Sacrificial Adhesion Promotion Layers for Copper Metallization of Device Structures

Yinfeng Zong, Xiaoying Shan, and James J. Watkins*

Department of Chemical Engineering, University of Massachusetts, Amherst, Massachusetts 01003

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The adhesion of copper films to adjacent device layers including TiN, Ta, and TaN diffusion barriers is a crucial reliability issue for integrated circuits. We report that ultrathin layers of poly(acrylic acid) (PAA) prepared on barrier surfaces or on the native oxide of Si wafers dramatically increase the interfacial adhesion of Cu films deposited by the H_2 assisted reduction of bis(2,2,7-trimethyloctane-3,5-dionato)-copper in supercritical carbon dioxide. Similar improvements were achieved on Si wafers using a simple vapor phase exposure of the substrate to acrylic acid prior to metallization. The deposited films and the substrate/Cu interfaces were analyzed by X-ray photoelectron spectroscopy (XPS), electron microscopy, atomic force microscopy, and variable-angle spectroscopic ellipsometry. No trace of the adhesion layer was detected at the interface, indicating it was sacrificial at the deposition conditions used. Moreover, the presence and subsequent decomposition of the PAA layer during deposition substantially reduced or eliminated metal oxides at the substrate interface. For depositions on PAA-treated Si wafers, copper was present primarily as Cu^0 at the interface and Si was present only as Si^0. On PAA-treated Ta substrates, XPS analysis indicated Ta was present primarily as Ta^0 at the metallized interface whereas Ta_2O_5 dominated the interface of samples prepared without the adhesion layers. The technique can be extended to patterned substrates using adsorption of acrylic acid or thermal/UV polymerization of acrylic acid.

Introduction

Copper has replaced aluminum as the material of choice for interconnect structures in advanced integrated circuits (ICs). This transition is due to copper's lower electrical resistance and higher electromigration resistance, both of which are required for deep sub-micrometer features currently in production. The integration of Cu, however, poses a number of challenges. It exhibits high diffusivity into Si, necessitating the use of barrier layers. It is easily oxidized, and the oxide layer does not form a self-passivation layer to limit further oxidization. Moreover, adhesion of Cu to adjacent device layers is a significant reliability issue. Excellent adhesion is required to survive the chemical mechanical planarization (CMP) step in the dual damascene process and to achieve acceptable electromigration resistance in interconnect structures.

Cu interconnects are currently produced in a two-step process that consists of the preparation of a continuous seed layer by physical vapor deposition (sputtering) followed by a bottom up fill of the features using electrochemical deposition. Continuity and conformality of the seed layer are crucial, as it serves as the cathode during plating. As the feature aspect ratio increases and device dimensions decrease below 45 nm, the deposition of conformal seed layers by PVD, nominally a line of sight technique, is problematic. This challenge, combined with the desire to replace current Cu barrier layers such as Ta and TaN with metal films such as Ru has renewed interest in alternative deposition techniques including chemical vapor deposition (CVD), atomic layer deposition (ALD), and supercritical fluid deposition (SFD).

SFD involves the chemical reduction of organometallic compounds in supercritical carbon dioxide to yield conformal depositions of high-purity films.[1−5] Recently we demonstrated the single-step deposition of void-free Cu within high aspect ratio, sub-100-nm features.[6] SFD is essentially a hybrid approach that offers the advantages of solution-based chemistry in a medium that exhibits transport properties similar to a gas. The precursor reduction chemistry is similar to that employed in CVD; however in SFD precursor transport occurs in solution. This obviates precursor volatility constraints and enables depositions at high precursor concentration, which eliminates mass transfer limitations in narrow, high aspect ratio features. The technique can also be applied to pure and doped Co, Pt, Pd, Au, Rh, and Ni films and their alloys.[1,6−9]

While acceptable adhesion for Cu films deposited by PVD can be realized, it has remained problematic for the alternative metallization techniques. This is particularly true of CVD, and poor adhesion remains a significant impediment to the commercialization of Cu CVD for IC fabrication. Poor adhesion for CVD films has been attributed to a number of factors including contamination of the film/substrate interface with fluorine from precursor ligands and the oxidation of adjacent barrier surfaces. The latter is supported by detailed X-ray photoelectron spectroscopy (XPS) analysis of Cu/barrier interfaces, particularly Ta, Ta/TaN, and TiN.[10−13] Similar issues are

* To whom correspondence should be addressed: watkins@ecs.umass.edu.

