Interplay between bond breaking and plasticity during fracture at a nanomolecularly-modified metal-ceramic interface

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Abstract

We reveal the roles of moisture and temperature on the interplay between interfacial work of adhesion γ_a and metal plasticity γ_p for a copper-silica interface modified with an organosilane nanolayer. We find that $\gamma_p \neq 0$ for interfaces with metal thicknesses $h_{Cu} > 12$ nm, and increases with h_{Cu} before it saturates at $h_{Cu} \sim 165$ nm. For a fixed h_{Cu} , γ_p increases due to temperature-induced yield stress decrease despite a decrease in γ_a with temperature because of water-induced siloxane bond weakening. These findings should be valuable for understanding the fracture mechanics of, and designing, nanomolecularly-functionalized interfaces subject to thermomechanical and chemical stresses.

Key Words: fracture, plasticity, interfaces, self-assembly, organosilane

The thermo-mechanical and chemical integrity of interfaces[1–4] often determines the functionality, reliability, and performance of many materials systems such as composites and thin film devices. The interfacial fracture energy Γ_{FT} is typically comprised of contributions from multiple processes such as bond-breaking[5] and crack-tip plastic energy dissipation.[6,7] Partitioning Γ_{FT} into the bond-breaking work of adhesion γ_a and plastic energy dissipation γ_p , e.g., as described by the Griffith-Irwin model,[5,6] is key to understanding atomistic fracture mechanisms in terms of the interface chemistry. However, experimentally partitioning Γ_{FT} is a challenge due to crack path uncertainties even for model heterointerfaces where plasticity is confined to only one material[8]. Recently we showed a new approach[9] to partition Γ_{FT} for a nanomolecularly-modified metal-ceramic interface. Copper-silica interfaces treated with a nanomolecular monolayer (NML) of a mercaptan-terminated organosilane are known to toughen due to Cu-S bonding and thermally-activated siloxane (Si-O-Si) bridging[10]. [Introducing organosilane NMLs at metal-silica interfaces can obviate crack path uncertainties because interfacial fracture occurs due to the scission of water-sensitive siloxane bridges \[9–11\]. Thus varying the water partial pressure \$p_{H_2O}\$ provides a means for adjusting \$\gamma_a\$ through siloxane hydrolysis, and deducing \$\gamma_p\$ by subtracting \$\gamma_a\$ from \$\Gamma_{FT}\$. Further, \$\gamma_p\$ is varied by changing the film thickness \$h_{Cu}\$ and temperature.](#)

Here, we describe the effects of p_{H_2O} , metal thickness h_{Cu} , and temperature, on the contributions of γ_a and γ_p to Γ_{FT} for a model Cu/NML/silica interface. Partitioning Γ_{FT} into γ_a and γ_p as a function of p_{H_2O} reveals that γ_p depends indirectly on the metal film yield stress, which decreases with film thickness h_{Cu} and temperature T . There is negligible Cu plasticity observed only for $h_{Cu}=12$ nm, where the yield strength is high enough to prevent γ_a from activating plasticity. The temperature-induced yield stress reduction increases γ_p , which offsets the decrease in γ_a due to water-induced siloxane bond weakening, leading to a net increase in Γ_{FT} with temperature. At high p_{H_2O} , Γ_{FT} is limited by low bond strength γ_a , while plasticity dominates at low p_{H_2O} . Our findings on the fracture behavior of molecularly modified

metal-ceramic interfaces should be important for designing heterointerfaces for applications involving exposures to thermo-mechano-chemical stresses.

We measured Γ_{FT} from four-point bending tests carried out at different water partial pressure between $0.158 \text{ kPa} \leq p_{H_2O} \leq 40.6 \text{ kPa}$ in the $278 \text{ K} \leq T \leq 358 \text{ K}$ range on rectangular beams of dummy-Si/epoxy/Ta/Cu/NML/SiO₂/Si(001) structures. We note that, in our experiments, $p_{H_2O} > 2.3 \text{ kPa}$ is only accessible above 298 K due to limitations of the humidity chamber. The test structures were fabricated using procedures described in detail elsewhere[12]. Briefly, we used molecular self-assembly to deposit NMLs of mercapto-propyl-tri-methoxysilane on surfaces of 85-nm-thick thermally grown silica films on Si(001) substrates. The substrates were dipped in a 5 mM solution of the organosilane in toluene for 30 minutes at 25 °C. Cu films of different pre-chosen thicknesses in the $12 \text{ nm} \leq h_{Cu} \leq 340 \text{ nm}$ range were sputter-deposited using a 7 mTorr Ar plasma in a 5×10^{-7} Torr base pressure CVC tool. A 150-nm-thick Ta layer was deposited *in vacuo* on the Cu to circumvent poor Cu-epoxy bonding via epoxy-Ta bonds used to glue to a dummy Si wafer. The Ta/Cu/NML/SiO₂/Si(001) stacks were annealed at 300 °C in 2×10^{-7} Torr vacuum for 30 minutes prior to gluing them to dummy Si wafers using an epoxy. The dummy-Si/epoxy/Ta/Cu/NML/SiO₂/Si(001) structures were sliced into 5 mm x 40 mm beams for four-point bend tests. A 0.13-mm-wide notch was scribed on the host Si(001) wafer for crack initiation.

