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Quantitative Interfacial Energy Measurements of Adhesion-Promoted Thin Copper Films by Supercritical Fluid Deposition on Barrier Layers

A fivefold increase in adhesion energy is observed for poly(acrylic acid) (PAA) modified Cu/TaN interfaces in which the thin copper films are deposited by the hydrogen assisted reduction of bis(2,2,7-trimethyloctane-3,5-dionato) copper in supercritical carbon dioxide. The PAA adhesion layer is sacrificial at the reaction conditions used, and X-ray photoelectron spectroscopy has shown that the Cu/TaN interface is free of contamination following deposition. The resulting average interfacial adhesion energy is just above 5 J/m^2, which meets adhesion requirements for integration in Cu interconnects. The adhesion measurements are performed with a custom built four-point bend fracture mechanics testing system. Comparison of the copper film thickness to the measured adhesion energy indicated that there is no effect on the adhesion energy as the film thickness changes. [DOI: 10.1115/1.4000283]

Keywords: fracture mechanics, adhesion, supercritical fluid deposition

1 Introduction

Copper is the material of choice for interconnects in advanced integrated circuits (ICs). While Cu offers higher electromigration resistance and lower electrical resistance than its predecessor, aluminum, the introduction of copper required notable manufacturing and materials changes. These include the introduction of barrier layers, such as TaN, to prevent Cu diffusion into the dielectric. The adhesion of copper to barriers such as TaN [1–4] has proven to be a critical reliability issue during the manufacturing and lifetime of ICs.

The production of copper interconnects for ICs is a two-step process. Initially, the deposition of a Cu seed layer by sputtering is performed. Next, electrochemical deposition is used to carry out a bottom-up fill of the interconnect trench. Because sputtering is essentially a line of sight technique, it is difficult to sputter conformal and defect-free copper seed layers in trenches as device dimensions are reduced below 32 nm. Subsequent electrochemical filling of these features can create voids and defects that cause high resistance and open circuits.

While the two-step physical vapor deposition (PVD) seed layer–electrochemical fill process has been adapted to meet the demands of current interconnect dimensions, there are serious concerns that this approach will fail to do so in the future. Consequently, alternative solutions are under consideration. These include atomic layer deposition (ALD), chemical vapor deposition (CVD) and supercritical fluid deposition (SFD). Although CVD can in principle be used to deposit conformal copper, it fails to do so in a high aspect ratio features. Additionally, it suffers from both inefficient consumption of the precursor and poor adhesion [5,6]. Low precursor conversion is attributed to low precursor concentrations, which is a function of the low precursor vapor pressure. Poor adhesion is attributed to contamination of the interface between the trench (barrier layer) and the deposited copper. Contamination is from precursor byproducts of the reaction, typically the ligand, and from oxidation of the barrier layer [5–8]. ALD is a CVD variant using alternating precursor gas exposure for self-limited reactions to form films with precise composition, conformal coverage, exceptionally high interfacial adhesion, and thickness control on the angstrom level. ALD, although a candidate for conformal films with precise composition control, is only a time effective solution at submonolayer thicknesses requiring significantly longer processing times for thicker films, thus making it unsuitable for industrial integration. Additionally, ALD provides no solution for the important Cu/Ta/TaN seed/barrier layer formation used for ICs [9–13]. SFD presents a unique solution for the single step, rapid, and conformal deposition of films in high aspect ratio features with near complete precursor conversion [14–17]. Unfortunately, films deposited with this method still have weak adhesion from oxidation at the barrier during deposition. It is the focus of this study to outline current progress in increasing interfacial adhesion of copper to barrier layers, of which SFD specific solutions have been identified, and to explore quantitative methods of analyzing this increased adhesion. This enhances the likelihood that a single step process for the efficient and conformal filling of Cu into Ta/TaN for seed/barrier systems of high aspect ratios can seamlessly be integrated into production.

There are a variety of reasons why poor adhesion is experienced with films deposited via reactive deposition. During CVD and SFD, which use reduction chemistry, significant contamination can occur at the interface, which reduces adhesion. The precursors used in SFD and CVD typically have a hydrocarbon or fluorine based ligand that is chelated to a metal core. The ligand is chosen to increase the solubility or volatility of the metal in whichever medium used [18–20]. The reduction reaction reduces the ligands and leaves behind the metal center for deposition [5,6]. However, the ligand decomposition products can become trapped at the interface, which reduces the number of sites available for bonding, thereby decreasing adhesion.

