Effect of passivation on stress relaxation in electroplated copper films

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(Received 5 January 2006; accepted 9 March 2006)

The present study investigated the effect of passivation on the kinetics of interfacial mass transport by measuring stress relaxation in electroplated Cu films with four different cap layers: SiN, SiC, SiCN, and a Co metal cap. Stress curves measured under thermal cycling showed different behaviors for the unpassivated and passivated Cu films, but were essentially indifferent for the films passivated with different cap layers. On the other hand, stress relaxation measured under an isothermal condition revealed clearly the effect of passivation, indicating that interface diffusion controls the kinetics of stress relaxation. The relaxation rates in the passivated Cu films were found to decrease in the order of SiC, SiCN, SiN, and metal caps. This correlates well with previous studies on the relationship between interfacial adhesion and electromigration. A kinetic model based on coupling of interface and grain-boundary diffusion was used to deduce the interface diffusivities and the corresponding activation energies.

I. INTRODUCTION

Copper (Cu) damascene structures with low *k* dielectrics are being implemented as on-chip interconnects to meet the demand for chip density and performance for 90 nm technology node and beyond. Recent studies on electromigration (EM) in the Cu interconnects have shown that mass transport is dominated by interface diffusion between Cu and the surrounding layers, especially at the interface subjected to chemical-mechanical polishing (CMP) and then passivated with a cap layer.[1,2] This has generated great interest in improving EM reliability of Cu interconnects by optimizing the interface materials and processes to suppress the interfacial mass transport. Various cap layer materials and processing techniques have been proposed, and their effects on EM lifetime of Cu interconnects have been examined.[3,4] In particular, Hu et al.[3] demonstrated a significant improvement in the EM lifetime by coating the Cu surface with a thin metal layer, such as Pd and CoWP. However, it is difficult to delineate the kinetics of mass transport directly from the EM lifetime, which is controlled by the mechanism of damage formation, a complex process depending on local defects, microstructures, and the geometry of the interconnects. As interconnect scaling advances beyond the 90 nm node, the interface to volume ratio continues to increase with decreasing line width, making the interface an increasingly dominant path for mass transport during EM. Therefore, it is important to understand the effect of passivation on the kinetics of interfacial mass transport and its correlation to EM reliability of Cu interconnects.

Previously, we developed a bending beam method for measuring isothermal stress relaxation in Cu damascene interconnects and we found that the effect of passivation on stress relaxation correlates well with EM results.[5–7] A numerical model was developed to simulate the stress relaxation in the Cu lines based on the kinetics of mass transport through interfaces and grain boundaries. Thus, it is possible to deduce the kinetics of mass transport from stress relaxation tests. The test procedure was further simplified by using electroplated Cu films instead of damascene lines,[8–10] for which a semi-analytical kinetic model was developed based on the coupling of grain boundary and interface diffusion. The deduced grain boundary and interface diffusivities were in good agreement with other studies. In this article, we report stress relaxation measurements of electroplated Cu films passivated with four different cap layers, based on which the

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DOI: 10.1557/JMR.2006.0196

interface diffusivities are deduced and the effect of passivation on interfacial mass transport is examined.

II. SAMPLES AND MEASUREMENTS

Samples of electroplated Cu films were prepared on 12-inch (100) silicon (Si) wafers. A thin layer of silicon oxide (100 nm) was deposited on the wafer surface, followed by the deposition of an etch-stop layer and a 450-nm layer of a low *k* material, carbon-doped oxide (CDO). A TaN/Ta diffusion barrier was then deposited before physical vapor deposition of a Cu seed layer. The rest of the Cu film was electroplated, followed by a CMP process. The final thickness of the Cu film was determined to be 0.8 μm. After a surface-cleaning procedure, the Cu film was passivated with a cap layer. Four different cap layers were used in this study, including SiN, SiC, SiCN, and a metal cap. A thin Co cap layer (about 10–20 nm) was used as the metal cap at the interface between the Cu film and a SiN passivation. The thickness of the other cap layers was 100 nm. Figure 1 shows the schematic of the film stack. No additional annealing process was applied during the preparation of the samples.