The dummy-Si/epoxy/Ta/Cu/NML/SiO₂/Si(001) structures were subject to four-point bending at a constant 10 nm/s displacement rate in a Cincinnati Sub-Zero ZP-8 chamber that allows independent control of relative humidity and temperature. The first load-displacement plateau at a critical driving energy Γ_c corresponds to the crack reaching the weakest interface.[13] Relaxing the load by arresting the external displacement at the plateau results in sub-critical interfacial delamination at monotonically decreasing velocities. The delamination velocity v approaches zero as the driving energy Γ diminishes to a threshold fracture energy Γ_{FT} . This corresponds to the free energy of hydrolysis of siloxane bridges at the NML-silica interface, as indicated by fracture surface analyses by X-ray photoelectron spectroscopy[9,10].

Our results show that the threshold fracture energy Γ_{FT} is a strong function of p_{H_2O} , temperature and the copper film thickness h_{Cu} . We first describe the role of p_{H_2O} for structures with $12 \text{ nm} \leq h_{Cu} \leq 340 \text{ nm}$ at $T = 298 \text{ K}$ (see Figure 1a), where decreasing p_{H_2O} from 2.22 kPa to 0.634 kPa increases Γ_{FT} at all h_{Cu} . The inverse linear correlation between Γ_{FT} and $\log_e p_{H_2O}$ is attributable to water-induced siloxane bridge scission via hydrolysis at the NML-silica interface by $\text{Si-O-Si} + \text{H}_2\text{O} \rightarrow 2 \text{ Si-OH}$, similar to stress corrosion cracking in glass[14].

From Figure 1b we determine that the plastic energy γ_p is negligible for $h_{Cu} = 12 \text{ nm}$, by fitting the interfacial work of adhesion purely as a function of the hydrolysis driving force and interfacial Si-O-Si bond density $N_{\text{Si-O-Si}}$ using

$$\gamma_a = \gamma_0 - N_{\text{Si-O-Si}} kT \log_e p_{H_2O} \quad (1).$$

We find that $N_{\text{Si-O-Si}} = 1.4 \times 10^{20} \text{ m}^{-2}$, which agrees well with $N_{\text{Si-O-Si}} = 7.0 \times 10^{19} \text{ m}^{-2}$ obtained by fitting the v - Γ characteristics for different p_{H_2O} to a reaction-rate kinetics model for water-induced fracture in orthosilicates[15,16]. In systems where plasticity is significant, the $N_{\text{Si-O-Si}}$ values determined by the two methods can differ by more than two orders of magnitude[17,18], which is clearly not the case here. Hence, we conclude that $\Gamma_{FT} = \gamma_a$, which is only a function of p_{H_2O} . Thus, Γ_{FT} is tantamount to the product of the $N_{\text{Si-O-Si}}$ and the free energy of siloxane hydrolysis $\Delta G_{\text{Si-O-Si}}$ for our interfaces with $h_{Cu} = 12 \text{ nm}$. Using the $N_{\text{Si-O-Si}}$ values, we estimate the NML-tailored interface fracture energy to be in $1.07 \text{ J/m}^2 \leq \Gamma_{FT} \leq 1.79 \text{ J/m}^2$ range, which corresponds to the $48 \leq \Delta G_{\text{Si-O-Si}} \leq 80 \text{ meV/bond}$. These values are typical of Si-O-Si bonds in the presence of water,[19] which is higher than van der Waals bonding strength (4.1-41 meV/bond[20]) and similar to weak hydrogen bonding strength (41-410 meV/bond[20]). This result suggests that the weak Si-O-Si bonding precludes plasticity for $h_{Cu}=12 \text{ nm}$.

