

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 calculations⁷ 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 attributed 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/SiO₂/Si(001) stacks for four point bend interfacial fracture tests as described in detail elsewhere.^{9,10} We prepared stacks with Au/SiO₂ interfaces by the same method.

We conducted four-point-bend fracture tests at water activities between $0.05 \leq a_{H_2O} \leq 0.8$ 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 curve¹¹ 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 toughness¹¹ 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_{H_2O} indicate that Γ_{FT}^{Cu} is sensitive to a_{H_2O} for copper-silica interfaces [see Fig. 2(a)]. Decreasing a_{H_2O} from 0.8 to 0.05 results in a nearly five-fold increase in Γ_{FT}^{Cu} from 1.1 to 5.4 J/m² for copper-silica interfaces. This value is comparable to 1.9 J/m² reported for Cu-SiO_xN_y interfaces¹² for 20%–40% humidity. In contrast, $\Gamma_{FT}^{Au} \approx 0.5 \pm 0.1$ J/m² is significantly lower and independent of a_{H_2O} . 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 formation¹³ 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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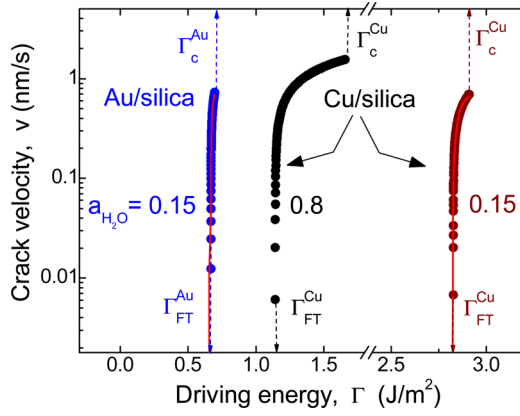


FIG. 1. (Color online) Crack velocity vs. driving energy (v - Γ) curves as a function of $a_{\text{H}_2\text{O}}$ at 323 K for copper-silica and gold-silica interfaces. The solid lines represent the reaction rate kinetics model fits for $a_{\text{H}_2\text{O}} = 0.15$.

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 $N_i^{\text{Au}} = 0.1 \times 10^{15}$ atoms/cm² is in reasonable agreement with 1.4 – 1.9×10^{15} atoms/cm² oxygen coverage on silica surfaces.¹⁶

For copper-silica interfaces, we observe two distinct regimes about $a_{\text{H}_2\text{O}} \sim 0.2$. In both regions, $\Gamma_{\text{FT}}^{\text{Cu}}$ increases linearly with decreasing $\log a_{\text{H}_2\text{O}}$, but the slope of toughness increase $|\frac{d\Gamma_{\text{FT}}^{\text{Cu}}}{d\log a_{\text{H}_2\text{O}}}|$ is four-fold higher for $a_{\text{H}_2\text{O}} < 0.2$ than that for $a_{\text{H}_2\text{O}} > 0.2$. We note that plotting $a_{\text{H}_2\text{O}}$ on a log scale connotes the water chemical potential $|\text{RT} \log a_{\text{H}_2\text{O}}|$, where R is the gas constant. For $a_{\text{H}_2\text{O}} \sim 0.2$, $\Gamma_{\text{FT}}^{\text{Cu}} \sim 2.1$ J/m², in good agreement with $\gamma_a = 2.2$ J/m² for copper-silica interfaces.¹⁶ For $a_{\text{H}_2\text{O}} > 0.2$, $\Gamma_{\text{FT}}^{\text{Cu}} < 2.1$ J/m² due to water-induced Cu-O-Si weakening and/or fissure. Thus, for $a_{\text{H}_2\text{O}} > 0.2$, the mechanical energy supplied is used solely for interfacial bond breaking, i.e., $\Gamma_{\text{FT}} = \gamma_a$. Since $\gamma_a \propto N_i \text{RT} \log a_{\text{H}_2\text{O}}$ at equilibrium ($v \rightarrow 0$), we obtain $N_i^{\text{Cu}} = 8.7 \times 10^{15}$ atoms/cm², which is within about an order of magnitude of the oxygen coverage on silica¹⁶ and $N_i^{\text{Cu}} = 0.4 \times 10^{15}$ atoms/cm² 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 $a_{\text{H}_2\text{O}} < 0.2$, copper-silica interfaces exhibit $2.1 < \Gamma_{\text{FT}}^{\text{Cu}} < 5.4$ J/m² which are significantly higher than γ_a . This result and the higher toughness increase rate for $a_{\text{H}_2\text{O}} < 0.2$ indicate an additional energy dissipation mechanism, identified to be copper plasticity.⁴ The linear increase in $\Gamma_{\text{FT}}^{\text{Cu}}$ with decreasing $\log a_{\text{H}_2\text{O}}$ for $a_{\text{H}_2\text{O}} < 0.2$ is consistent with increasing plasticity because the plastic zone size is expected to linearly increase⁴ with γ_a . Thus, at low water activities $a_{\text{H}_2\text{O}} < 0.2$ 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 $\Gamma_{\text{FT}}^{\text{Cu}}$. We extract γ_p from the difference between $\Gamma_{\text{FT}}^{\text{Cu}}$ and γ_a by extrapolating the linear fit of γ_a vs. $|\log a_{\text{H}_2\text{O}}|$ plot to the desired $a_{\text{H}_2\text{O}}$ in the low-humidity region. This extrapolation is valid since γ_a is dependent solely on $a_{\text{H}_2\text{O}}$. 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