The Cu films were cut into 5 × 40-mm stripes for bending beam measurements using a system developed in our laboratory.[11] The surface curvature of each beam was monitored as a function of temperature and time in a vacuum chamber under a nitrogen atmosphere at a pressure of 50 Torr. An optical system was designed to monitor the curvature change during the experiment and measure it with a quadratic position sensor. A reference radius of curvature, R_0, was measured under the same condition, using the same film stack but with the Cu film and passivation etched off. The stress was then determined using Stoney's equation

$$\sigma = \frac{M_s h_s^2}{6h}\left(\frac{1}{R} - \frac{1}{R_0}\right) \quad , \tag{1}$$

where σ is the stress in the Cu film, h is the film thickness, h_s is the substrate thickness, M_s is the biaxial modulus of the Si substrate, and R is the measured radius of curvature of the sample with the Cu film. Because the passivation layer is much thinner than the Cu film, its contribution to the curvature change is negligible. The estimated system error in the stress measurement is about 5%, largely from the determination of the reference curvature. The error of measuring the relative curvature change is about 2%.

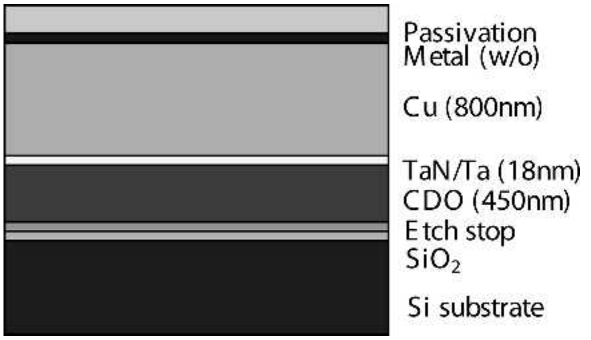

FIG. 1. Schematic of the film stack of the samples.

III. THERMAL CYCLING EXPERIMENTS

Stress in the Cu films was first measured under thermal cycling conditions. Each sample was annealed at 450 °C for 30 min during the first cycle to stabilize the microstructure. In the subsequent cycles, the temperature varied from room temperature to 400 °C, 350 °C, or 300 °C, where the peak temperature was adjusted to equalize the starting stress for subsequent isothermal measurements at different temperatures. The ramping rate was set to be 4 °C per minute, but could not be held constant as cooling below 200 °C. Figure 2 shows the stress-temperature curves for an unpassivated Cu film (first cycle not shown). The stress hysteresis differs from our previous measurement using unpassivated, electroplated Cu films from a different source.[9] In particular, the compressive stress in this study was sustained at a much lower level as heating above 250 °C, with an inflection point indicating the onset of more extensive plastic yield in the Cu film in comparison with the previous measurement. This can be largely attributed to the effect of the CMP process, which was applied on the Cu surface in the present study but not in the previous study. The shape of the stress hysteresis is similar to those reported for e-beam and sputter-deposited Cu films from other groups.[12–16]

Figures 3(a)–3(d) plots the measured stress-temperature curves in four Cu films passivated with SiN, SiC, SiCN, and the metal cap, respectively. Different from Fig. 2 for

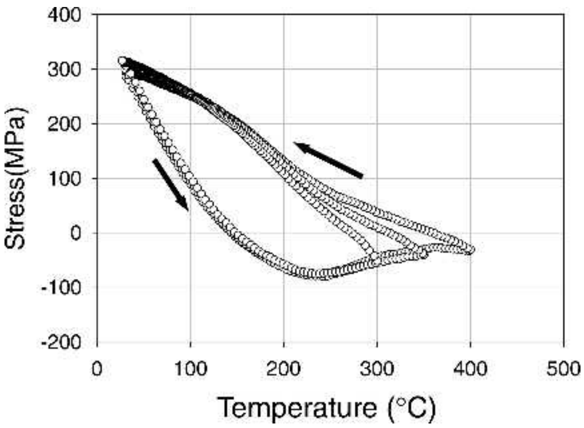

FIG. 2. Measured stress hysteresis in an unpassivated, electroplated Cu film during three thermal cycles. Arrows indicate the heating and cooling directions.

