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Self-assembled subnanolayers as interfacial adhesion enhancers and diffusion barriers for integrated circuits

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Preserving the structural and functional integrity of interfaces and inhibiting deleterious chemical interactions are critical for realizing devices with sub-50 nm thin films and nanoscale units. Here, we demonstrate that ~ 0.7-nm-thick self-assembled monolayers (SAMs) comprising mercapto-propyl-tri-methoxy-silane (MPTMS) molecules enhance adhesion and inhibit Cu diffusion at Cu/SiO_2 structures used in device metallization. $Cu/SAM/SiO_2/Si(001)$ structures show three times higher interface debond energy compared to Cu/SiO_2 interfaces due to a strong chemical interaction between Cu and S termini of the MPTMS SAMs. This interaction immobilizes Cu at the Cu/SAM interface and results in a factor-of-4 increase in Cu-diffusion-induced failure times compared with that for structures without SAMs. © *2003 American Institute of Physics.*
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Isolating individual components of nanoscale architectures comprised of thin films or nanostructures, without significantly impacting their functionalities, is a critical challenge in micro- and nanoscale device fabrication. One important example that illustrates this challenge is seen in Cu-interconnected sub-100 nm devices structures, which require <5-nm-thick interfacial layers to inhibit Cu diffusion into adjacent dielectrics, and to enhance interfacial adhesion.[1] Currently used interfacial barrier materials such as Ta, TaN, and TiN, deposited by conventional methods cannot form uniform and continuous layers below 10 nm thickness, especially in high depth-to-width aspect ratio features. Thicker layers take up the space meant for low-resistivity Cu, neutralizing the advantages of miniaturization. Newly emerging methods such as atomic layer deposition have the potential to obviate some of these concerns. However, even if <5-nm-thick conformal films of conventional barrier materials are achieved, it is not clear if they will be effective due to high defect densities and fast diffusion paths such as nanopipes[2] or grain boundaries. Hence, there is a great deal of interest in exploring alternative materials and processing methods.

Recently we reported the concept of using self-assembled molecular layers (SAMs) of organosilanes to inhibit Cu diffusion into SiO_2 in microelectronics devices.[3] SAMs have been widely studied due to their attractive properties, which can be tuned through suitable choice of chain length and terminal groups, for a number of applications such as molecular devices, lithography, and micromachines.[4]

Here, we use sub-nanometer-thick SAMs to enhance both diffusion barrier and adhesion properties of Cu/SiO_2 interfaces through strong local chemical interaction between interfacial Cu and the terminal groups of SAMs. This strategy realizes two concepts: (a) a strong interfacial bonding which also immobilizes Cu, and (b) creation of a vacuum-like potential barrier between the Cu and the dielectric layer to inhibit Cu ionization and transport.[5] The first criterion can be achieved through strong, local chemical interactions by choosing appropriate terminal groups, and the second can be accomplished by using SAMs with suitable chain lengths. This approach offers the potential for tailoring effective barriers with decreased thicknesses (e.g., 1–2 nm) because strong local chemical bonding obviates the need for interfacial mixing that is generally necessary for obtaining adhesion with conventional barriers. Interfacial mixing in nanometer-thick barriers is undesirable because the resultant effects such as crystallization, phase formation or grain boundary generation can dramatically degrade barrier properties.

We demonstrate the dual use of ~ 0.7-nm-thick SAMs comprising mecapto-propyl-trimethoxy-silane $[(HS\text{-}(CH_2)_3\text{-}Si\text{-}(OCH_3)_3\text{—}MPTMS]$ molecules for inhibiting Cu diffusion and enhancing adhesion at Cu/SiO_2 interfaces. The strong chemical interactions between Cu and thiol (–SH) termini in MPTMS SAMs at Cu/SiO_2 interfaces enhance interfacial adhesion by a factor of 3 and increase failure times for Cu-transport-induced SiO_2 breakdown by a factor of 4.

