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Polyelectrolyte nanolayers as diffusion barriers for Cu metallization

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Cu interconnect technology requires the use of <5-nm-thick interfacial layers to inhibit Cu transport into adjacent dielectric layers. We demonstrate the use of 3.5-nm-thick polyelectrolyte layers comprising polyethyleneimine (PEI) and polyacrylic acid (PAA) for this application. $Cu/PAA/PEI/SiO_2/Si$ structures show more than a factor-of-5 greater failure time compared to that observed in $Cu/SiO_2/Si$ structures. Increasing the number of PAA/PEI bilayers does not show any further improvement in barrier properties. Spectroscopic probing of the Cu/PAA interface reveals that polychelation of Cu with carboxyl groups in PAA is the primary reason for Cu immobilization. Our study suggests that polyelectrolyte nanolayers are attractive for applications such as tailoring barrierless low-k polymeric dielectrics, and for isolating nanoscale components in future device systems. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1618951]

Cu interconnect technology for sub-100-nm-scale devices requires the use of <5-nm-thick barrier layers to prevent Cu transport into adjacent dielectric materials, which degrades device reliability and performance. Currently used interfacial barrier layers based on transition metals[1] formed by conventional deposition methods are not continuous and uniform at thicknesses $\lesssim 10$ nm, especially in high-aspect-ratio features. Higher barrier thicknesses take up the space meant for low-resistivity Cu and neutralize the advantages of Cu metallization. Furthermore, it is not clear if <5-nm-thick conventional barrier materials will be effective due to issues such as the presence of fast diffusion paths, grain boundary generation, and phase formation caused by interfacial intermixing. Thus, there is interest in exploring nanolayers of alternative barrier materials formed by different types of processing techniques.

We recently demonstrated the use of nanolayers[2] and subnanolayers[3] of self-assembled amphiphilic organosilanes as diffusion barriers. The underlying rationale is to immobilize Cu through strong local interfacial bonding with short-chained molecular moieties, and create a vacuum-like potential barrier between the Cu and the dielectric to prevent Cu ionization and transport. Here, we describe a variant of this overall approach: harnessing polyelectrolyte nanolayers to inhibit Cu diffusion across dielectrics.

Previous works have reported the use of polyelectrolytes with appropriate functional groups to immobilize metal ions through electrostatic, covalent or coordinate-covalent interactions.[4,5] Forming ultrathin polymeric films through electrostatic adsorption is a simple, versatile technique[6] that can be integrated with current fabrication methods. Furthermore, the use of polymeric structures as barriers could open up possibilities of integrating them, or their constituents, with low-k dielectric materials or their precursors, thereby obviating the need for barriers for Cu/low-k metallization technology.

The substrates used in our experiments were device-quality n-type Si(001) wafers with an 85-nm-thick thermal SiO_2 layer. Each wafer was successively rinsed ultrasonically in acetone, methanol and deionized water. A 500-nm-thick Al back-contact was sputter-deposited in a 5-mTorr Ar plasma after stripping the back oxide with HF. Polymer bilayers of polyethyleneimine (PEI) and polyacrylic acid (PAA) layers were adsorbed onto the $SiO_2/Si(001)/Al$ structures by sequential immersion in 10 mM solutions (pH $=8.69$ for PEI and 3.52 for PAA) of the respective polyelectrolytes, for 20 min at room temperature. PEI was obtained from Sigma-Aldrich® and the PAA was obtained from Acros organics®.[7] PEI was the first layer on SiO_2, and PAA polyanion layer was electrostatically attached to PEI. Each adsorption step was followed by a 5-min water rinse to remove unattached molecules, and the sample was dried gently in flowing N_2. The thickness of each polyelectrolyte layer, characterized by variable angle spectroscopic ellipsometry, was ~ 1.5–2 nm. PAA surfaces exhibit contact angles of $34\pm 3°$, consistent with the hydrophilic characteristics of the constituent carboxyl (–COOH) groups, while PEI surfaces show a significantly higher value of $47\pm 3°$.