Additional causes of poor adhesion include process defects and oxidation at the interface. Process defects, typically gaps and

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cracks formed by stress, greatly reduce adhesion. Oxidation is an important aspect of adhesion that is usually overlooked. By directly addressing the oxidation at the interface, it is possible to increase the number of sites with which the deposited film can bond with the previous layer. Copper is easily oxidized in the presence of oxygen in very small quantities. Therefore, for the reduction of precursors for copper deposition, it is advantageous to work in an inert or reducing atmosphere. In SFD, a high density CO_2 atmosphere containing a few percent hydrogen is used, which drastically reduces the potential for copper oxidation.

There are multiple approaches that have been used toward the end goal of increasing adhesion between copper and its barrier layer. Self-assembled molecular nanolayers (MNLs) have been employed in order to increase adhesion from the angle of improving interfacial bonding. 3-mercapto-propyl-tri-methyoxy-silane (MPTMS) MNLs have been used for PVD deposited Cu/SiO_2 interfaces resulting in a threefold increase in adhesion [21–23]. Multilayers of vinyl silane monomers were cross-linked to form C–Si films, which increase adhesion [24,25]. Poly(dimethylsiloxane) was used to cold weld gold contacts together at ambient conditions [26]. Unfortunately, these MNLs have low stability at temperatures exceeding 400°C due to desorption or degradation. Gandhi et al. [27] recently reported the use of the same MPTMSs previously reported, however, with the improvement of stability at temperatures exceeding the MNLs' desorption temperature. Additional methods for increasing adhesion by improving interfacial bonding include the alloying of other metals, such as aluminum, magnesium, and ruthenium to copper [28–35]. Even though these alloyed metals show the potential for two- and threefold increases in adhesion, they are currently not used.

Zong et al. [36] reported the use of ultrathin layers of poly-(acrylic acid) (PAA) on diffusion barrier layers of TiN, Ta, and TaN to dramatically increase the adhesion of copper films deposited by SFD to these barrier layers. The pretreatment of the silicon substrates with PAA was performed by either spin coating of PAA or vapor phase exposure of PAA. Additionally, it was suggested that this method be extended to more complex substrates by the adsorption of acrylic acid to the substrate and subsequent thermal or UV polymerization to PAA to achieve the same pretreatment effect. Postcopper deposition X-ray photoelectron spectroscopy (XPS) indicated that there was no PAA layer at the copper/barrier interface, which indicates that the PAA layer was completely sacrificial at the reaction conditions used. The increased adhesion was attributed to the reduction of oxides at the interface, likely due to etching or reduction by the degradation products of the PAA layer at the interface.

Within the microelectronics industry, there exists a need for a standard quantitative method of measuring adhesion. However, the majority of techniques used (scribed tape test, scratch test, peel test, and many others [37–44]) are qualitative since they only allow for visual comparison for quality control purposes. Quantitative measures enable then a direct comparison of critical energies to be made and understanding the energy dissipative mechanisms of interfacial adhesion would be possible.

Quantitative tests include micro-indentation, the pull-off test, the blister test, the edge-delamination test, and the four-point bend test [45–50]. Unfortunately, the majority of these are designed for macroscale films. A few, however, can be extended to thin film adhesion; of these, some still suffer further from difficult sample preparation methods. Over recent years, four-point bend has emerged as the industry standard [51–62]. It is the method of choice in spite of relatively difficult sample preparation because the experimental data are relatively easier to interpret. This is primarily because the method is based on established fracture mechanics and the film is bonded to one substrate in the crack wake, and consequently the residual stress in the film is not relieved to contribute to the crack driving force (energy release rate).

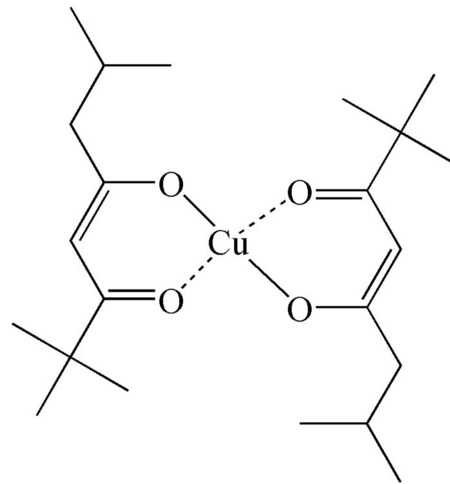

Fig. 1 Chemical structure of bis(2,2,7-trimethyloctane-3,5-dionato) copper, $Cu(tmod)_2$