$Cu/MPTMS/SiO_2$ structures were fabricated on n-type, device-quality Si(001) wafers with a 100-nm-thick dry thermal SiO_2 layer grown at 1000 °C. The wafers were cleaned successively in xylene, acetone, isopropanol, and de-ionized (DI) water, and dried in flowing N_2. The SiO_2 surfaces were
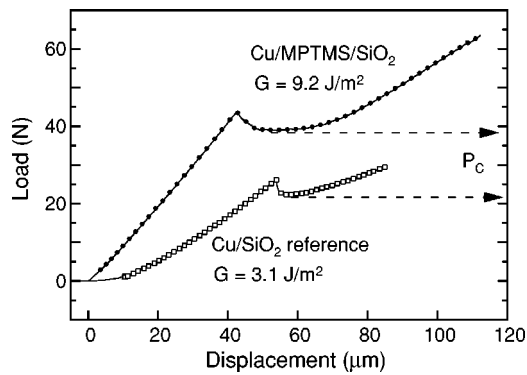

FIG. 1. Load vs displacement plots for Cu/MPTMS/SiO$_2$/Si and Cu/SiO$_2$/Si structures. Arrows indicate the critical load P_C at which interfacial delamination occurs.

FIG. 2. Representative XPS survey spectra from SiO$_2$ fracture surface of a delaminated Cu/MPTMS/SiO$_2$ sample, and an untreated SiO$_2$ reference sample.

either treated in a 30% H$_2$O$_2$–70% H$_2$SO$_4$ solution at 60 °C for 30 min, or an ozone plasma for 15 min, to facilitate SAM formation through surface hydroxylation. MPTMS SAMs were formed on SiO$_2$ by dipping the wafers in a 5 mM MPTMS solution in toluene for 30 min, and dried, in a N$_2$ glove box. The samples were rinsed with toluene and methanol, and dried with a N$_2$ jet to remove excess MPTMS molecules unattached to SiO$_2$.

Variable angle spectroscopic ellipsometry (VASE) carried out in a VASE M-44 instrument at 60°–70° incident angles show that our MPTMS SAMs have a thickness of 0.67±0.1 nm, in good agreement with the theoretical molecular length ($\sim$0.7 nm)[6] of MPTMS. Sessile 50 μL DI water drops on MPTMS exhibit a contact angle of 46.6° ±1.6°, characteristic of thiol-terminated hydrophilic SAM surfaces. These results indicate that MPTMS molecules organize themselves at a canted angle forming an ordered monolayer.[7]

A 65-nm-thick Cu layer was deposited on the SAM/SiO$_2$/Si(001) and reference SiO$_2$/Si(001) structures in a CVC dc sputter tool (base pressure 9×10^{-7} Torr). The Cu/SAM/SiO$_2$/Si(001), and Cu/SiO$_2$/Si(001), stacks were bonded onto a Si(001) support wafer with an epoxy for interfacial adhesion tests. Interfacial debond energies were measured from the load-displacement curves obtained at a strain rate of 300 nm/s using a high-stiffness four-point-bend micromechanical test system, as described previously.[8] At least six tests were conducted on each sample-type to verify reproducibility. X-ray photoelectron spectroscopy (XPS) measurements were carried out to investigate interface chemistry on as-prepared and fracture surfaces in a PHI 5400 instrument with a Mg K_α probe beam.

Figure 1 shows representative load versus displacement plots obtained from adhesion test samples of Cu/SAM/SiO$_2$ and Cu/SiO$_2$ structures. The plateaus observed in the two curves correspond to the respective critical loads P_C at which debonding occurs at the weakest interface. Cu/MPTMS/SiO$_2$ structures show a P_C of $\sim$38 N, which is a factor of 1.7 higher than the critical load of $\sim$22 N needed to debond the Cu/SiO$_2$ interface. Since plastic flow in SiO$_2$ and Cu are constrained under our loading conditions, the interfacial debond energy (G) was determined from the equation $G = K(1 - \nu^2)P_C^2/E$.[8] E and ν are the elastic modulus and poisson's ratio of the substrate, respectively, and K is
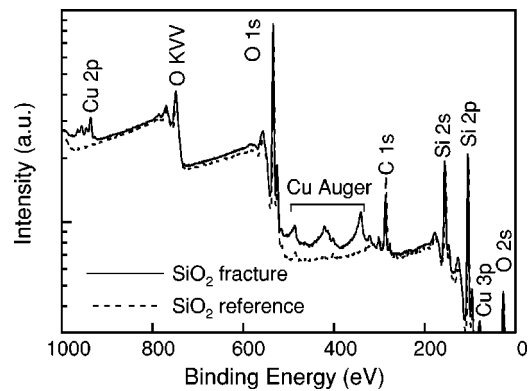
a constant that is dependent on the loading geometry and the substrate thickness. Our results show that Cu/MPTMS/SiO$_2$ structure has a debond energy of 9.2 J/m^2, which is $\sim$3 times higher than that of pristine Cu/SiO$_2$ interfaces (3.1 J/m^2).