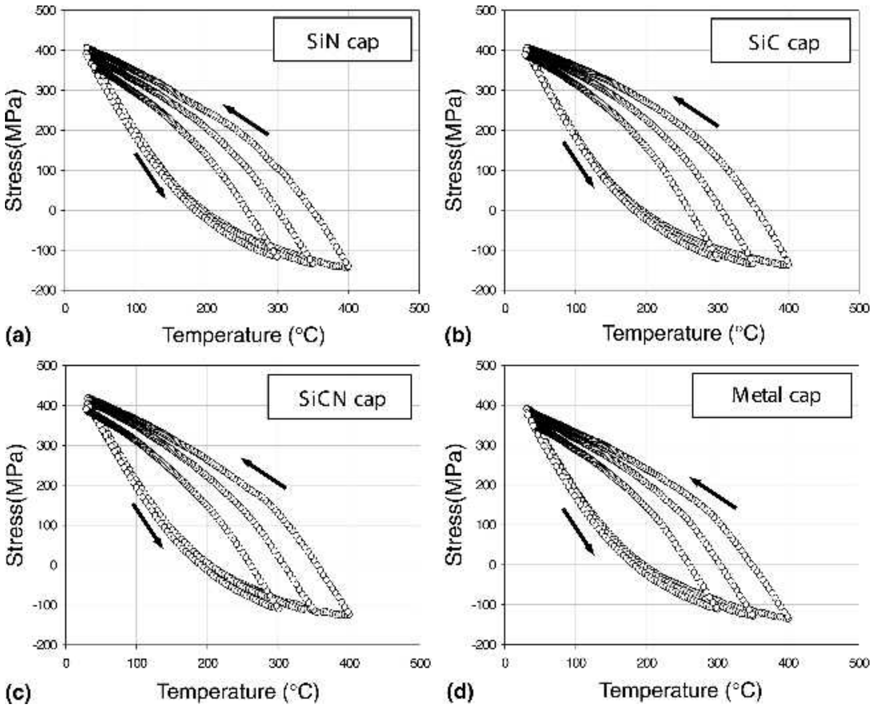

FIG. 3. Measured stress hysteresis in the electroplated Cu films passivated with different cap layers: (a) SiN, (b) SiC, (c) SiCN, and (d) the metal cap. Arrows indicate the heating and cooling directions.

the unpassivated Cu film, the passivated Cu films retained relatively higher compressive stresses at the elevated temperature range, with the residual stress at room temperature also being higher. No inflection in the cooling or the heating curve was observed. The different behavior of the stress hysteresis for the passivated and unpassivated Cu films reveals a passivation effect for all the cap layers of this study in reducing plastic yield and stress relaxation during thermal cycling, which has been widely reported in the literature.[17,18] However, the stress curves in Fig. 3 for the four cap layers are virtually indistinguishable, making it difficult to compare the passivation effect among these cap layers. This observation indicates that, although stress behavior under thermal cycling test is commonly used to investigate the mechanical properties of thin films,[12–19] it is not sensitive enough to differentiate the effect of different cap layers. It is well known that during thermal cycling, multiple deformation mechanisms can contribute to the overall stress characteristics as the temperature and the stress vary simultaneously.[19] Thus, it is difficult to delineate the dominant mechanisms as the temperature varies quite rapidly within a few tens of minutes. Although the mechanism involving interfacial mass transport would depend on the cap layer, the effect may be masked by contributions from other mechanisms. Therefore, thermal cycling measurements are not suitable for studying the kinetics of interfacial mass transport. As in the previous study,[9] we next turn to isothermal stress relaxation tests to investigate the passivation effect on interfacial mass transport in the Cu films.