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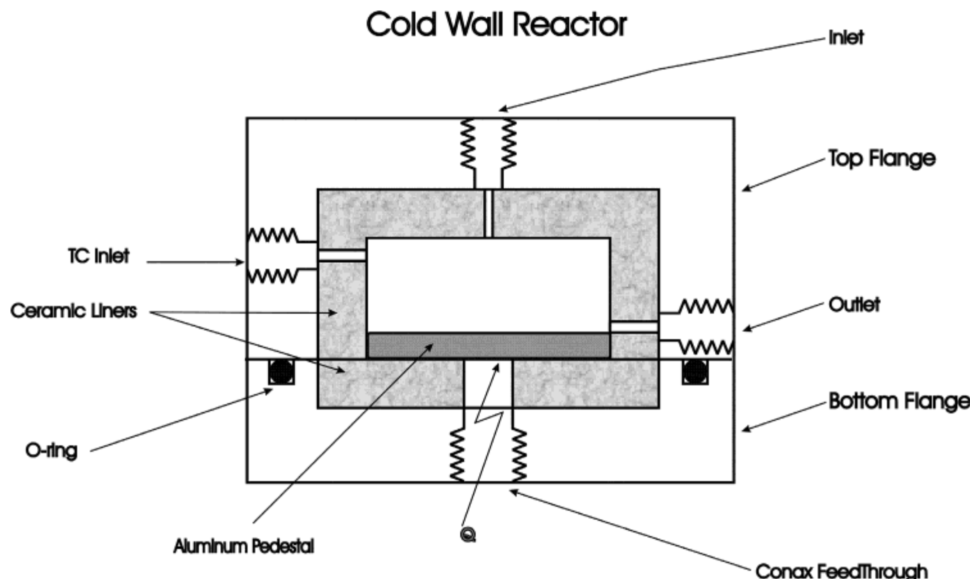

Figure 1. Schematic of a cold wall reactor for supercritical fluid deposition.

likely to dominate for films deposited by SFD and ALD, both of which employ reduction chemistry at the substrate interface.

Previous attempts to improve Cu adhesion to barrier interfaces focused on improving interfacial bonding rather than directly addressing oxidation at the interface. For example, Ramanath et al. employed self-assembled monolayers (SAMs) of (mercaptopropyl)trimethoxysilane prepared on SiO_2 to enhance the adhesion of Cu films deposited by PVD at the SiO_2 interface by a factor of 3.[14] The enhancement was attributed to the strong interactions between the thiol terminus of the silane coupling agent and Cu and thus relies on the presence and stability of the SAM. The presence of the organic layer at the Cu/substrate interface is a potential concern for reliability. Other approaches include alloying Cu with elements including Mg or Al that bond to the barrier surface.[15] In this paper we focus on using PAA as a sacrificial adhesion promotion layer. The adhesion layer is completely consumed during deposition by SFD and its decomposition reduces or eliminates metal oxides at the metal/substrate interface.

Experimental Section

Bis(2,2,7-trimethyloctane-3,5-dionato)copper, [Cu(TMOD)$_2$], was obtained from Epichem, Inc. (Allentown, PA), and used as received. Poly(acrylic acid) (PAA) (25% solution in water, M_w ~90 000) was obtained from Polysciences, Inc. (Warrington, PA), and diluted for spin coating. Acrylic acid was purchased from Sigma-Aldrich Co. (St. Louis, MO) and used as received. N_2 (prepurified grade), H_2 (ultrahigh purity grade), and CO_2 (Coleman grade) were obtained from Merriam Graves Corp. (Charlestown, NH).

Cu deposition was carried out in a cold wall reactor (Figure 1). The reactor consists of opposing 316 stainless steel flanges and has an internal volume of approximately 65 cm^3. The reactor walls were heated by four cartridge heaters. A custom designed 450 W, 2.3 in. diameter aluminum stage heater was installed on the bottom flange using a split gland fitting (Conax Buffalo Corp.). The temperatures of the heated stage and the reactor walls were controlled independently. The reactor walls were insulated internally using nonporous ceramic liners. The top liner has a showerhead design, which evenly distributes the inlet flow. The flanges were bolted together and sealed with a Buna O-ring.

Cu was deposited by H_2 reduction of Cu(TMOD)$_2$ in batch mode. In a typical experiment, the substrate and precursor were loaded into the reactor, the reactor was sealed and flushed with N_2, and the reactor walls were heated to 60 °C. CO_2 at 60 °C and 125 bar was then transferred into the reactor using a high-pressure pump (model 500D, ISCO, Inc.). The reactor was maintained at these conditions for 30−45 min to ensure complete dissolution of the precursor. H_2 was then loaded into the reactor using a high-pressure manifold, and the stage was heated to the desired temperature (225−270 °C) to initiate deposition. The reaction time was 10−20 min in most cases. After the reaction, CO_2 was used to purge the reactor thoroughly to eliminate remaining precursor and byproducts. The effluent was then vented through an activated carbon bed.

The substrates used in the study were Si with ~2 nm native SiO_2 layer (SiO_2/Si), a Si wafer with 1000 Å of copper deposited by PVD (Cu/Si), a Si wafer with 300 Å of TiN deposited by CVD (TiN/Si), a Si wafer with 300 Å of Ta deposited by PVD (Ta/Si), and a Si wafer with 300 Å of TaN deposited by CVD (TaN/Si). Thin films of PAA were spin coated on the substrates from PAA/water solutions.