A 100-nm-thick Cu film was sputter-deposited on the polyelectrolyte bilayers or multilayers through a shadow mask to obtain $Cu/polymer/SiO_2/Si(001)/Al$ metal-oxide-semiconductor (MOS) capacitor structures with 1.2-mm-
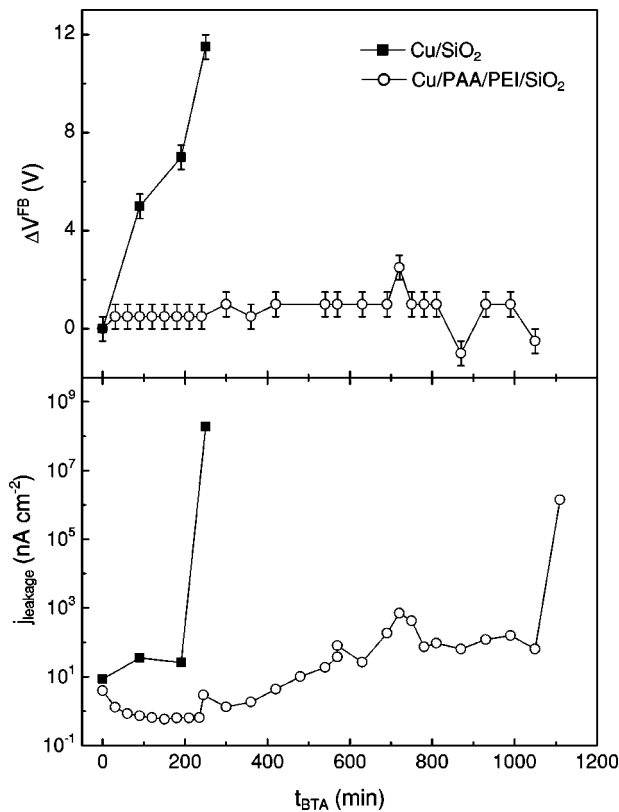
FIG. 1. ΔV^{FB} and $j_{leakage}$ plotted vs t_{BTA} for Cu/PAA/PEI/SiO$_2$/Si/Al (closed legend) and Cu/SiO$_2$/Si/Al capacitors (open legend).
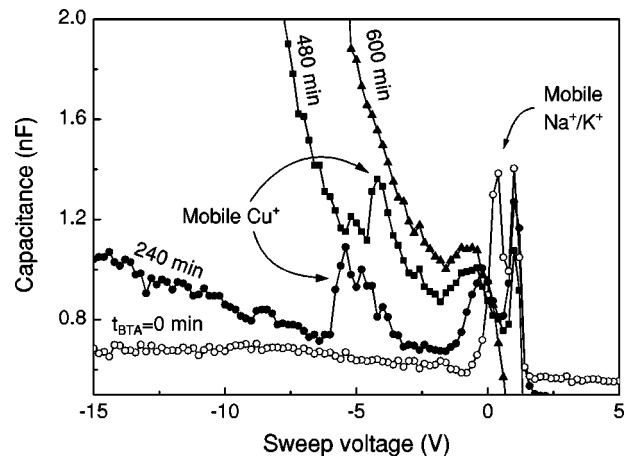

FIG. 2. Triangular voltage sweep spectra obtained at a 0.02 V/s sweep rate for Cu/PAA/PEI/SiO$_2$/Si/Al capacitors annealed at 200 °C in a 2 MV/cm electric field for different t_{BTA}.

diameter gate contacts. Reference samples of Cu/SiO$_2$/Si/Al MOS structures without the polymer layers were also fabricated. Bias thermal annealing (BTA) tests on the MOS structures were carried out in flowing N$_2$ at 200 °C and a 2-MV cm^{-1} electric field. The samples were rapidly cooled to 30 °C at 30-min intervals to record leakage-current versus voltage (I–V), and triangular voltage sweep (TVS) characteristics using HP4280 and HP4140 instruments. The C–V and I–V results were similar to what has been reported previously.[2,3]