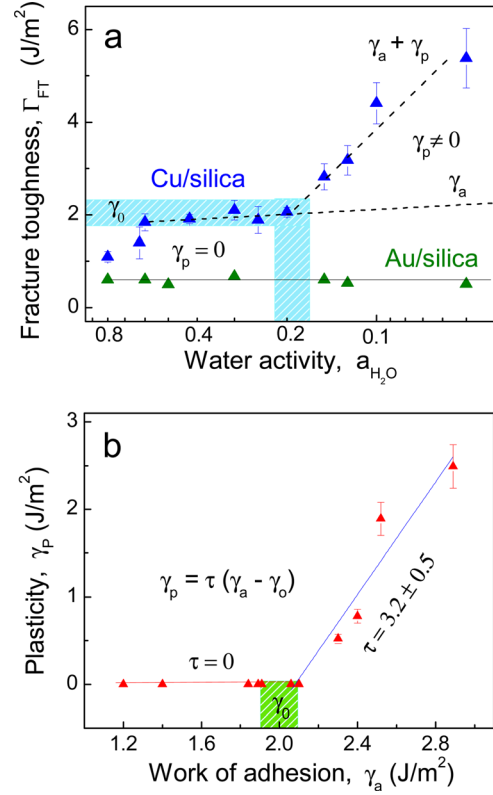


FIG. 2. (Color online) (a) Fracture toughness Γ_{FT} plotted as a function of $a_{\text{H}_2\text{O}}$ at 323 K for copper-silica and gold-silica interfaces. In this plot, $a_{\text{H}_2\text{O}}$ is on a log scale, (b) Copper plastic energy γ_p vs interfacial work of adhesion γ_a at 323 K.

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 $\text{Cu-O} + \text{H-O-H} \rightarrow \text{Cu-OH} + \text{OH}$ with $\Delta G_{\text{hydrolysis}}^{\text{Cu-O}} = 3.3$ eV and $\text{Si-O} + \text{H-O-H} \rightarrow \text{Si-OH} + \text{OH}$ with $\Delta G_{\text{hydrolysis}}^{\text{Si-O}} = 9.2$ eV. Since $\Delta G_{\text{hydrolysis}} > 0$ 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 code¹⁹ with the PW91 generalized gradient approximation²⁰ and projector-augmented wave approach.^{21,22} Assuming that interfacial

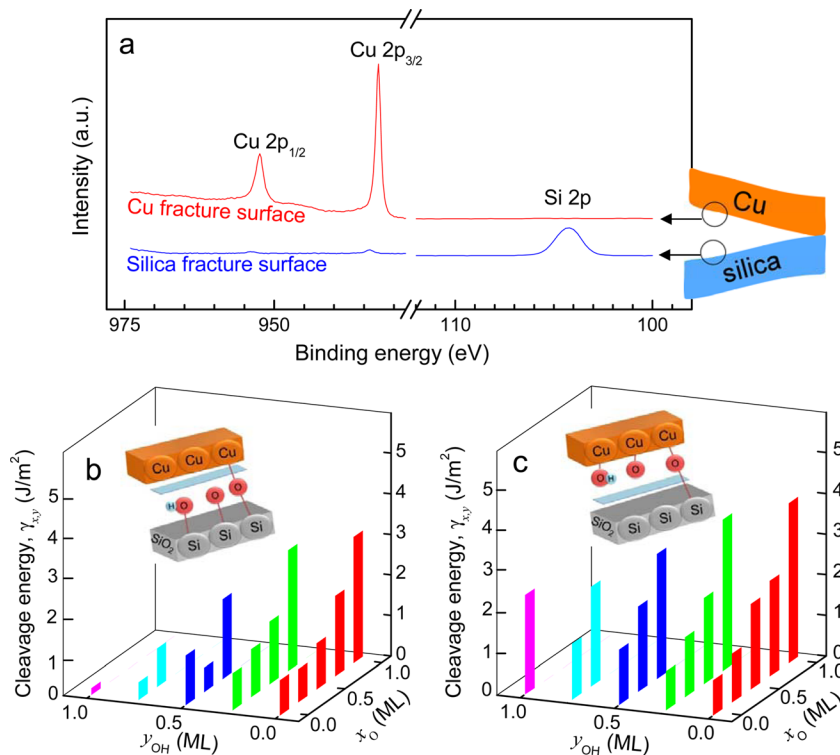


FIG. 3. (Color online) (a) Core-level Cu 2p sub-band and Si 2p sub-band from a Cu/SiO₂ interface, measured by x-ray photoelectron spectroscopy at $a_{\text{H}_2\text{O}} = 0.85$ and $T = 323$ K. Cleavage energy γ_{xy} plotted as a function of interfacial O and OH coverages for (b) breaking Cu-O/Cu-OH 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 $\gamma_{xy} = E_{\text{Cu}} + E_{\text{SiO}_2} - E_{xy}$, where E_{Cu} , E_{SiO_2} , and E_{xy} are the DFT energies for the cleaved fragments of Cu and SiO₂, 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/m² at low water content, e.g., $y_{OH} < 0.25$, and more pronounced at $\Delta\gamma_{xy} \sim 1.5$ J/m² 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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