Adhesion was assessed using a scribe tape test. The test involves scoring the copper film in a crosshatched pattern followed by application and removal of a pressure-sensitive adhesive (PSA). A sample is deemed to pass if no metal is transferred to the PSA after its removal. Although qualitative in nature, the scribe tape method is a demanding test that is commonly employed to assess film adhesion. A Sloan DEKTAK^3 surface profiler was used to obtain the film thickness. The resistance was measured using a Jandel four-point probe. The film surface morphology was imaged using a JEOL JSM-6320FXV field emission scanning electron microscope. Film composition was studied by Quantum 2000 scanning ESCA microprobe (Physical Electronics USA) equipped with an Ar^+ ion sputtering gun. Samples were analyzed using a takeoff angle of 45° and monochromatic Al Kα (1486.6 eV) as the X-ray source. The ion gun sputtering setting was 1 kV, 700 nA, with a 2 mm × 2 mm crater dimension. At these conditions the sputtering rate was approximately 1 nm of Cu/min. The XPS data were analyzed using Multipak (version 6.1A, Physical Electronics USA). The polymer adhesion layer thickness and refractive index were determined using Sopra GES-5 variable-angle spectroscopic ellipsometry with WINELLI V4.07 simulation and analysis program. The surface root mean square roughness of the polymer

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Table 1. Experiment Results of Cu Deposition with PAA Layer

expt	substrate material	PAA thickness (nm)	temp (°C)	pressure (bar)	precursor loading (g)	film thickness (nm)	sheet resistance ($\mu\Omega$ cm)	scribe tape test
1	Si	22.3	225	252	0.2000	no film	N/A	N/A
2	Si	8.6	250	169	0.2022	257.5	2.83	passed
3	Si	17.3	270	227	0.3129	326.5	2.50	passed
4	Si	14.5	270	210	0.3060	479.4	2.39	passed
5	Si	6.8	270	190	0.3075	500.0	2.19	passed
6	Si	6.4	270	193	0.0175	43.6	N/A	passed
7	Si	5.6	270	197	0.0873	169.1	2.30	passed
8	Si	5.0	270	224	0.0253	30.0	N/A	passed
9	Si	4.8	270	197	0.1006	195.4	2.64	passed
10	Si	3.5	270	207	0.3040	267.7	2.21	passed
11	TiN	17.3	270	197	0.3029	388.8	2.50	passed
12	TaN	17.3	270	190	0.3079	350.0	2.50	passed
13	TiN	5.0	270	221	0.0803	118.0	2.93	passed
14	Ta	5.0	270	200	0.0653	143.0	N/A	passed
15	TaN	5.0	270	200	0.0653	226.0	N/A	passed

layers was obtained by using NanoScope IIIa scanning probe microscope (Veeco Instruments).

Results and Discussion

Depositions were conducted between 225 and 270 °C at pressures between 169 and 252 bar (Table 1). In all cases, films deposited onto substrates containing the PAA layer passed the scribe tape test. PAA film thickness as low as 3.5 nm, which was the practical limit for spin-coating uniform films, was effective. Without the PAA layer, Cu films deposited onto these substrates showed much weaker adhesion, failed the scribe tape test, and often delaminated during a simple tape test in which the PSA was applied to the film surface without scoring.

The presence of the PAA adhesion layer increased the temperature required for deposition. Previously we reported that copper could be readily deposited at 225 °C[6] on Si and several barrier layers. On PAA-modified substrates, the required deposition temperature increased to ~250 °C. The resistance of copper films deposited on PAA-modified substrates was as low as 2.2 $\mu\Omega$ cm (Table 1), which meets the requirements of the Semiconductor Industry Association's International Technology Roadmap for Semiconductors.

Field emission scanning electron microscopy (FE-SEM) revealed that Cu films deposited at these conditions are composed of 150–200 nm well intergrown spherical grains (Figure 2). Film purity was assessed by XPS. Figure 3 is an XPS depth profile of a 170 nm thick copper film on a PAA-coated Si substrate (experiment 7) that shows composite spectra for the upper 40 nm of the film. The surface survey is at the bottom, followed by spectra collected at 4 nm intervals. The analysis indicates that carbon and oxygen contamination are present only at the surface and are attributed to ambient contamination. The C 1s signal (284.5 eV) was not detected after the first 4 nm sputtering. The oxygen 1s signal (531.0 eV) was detected only within the first 8 nm of the film and is likely present due to ambient oxidation. The bulk film is essentially free of impurities, which is consistent with the low resistivities measured for these films. It is worth noting that excess H_2 present during Cu film growth suppresses oxidation of Cu during deposition.[7]

The nature of the Cu/substrate interface was studied in detail by careful XPS depth profiling. Figure 4 shows a depth profile of a Cu film deposited on ~5 nm PAA coated Si substrate at 250 °C and 170 bar. The analysis revealed a ~50 nm wide region containing significant concentrations of C and O at the Cu/substrate interface, which are likely vestiges of the polymer adhesion layer.

