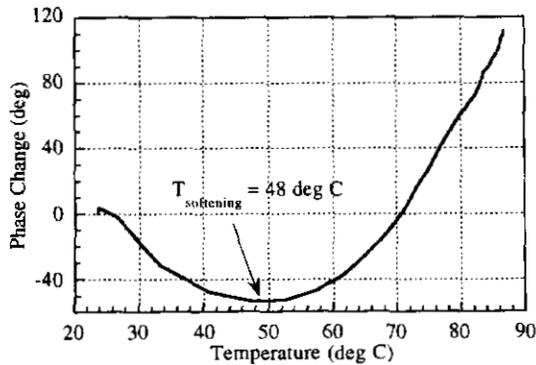
Figure 7: Phase change at 280 MHz vs. temperature during prebake.

CONCLUSIONS

We have developed an *in situ* ultrasonic method that can measure the glass transition temperature of prebaking photoresist by monitoring the phase of a high frequency reflection from the silicon/resist interface. Since it is at the glass transition temperature that the resist softens and the diffusion and evaporation of the *solvent molecules in* the resist become significant, a measure of the glass transition temperature allows us to determine resist cure state.

ACKNOWLEDGEMENTS

REFERENCES

[1] L.F. Thompson, "Resist Processing", Chapter 5 in Introduction to Microlithography, 2nd ed. , ed. by Thompson, et al., American Chemical Society, Washington, D.C., 1994.

[2] E. Tegou, et al. Microelectronic Engineering, Vol. 35, 1997, pp. 141-144.

[3] A. Schiltz , et al. Microelectronic Engineering, Vol. 27, 1995, pp. 413-416.

[4] J.W. Grate, et al. *Anal. Chem.,* Vol. 64, No. 4, Feb. 15, 1992, pp. 413-423.

[5] H. Wohltjen and R. Dessy. *Anal. Chem.,* Vol. 51, No. 9, August 1979, pp. 1470-1475.

[6] T.E. Metz, et al. *Process Module Metrology, Control, and Clustering, SPIE,* Vol. 1594, 1991, pp. 146-152.

[7] L.E. Kinsler, et al. "Transmission Phenomena", Chapter 6 in Fundamentals of Acoustics, 3rd ed, John Wiley and Sons, New York: 1982, pp. 127-128.

[8] H.J. McSkimin, et al. *J. Appl. Phys.,* Vol. 24, No. 8, August 1953, pp. 988-997.

Mailing Address:
Susan L. Morton
Ginzton Laboratory, N 121
Stanford, CA. 94305
smorton@macro.stanford.edu
(650) 725-2990