Flatband voltage shifts (ΔV^{FB}) and increases in leakage current density $j_{leakage}$ in Cu/SiO$_2$/Si/Al MOS structures are characteristic signatures of Cu ion diffusion into SiO$_2$. Comparisons of ΔV^{FB} and $j_{leakage}$ characteristics of Cu/PAA/PEI/SiO$_2$/Si/Al structures and reference structures without the polymer bilayer indicate that the PEI/PAA bilayer inhibits Cu diffusion into SiO$_2$. Figure 1 plots ΔV^{FB} and $j_{leakage}$ values as a function of BTA time (t_{BTA}), for MOS structures with, and without (reference sample), a PAA/PEI bilayer at the Cu/SiO$_2$ interface. In the reference samples, ΔV^{FB} rapidly increases with t_{BTA} reaching ~ 7 V at ~ 190 min. In contrast, the ΔV^{FB} of structures with a PAA/PEI bilayer are nearly constant: at $\lesssim 1$ V even at $t_{BTA} = 1050$ min. These results bear a strong correlation with the $j_{leakage} - t_{BTA}$ characteristics for the two types of MOS structures. In the reference sample, $j_{leakage}$ rapidly increases to $> 10^3$ nA/cm^2 at $t_{BTA} \sim 190$ min, indicating the dielectric breakdown of SiO$_2$ due to Cu ion drift.[8] The $j_{leakage}$ in MOS capacitors with the polymer bilayer was only ~ 10 nA/cm^2 up to $t_{BTA} = 1050$ min, after which the SiO$_2$ dielectric breakdown occurs. Thus, the use of a PAA/PEI bilayer at the Cu/SiO$_2$ interface increases the SiO$_2$ breakdown time by

more than a factor of 5. We further note that at t_{BTA} corresponding to SiO$_2$ breakdown in the reference sample, the $j_{leakage}$ in samples with the polyelectrolyte bilayers is more than 5 orders of magnitude smaller.

Triangular voltage sweep spectra from Cu/PAA/PEI/ SiO$_2$/Si/Al MOS structures indicate that the leakage currents reported here arise due to Cu ion drift. This is seen from the emergence of a distinct peak at ~ -5 V due to mobile Cu ions[9] after BTA for 240 min (see Fig. 2). While further annealing increases the intensity of this peak, it is relatively small and is obscured by the leakage current increase due to the onset of SiO$_2$ degradation. Note that the Cu peak is absent at $t_{BTA} = 0$. The peaks near 0 V present in all the spectra are from residual Na$^+$ or K$^+$ mobile ions in SiO$_2$.[10]

We carried out BTA tests of MOS structures with multilayers consisting of different number of alternating PAA and PEI layers at the Cu/SiO$_2$ interface to probe the barrier mechanism. Figure 3 shows the SiO$_2$ breakdown time for MOS structures as a function of total thickness of polyelectrolyte layers. Our results show no significant differences in failure times of MOS structures with a PAA/PEI bilayer and those with a PAA/PEI/PAA/PEI quadruple layer. We note that in both these cases, the PAA layer is in contact with Cu. In contrast, MOS structures with 3 and 5 polyelectrolyte
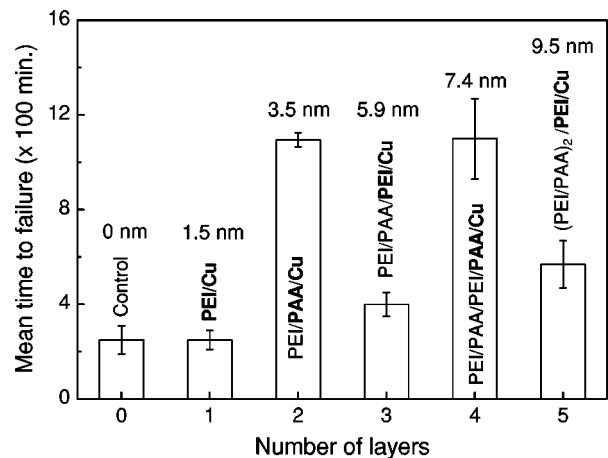

FIG. 3. Device failure times of Cu/SiO$_2$/Si/Al MOS structures plotted as a function of the number of polyelectrolyte layers at the Cu/SiO$_2$ interface. The polyelectrolyte multilayer thickness is also shown for each structure.
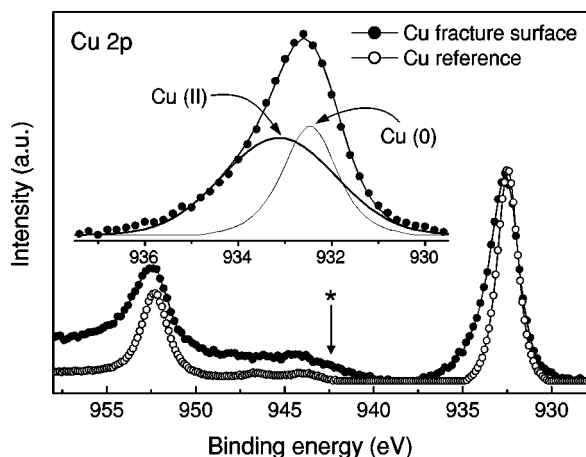
FIG. 4. High-resolution XPS spectra of the Cu $2p$ band obtained from a Cu/PAA/PEI fracture surface (closed circles) and a Cu surface without a surface oxide (open circles).* points to the expected Cu(II) satellite peak position for Cu oxides—absent in our samples. Inset shows a magnified version of the Cu $2p_{3/2}$ band with the two subband components.

