Thermally induced stress relaxation and densification of spin-on-glass thin films

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The stress–temperature relationship of silica spin-on-glass thin films on silicon wafers was studied. Upon heating, the stress–temperature curves showed a dramatically increasing slope when the temperature of the film was greater than 340 °C. At 450 °C, a significant, irreversible change in the stress of the film was observed. This change in stress was correlated with an increase in film electron density and a decrease in film thickness. The observed thermally activated stress–relaxation behavior was interpreted in terms of reflow of the glassy hydrogen–silsesquioxane-based material. © *2000 American Institute of Physics.* [S0003-6951(00)02704-2]

Spin-on-glass dielectrics based on hydrogen–silsesquioxane[1] (HSQ) are emerging as a viable low-*K* interplanar dielectric for next-generation very-large-scale-integrated (VLSI) circuitry.[2,3] The ability to spin coat a silicon-based prepolymer onto a wafer and convert it at low temperature to silica offers several important advantages. The most important of these is the ability to planarize complex metal topography via the spin-coating process, thereby reducing the reliance on expensive planarization processes such as chemical–mechanical polishing.[4] A second major benefit is a lower dielectric constant ($k \leq 3$) compared to silica deposited by chemical-vapor deposition.[3] This allows for faster signal propagation with less power dissipation and reduced cross talk. Finally, reflow of HSQ at high temperature, that is, the ability of the spin-on-glass to flow and find its own level during processing further enhances its ability to planarize metal topography and fill narrow gaps. However, as the various layers of circuitry are built up, the previously deposited lower layers must maintain their integrity.[5] Thus, reflow at elevated temperatures poses some complications in the design of spin-on-glass processes when multilevel circuitry is involved. Therefore, an understanding of the thermal behavior and dimensional stability of spin-on glass and similar dielectrics is one of the most important issues in developing high-speed electronic circuitry.[6]

In this letter we report the stress, electron density, and thickness behavior of HSQ thin films on silicon wafers upon heating from room temperature to 450 °C, a typical processing temperature. The stress was measured using a wafer-curvature method. The thickness and density were found using x-ray reflectivity. This information, collected from the same set of specimens, provides a detailed thermal–mechanical description of the reflow of spin-on glass.

Spin-on-glass thin films were prepared according to the manufacture's specifications by spin coating the precursor solution onto 8-in.-diam silicon wafers with subsequent curing at 400 °C for 1 h. The final film thickness was nominally 400 nm for all samples. Film stress was calculated using the original, as-cured film thickness from the change of curvature of the silicon wafer before and after the film was coated. According to Stoney's equation,[7] the film stress σ is given by

$$\sigma = E_b d^2 / (6Rt), \qquad (1)$$

where $E_b = E/(1 - \nu)$ the biaxial modulus of the wafer, E is the elastic modulus of silicon, ν is the Poisson's ratio of silicon, R is the radius of the curvature of the wafer, and d and t are the thickness of the wafer and the film, respectively. The stress–temperature curves were measured by heating the sample under flowing nitrogen at 2 °C/min (except when the temperature fell below 60 °C and the cooling rate slowed down). The uncertainty of the temperature at the high-temperature end was estimated to be 5 °C as measured by a thermocouple. The uncertainty of the calculated stress values is estimated to be 5% at room temperature by repeating the entire procedure on test films known to have reproducible behavior.