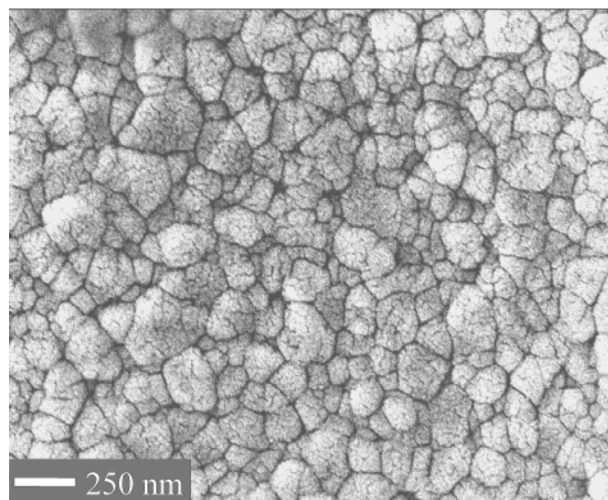

Figure 2. FE-SEM image of a Cu film deposited onto PAA-coated substrate by the H_2-assisted reduction of $Cu(TMOD)_2$ in supercritical CO_2 at 270 °C and 200 bar.

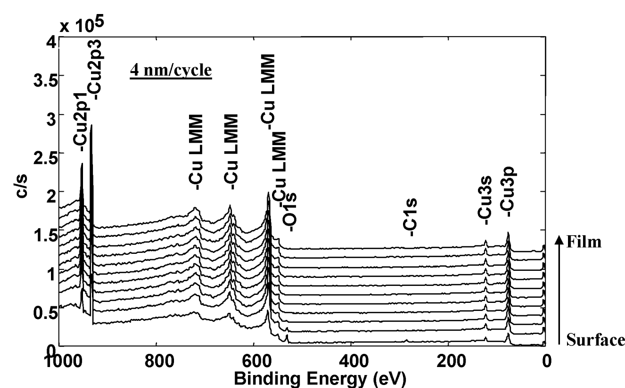

Figure 3. XPS depth profile of a 170 nm thick copper film deposited on a PAA-coated Si substrate by the H_2-assisted reduction of $Cu(TMOD)_2$ in supercritical CO_2 at 270 °C and 197 bar. The spectra are offset for clarity. Only the first 40 nm of film was studied. The bottom spectrum is the surface survey. From the second to bottom spectrum to the top, the surveys were taken at intervals of ~4 nm.

Figure 5A shows an XPS depth profile of a copper film deposited at 270 °C and 170 bar on ~3.5 nm PAA film prepared on the native oxide of Si. Notably absent in the spectrum is any evidence of a carbon- and oxygen-rich region that would be expected for a polymer layer at the Cu/wafer interface. The PAA film if present should be easily detected by depth profiling, even if it were subject

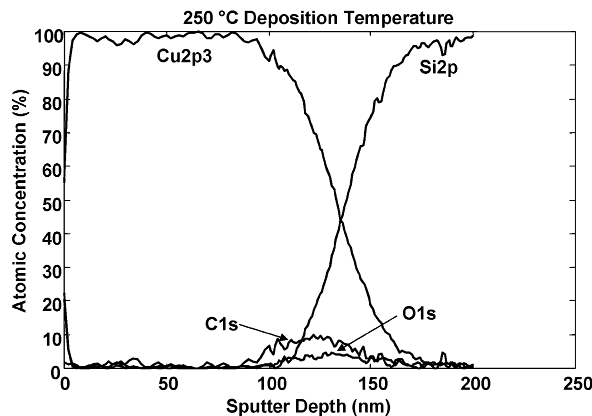

Figure 4. XPS depth profile of a copper film deposited on PAA-coated Si substrate by the H_2-assisted reduction of $Cu(TMOD)_2$ in supercritical CO_2 at 250 °C and 170 bar. High concentrations of carbon and oxygen at the interface are likely vestiges of the PAA layer.

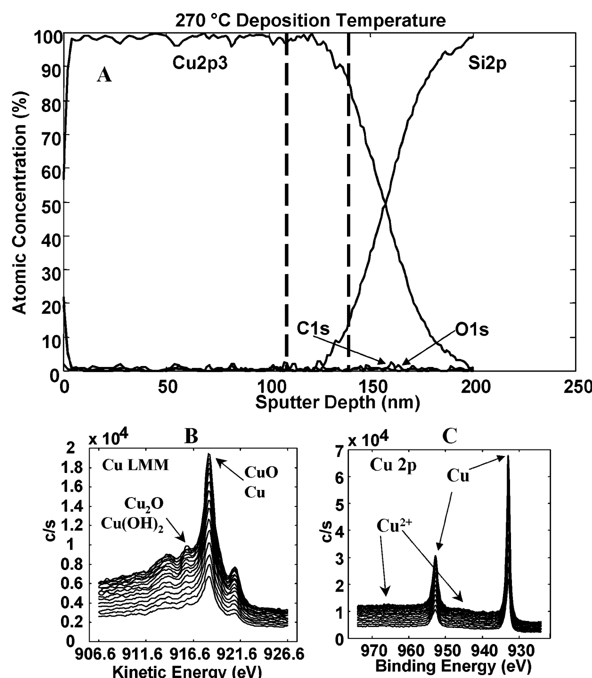

Figure 5. XPS analysis of a copper film deposited on a PAA-coated Si substrate by the H_2-assisted reduction of $Cu(TMOD)_2$ in supercritical CO_2 at 270 °C and 170 bar: (A) depth profile of the film; (B) Cu LMM Auger spectra acquired between the dashed lines shown in the depth profile; (C) Cu 2p spectra acquired between the dashed lines shown in the depth profile. At 270 °C, there is essentially no evidence of the PAA adhesion layer, which is consumed during the deposition.

