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Atomistic mechanisms of moisture-induced fracture at copper-silica interfaces

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Tailoring the chemo-mechanical properties of metal-dielectric interfaces is crucial for many applications including nanodevice wiring, packaging, composites, and catalysis. Here, we combine moisture-induced fracture tests, electron spectroscopy, and density functional theory calculations to reveal fracture toughness partitioning and atomistic delamination mechanisms at copper-silica interfaces. Copper plasticity is supported above a threshold work of adhesion and delamination occurs by moisture-induced Cu-O bond scission in Cu-O-Si bridges. These results provide insights into the effects of the nature of metal-oxygen bonding on moisture-induced delamination of metal-dielectric interfaces. © *2011 American Institute of Physics*. [doi:10.1063/1.3622304]

Metal-ceramic interfaces are of key importance in diverse applications including nanoelectronics, sensors, communication devices, composites, and catalysis.[1] Heterointerfacial fracture toughness Γ_{FT} typically consists of the interfacial bond-breaking work of adhesion γ_a (Ref. 2) and plasticity γ_p, in the layers.[3] Plasticity is often a function of γ_a, which in turn is sensitive to the crack-tip chemical environment.[3,4] Unveiling the fracture mechanism and partitioning Γ_{FT} into γ_a and γ_p are crucial for tailoring the chemo-mechanical properties and stability of heterointerfaces for applications.

Although copper-silica interfaces are known to be susceptible to stress corrosion-cracking, e.g., in water, alcohols and amides,[5,6] the atomistic fracture mechanism is yet to be understood. Theoretical calculations[7] have shown that strong Cu-O bonds promote, and hydroxyl groups degrade, copper-silica interfacial adhesion. Oxygenated copper films exhibiting a 40% higher copper-silica interface toughness has been atrributed to Cu-O-Si bridging.[8] Involvement of dissociative adsorption of reactive species at Cu-O-Si bridges in the fracture mechanism has also been hypothesized,[5] but is yet to be verified.

Here, we combine moisture-induced fracture tests, electron spectroscopy and density functional theory calculations to reveal the atomistic delamination mechanisms at copper-silica interfaces. We show that copper plasticity is supported above a threshold work of adhesion, and delamination occurs by moisture-induced Cu-O bond scission in Cu-O-Si bridges. These findings provide insights into the effects of the nature of metal-oxygen bonding on the delamination of metal-dielectric interfaces.

We sputter-deposited 50-nm-thick copper films followed by a 150-nm-thick Ta overlayer at a 7 mTorr Ar^+ plasma without vacuum break in a 7×10^{-7} Torr base pressure CVC sputter tool on Si(001) wafers capped with a 85-nm thick thermal silica layer. The Ta layer offsets the poor adhesion between Cu and an epoxy used to obtain 50 mm $\times$ 5 mm rectangular beams of dummy-Si/epoxy/Ta/Cu/SiO_2/Si(001) stacks for four point bend interfacial fracture tests as described in detail elsewhere.[9,10] We prepared stacks with Au/SiO_2 interfaces by the same method.

We conducted four-point-bend fracture tests at water activities between $0.05 \le a_{H2O} \le 0.8$ at T = 323 K in a Cincinnati Sub-Zero PZ series chamber. The test structure beams were displaced at 10 nm/s in a high stiffness micromechanical system operated at a 43° phase angle.[11] The interfacial crack emanates from a notch scribed using a diamond saw on the Si wafer hosting the Cu film. The first plateau in the load-displacement curve[11] corresponds to a critical crack driving energy Γ_c at which the crack reaches and propagates along the weakest interface at the given displacement rate. Arresting the displacement at the plateau relaxes the load monotonically at a continually decreasing crack velocity v. As v $\rightarrow$ 0, the crack driving energy Γ diminishes to the equilibrium fracture toughness[11] Γ_{FT}. Since Γ_{FT} is extracted from the steep part of the v-Γ curves, Γ_{FT} connotes reaction-kinetics-limited delamination at the crack tip.