2 Experimental

2.1 Materials. bis(2,2,7-trimethyloctane-3,5-dionato) copper, $Cu(tmod)_2$, is used as received without any further purification (Epichem, Inc., Allentown, PA), Fig. 1. PAA [9003-01-4] (25% solution in water, $M_w \sim 90{,}000$) is diluted and used for spin coating (Polysciences, Inc., Warrington, PA). Acrylic acid [79-10-7] is used as received without further purification (Sigma-Aldrich Co., St. Louis, MO). EPO-TEK 353ND is used as received (Epoxy Technology, Billerica, MA). Approximately 98% pure *n*-heptane [142-82-5] (Fisher Scientific, Pittsburgh, PA) is used as received without any further purification. Coleman grade (99.99%) carbon dioxide and ultrahigh purity (99.999%) hydrogen are used as received (Merriam Graves Corp, Charlestown, NH). A buna-N o-ring, size 2-236, is used for the high pressure and high temperature reactor seal (Marco Rubber and Plastic Products, Inc., North Andover, MA). Copper films are deposited on 35×45 mm^2 silicon substrates with a TaN passivation layer (Si crystal orientation ⟨100⟩, 300 Å TaN by CVD, 1–100 $\mu\Omega$ cm, and 750 μm total thickness) (Novellus, San Jose, CA). A 35×45 mm^2 silicon wafer (crystal orientation ⟨100⟩, 500 nm thermally grown oxide, 1–100 $\mu\Omega$ cm, and 750 μm total thickness) (Novellus, San Jose, CA) is used for the support side of the sample stack.

2.2 Sample Preparation. PAA is spun at 4000 rpm onto a TaN coated Si substrate from a 1% solution of PAA in water to form a 15 nm thick layer. Data for PAA film thickness versus spin seed at various PAA/water concentrations were previously determined [63]. Film thickness was confirmed with variable angle spectroscopic ellipsometry (VASE).

The deposition of copper onto PAA pretreated and untreated substrates is carried out via supercritical fluid deposition, previously reported [36,64] with reaction conditions yielding conformal deposition. The reactor, however, is a cold wall reactor, Fig. 2. The reactor consists of two opposed 316 stainless steel flanges sealed with a 2-236 buna-N o-ring. The internal volume of the reactor is approximately 70 cm^3. A custom designed 2.3 in. (5.8 cm) diameter aluminum sample stage with a 450 W coiled resistive heater (Belilove Co. Engineers, Hayward, CA) is installed at the bottom of the reactor with a high pressure sealing split gland fitting (Conax Buffalo Corp., Buffalo, NY). The wall of the stainless steel reactor is heated using four 3 in. (7.6 cm) long, 120 V, 170 W cartridge heaters and is maintained at a lower temperature than the reaction stage in order to induce selective deposition to the higher temperature sample stage. The heated sample stage and reactor wall are controlled and heated separately using custom built temperature controllers consisting of a solid state relay

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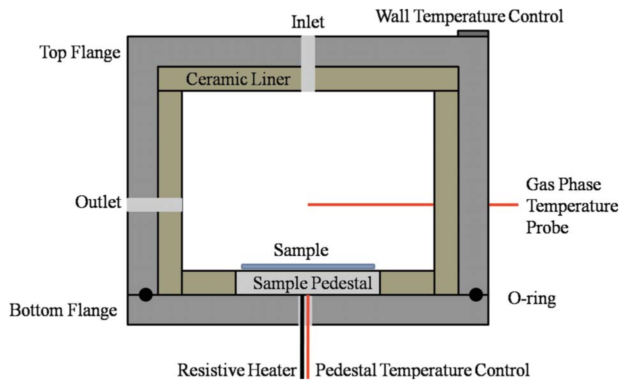

Fig. 2 Custom built 316 stainless steel cold wall reactor with resistive heated aluminum sample stage

(Omega Engineering Inc., Stamford, CT) and microprocessor-based temperature controller, model CN76000 (Omega Engineering Inc., Stamford, CT) encased in an aluminum enclosure.