IV. ISOTHERMAL STRESS RELAXATION

In the present study, isothermal stress relaxation measurements were performed for the electroplated Cu films passivated with four different cap layers. All of the samples were annealed to a peak temperature of 450 °C in the first thermal cycle, and were then cooled from 350 °C to 210 °C in the second cycle to start the isothermal run. The temperature was held constant at 210 °C for 30 h while the stress was being measured by the bending beam method. The starting stresses were equalized for all samples to about 190 MPa. The measured stress relaxation curves are shown in Fig. 4. It is clear from the figure that the isothermal stress relaxation behavior is very sensitive to the cap layer, which suggests that the dominant mechanism for the stress relaxation is controlled by the mass transport at the interface. Contributions from other stress relaxation mechanisms may have been largely consumed during thermal cycling plus a relatively short initial stage upon annealing, leaving interfacial mass transport as the dominant mechanism for long-term stress relaxation. Figure 4 shows that the Co cap layer most effectively reduced the interfacial mass transport, followed in order by SiN, SiCN, and SiC. The order of the stress relaxation rates for the four cap layers correlates very well to the EM results of Cu interconnects

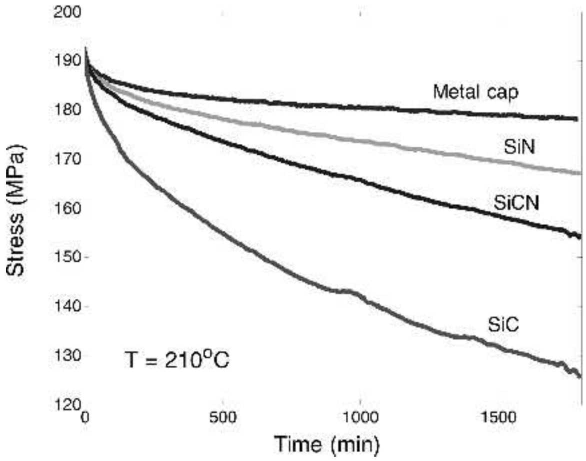

FIG. 4. Isothermal stress relaxation in electroplated Cu films passivated with four different cap layers, measured at 210 °C.

passivated with similar cap layers.[20] Therefore, the isothermal stress measurement of Cu films provides an effective method to evaluate the cap layers for improving EM reliability of Cu interconnects.

In a previous study,[9] we showed that stress relaxation under isothermal annealing at moderate temperatures can be used to measure the kinetics of mass transport at interfaces and grain boundaries of thin Cu films. A kinetic model for isothermal stress relaxation of polycrystalline thin films was developed based on the coupling of grain boundary and interface diffusion.[10] The model assumes that the film consists of a periodic array of grains with grain boundaries perpendicular to the interface (Fig. 5). The biaxial in-plane stress in the film is relaxed by diffusional flow of atoms via the grain boundaries and the interface with a cap layer. Diffusion at the film/substrate interface and in the bulk of the film was considered negligible. A parametric study of the model showed that the stress relaxation curve strongly depends on the interface diffusivity when the interface diffusion is slower than the grain-boundary diffusion. In the limiting case when the grain-boundary diffusion is much faster, stress relaxation is fully controlled by interface diffusion. An analytical solution was obtained for this limiting case, which leads to

$$\sigma(t) = \sigma_0 \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp[-(2n+1)^2 t/\tau_I]}{(2n+1)^2} \quad , \tag{2}$$

where

$$\tau_I = \frac{kThl^2}{\pi^2 M \Omega \delta_I D_I} \quad , \tag{3}$$

and σ_0 is the initial stress, M is the biaxial modulus of the film, h is the film thickness, l is the grain size, δ_I is the effective thickness of the interface, D_I is the interface diffusivity, Ω is the atomic volume, k is Boltzmann's constant, and T is the absolute temperature. A similar model was also developed for unpassivated films, where the grain-boundary diffusion controls the stress relaxation behavior. By fitting the model with experimental data from isothermal stress relaxation measurements for unpassivated and passivated films, the grain boundary and the interface diffusivities can be deduced. The corresponding activation energies can then be determined from the temperature dependence of the diffusivities.