to degradation during Ar^+ sputtering. The Beer–Lambert relationship [16] can be used to calculate the intensity of electrons (I) emitted from a depth (d) via

$$I = I_0 \exp(-d/\lambda \sin \theta)$$

where I_0 is the intensity from an infinitely thick clean substrate, θ is the electron takeoff angle, and λ is the inelastic mean free path (IMFP) of an electron. The XPS analysis depth is described by $3\lambda \sin \theta$. The IMFP of the C 1s electron in the copper is 1.9 nm.[17] Following this analysis, the carbon signal from the polymer layer can be detected beneath 4 nm of copper. None-the-less, no

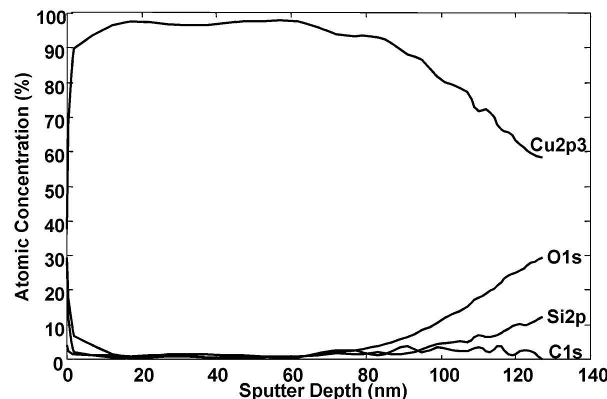

Figure 6. Depth profile of a copper film deposited by the hydrogen-assisted reduction of $Cu(TMOD)_2$ in CO_2 onto a Si substrate with native oxide layer without PAA treatment at 250 °C and 170 bar.

significant C 1s signal is detected near the interface. The analysis of the IMFP suggests that the absence of carbon signal is not simply due to the decomposition of the polymer caused by high-energy ion gun sputtering, as the adhesion layer could be detected while still protected beneath a thin Cu film during the depth profile. Rather the absence of the carbon signal strongly suggests that the PAA layer was completely degraded at 270 °C and the decomposition products extracted into the CO_2 phase during Cu deposition. We will return to this point later.

Gradual depth profiling was also used to study the chemical states of the elements at the interfaces. Parts B and C of Figure 5 are XPS studies of the Cu Auger peak and Cu 2p regions for the Cu film at the substrate interface following deposition on a PAA-coated SiO_2/Si wafer, respectively. The region studied is marked by the dashed lines in the depth profile (Figure 5A). By combining Cu 2p and X-ray induced Auger peaks, it is possible to identify four chemical states of Cu: Cu^0, Cu_2O, CuO, and $Cu(OH)_2$.[13] The binding energy of Cu^0 is 932.7 eV. It is difficult to separate Cu_2O from Cu^0 as the difference of the binding energy is only about 0.1 eV. However, there is a significant difference in the kinetic energy of the Auger peak between Cu^0 and Cu^+. For Cu^{2+}, two apparent satellite peaks appear at higher binding energies relative to the $2p_{1/2}$ and $2p_{3/2}$ peaks, respectively. The results of the depth profile indicate that Cu is present primarily as Cu^0 at the interface.

We also determined the chemical state of Si at the interface of Cu deposited on a SiO_2/Si substrate coated with PAA via XPS depth profiling and compared this result to an experiment in which Cu was deposited on the same type of substrate without the PAA adhesion layer. Figure 6 is a depth profile of a copper film deposited on a Si substrate without a PAA layer. The presence of oxygen at the interface of Cu and Si from the native Si oxide layer is clear. Figure 7 is a comparison of the Si 2p signal after the deposition on the substrate with PAA (Figure 7A) and without PAA (Figure 7B). The spectra were taken during depth profiling across the copper/substrate interface as indicated in the figures. For SiO_2, the Si has a binding energy of 103.3 eV. This peak is clearly identified for Cu SFD deposition without a PAA layer (Figure 7B). However, after deposition with a PAA layer, we found that Si is present as Si^0, which has a binding energy of 99.5 eV.

We also characterized copper films deposited on PAA-coated TiN, TaN, and Ta substrates by using XPS.