EPO-TEK 353ND epoxy is used to bond the copper deposited silicon substrate to a support silicon substrate similar to the substrate used for copper deposition. The epoxy is spun on at 7500 rpm for 45 s, and then cured at 140°C at 8 kPa for 40 min resulting in an epoxy layer thickness of approximately 5 μm. Then, a notch is machined with a high speed dicing saw, model ADA-321 (DISCO, Tokyo, Japan), into the sample stack to within approximately 50 μm of the interface. Finally, the sample stacks are diced into three 45 mm$(L)\times 4.5$ mm$(W)\times 0.73$ mm(H) samples using the dicing saw at a speed of 0.3 mm/s to achieve a sufficiently smooth finish. The representation of the final sample stack for untreated and PAA pretreated films is shown in Figs. 3 and 4, respectively.

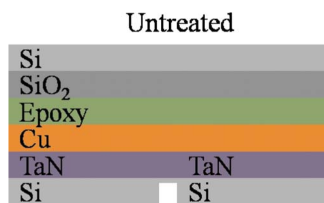

Fig. 3 Experimental sample stack for mechanical adhesion testing of copper deposited film on unmodified TaN capped substrates. Si, SiO_2, epoxy, and TaN thicknesses are approximately 700–750 μm, 500 nm, 5 μm, and 30 nm, respectively. Cu thickness varies according to Table 1.

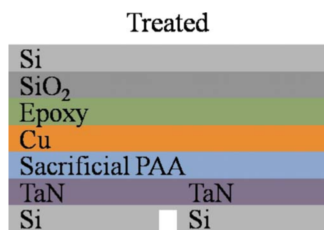

Fig. 4 Experimental sample stack for mechanical adhesion testing of copper deposited film on poly(acrylic acid) modified TaN capped substrates. PAA thickness is approximately 15 nm.

2.3 Mechanical Testing. The samples were tested using a custom built four-point bending mechanical test system [62], which works in displacement controlled mode with the loading continuously measured with a high-sensitivity load cell. The system also features high rigidity as well as an integration of a closed environmental cell to finely control both the relative humidity and temperature inside the cell.

The delamination experiments to determine the adhesion energy of the Cu/TaN interface are performed using the four-point bending technique, Fig. 5. All samples are tested at 21 ± 0.3°C in an environmental cell with N_2 flow, relative humidity below 10%, immediately after the samples are cured. Before further testing, a 3 h stabilizing period is allowed to achieve thermal equilibrium and minimize thermal fluctuation during test. The default loading rate, crosshead speed, is 0.1 μm/s. Four-point bend geometry is $S=20$ mm and $L=8$ mm. Four samples are tested at each condition for statistical information. The energy release rate G to drive the crack along the Cu/TaN interface under these conditions is taken to be the adhesion energy of the interface, with G calculated from the following [55]:

$$G=\frac{21P^2L^2(1-\nu^2)}{16Eb^2h^3}$$

where P is the steady load taken as the average value over the plateau region in the load-displacement curve after the major load drop, b is the width, and h is the half thickness of the sample. E $=168.9$ GPa and $\upsilon=0.064$ are Young's modulus and Poisson's ratio of Si as appropriate for the crystallographic orientation of the samples [65].

3 Results

Copper films are deposited by the hydrogen assisted reduction of $Cu(tmod)_2$ in supercritical carbon dioxide on TaN barriers. The barrier layers are treated with PAA, a known interfacial adhesion enhancer for copper deposited by SFD, prior to deposition. Four-point bend fracture mechanics are then used to quantify the interfacial adhesion energy of the Cu/TaN interface, Table 1.

The copper SFD reaction temperature is between 270°C and 285°C for all depositions. Precursor concentration is between 0.2 wt % and 0.9 wt %, and hydrogen concentration is approximately 0.5 wt % for all depositions. The hydrogen concentration is always in excess of 100 times the necessary amount needed for complete conversion of the loaded $Cu(tmod)_2$. XPS is used to confirm crack propagation at the interface of interest.

