

**Chemistry-Property Relationships at Molecularly Modified  
Copper-Silica Interfaces**

by

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## ABSTRACT

Self-assembled molecular nanolayers (MNLs) present a convenient and versatile platform to tailor the surface and interfacial properties of metals, ceramics and metal-oxides and render them useful for a variety of technological applications. MNLs provide a methodology for toughening metal-dielectric interfaces through chemical bonding. MNLs can also inhibit chemical mixing through strong bonding between the terminal moieties of the MNL and the metal. In addition, this framework can be adapted to eliminate separate glue layer altogether, by modifying dielectric materials with functional groups responsible for interfacial toughening to obtain adherent metal-dielectric interfaces. It is crucial to develop a fundamental understanding of the MNLs with respect to the parameters such as functional groups, chain length and thermal stability to fully utilize them in nanodevice applications. This work addresses some of the key challenges related to modifying Cu-silica interfaces with MNLs and examines the effect of functional group and interface chemistry on the mechanical properties of the engineered bimaterial interfaces.

Thermal annealing of Cu-silica interfaces tailored with MNLs lead to interface toughening through the formation of strong bonding. An important finding of this thesis is the application of strained low-polarizability cyclic rings as MNLs, which can toughen the interface through Cu-catalyzed bonding. Seven fold increase in interface toughening is reported through annealing by using cyclic moieties in MNL at Cu-silica interface. The increase is due to strong chemical bonding at the Cu-MNL and MNL-silica interface. These findings open up possibilities for directly integrating metals with low-permittivity dielectrics without using an additional glue layer, for various technological applications. Another important conclusion is that the cyclic moieties can be used to clean the native-oxide of the copper through chemical interaction. This process of chemical reduction of copper-oxide could be exploited for cleaning and passivation of Cu wiring which results in lowering of surface-scattering induced resistivity.

A crucial finding of this thesis is the fundamental understanding of the MNL decomposition induced interface toughening of Cu-silica interface. The results indicate that thermal decomposition of MNL into its inorganic constituents and consequent intermixing can provide an interface toughening mechanism. Organogermane and

organosilane MNLs are compared to study the effect of chemical bonding. Germanium transport from organogermane MNLs in integrated structures results in the formation of nano-islands of copper silicate, which is not observed in organosilane MNL. This shows that subtle changes in the MNL chemistry can have a profound influence on the interfacial phase formation at Cu-silica interface. These findings reveal that MNL decomposition at a buried Cu-silica interface could result in interface toughening and by appropriate choice of MNL, this concept can be extended to other bimaterial systems.

Self assembled molecular nanolayers composed of organic functional groups and short methylene chain length are an attractive alternative as diffusion barriers and adhesion promoters at Cu-silica interface. This work demonstrates that low-polarizability hydrophobic moieties in MNLs can inhibit copper diffusion by suppressing the Cu ion formation at the interface. This is due to the decreased interface moisture which can suppress copper-oxide formation and hence formation of Cu ions. Results show that the barrier properties are enhanced in the absence of chemical bonding across copper-MNL interface indicating that the fluoroalkyl moieties in MNL inhibit Cu ion formation and transport.

This work also develops the fundamental understanding of the energy dissipation processes which contributes to the measured interface toughness obtained from a four-point bend test. The fracture toughness was studied as a function of different corrugation orientations and aspect ratios. The results reveal up to a ten-fold increase in interface toughness due to increased debonding area, debond shielding at corrugation asperities and plasticity. The results show that debond shielding and plasticity are coupled. This study also presents an alternative methodology to toughen the heterogeneous interfaces where other chemical functionalization or treatments may be undesirable.