The v-Γ plots obtained from structures with copper-silica and gold-silica interfaces (Figure 1) at different a_{H2O} indicate that Γ_{FT}^{Cu} is sensitive to a_{H2O} for copper-silica interfaces [see Fig. 2(a)]. Decreasing a_{H2O} from 0.8 to 0.05 results in a nearly five-fold increase in Γ_{FT}^{Cu} from 1.1 to 5.4 J/m^2 for copper-silica interfaces. This value is comparable to 1.9 J/m^2 reported for Cu-SiO_xN_y interfaces[12] for 20%–40% humidity. In contrast, $\Gamma_{FT}^{Au} \approx 0.5 \pm 0.1$ J/m^2 is significantly lower and independent of a_{H2O}. These differences can be understood in terms of the vastly different oxidation potentials of copper and gold. While Γ_{FT}^{Cu} is dependent on Cu-O-Si bond formation and its susceptibility to water,[5,8] the low Γ_{FT}^{Au} stems from the lack of thermodynamic driving force for Au-O bond formation[13] at room temperature, thereby precluding further moisture-induced weakening. Fitting v-Γ characteristics of the Au/silica interface to a reaction rate kinetics model for water-induced fracture in orthosilicates[14,15] yields a crack propagation activation

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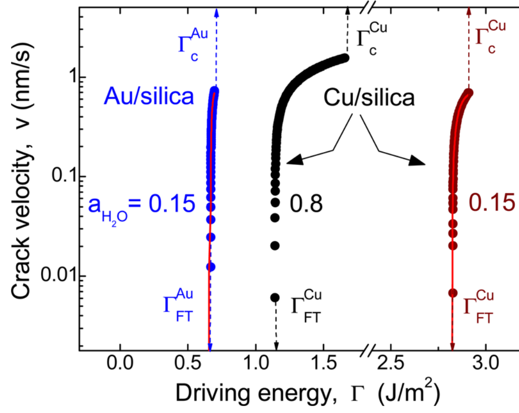

FIG. 1. (Color online) Crack velocity vs. driving energy (v-Γ) curves as a function of a_{H2O} at 323 K for copper-silica and gold-silica interfaces. The solid lines represent the reaction rate kinetics model fits for $a_{H2O} = 0.15$.

energy of 0.193 ± 0.002 eV that is lower than that for Si-O-Si hydrolysis,[14] suggesting that Au-O-Si hydrolysis is kinetically favored. The extracted interfacial bond density $N_i^{Au} = 0.1 \times 10^{15}$ atoms/cm^2 is in reasonable agreement with $1.4–1.9 \times 10^{15}$ atoms/cm^2 oxygen coverage on silica surfaces.[16]

For copper-silica interfaces, we observe two distinct regimes about $a_{H2O} \sim 0.2$. In both regions, Γ_{FT}^{Cu} increases linearly with decreasing log a_{H2O}, but the slope of toughness increase $\left|\frac{d\Gamma_{FT}^{Cu}}{d\log a_{H_2O}}\right|$ is four-fold higher for $a_{H2O} < 0.2$ than that for $a_{H2O} > 0.2$. We note that plotting a_{H2O} on a log scale connotes the water chemical potential $|RT \log a_{H2O}|$, where R is the gas constant. For $a_{H2O} \sim 0.2$, $\Gamma_{FT}^{Cu} \sim 2.1$ J/m^2, in good agreement with $\gamma_a = 2.2$ J/m^2 for copper-silica interfaces.[16] For $a_{H2O} > 0.2$, $\Gamma_{FT}^{Cu} < 2.1$ J/m^2 due to water-induced Cu-O-Si weakening and/or fissure. Thus, for $a_{H2O} > 0.2$, the mechanical energy supplied is used solely for interfacial bond breaking, i.e., $\Gamma_{FT} = \gamma_a$. Since $\gamma_a \propto N_i RT \log a_{H2O}$ at equilibrium ($v \to 0$), we obtain $N_i^{Cu} = 8.7 \times 10^{15}$ atoms/cm^2, which is within about an order of magnitude of the oxygen coverage on silica[16] and $N_i^{Cu} = 0.4 \times 10^{15}$ atoms/cm^2 obtained by fitting the v-Γ data to a reaction-rate kinetics model. This fit also yields a crack-propagation activation energy of 0.204 ± 0.002 eV/bond for Cu-O-Si hydrolysis, implying that Cu-O-Si bond breakage is kinetically favored over siloxane bridge scission.