Untreated sample stacks have a copper thickness range 68–180 nm. PAA pretreated stacks have a copper thickness range 130–266 nm. It is observed that the copper film thickness is greater with

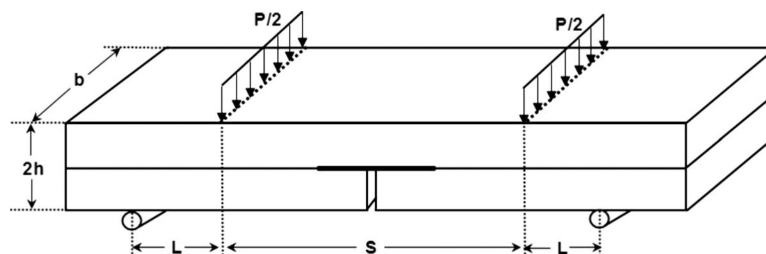

Fig. 5 Schematic and force diagram for four-point bend technique

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Table 1 Table of adhesion energy for untreated and poly(acrylic acid) treated samples

Sample group		Cu thickness (nm)	Cu/TaN adhesion energy (J/m^2)	Variation (J/m^2)
Untreated	A-1	68	0.55	0.25
	A-2	97	1.40	0.37
	A-3	126	0.56	0.05
	A-4	131	1.56	0.20
	A-5	180	0.50	0.03
Treated	B-1	130	>5.3[a]	N/A
	B-2	172	3.36	0.57
	B-3	190	4.69	0.20
	B-4	192	>5.3[a]	N/A
	B-5	266	5.32	0.92

[a]Precrack failed to grow into interface.

PAA pretreated samples as compared with samples that did not have a pretreatment for equivalent reaction conditions.

A typical load-versus-displacement curve for an untreated and PAA pretreated stack is shown in Figs. 6 and 7, respectively. The steady state load is determined after the major load drop. Finally, the average interfacial adhesion energy of the Cu/TaN interface is calculated [55] and is found to be approximately 1 J/m^2 for untreated stacks and approximately 5 J/m^2 for PAA pretreated stacks, Fig. 8.

Visual inspection of the deposition side, graphical representation in Fig. 9, of the substrate shows a copper-free surface. XPS is used to confirm these results, Fig. 10. No trace of the copper $2p_{1/2}$ and $2p_{3/2}$ signature XPS peaks is observed. Visual inspection of

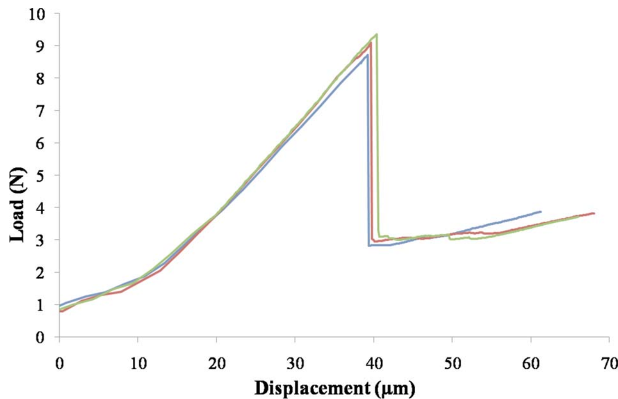

Fig. 6 Load-versus-displacement plot for sample A-5, unmodified surface

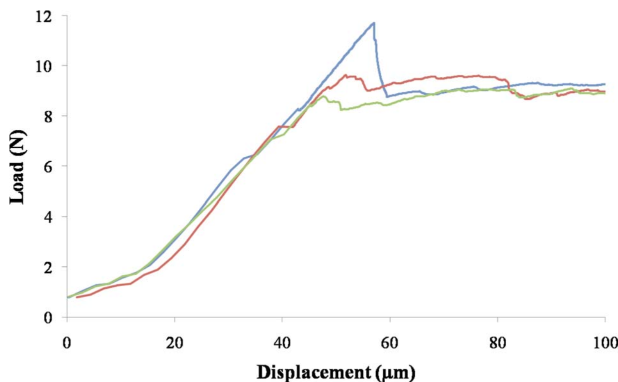

Fig. 7 Load-versus-displacement plot for sample B-3, poly(acrylic acid) modified surface

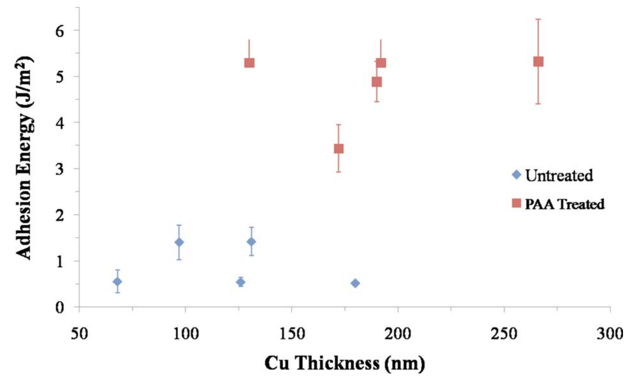

Fig. 8 Statistical data for adhesion energy versus thickness of the deposited copper film for both treated and untreated substrates

the support side shows a shiny copper film. XPS survey scan and sputter depth profiling of this side, Fig. 11, immediately show a high purity copper film eventually moving into a high carbon count region. The results do not differ for all samples, regardless of it being untreated or PAA pretreated, which confirms the sacrificial nature of the PAA at the reaction conditions used.