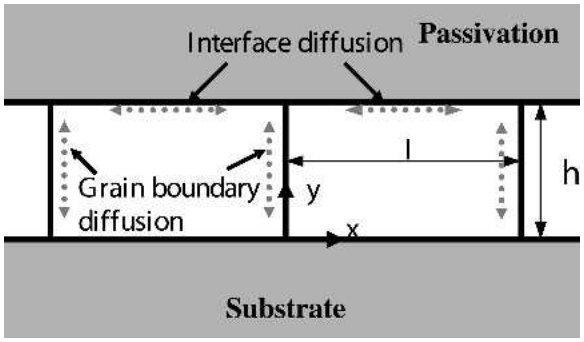

FIG. 5. Schematic illustration of the grain structure and diffusion paths in the kinetic model for passivated Cu films.

To measure the temperature dependence of stress relaxation, we adjusted the peak temperatures in the second thermal cycle (Fig. 3) to normalize the starting stress of the samples for the isothermal stress measurements. In this way, the isothermal measurements were set up with similar initial stresses at different temperatures to minimize the effect of initial stress. Figure 6 shows the stress relaxation curves of the four passivated Cu films, each measured at three temperatures, 179 °C, 210 °C, and 247 °C. The samples were cooled from 300 °C, 350 °C, and 400 °C, respectively. The initial stresses were around 190 MPa for all the samples. Because the stress hysteresis under thermal cycling is nearly identical for all the cap layers, the same thermal history was used. The microstructures of the Cu films should be similar in all the samples after the high-temperature annealing in the first cycle.[21]

The kinetic model was used to deduce the interface diffusivities by a data-fitting procedure. The grain boundary diffusivity deduced from the previous study[9] was adopted, as listed in Table I. The interface diffusivity for each cap layer was varied to obtain the best fit between the model and the experimental data by means of the least square optimization. Other parameters used in the model calculations are: grain size, $l = 1.04$ μm; modulus, $M = 155$ MPa; and atomic volume, $\Omega = 1.18 \times 10^{-29}$ m^3. For the SiN, SiC, and SiCN cap layers, the model was solved numerically with coupled grain boundary and interface diffusion.[10] For the metal cap layer,