Film thickness was measured with single-wavelength specular x-ray reflectivity[8] over an incident angular range of 0.05° to 0.6° with copper $K\alpha$ radiation having a fractional-wavelength spread of $\Delta\lambda/\lambda = 1.3 \times 10^{-4}$ and an angular divergence of 12 s. The motion of the goniometer was controlled by a closed-loop active servo system with an angular reproducibility of 0.0001°. The critical angle for x-ray reflection is a sensitive measure of the mean-electron density of the film. However, small sample tilt misalignments on the order of thousandths of a degree in the direction of reflection can cause significant errors in determining this critical angle. To overcome this sample-alignment problem, x-ray reflectivity can be performed at many different wavelengths simultaneously. This is done by using not just the characteristic intensities of the x-ray tube (for example, the $K\alpha$ line of a Cu tube like the one used in these experiments), but also the broad-wavelength spectrum known as the bremsstrahlung. An energy-dispersive lithium-doped silicon x-ray detector
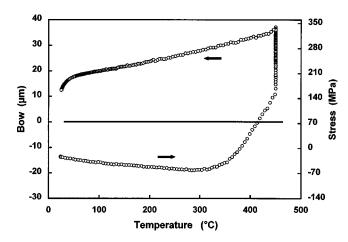
FIG. 1. Typical stress–temperature curve for the hydrogen–silsesquioxane spin-on-glass thin film. Arrows indicate heating and cooling directions. The left scale gives the measured wafer bow, the right scale gives the film stress found from Eq. (1).

FIG. 2. Total stress change as a function of time at 450 °C. The point given at a time of 0.01 min is for the unannealed sample.

with 200 eV resolution is employed and its output directed through amplifiers to a multichannel analyzer (MCA). Regions of interest (ROI) are defined on the MCA at various, distinct wavelengths. Each ROI will result in a different reflectivity curve. Data are collected by incrementally varying the angle of incidence of the x-ray beam to the surface under study and measuring the intensity of the reflected x rays on the multichannel analyzer in each ROI at each increment. A full description of this approach, its error analysis, and its demonstration of standard materials has been published.[9]

Figure 1 shows a full-cycle stress–temperature curve ($S-T$ curve) reaching a maximum temperature of 450 °C. Upon heating, the stress of the HSQ thin film changed slowly at temperatures below 340 °C. Above 340 °C the film stress rapidly increased with temperature. A stable state of stress was found when holding at 450 °C. Upon cooling, a slow variation of the stress was observed, but this time opposite in sign to the stress seen upon heating. The film stress remained high even upon returning to room temperature; however, it did begin to relax toward the original value after many days at room temperature and ambient conditions. This behavior has been attributed to moisture absorption in the film.[10] The thermal histories of four wafers used in this study are listed in Table I. Some samples were cycled several times between room temperature and 250 °C. In these cases the stress of the film simply retraced the lower portion of the $S-T$ curve in Fig. 1. When the samples were subjected to multiple heating cycles to 450 °C with little or no time at ambient conditions, the stress–temperature curves remained high and similar to that of the top portion of the curve in Fig. 1. Several months after the heat treatments, the film stress at room temperature was measured again and found to have remained high. Thus,
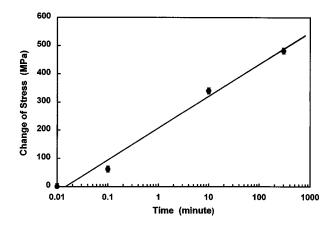
the thermal change in this case was permanent, or at least very long lived. This indicated that at sufficiently long times a state of quasiequilibrium could be achieved indicative of structural changes in the glassy HSQ.

To verify this, the changes in thickness and the electron density of the sample in Fig. 1 before and after heating at 450 °C were measured by x-ray reflectivity. A decrease in film thickness (with estimated standard uncertainties) from (430 ± 47) to (380 ± 30) nm was observed. Likewise, a mean-electron density increase from $(4.99 \pm 0.1) \times 10^{23} \ e^-/cm^3$ to $(6.02 \pm 0.1) \times 10^{23} \ e^-/cm^3$ was observed. This indicates there was a change in thickness, and a reciprocal change in electron density between 10% and 20%. Since the thermal effect is cumulative, as shown by the repeated heating of a single sample, we can measure the effect for all the films studied by classifying them in terms of the time spent at 450 °C. The total change in film stress at 450 °C was estimated using the stresses at the low-temperature portion of the heating curve as a base line. Figure 2 shows the correlation between the total change of the stress and the holding time at 450 °C. The fit to this data shows the heating effect is exponential with time. Figures 3 and 4 show the electron density and thickness of HSQ thin films as a function of annealing time at 450 °C (time corresponding to 0.01 min is for unheated samples). We also observed an exponential relation, similar to that found for the film stress.