layers, namely, PEI/PAA/PEI and PEI/PAA/PEI/PAA/PEI respectively, both of which have PEI in contact with Cu—show a factor-of-2 lower failure time compared to the PAA/PEI bilayers. These results strongly suggest that the Cu/polyelectrolyte interface chemistry is the major factor in blocking Cu diffusion.

In order to investigate if Cu ions are immobilized by PAA, we probed the chemistry of the Cu/PAA interface. Cu/PAA/PEI/SiO$_2$/Si structures subject to four-point bending[11] delaminate at the PEI/SiO$_2$ interface. The retention of the Cu/PAA/PEI structure on one end of the fracture surface suggests good adhesion between Cu and PAA. Indeed Cu $2p_{3/2}$ x-ray photoemission spectroscopy (XPS) spectra collected from the PAA/PEI side of the Cu/PAA/PEI fracture surface (see Fig. 4) show a higher binding energy component in addition to the Cu(0) state at $\sim$932.5 eV observed in elemental Cu obtained by sputtering the surface oxide. The inset shows the two Cu $2p_{3/2}$ component subbands superimposed on a high-resolution spectrum obtained from a Cu/PAA/PEI fracture surface. The higher binding energy band centered at $\sim$933.2 eV is consistent with the reported peak position of Cu(II) subband in Cu oxides.[12] However, the absence of satellite peaks associated with the Cu(II) state (see arrow at the expected location) indicates the absence of the Cu oxides at the Cu/PAA interface.

Based upon our results, we propose that the Cu(II) state arises from polychelation between Cu(II) and oxygen in the –COOH groups of the PAA. This attractive interaction results in a higher binding energy Cu(II) peak compared to that of elemental Cu. The absence of satellite peaks, which are typically observed in Cu oxides and many Cu-coordination compounds due to poor screening of core-hole charge by the Cu $3d$ electrons,[13] suggests the prevalence of a metal-like atmosphere at the Cu/PAA interface. This is most likely due to interaction of interfacial Cu with lone pairs of electrons from *several* carboxyl groups at the interface. The proposed scenario is consistent with previous works showing *polychelation* between Cu and carboxyl groups in PAA[5] in the liquid phase.

In PEI-terminated multilayers, the interaction between Cu ions and the PEI cation layer is repulsive, and is hence ineffective in immobilizing of Cu. The inner PAA layers do not immobilize Cu, as seen from the negligible effect of multilayering on devices failure time for PAA-terminated barriers. We attribute this to imidization at PEI/PAA/PEI interfaces and the resultant decrease in the density of carboxyl moieties available for chelating with Cu. This explanation is supported by XPS spectra[14] from PAA/PEI barriers revealing a strong N $1s$ imide subband[15] at 400.5 eV, in addition to the sole peak at $\sim$399.6 eV seen in PEI reference samples.

Thus, polychelation of Cu with PAA at the Cu/PAA interface in PAA-terminated bilayers or multilayers provides a mechanism for immobilizing Cu and for inhibiting its diffusion across the barrier layers. Inducing interfacial polychelation could be a potential tool to offset degradation of barrier properties that have been attributed to interfacial oxygen in metal/polymer structures.[16]

In summary, we have demonstrated that 3.5-nm-thick PAA/PEI polyelectrolyte bilayers inhibit Cu diffusion across Cu/SiO$_2$ interfaces. Cu immobilization through polychelation between Cu and carboxyl groups at the Cu/PAA interface, is the primary barrier mechanism. Multilayering does not further improve the barrier properties exhibited by a single PAA/PEI bilayer. An important consequence of our results is that it is possible to design ultrathin (e.g., <3 nm) polymer layers that inhibit diffusion through strong, highly local, chemical interactions at the interface. This implies that thinner barriers can be as good as thicker versions of the same materials. We expect our findings to open up avenues for improving the integrity of metal/dielectric interfaces, and evolving barrierless polymeric dielectrics.

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