4 Discussion

PAA is used at the Cu/TaN interface to maintain an oxide- and contamination-free interface during SFD deposition of copper. PAA, at the reaction conditions used, will degrade and is ultimately sacrificial, as seen in the XPS sputter depth profiles in Figs. 10 and 11. Along with its decomposition products, PAA, a weak acid ($pKa=4.28$), acts as an etching agent to clean the surface of any oxides or ligand contamination that are formed or left behind during the reduction reaction. A comparison of the adhesion energy of untreated stacks versus PAA pretreated stacks indicates that there is a fivefold increase in adhesion energy of the Cu/TaN interface when pretreated with a 15 nm thick layer of spun on PAA from a 1% PAA in water solution. This increase in adhesion energy allows copper deposited by SFD to meet industry standards. Interfaces with an adhesion energy of less than 5 J/m^2 exhibit delamination or cracking during chemical mechanical polishing (CMP), and for this reason, 5 J/m^2 is the adhesion energy required in the semiconductor industry [57].

It is important to note that in Figs. 10 and 11, there is a slight carbon count at the beginning of each sputter depth profile for one cycle; this is attributed to contamination from the air after mechanical testing and not the presence of the PAA layer.

Although film thickness is known to affect adhesion energy as a result of plasticity in the film, this is only common for relatively

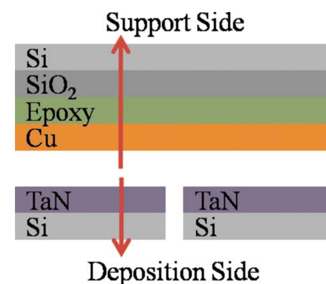

Fig. 9 Representation of the postmechanical tested sample stack with directionality indication of XPS for sputter depth profiling

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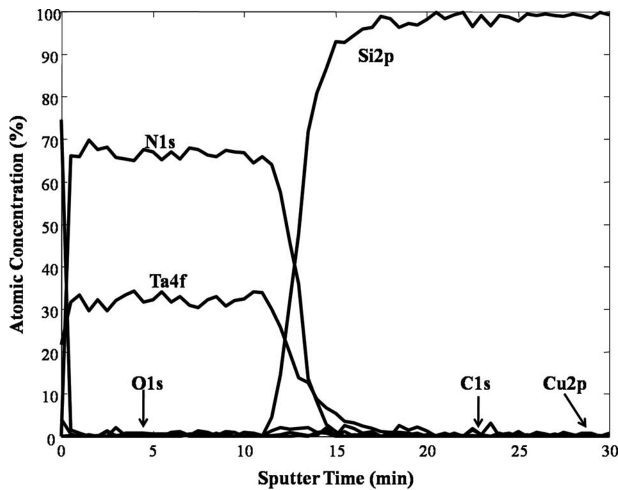