The temperature dependence of the stress of the HSQ film is mostly due to mismatch of the coefficients of thermal expansion (CTE) between HSQ and silicon. Smooth, continuously varying, linear changes in film stress are expected for the $S-T$ curve of an unchanging film on a silicon wafer. The large, irreversible stress deviations observed at temperatures higher than 340 °C indicate that there is some structural or chemical changes occurring in the film. Two possible ex-

TABLE I. Processing conditions and measured properties for selected samples.

Processing and properties	Wafer 13	Wafer 19	Wafer 12	Wafer 11
Total time at 450 °C (min)	0	0.1	10	300
Initial stress (MPa)[a]	23.8	37.0	23.1	23.6
Final thickness (nm)	426.9	415.2	398.9	381.1
Electron density ($10^{23}/cm^3$)	4.99	5.22	5.60	6.04
Density relative to quartz	79%	83%	89%	96%

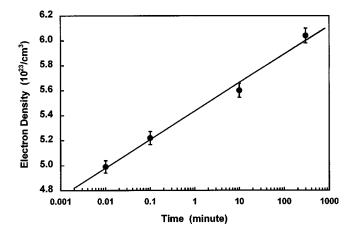[a]Estimated from the ratio of stress changes at 250 to that of 450 °C.

FIG. 3. Electron density as a function of annealing time at 450 °C. The point given at a time of 0.01 min is for the unannealed sample.

planations arise. The first is that there has been an incorporation of oxygen into the thin film through oxidation of the film itself. This may occur if the slowly flowing nitrogen did not provide a sufficiently low oxygen partial pressure (less than 100 ppm) (Ref. 3) to prevent the conversion of any residual $\equiv$SiH bonds to $\equiv$Si—O—Si$\equiv$ bonds:

$$2[\equiv SiH] + O_2 \rightarrow [\equiv SiOSi\equiv] + H_2O. \tag{2}$$

However, this reaction can only account for about a small change in the electron density of HSQ thin films when calculated strictly from atomic volume considerations. Specifically, for the sample in Fig. 1, the product of density and thickness of the film was used to determine the mass conservation of the HSQ film. The 8% increase in the mass of the film that was found is likely due to oxidation.
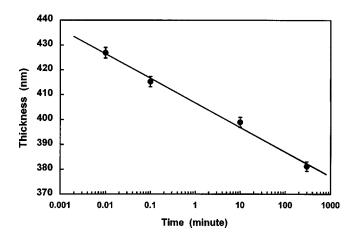

FIG. 4. Film thickness as a function of annealing time at 450 °C. The point given at a time of 0.01 min is for the unannealed sample.

If the change of the stress and the large increase in electronic density of about 20% could not all come from oxidation, a second explanation needs to be found. Recourse can be made to the fact that the HSQ films are glassy materials prepared under highly nonequilibrium conditions. When a glass (which is strictly never at thermodynamic equilibrium) is heated, the material starts to move toward equilibrium by flowing and reducing free volume, thereby becoming denser.[11] This explains the increase in HSQ film density with annealing measured here, which has been recently examined by positron annihilation lifetime spectroscopy.[12,13] The increase in density will also work to increase film modulus as well, which may lead to the observed increase in film stress.

The reflow of the interlayer dielectric studied here has repercussions on circuit reliability. The oxidation of residual $\equiv$SiH groups would tend to retard this reflow process by forming more chemical cross links within the system, thus creating a more rigid, flow-resistant network. This effect is apparently not great enough to completely prevent reflow for the times and temperatures studied here, but may prove more significant when lower processing temperatures are used, especially for newer silsesquioxane spin-on glasses intended to be cured at lower temperatures.[14] Finally, we note that the observed increase in film density would be expected to lead to an increase in the dielectric constant. From the work of Hrubesh, Keene, and Latorre[15] on silica aerogels of variable mass density, we find that a density increase of 20% leads to a dielectric constant increase of several percent. However, this does not take into account possible composition changes due to oxidation, which will also effect the dielectric constant.

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