

## In situ ultrasonic measurement of photoresist glass transition temperature

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We have developed a method to measure the glass transition temperature of photoresist *in situ*. The purpose of photoresist prebake is to evaporate excess solvent from the photoresist and to allow the polymer chains to relax into an ordered matrix. The phase of a high frequency ultrasound signal was monitored as it was reflected from the silicon/photoresist interface during the photoresist prebake. There was an initial decrease in phase followed by a rapid increase once a given temperature was reached. It is believed that this repeatable temperature is the glass transition temperature of the resist/solvent mixture and that the rapid increase in phase following it is a result of solvent evaporation. The glass transition temperature ( $T_g$ ) for a freshly spun 2.2  $\mu\text{m}$  Shipley 1813 resist was measured to be 50 °C. The  $T_g$  measured increased from 50 to 66 °C as the time delay between coating and prebaking was increased from 0 to 20 min. It is believed that this change in  $T_g$  is a result of solvent evaporation. © 1998 American Institute of Physics. [S0003-6951(98)00319-2]

During the pre-exposure bake process of semiconductor fabrication, it is important that the temperature exceed the glass transition temperature ( $T_g$ ) of the resist/solvent mixture. This ensures the diffusion of solvent molecules and polymer chains that is necessary for prebake to occur.<sup>1</sup> If the solvent is not fully evaporated or if the prebake time is too long, then feature sizes in exposed and developed photoresist may not be congruent to those on the mask. Several techniques are available to measure  $T_g$  but none of them has been applied *in situ* for endpoint detection of photoresist softbake.<sup>2,3</sup> Endpoint detection based on optical monitoring of the thickness of the photoresist has been used.<sup>4</sup> 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 photoresist.

Figure 1 shows a schematic of the experimental measurement scheme. An 8  $\mu\text{m}$  thick zinc oxide (ZnO) film was deposited on a sapphire buffer rod which is placed in contact with the back side of the wafer. The transducer was excited with a high voltage spike which launched a longitudinal wave that was coupled to the silicon wafer. The reflected signals from the silicon/photoresist interface were converted to an electrical signal by the transducer and were digitized and stored in a digital computer. A sample reflection signal, consisting of multiple reflections, is shown in Fig. 2. The phase was determined by subtracting the phase of the first

two reflections, eliminating systematic effects unrelated to cure state. It was calculated at many frequencies, and its variation monitored as the wafer was heated. Wafer temperature was measured using a thermocouple.

The reflection coefficient for a longitudinal plane wave incident from a medium on a layer can be calculated using classical reflection theory.<sup>5</sup> We expect a phase change in the reflected signal as the photoresist layer properties change and as the wafer changes temperature. The phase change accompanying photoresist thickness and impedance changes is expected as a result of thin film interference effects. With regard to temperature effects, Eq. (1) gives the expected phase change due to changes in the temperature of the silicon wafer. In this equation,  $d$  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, and  $k_v$  is the temperature sensitivity coefficient of the wave velocity. This relationship is approximately linear in the temperature range of prebake<sup>6</sup> and can be calibrated out using a thermocouple. For the films of interest, the thickness of the layer is less than a wavelength, and we do not expect separate reflections from the front and back of the layer:

$$\Delta\varphi(T) = 4\pi f d \left[ \frac{1}{v(T_0)[1 - k_v(T - T_0)]} - \frac{1}{v(T_0)} \right]. \quad (1)$$

In a first experiment, we determined the change in phase

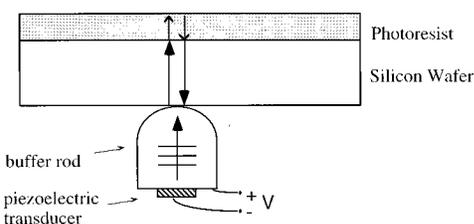


FIG. 1. Illustration of measurement technique (not to scale).

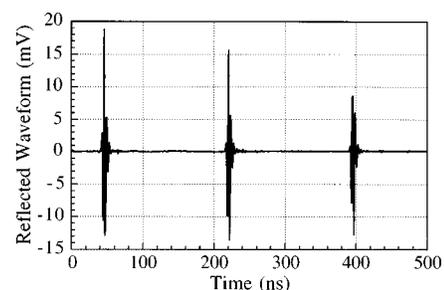


FIG. 2. Multiple reflections from the wafer/photoresist interface that are used to calculate the phase change.

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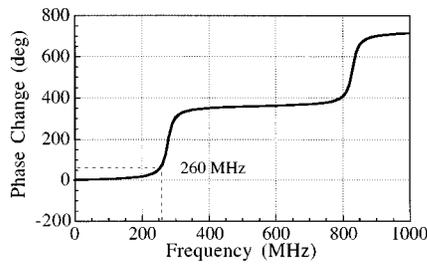


FIG. 3. Expected phase change vs operating frequency when 2.4  $\mu\text{m}$  photoresist is removed.

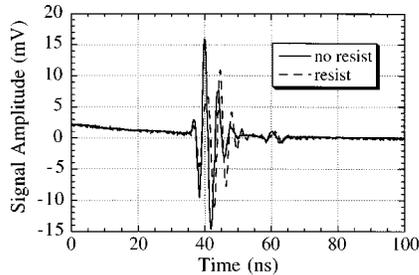


FIG. 4. Reflected ultrasound signal before and after photoresist removal. These are shown as dashed and solid lines, respectively.