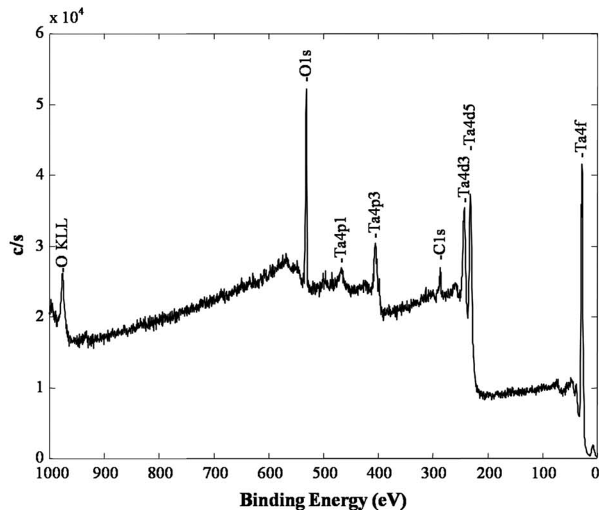
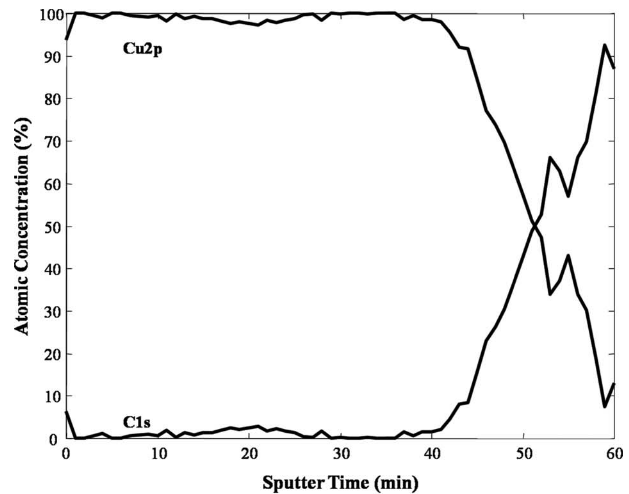


Fig. 10 XPS sputter depth profile (top) and survey scan (bottom) of sample A-5, deposition side. No Cu layer is detected prior to the TaN region, which confirms that the crack propagated at the desired interface.



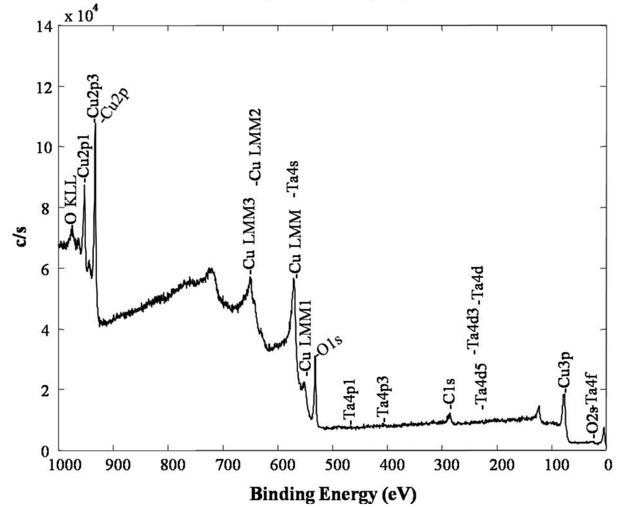


Fig. 11 XPS sputter depth profile (top) and survey scan (bottom) of sample B-5, support side. The lack of presence by the TaN layer prior to the copper rich region confirms propagation of the crack at the desired interface.

thicker films than those studied. There is no obvious trend in adhesion energy as a function of film thickness in either the untreated or PAA pretreated stacks.

During mechanical testing, the load-versus-displacement curves show a common trend with a major load drop, which is consistent with four-point bend tests. This load drop occurs as the precut notch initiates the interfacial crack. More often than not, the initiation of interfacial crack is asymmetric and the crack will propagate down one side of the sample initially. If the sample does not break, the energy will be enough to begin a crack that propagates down the other side of the sample. This is evident when a second major energy drop occurs, which corresponds to the crack propagating into the other side of the sample. As the crack propagates, the load begins with a plateau regime during which the energy release rate remains constant. The crack arrests as it approaches the inner loading pins, manifested as a steady increase in load without further crack extension.

A broken sample, in which the crack does not propagate into the interface but instead the entire stack immediately fails, indicates superior adhesion, as the crack always chooses a path with minimum energy dissipation. If the intended interface is sufficiently tough, it is energetically more favorable to propagate through the film then bulk silicon substrate, than along the tough interface.

5 Summary and Conclusions

A fivefold increase in adhesion is observed for PAA pretreated Cu/TaN interfaces in which the copper films are deposited by the hydrogen assisted reduction of bis(2,2,7-trimethyloctane-3,5-dionato) copper in supercritical carbon dioxide. The pretreatment of PAA is done via spin coating, and the remaining 15 nm layer at the interface becomes sacrificial at the reaction conditions used, leaving behind no trace of the PAA. The resulting average interfacial adhesion energy is 5 J/m^2, which meets adhesion standards in the semiconductor industry. The adhesion measurements are performed with a custom built four-point bend fracture mechanics testing system. Finally, film thickness is found to have no affect on the adhesion energy.

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