In order to understand the delamination mechanism, we probed the fracture surfaces using XPS. Figure 2 compares representative spectra (plotted on a log scale to reveal weak peaks) obtained from a SiO$_2$ fracture surface, and a SiO$_2$ reference sample. The low-intensity Cu 2p, and 3p bands, and Auger peaks—arising from trace amounts of Cu on SiO$_2$ fracture surfaces—indicate that the measured debond energies provide a lower bound estimate for MPTMS-treated Cu/SiO$_2$ interfaces.

High-resolution XPS measurements, described later, show that S is bound to the Cu fracture surface and is covered by silyl-propyl [−CH$_2$)$_3$−Si<−] moieties which detach from the SiO$_2$ surface. SiO$_2$ fracture surfaces did not show any detectable S 2p bands [see Fig. 3(a)], while Cu fracture surfaces exhibit a weak S 2p peak at $\sim$162.5 eV. This band is $\sim$1.5 eV lower than that obtained from reference MPTMS SAMs on SiO$_2$, suggesting a chemical interaction between S and Cu. This inference is corroborated by Cu fracture surfaces [see Fig. 3(b)] showing a Cu(II) subband at $\sim$934.5 in addition to the elemental Cu(0) band at $\sim$932 eV. At least a part of this Cu(II) subband intensity is due to Cu–S interactions,[9] confirmed by a much weaker Cu(II)/Cu(0) intensity ratio observed in reference Cu samples with a surface oxide.

Cu fracture surfaces also exhibit a Si 2p band [Fig. 3(c)] at $\sim$101.7 eV, which is a signature of silyl-alkyl moieties.[10,11] This band is seen in reference samples of MPTMS on SiO$_2$ as a low-energy shoulder to the Si 2p peak at $\sim$103.5 eV from SiO$_2$, but is absent in spectra from pristine as well as fracture surfaces of SiO$_2$. The presence of silyl-alkyl groups is consistent with Cu fracture surfaces showing a strong C 1s band (Fig. 2) and a weak S 2p band intensity, the latter due to signal attenuation.

The earlier results demonstrate that Cu/MPTMS/SiO$_2$ structures delaminate at the SAM/SiO$_2$ interface. The terminal S atoms of the SAM are strongly bound to the Cu surface, and the propyl-silane moieties end up on the Cu fracture surface by detaching from the SiO$_2$ surface. Since Si–O–Si bonds are strong compared to Cu–S interactions,[11] we
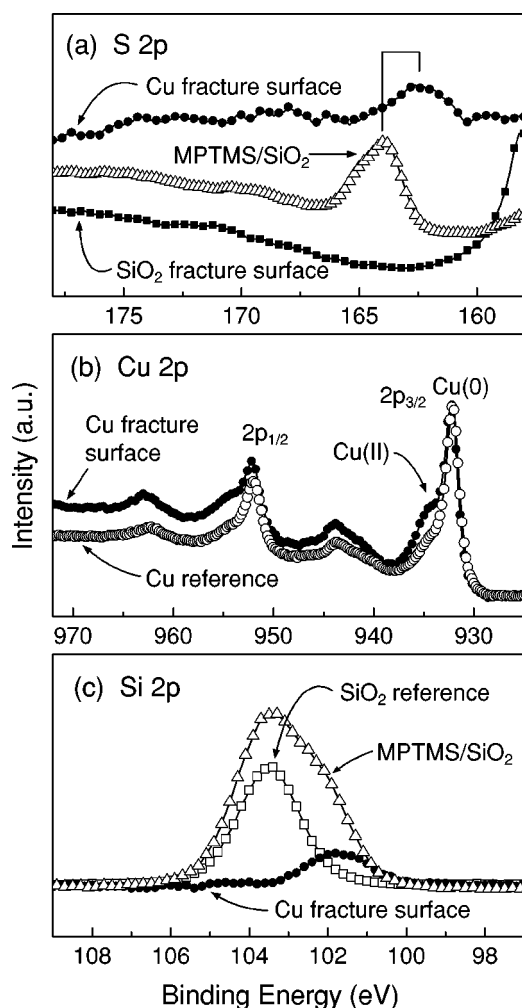
FIG. 3. High-resolution XPS spectra showing (a) S $2p$, (b) Cu $2p$, and (c) Si $2p$ bands from Cu and SiO_2 fracture surfaces (filled legends). Reference spectra (open legends) from untreated SiO_2, Cu, and MPTMS SAM surfaces are also shown.
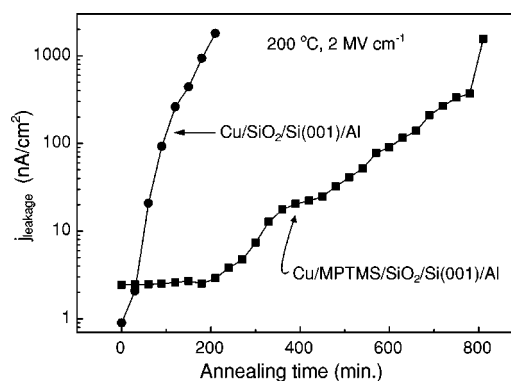