For $a_{H2O} < 0.2$, copper-silica interfaces exhibit $2.1 < \Gamma_{FT}^{Cu} < 5.4$ J/m^2 which are significantly higher than γ_a. This result and the higher toughness increase rate for $a_{H2O} < 0.2$ indicate an additional energy dissipation mechanism, identified to be copper plasticity.[4] The linear increase in Γ_{FT}^{Cu} with decreasing log a_{H2O} for $a_{H2O} < 0.2$ is consistent with increasing plasticity because the plastic zone size is expected to linearly increase[4] with γ_a. Thus, at low water activities $a_{H2O} < 0.2$ the Cu-O-Si interfacial bonds are strong enough to support plastic deformation in copper, leading to significant contributions from both γ_p and γ_a to Γ_{FT}^{Cu}. We extract γ_p from the difference between Γ_{FT}^{Cu} and γ_a by extrapolating the linear fit of γ_a vs. $|\log a_{H2O}|$ plot to the desired a_{H2O} in the low-humidity region. This extrapolation is valid since γ_a is dependent solely on a_{H2O}. Thus, γ_p can be described as a function of γ_a [see Fig. 2(b)]: $\gamma_p = \tau(\gamma_a - \gamma_0)$, where $\gamma_a = \gamma_0$ at yield

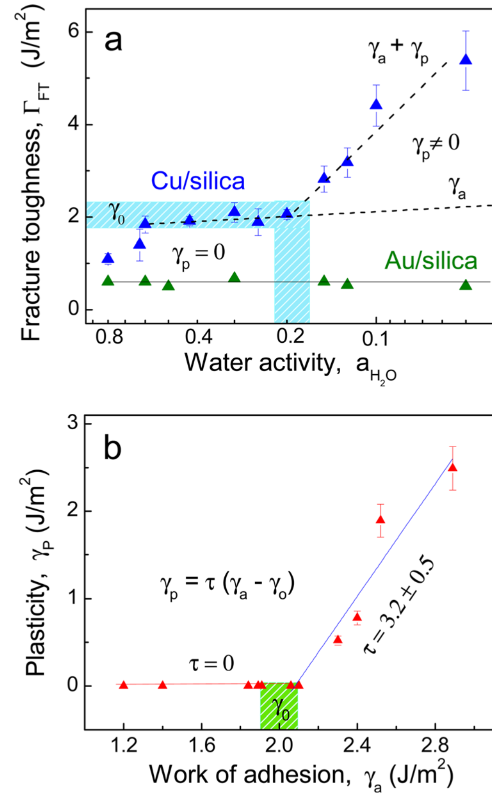

FIG. 2. (Color online) (a) Fracture toughness Γ_{FT} plotted as a function of a_{H2O} at 323 K for copper-silica and gold-silica interfaces. In this plot, a_{H2O} is on a log scale, (b) Copper plastic energy γ_p vs interfacial work of adhesion γ_a at 323 K.

point.[17] For $\gamma_a < \gamma_0$, $\gamma_p = \tau = 0$, but γ_p increases linearly with γ_a with $\tau \sim 3$ for $\gamma_a > \gamma_0$, consistent with $0.2 < \tau < 8$ predicted by analytical models for heterointerfaces.[2]

Fracture surface analysis by X-ray photoelectron spectroscopy reveals that delamination occurs through bond-breaking at the metal-dielectric interface. The Cu fracture surfaces show strong Cu $2p_{3/2}$ and $2p_{1/2}$ sub-bands at 932.7 eV and 953 eV, respectively [see Fig. 3(a)], these peak intensities are very low in spectra acquired from the silica fracture surfaces. The Si 2p band centered at 103.3 eV is observed only on the silica fracture surface and is undetectable on the Cu fracture surface.

In order to understand the bond-breaking mechanisms at the crack tip, we consider the energetics of hydrolysis of Cu-O and Si-O bonds, expressed by Cu-O + H-O-H → Cu-OH + OH with $\Delta G_{hydrolysis}^{Cu-O} = 3.3$ eV and Si-O + H-O-H → Si-OH + OH with $\Delta G_{hydrolysis}^{Si-O} = 9.2$ eV. Since $\Delta G_{hydrolysis} > 0$ for both reactions, calculated using the relevant bond free energies[15,18] at 323 K, the hydrolysis of neither Cu-O nor Si-O bonds is thermodynamically favored. However, the mechanical driving force in our experiments can offset this constraint. The free energy magnitudes of the reactions indicate that the Cu-O bonds need a lower mechanical driving force to break via hydrolysis than Si-O bonds. This inference is supported by the results of density functional theory (DFT) calculations carried out to assess the impact of moisture on the copper-silica interface strength.