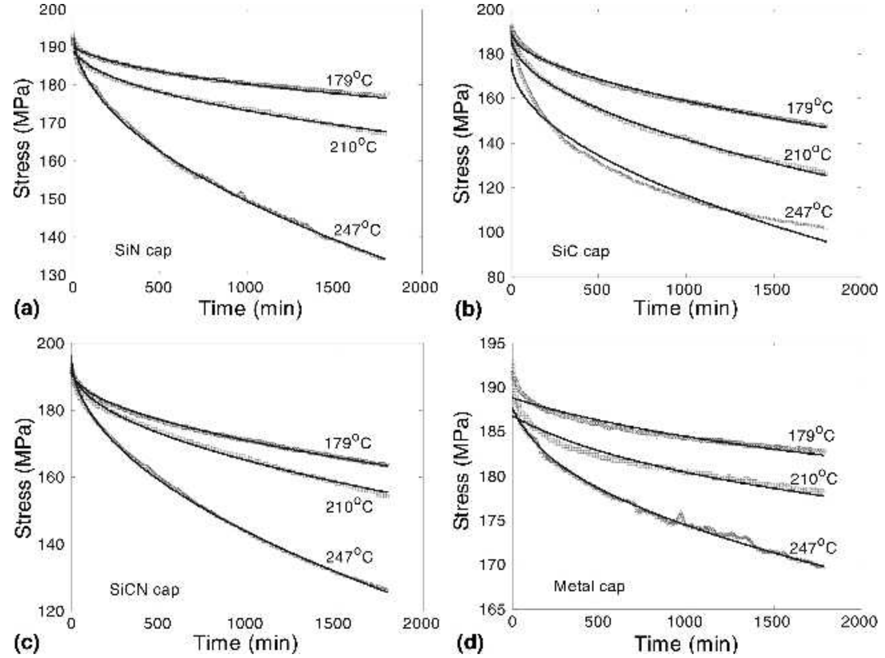

FIG. 6. Isothermal stress relaxation of electroplated Cu films passivated with (a) SiN, (b) SiC, (c) SiCN, and (d) metal cap layers. The thin solid lines are fitting curves of the kinetic model using deduced diffusivities in Table I.

because the interface diffusion is significantly slower than the grain-boundary diffusion, the analytical solution, Eq. (2), was used. Because of the uncertainty in the initial condition and possible contributions from other relaxation mechanisms in the initial stage, the initial stresses were also adjusted in the model calculations to yield the best overall fitting. The deduced interface diffusivities for different cap layers at different temperatures are listed in Table I. The stress relaxation curves calculated from the kinetic model using the deduced diffusivities are plotted in Fig. 6 as the thin solid lines to compare with the experimental data. The activation energy for the interface diffusion with each cap layer is then determined by the Arrhenius plot in Fig. 7, where the previously deduced grain-boundary diffusivities are also plotted for comparison. The dependence of the diffusivities on temperature is summarized as the exponential functions in Table I.

V. DISCUSSION

The isothermal stress relaxation measurements (Figs. 4 and 6) clearly show the effect of passivation on the kinetic process. Experiments using a similar film stack without the Cu film exhibited negligible stress relaxation during isothermal annealing, which indicates that the measured stress relaxation is associated with the Cu film. Among the four cap layers used in this study, the Co cap layer provides the most significant reduction in the stress relaxation rate, most likely from suppression of the mass transport at the interface between Cu and the cap layer. The order of decreasing relaxation rates in the Cu films passivated with SiC, SiCN, SiN, and the metal cap agrees well with previous studies on the relationship between interfacial adhesion and electromigration,[4,20] which was attributed to increasingly enhanced chemical bonding at the interfaces. However, the correlation of the EM

TABLE I. The deduced interface diffusivities for the electroplated Cu films passivated with four different cap layers (the grain boundary diffusivities are adopted from our previous study[9]).

	Diffusivity, δD (m^3/s)			
Diffusion path	179 °C	210 °C	247 °C	f(T)
Grain boundary	1.3×10^{-26}	7.5×10^{-26}	4.7×10^{-25}	$1.1 \times 10^{-14} \exp(-1.07\ \text{eV}/kT)$
SiN/Cu	2.8×10^{-29}	7.7×10^{-29}	6.0×10^{-28}	$3.4 \times 10^{-19} \exp(-0.91\ \text{eV}/kT)$
SiC/Cu	3.3×10^{-28}	6.6×10^{-28}	1.3×10^{-27}	$1.2 \times 10^{-23} \exp(-0.41\ \text{eV}/kT)$
SiCN/Cu	1.2×10^{-28}	2.2×10^{-28}	8.1×10^{-28}	$1.6 \times 10^{-22} \exp(-0.56\ \text{eV}/kT)$
Metal cap/Cu	8.2×10^{-30}	1.5×10^{-29}	5.8×10^{-29}	$2.4 \times 10^{-23} \exp(-0.59\ \text{eV}/kT)$