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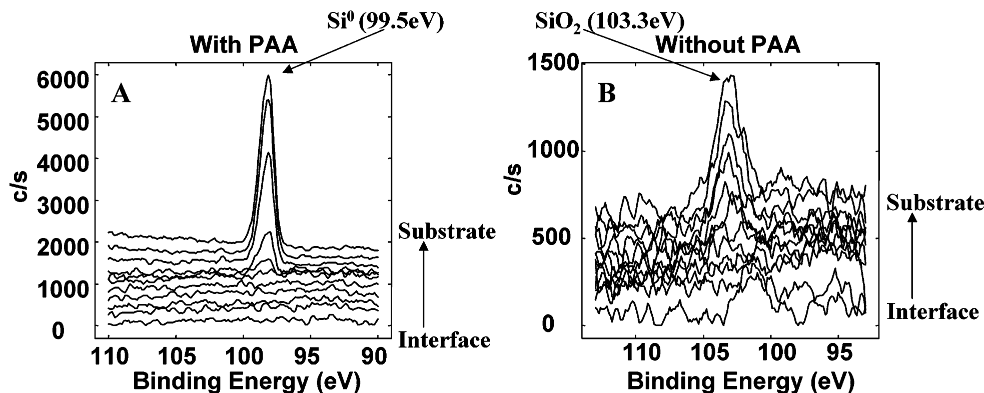

Figure 7. XPS study of Si 2p at the interface: (A) Si chemical state at the interface after H_2-assisted Cu SFD on PAA/native SiO_2/Si substrate at 270 °C and 170 bar; (B) Si chemical state at the interface after a H_2-assisted reduction Cu SFD on native SiO_2/Si substrate at 250 °C and 170 bar without the adhesion layer.

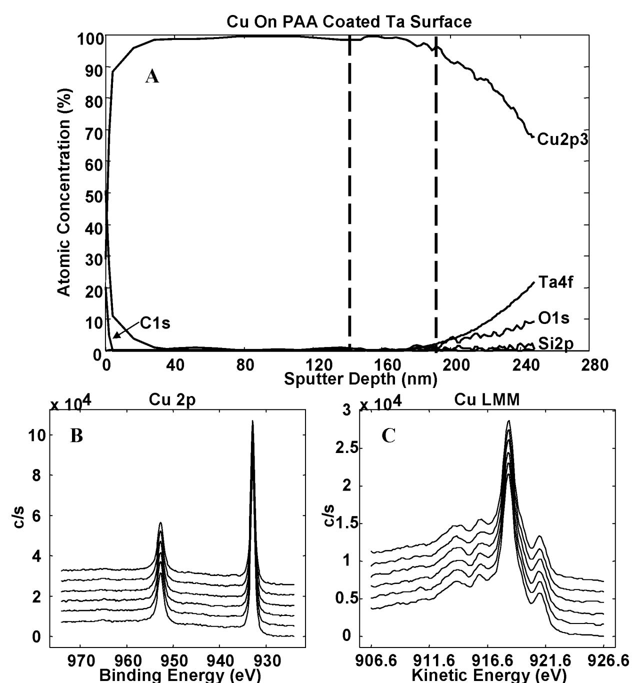

Figure 8. XPS analysis of a copper film deposited by H_2-assisted reduction Cu SFD on a 5 nm PAA-coated Ta/Si substrate at 270 °C and 200 bar: (A) depth profile of the copper film; (B) Cu 2p spectra between the dashed lines in depth profile; (C) Cu LMM Auger spectra acquired between the dashed lines shown in the depth profile.

Adhesion enhancement was observed for all cases, and each film passed the scribe tape test. Figure 8A is the depth profile of a Cu film deposited on 5 nm of a PAA-coated Si substrate with 30 nm PVD Ta layers (experiment 14). A sputtering rate equivalent to ~4 nm/cycle was used for the region of the Cu film closest to the surface, then the sputtering cycles were reduced to ~1 nm/cycle at a distance of 20 nm above the substrate to capture the interface in detail. Again, there was no evidence of the PAA adhesion layer at the interface (a C1s peak was not detected). Carbon and oxygen attributed to ambient exposure were detected only at the free surface of the copper film. The state of Cu at the interface is shown in Figure 8B,C. The spectra were taken from the region between the dashed lines in Figure 8A. Using the same analysis as described earlier, we conclude that copper is again present primarily as Cu^0 at the interface. The chemical state of Ta at the interface was compared for films deposited with and without the adhesion layer using the signal for Ta 4f, as shown in Figure 9. Figure 9A shows the results for films deposited directly on Ta/Si. Peaks attributed to Ta^0 ($4f_{7/2} = 21.9$ eV) and Ta_2O_5 ($4f_{7/2} = 26.7$ eV) are clearly visible. Figure 9B shows results for Cu deposited on the substrate with the adhesion promotion layer. The Ta 4f signal attributed to Ta^0 is dominant, and the peaks assigned to Ta_2O_5 are weakened dramatically but are not completely eliminated. This may be due to the complexity of the Ta oxide. Nonetheless, it is clear that the oxidation of Ta at the interface is significantly lower for films deposited on substrates treated with the adhesion promotion layer.