Our DFT calculations used the VASP code[19] with the PW91 generalized gradient approximation[20] and projector-augmented wave approach.[21,22] Assuming that interfacial

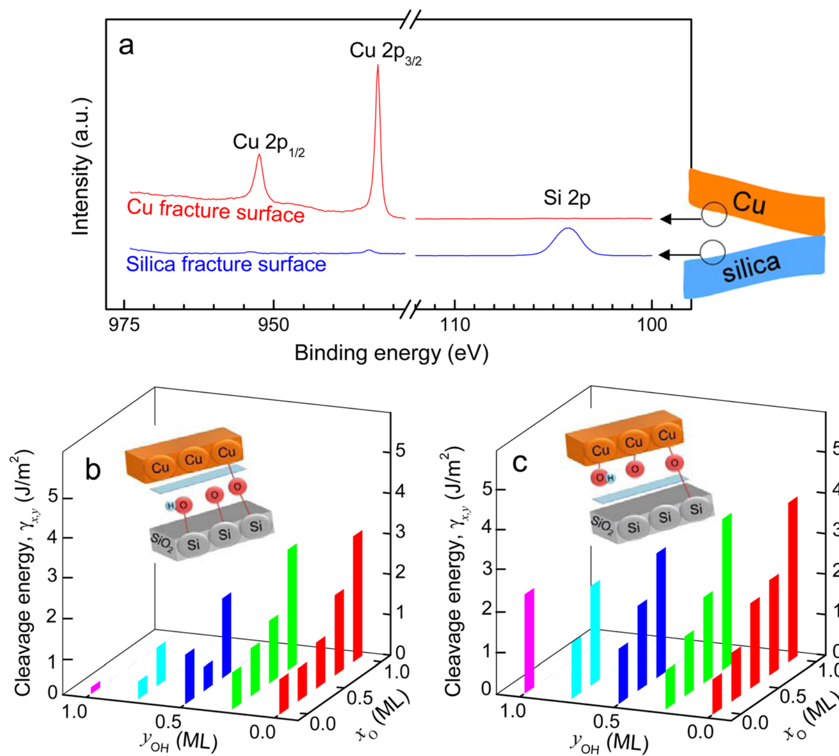

FIG. 3. (Color online) (a) Core-level Cu 2p sub-band and Si 2p sub-band from a Cu/SiO_2 interface, measured by x-ray photoelectron spectroscopy at $a_{H2O} = 0.85$ and $T = 323$ K. Cleavage energy γ_{xy} plotted as a function of interfacial O and OH coverages for (b) breaking Cu-O/Cu-OH bonds and (c) breaking Si-O/Si-OH bonds. The schematic sketches indicate the location of Cu-O-Si bridge scission.

moisture produces hydroxyl species, we considered copper-silica interfaces with different O and OH coverages, x_O and y_{OH}, respectively, for cleavage at Cu-O or Si-O bonds [see Figs. 3(b) and 3(c)]. We note that cleaving *interfacial* Cu-O bonds results in Si-OH and Si-O passivated surfaces, while breaking *interfacial* Si-O bonds forms Cu-OH and Cu-O species at the interface. These reaction pathways and energetics of hydrolysis of *interfacial* Cu-O or Si-O bonds are different from that of *stand-alone* Cu-O and Si-O bonds described above. The cleavage energy γ_{xy} can be computed for various values of x_O and y_{OH} using $\gamma_{xy} = E_{Cu} + E_{SiO2} - E_{xy}$, where E_{Cu}, E_{SiO2}, and E_{xy} are the DFT energies for the cleaved fragments of Cu and SiO_2, and their heterointerface, respectively. We find that γ_{xy} increases with x_O, as expected [Figs. 3(b) and 3(c)], pointing to the importance of oxygen-bridged bonds at copper-silica interfaces. Cu-O scission requires a lower γ_{xy} than for Si-O bond fissure for the x_O and y_{OH} ranges explored. However, the energy difference between Cu-O and Si-O cleavage given by $\Delta\gamma_{xy}$, which is <0.4 J/m^2 at low water content, e.g., $y_{OH} < 0.25$, and more pronounced at $\Delta\gamma_{xy} \sim 1.5$ J/m^2 at higher moisture levels, e.g., $y_{OH} > 0.75$. Thus, the Cu-O bond is the weaker link especially at higher moisture contents, supporting the claim that copper-silica interfaces fracture via water-induced scission of Cu-O-Si bridges at the Cu-O bonds.

In conclusion, the work of adhesion at copper-silica interfaces is determined by moisture-induced scission of Cu-O bonds in Cu-O-Si bridges. Above a threshold work of adhesion, the interfacial bonds support copper plasticity. Our findings provide atomistic insights into environmental effects of delamination of metal-dielectric interfaces, and are relevant to many applications ranging from microelectronics to biological implants.

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