For $h_{Cu} = 35 \text{ nm}$, we observe two regimes in the $0.634 \text{ kPa} \leq p_{H_2O} \leq 2.22 \text{ kPa}$ range at 298 K (Figure 1b). For $kT \log_e p_{H_2O} \geq 6.1 \text{ meV}$, Γ_{FT} decreases linearly by 0.5 Jm^{-2} as $kT \log_e p_{H_2O}$ increases up to 20 meV, reminiscent of the free energy dependence[15] of an equilibrium reaction. We attribute the linear

behavior[9] in regime I at high $p_{\text{H}_2\text{O}}$ to the γ_a increase with decreasing water chemical potential, as seen for $h_{\text{Cu}} = 12$ nm. If we assume that *only* γ_a changes, from Eq. 1 we obtain $N_{\text{Si-O-Si}} = 2.72 \times 10^{20} \text{ m}^{-2}$ for $kT \log_e p_{\text{H}_2\text{O}} \geq 6.1$ meV, and $N_{\text{Si-O-Si}} = 4.93 \times 10^{20} \text{ m}^{-2}$ for $kT \log_e p_{\text{H}_2\text{O}} \leq 6.1$ meV. In regime II, the $N_{\text{Si-O-Si}}$ values are two- to three-fold higher than that seen for $h_{\text{Cu}} = 12$ nm. This indicates that besides γ_a , which is independent of h_{Cu} , Γ_{FT} for $h_{\text{Cu}}=35$ nm includes metal film plasticity[9,17-18] that is sensitive directly to h_{Cu} and indirectly to $p_{\text{H}_2\text{O}}$. Indeed, the interface fracture energy $\Gamma_{\text{FT}} \sim 2 \text{ Jm}^{-2}$ at $kT \log_e p_{\text{H}_2\text{O}} \sim 6.1$ meV for $h_{\text{Cu}} = 35$ nm corresponds to a film stress of $\sigma_{\text{film}} \sim 2.9$ GPa,[9] which is within 15% to 32% of the Cu film yield stress σ_y determined from nanoindentation measurements on blanket films[9] and molecular dynamics simulations[21].

For $h_{\text{Cu}} > 35$ nm (Fig. 1) plasticity is expected to set in at lower fracture energies (higher $p_{\text{H}_2\text{O}}$) because of the lower yield stress in thicker films. We are unable to capture this transition for $h_{\text{Cu}} > 35$ nm in Figure 1 because of a 20 meV cap in the water chemical potential at room temperature in our humidity chamber. However, we show later below that the plasticity onset can be captured in thicker films (e.g., $h_{\text{Cu}}=100$ nm) at higher temperatures (e.g., $>323\text{K}$) that allow access to higher water chemical potentials.

Based on γ_a for $h_{\text{Cu}} = 12$ nm, we can estimate γ_p for thicker films (e.g., $h_{\text{Cu}} = 35$ nm) by

$$\gamma_p = \Gamma_{\text{FT}} - \gamma_{a \text{ 12 nm}} \quad (2),$$

where $\gamma_{a \text{ 12 nm}}$ is the adhesion energy for $h_{\text{Cu}} = 12$ nm. Figure 2 plots the maximum plastic energy $\gamma_{p\text{-max}}$ and minimum plastic energy $\gamma_{p\text{-min}}$ and the slope of $d\Gamma_{\text{FT}}/d\log_e p_{\text{H}_2\text{O}}$ for various h_{Cu} . The increase in $d\Gamma_{\text{FT}}/d\log_e p_{\text{H}_2\text{O}}$ with h_{Cu} is consistent with theoretical predictions[2] for Cu films at high γ_a . The difference between the $\gamma_{p\text{-max}}$ and $\gamma_{p\text{-min}}$ at a given h_{Cu} is attributable to the difference in γ_a due to $p_{\text{H}_2\text{O}}$. Both $\gamma_{p\text{-max}}$ and $\gamma_{p\text{-min}}$ increase with h_{Cu} at all accessible $p_{\text{H}_2\text{O}}$, but saturate for $h_{\text{Cu}} > 165$ nm (Figure 2). Even $\gamma_{p\text{-min}}$ measured at the highest $p_{\text{H}_2\text{O}}$ increases by more than an order of magnitude from $\gamma_{p\text{-min}} = 0.4 \text{ Jm}^{-2}$ for $h_{\text{Cu}} = 35$ nm to $\gamma_{p\text{-min}} = 6.1 \text{ Jm}^{-2}$ for $h_{\text{Cu}} = 165$ nm. The linear increase in $\gamma_{p\text{-max}}$ and $\gamma_{p\text{-min}}$ is due to the

expected[22–24] yield stress reduction with increasing film thickness up to $h_{\text{Cu}} \sim 165$ nm. Saturation in γ_p for $h_{\text{Cu}} > 165$ nm is indicative of a σ_y plateau above this thickness.