While we have not established a definitive mechanism for the suppression of Cu oxides at the substrate interface, the literature and additional experimentation provide some insight. It is well-known that Cu oxides can be dry etched from Cu by exposure to volatile acids[18−23] and decomposition of PAA is known to produce low molecular weight acidic species.[24] In addition, we have demonstrated that the presence of excess H_2 during Cu SFD suppresses Cu oxidation in the bulk during film deposition[7] and others have shown that H_2 can reduce both CuO and CuO_2.[25] Finally, Kirsch et al. found that Cu oxides could be reduced at low temperature by radical species, including methyl radicals.[26] Radicals could be generated by the decomposition of PAA during our deposition experiments.[27] These factors alone, or more likely in combination, can explain the elimination of Cu oxides. To assess the first, 5 nm of PAA was spin coated onto 100 nm thick PVD Cu films on SiO_2/Si substrates. The test stack was then exposed to pure CO_2 at 270 °C and 207 bar for 30 min. Figure 10 shows XPS spectra of the films before and after the high-temperature CO_2 soak. The top two spectra are the Cu signal at the PAA/PVD Cu interface before the CO_2 treatment. The presence of Cu_2O is indicated by the binding energies of the Cu LMM Auger peaks. The satellite

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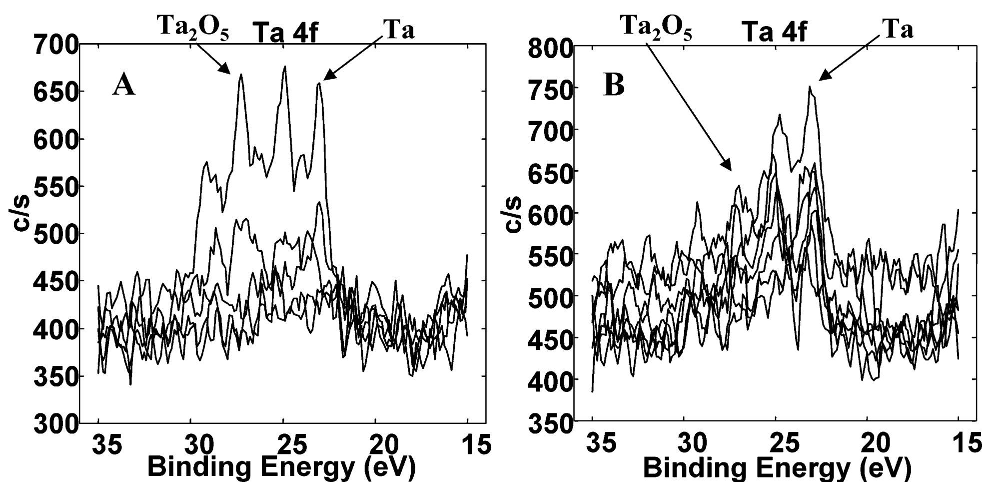

Figure 9. XPS study of Ta chemical state at the interface of Cu and PVD Ta: (A) chemical state of Ta at the Cu/Ta interface after H_2-assisted Cu SFD on 30 nm PVD Ta/native SiO_2/Si substrate at 250 °C and 200 bar without the PAA layer; (B) chemical state of Ta at the Cu/Ta interface after H_2-assisted Cu SFD on 5 nm PAA/30 nm PVD Ta/native SiO_2/Si substrate at 270 °C and 200 bar.