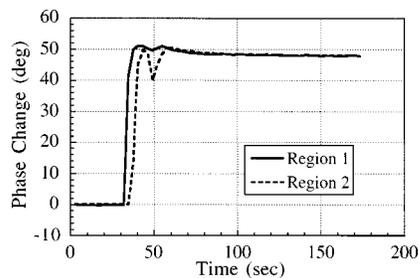


FIG. 5. Experimental phase change before and after resist removal at two points on the wafer.

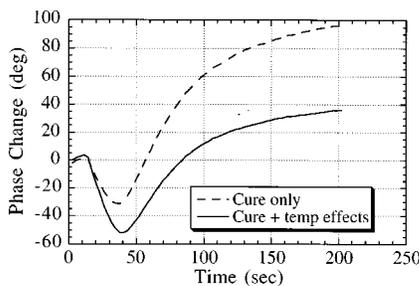


FIG. 6. Phase change vs time of cure with and without temperature effects. These are shown as solid and dashed lines, respectively.

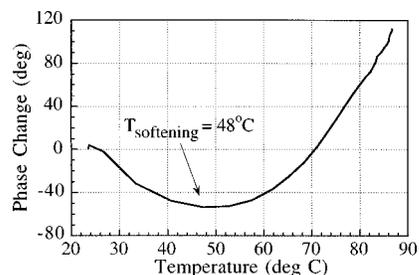


FIG. 7. Phase change vs temperature during prebake.

of the reflected signal as a 2.4  $\mu\text{m}$  layer of Shipley 1813 photoresist was removed. This experiment was designed to provide a measure of the properties of the resist and to validate the measurement scheme. Figure 3 is a plot of the expected phase change of the reflection coefficient after a 2.4  $\mu\text{m}$  photoresist layer has been removed from the wafer surface. This expected change is plotted versus measurement frequency to determine the frequency at which the highest sensitivity is achieved. At 260 MHz, the frequency of the current transducer, the expected phase change is  $50^\circ$  which is large enough that a higher frequency transducer is not needed. A sample was prepared by cleaning an 8 in. wafer, coating it with a 2.4  $\mu\text{m}$  layer of Shipley 1813 resist, and then prebaking the resist. Approximately 30 s into data acquisition, acetone was applied to the wafer to remove the resist layer. Figure 4 shows the reflected signal before and after resist removal; note the significant phase change. Figure 5 shows the measured phase change versus time at 260 MHz. As can be seen from the plot, about 30 s of data were taken prior to the removal of the resist to determine the phase noise level associated with the measurement; this noise was about  $\pm 0.2^\circ$ . Then, when the acetone was applied at about 30 s, a  $48^\circ$  jump in phase was measured as the resist dissolved. The experiment was repeated at another point on the wafer with similar results (dotted line on the same graph). The second jump in the dotted curve is attributed to a second solvent application and the temperature changes that result from its subsequent evaporation.

In the next experiment, the goal was to measure the phase change *in situ* during resist prebake. The change in phase once the resist decreased in thickness and increased in density was expected to be about  $300^\circ$ , excluding temperature effects. The calculations assumed a typical thickness change from 1.50 to 1.15  $\mu\text{m}$ . A wafer was coated with Shipley 1813 resist at a spin speed of 3000 rpm. Reflected wave forms were obtained along with temperature readings for about 200 s of heating, beyond the usual bake time of 90 s. The total phase change versus time and temperature was calculated and the temperature effects subtracted using a phase versus temperature slope determined prior to the experiment.

The measured phase versus time of cure is plotted in Fig. 6, both with and without the temperature effect. There was an initial decrease in phase followed by a rapid increase which eventually began to level off. We believe that the initial decrease in phase was due to a decrease in wave velocity that accompanied film softening during heating. The rapid increase in phase that is shown following the minimum was likely due to the onset of solvent evaporation. To support this hypothesis, a separate study was conducted in which the solvent was allowed to evaporate without heating the wafer and resist. In this case, there was just a small monotonic increase in phase due to solvent evaporation, with no decrease measured. Thus, we know that the initial decrease in phase is a heating effect, and we believe it to be a measure of the resist softening.

Figure 7 shows the change in phase again, this time plotted against temperature. There is a repeatable phase minimum occurring at about  $48^\circ\text{C}$ . The temperature of this minimum represents the characteristic glass transition

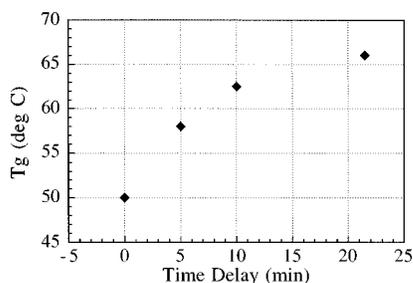


FIG. 8. Change in glass transition temperature as the prebake is delayed.

temperature of the resin/solvent mixture. For both Figs. 6 and 7, the final thickness of the resist after prebake was 2  $\mu\text{m}$ . Figure 8 shows the effect of increasing the time delay between coating and prebaking the wafer; it was expected that a longer delay would allow more solvent to evaporate and increase  $T_g$ .<sup>7</sup> As seen from Fig. 8, this effect was confirmed.

We have developed a sensor that can measure the glass transition temperature of prebaking photoresist. This is an important step in determining cure state of the resist 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. Since photoresist prebake involves removal of excess solvent as well as relaxation of the polymer molecules into an ordered matrix, the glass transition temperature gives us a measure of the cure state of the resist during prebake. In a noncontact environment, laser-based ultrasound could be applied to generate the ultrasonic signal without direct contact to the wafer.

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