FIG. 4. Leakage current density plotted as a function of bias-thermal annealing time for MOS capacitors with and without MPTMS SAM at the interface.

sample to room temperature for each measurement, until electrical breakdown of SiO_2 characterized by $j_{leakage}$ > 1000 nA cm^{-2}. Our results (see Fig. 4) demonstrate that MPTMS SAMs indeed hinder Cu diffusion into SiO_2. Capacitors with MPTMS at the interface show lower leakage currents and a factor of 4 increase in time for Cu-transport-induced SiO_2 breakdown, compared with those measured from capacitors without a SAM.

In summary, subnanometer layers comprised of molecules such as MPTMS offer an attractive mechanism for enhancing interfacial adhesion and inhibiting Cu transport across Cu/SiO_2 interfaces through local chemical immobilization of Cu. Similar strategies with SAMs of difunctional molecules open up possibilities for preserving structural and functional integrity of interfaces between nanoscale units of newly evolving device structures.

[1] S. P. Murarka, Mater. Sci. Technol. **17**, 749 (2001).
[2] G. Ramanath, J. R. A. Carlsson, J. E. Greene, L. H. Allen, V. C. Hornback, and D. J. Allman, Appl. Phys. Lett. **69**, 3179 (1996).
[3] A. Krishnamoorthy, K. Chanda, S. P. Murarka, J. G. Ryan, and G. Ramanath, Appl. Phys. Lett. **78**, 2467 (2001).
[4] A. Ulman, *Introduction to Ultathin Organic Films: From Langmuir-Blodgett to Self-Assembly* (Academic, San Diego, 1991).
[5] J. D. McBrayer, R. M. Swanson, and T. W. Signmon, J. Electrochem. Soc. **133**, 1243 (1986).
[6] E. T. Vandenberg, L. Bertilsson, B. Liedberg, K. Uvdal, R. Erlandsson, H. Elwing, and I. Lundstrom, J. Colloid Interface Sci. **17**, 103 (1991).
[7] M. Hu, S. Noda, T. Okubo, Y. Yamaguchi, and H. Komiyama, Appl. Surf. Sci. **181**, 307 (2001).
[8] R. H. Dauskardt, M. Lane, Q. Ma, and N. Krishna, Eng. Fract. Mech. **61**, 141 (1998).
[9] G. Seshadri, H. C. Xu, and J. A. Kelber, J. Electrochem. Soc. **148**, B222 (2001).
[10] R. L. Schmitt, J. A. Cardella, J. H. Magill, and R. L. Chin, Polymer **28**, 1462 (1987).
[11] *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide (CRC Press, Cleveland, OH, 1999).

attribute delamination at the MPTMS/SiO_2 interface to the inadequate number of Si–O–Si bonds between MPTMS and SiO_2 during self-assembly. Formation of lateral siloxane linkages between adjacent organosilane molecules is the likely reason for insufficient Si–O–Si bonds with the substrate. Devising processes to form SAMs with increased siloxane linkages with the substrate are expected to lead to further enhancements in adhesion.

In order to investigate if the strong chemical interactions between Cu and S in MPTMS SAMs inhibit Cu diffusion into SiO_2, we carried out bias thermal annealing tests on Cu/SAM/SiO_2/Si(001)/Al metal–oxide–semiconductor (MOS) capacitors in flowing N_2 at 200 °C in a 2 MV/cm electric field. The MOS structures were fabricated by standard procedures described previously.[3] The leakage current $j_{leakage}$, due to Cu diffusion,[3,5] was recorded at 30 min intervals using a HP4140 picoammeter, after cooling the