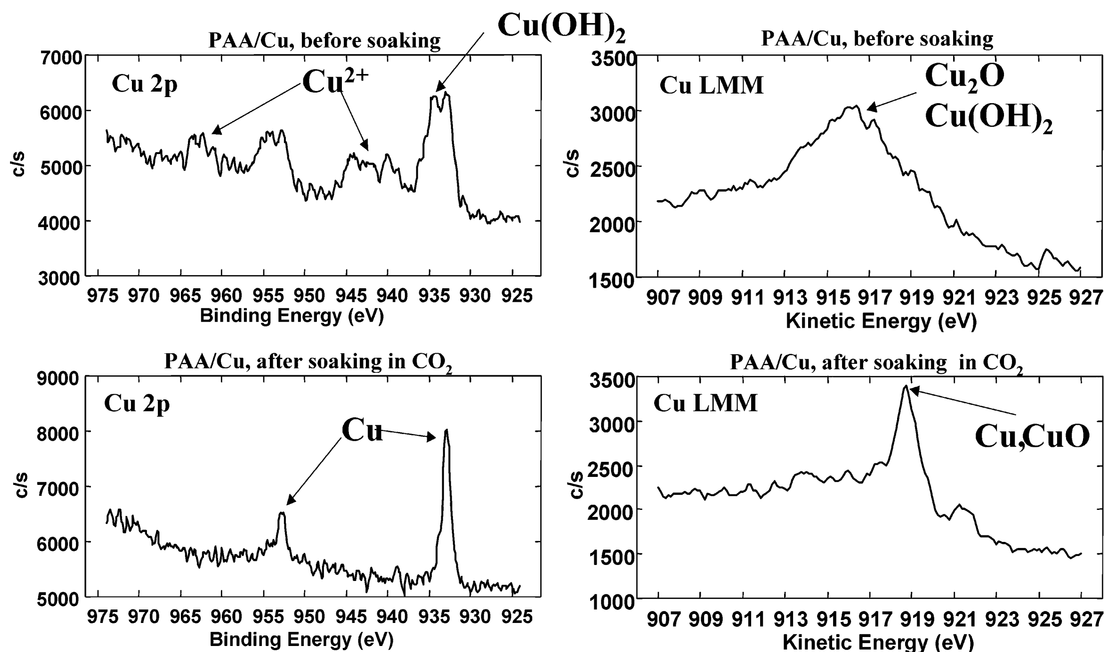

Figure 10. XPS study of the chemical state of Cu at the copper/PAA layer interface before (top) and after (bottom) soaking in CO_2 at 270 °C and 207 bar.

peaks in Cu 2p spectrum and the split in both Cu 2p and Cu LMM indicate that $Cu(OH)_2$ is also present on the surface. However, after the PAA/Cu sample was exposed to CO_2 in the reactor at 270 °C, only peaks attributable to Cu^0 appear in the XPS spectra (bottom two spectra in Figure 10). The experiment indicates that the PAA layer can reduce or strip copper oxides and copper hydroxide in the absence of H_2.

It is well-known that dilute HF can be used to strip the native SiO_2 oxide from Si wafers (in a standard RCA wafer cleaning procedure). Ti and Ti oxides can also be etched by dilute HF [28] or weak base, such as H_2O_2/NH_4OH (pH = 7.0−9.5).[29] It has also been reported that acidic solutions, such as dilute HF solution, can be used to etch Ta_2O_5.[30]

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By comparison PAA is a weak acid ($pK_a = 4.28$). However at the high temperatures (270 °C) used for the deposition, PAA and its decomposition products could likely serve as etching agents for the native oxides of Si, Ti, and Ta. It is unlikely that these oxides are reduced by H_2 at 270 °C.

Finally, it is clear from the experiments that the PAA adhesion layer is completely consumed during the Cu SFD at 270 °C. We assessed the stability of 6−7 nm thick PAA films on Si wafers and in Cu/Si wafers at conditions relevant to the depositions using spectroscopic ellipsometry, atomic force microscopy, and SEM. The thickness and refractive index of PAA films (ca. 1.58) exposed to CO_2 or CO_2/H_2 mixtures ($CO_2:H_2 \approx 15:1$) at 270 °C and 207 bar for 30 min on SiO_2/Si remained relatively constant, indicating little if any decomposition at these conditions in the absence of Cu.

By comparison, exposure of PAA films coated onto Cu/Si wafers in CO_2/H_2 mixtures ($CO_2:H_2 \approx 15:1$) resulted in significant decomposition of the film, as evidenced by a dramatic reduction of the refractive index of the PAA layer

(1.18) and a significant increase in the root mean square roughness of the PAA film as measured by atomic force microscopy (from 1.1 to 4.7 nm). Exposure of PAA films on Cu/Si substrates in neat CO_2 at the same conditions reduced the refractive index of the film to 1.3 and increased roughness slightly (2.2 nm). SEM studies were consistent with these results, indicating the as-prepared films were relatively smooth while the films exposed to neat CO_2 and CO_2/H_2 were progressively rougher. The experiments suggest that the adhesion layer is degraded by a H_2-assisted decomposition of PAA that is catalyzed by Cu. Rapid degradation during the Cu deposition may be attributed in part to the very large surface area of Cu available during the initial stages of film nucleation.

The experiments described above were carried out by spin coating PAA onto planar test wafers. Extension to patterned wafers containing sub-100-nm device features will require an alternative means of depositing the adhesion promotion layer. Simple vapor phase exposure of Si wafers to acrylic acid prior to Cu SFD resulted in excellent adhesion. The same treatment however was not effective on TiN layers. This is most likely due to the desorption of acrylic acid from TiN in the presence of CO_2 prior to deposition. This difficulty for TiN and other barrier layers on patterned surfaces can likely be overcome by simple thermal, UV, or plasma induced polymerization of acrylic acid from the vapor phase, by using multifunctional or higher molecular weight sources of acidic organics that do not readily desorb from barrier substrates in CO_2, by using SAMs, or by combinations of these approaches.

Conclusion

We have shown that poly(acrylic acid) can be used as an adhesion-promoting layer for copper metallization in supercritical fluid deposition. The layer thickness was as thin as 3.5 nm. XPS analysis indicated that the polymer layer was sacrificial. In addition, Cu is present as Cu^0 at the interface, and the substrate oxides are significantly reduced at the interface. Finally, we extended the study to patterned Si wafers by surface pretreatment with acrylic acid. The same approached may be effective for adhesion enhancement for films deposited by CVD or ALD.

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