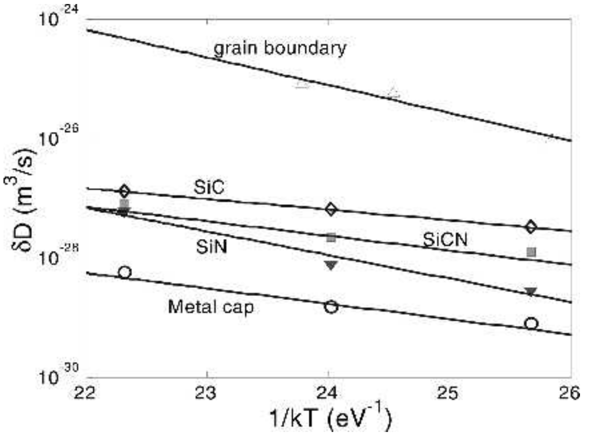

FIG. 7. Temperature dependence of the interface diffusivities in electroplated Cu films passivated with four different cap layers. The grain boundary diffusivities deduced from our previous study[9] are plotted for comparison.

activation energy to the interfacial bonding energy is indirect because of the complexity of the EM damage processes in Cu interconnects. This study on stress relaxation measures directly the cap layer effect on interfacial mass transport, thus providing a better understanding of the mechanism for EM reliability improvement.

The kinetic model provides a quantitative framework for evaluating the kinetics of the mass transport process responsible for stress relaxation. Figures 6(a)–6(d) shows that the model can well account for the stress relaxation behavior under isothermal annealing. A relatively large discrepancy is noted at the initial stage of stress relaxation, which may be attributed to the uncertainties in the determination of the initial stress state and possible contributions from other stress relaxation mechanisms. This is mitigated by adjusting the initial stresses in the modeling analysis. Nevertheless, most of the stress relaxation curves were closely reproduced by the model. The deduced interface diffusivities appear to be reasonable. The activation energies, however, are systematically lower than the activation energy (0.8–1.0 eV) deduced from EM lifetime measurements of Cu interconnects.[1] In addition to the complexity of the EM damage process, the difficulty may rest with the stress relaxation measurement. The sensitivity of this measurement requires a reasonable starting stress value, thus limiting the experiments to a relatively narrow temperature range around 180 °C to 250 °C and increasing the experimental error.

Figure 7 shows that the interface diffusion is considerably slower than the grain-boundary diffusion in the temperature range of the present study. This agrees with the general understanding about the passivation effect on the thermomechanical behavior in thin films subjected to thermal cycling.[17,18] By comparing the stress hysteresis in Figs. 2 and 3 for unpassivated and passivated Cu films, it is clear that the grain-boundary diffusion leads to rapid stress relaxation at high temperatures for the unpassivated films, whereas for the passivated films, stress relaxation controlled by interface diffusion is considerably reduced. The difference among the four cap layers, however, is less significant and not readily observable from the thermal cycling behavior. The cap layer effect is better revealed by isothermal stress measurements (Fig. 4), where long-term annealing allows appreciable stress relaxation via the process of interface diffusion. The present study shows that among the four cap layers, the SiC cap gives the fastest interface diffusion, and the metal cap is the most effective in reducing the interfacial mass transport. Quantitatively, the interface diffusivity decreases by two orders of magnitude from SiC to the metal cap layer.

VI. SUMMARY

The present study demonstrates that isothermal stress relaxation measurements can be used to evaluate the effect of cap layers on the kinetics of interfacial mass transport in Cu films. Stress relaxation in unpassivated and passivated electroplated Cu films was measured under thermal cycling and isothermal annealing conditions. The thermal cycling measurements showed the effect of passivation, but were not able to differentiate different cap layers. The isothermal stress relaxation experiments clearly revealed the cap layer effect, indicating that the interface diffusion controls the kinetic process of the stress relaxation in the Cu films. A kinetic model was used to deduce the interface diffusivities and the corresponding activation energies for interface diffusion. The effect of the cap layers on isothermal stress relaxation of Cu films correlates well with their effect on the EM lifetime of Cu interconnect.

ACKNOWLEDGMENTS

This work was supported in part by the Advanced Technology Program of the Texas High Education Coordinating Board and by Intel Corporation. The authors thank Jun He of Intel for helpful discussions.

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