Nanoindentation measurements on Cu films[9] show that σ_y decreases rapidly with h_{Cu} for $h_{\text{Cu}} \leq 165$ nm (Figure 3a). Since plastic zone size[24] R_0 can be related to σ_y through

$$R_0 = \frac{E\gamma_a}{3\pi(1-\nu^2)\sigma_y^2}, \quad (3)$$

where E is the Cu stiffness and ν the Poisson's ratio, we find that for $h_{\text{Cu}} > 75$ nm $R_0 \leq 4$ nm calculated with $\gamma_a = 1.79$ J m⁻² at $p_{\text{H}_2\text{O}}=0.634$ kPa while $R_0 \geq 1$ nm calculated with $\gamma_a = 0.78$ J m⁻² at $p_{\text{H}_2\text{O}}=2.2$ kPa (Figure 3a). Although R_0 scales with h_{Cu} , our results showing that $R_0 \ll h_{\text{Cu}}$ suggests that plasticity is localized near the interfacial crack tip where debonding occurs. Examining the variations of γ_p (Figure 2) and R_0 (Figure 3a) with respect to h_{Cu} , we find that γ_p scales linearly with R_0 (Figure 3b) as expected for small-scale yielding[25]. This trend is consistent with our observation of $\gamma_p=0$ for $h_{\text{Cu}} \leq 12$ nm due to high σ_y in thinner films.

In order to assess temperature and moisture effects, we measured the interfacial fracture energy Γ_{FT} of structures with a fixed $h_{\text{Cu}}=100$ nm for $278 \text{ K} \leq T \leq 358 \text{ K}$ and $0.158 \text{ kPa} \leq p_{\text{H}_2\text{O}} \leq 40.6 \text{ kPa}$. For a constant $p_{\text{H}_2\text{O}}$, Γ_{FT} increases with temperature (Figure 4). This overall trend is attributable to increased γ_p due to temperature-induced reduction in yield stress[26] despite any decreases in γ_a . At temperatures >300 K, we observe two different rates of Γ_{FT} increase as $p_{\text{H}_2\text{O}}$ decreases. At high $p_{\text{H}_2\text{O}}$ (regime I) at a given temperature, the rate of Γ_{FT} increase is small, which is consistent with limited localized crack tip plasticity expected at low γ_a . Decreasing $p_{\text{H}_2\text{O}}$ increases γ_a due to diminution of moisture-induced siloxane bond weakening and scission[10]. The increased γ_a at lower $p_{\text{H}_2\text{O}}$ supports a much higher γ_p , leading to a higher Γ_{FT} (regime II). We do not observe the bond-breaking regime I for thicker films at $T < 323$ K because water chemical potentials above 20 meV are inaccessible in our experiments at these temperatures. This single regime of plasticity is analogous to linear increase in plasticity with increasing h_{Cu} due to σ_y

reduction with Cu film thickness, described earlier. Collectively, these results thus indicate that the temperature-induced yield stress decrease significantly increases γ_p , offsetting any decreases in γ_a .

In summary, we have investigated the effects of moisture and temperature on the work of adhesion and metal plasticity for a metal-dielectric heterointerface modified with a nanomolecular layer. Our results indicate that copper film yielding occurs only above a critical film thickness. While humidity decreases the work of adhesion and the fracture energy at all thicknesses, increasing the temperature increases the fracture energy by lowering the yield stress for films above a critical thickness. These findings provide an atomistic understanding of heterointerfacial fracture, which should be important for designing heterointerfaces for applications involving exposures to thermo-mechano-chemical stresses.

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Figure 1. Fracture energy Γ_{FT} at 298 K as a function of chemical potential for a Cu film thickness (a)

$12\text{ nm} \leq h_{Cu} \leq 340\text{ nm}$ and (b) $h_{Cu} = 12\text{ nm}$ and $h_{Cu} = 35\text{ nm}$.

Figure 2. Plots capturing the effects of h_{Cu} on the minimum plasticity $\gamma_{\text{p-min}}$ at $p_{\text{H}_2\text{O}} = 2.22$ kPa and maximum plasticity $\gamma_{\text{p-max}}$ at $p_{\text{H}_2\text{O}} = 0.633$ kPa, and the rate of increase of fracture energy Γ_{FT} with respect to the natural logarithm of water partial pressure.

Figure 3. (a) Plastic zone radius (open symbols) and yield stress (closed triangle) calculated from the adhesive strength γ_a at $p_{H_2O} = 0.633 \text{ kPa}$ (circles) and at $p_{H_2O} = 2.22 \text{ kPa}$ (squares) and nanoindentation measurements on Cu films with $h_{Cu} > 75 \text{ nm}$. (b) Linear relationship between calculated plastic zone radius and interface plastic energy, yields a slope of 2.07 GPa.

Figure 4. Fracture energy of Cu/NML/silica interfaces obtained as a function of chemical potential at different temperatures and water partial pressures for structures with $h_{Cu} = 100$ nm. Two regimes are seen at 358 K (stars) and 323 (triangles), while at 284 K (squares) and 278 K (circles) only the second regime is seen.

Graphical Abstract