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Chromium and tantalum adhesion to plasma-deposited silicon dioxide and silicon nitride

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Abstract—Thin layers of Ta and Cr deposited onto plasma-deposited silicon dioxide (SiO_2) and silicon nitride (SiN) surfaces promote adhesion of Cu to the underlying insulating surfaces. In this paper, the peel adhesion strength of the Ta and Cr layers to the reactive ion etched (RIE) and Ar-sputtered insulating surfaces is measured after Cu deposition. Peel tests, which provide a measure of the adhesion strength of the metallic (Cu + Ta or Cr) layer to the insulators, indicate that both Ta and Cr adhere better to SiN than to SiO_2. Cohesive failure of the peel strip occurred for the Ta/SiN system rather than failure at the interface. The freshly exposed surfaces of the peeled metallic strip and the underlying insulator, which represent the locus of adhesion failure, were analyzed by X-ray photoelectron spectroscopy (XPS). Characterization of the chemistry at the surfaces and their relationship to adhesion is discussed.

Keywords: Adhesion; metal adhesion to SiO_2; metal adhesion to Si-nitride.

1. INTRODUCTION

Copper–polyimide (Cu–PI) interconnect structures have been under development for a number of years in microelectronics applications. Significant chip performance improvement is expected with Cu–PI integrated circuits as compared to aluminum-silicon dioxide (Al–SiO_2) circuits [1]. The performance improvement is realized from a reduction in the resistance (R) and capacitance (C) of the interconnections between individual devices [1]. The 3-D capacitance reduction is $\approx 20\%$, while the RC delay reduction is over 50% [1]. To achieve these improvements in performance it is necessary to fabricate the Cu–PI structures reliably. Cu adhesion to PI is poor [2]. To provide adequate Cu adhesion to PI, thin Cr or Ta layers between Cu and PI are used as adhesion promoters [2, 3]. The Ta or Cr layers function also as Cu diffusion barriers [2, 4]. A schematic illustration of the fabrication of a typical Cu–PI structure [5] is shown in Fig. 1.

The Cu–PI structure is fabricated by first depositing PI onto a Si–nitride (SiN) coated Si-wafer and curing at 400°C in an inert ambient. Photoresist is applied and the pattern defined (Fig. 1A). The photoresist is completely removed during O_2–RIE of the PI (Fig. 1B). The top SiN or SiO_2 layer serves both as a plasma etch barrier for

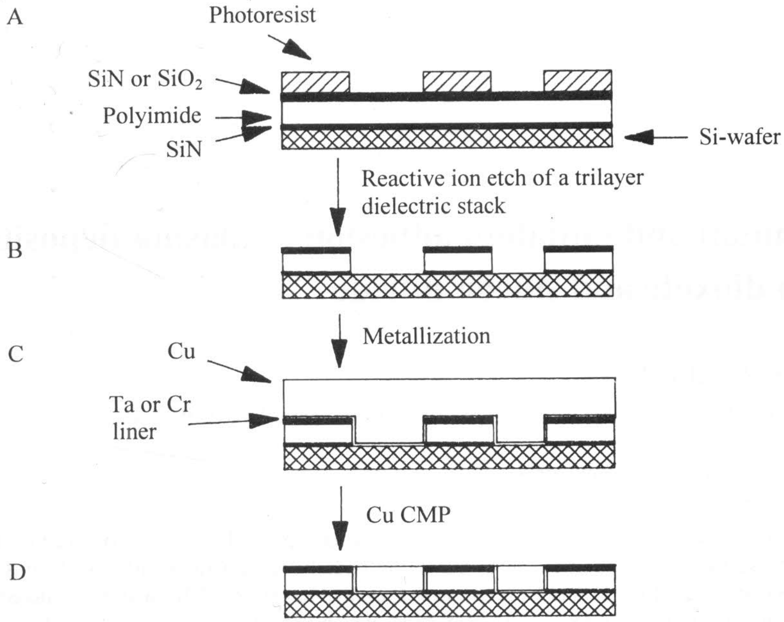

Figure 1. Fabrication of a Cu–PI structure. CMP = chemical–mechanical polish.

pattern definition in the PI (Fig. 1B) and as a chemical–mechanical polishing (CMP) stop (Fig. 1D) [5].

The last step in pattern definition is CF_4–RIE removal of the bottom SiN insulator (Fig. 1B, this etching also chemically modifies and reduces the thickness of the top inorganic insulator). In a metal deposition chamber, the inorganic insulator surfaces are exposed to Ar-sputtering just prior to deposition of the Ta or Cr layer (liner, Fig. 1C). Adhesion of the Ta or Cr to the CF_4–RIE and Ar-sputter modified top insulating layer is important for successful CMP process completion.

Although Ta adhesion to the SiO_2 or SiN surfaces has not been reported, adhesion of Cr and other metals, such as Cu, Ti, and Al on similar surfaces has been studied. Poley and Whitaker [6] found that the peel strength of Cr evaporated onto soda lime glass (12% Na_2O, 12% CaO, and 74% SiO_2) ranged between 6 J/m^2 to about 310 J/m^2 depending on the glass surface treatment and the Cr thickness (20 nm or 100 nm backed with $\geqslant 4$ μm copper). Cu peel strengths to Al_2O_3 and SiO_2 have been measured [7, 8]. Initially, the peel strength of Cu to Al_2O_3 was near zero but improved by exposing the interface to He^+ or Ne^+ ion beam bombardment through an overlying 70 nm thick Cu film. Peel strengths were a function of ion dose; the highest peel strengths were obtained after ion bombardment with an ion dose of $2 - 3 \times 10^{16}$ ions/cm^2. After Ne^+ ion bombardment, the peel strength required to peel a 10 μm thick Cu film off the Al_2O_3 surface reached 80 J/m^2. The initial Cu peel strength to SiO_2 (quartz) was a mere 2 J/m^2, but increased to ≈ 190 J/m^2 by implanting Ti^+ ions at the interface [8] through an overlying 70 nm thick Cu film. On the other hand, ion implantation of Cr^+ at the interface did not improve Cu/SiO_2 peel adhesion.

Table 1.
Peel strength of Ti on various substrates as a function of substrate properties

Substrate	E (GPa)	Peel strength (J/m^2)	Cu film thickness (μm)
Al_2O_3	480	> 1800	50
MgO	250	400–780	20–30
SiO_2 quartz	100	59	10
SiO_2 fused	70	13	10

Ti is used as an adhesion layer to promote Au adhesion to SiO_2 surfaces [9]. Kim *et al.* [10] discuss the adhesion and reaction of Ti with SiO_2. The peel strength of Ti coated with 10 μm of Cu on a detergent cleaned SiO_2 surface was only 7–12 J/m^2. If the SiO_2 surface is cleaned with *in-situ* Ar^+-ion beam instead of the detergent cleaning, the Ti peel strength increased to 40 J/m^2, which is attributed to removal of surface contamination [10]. Ti could not be peeled from MgO or Al_2O_3. *In-situ* XPS analyses indicate that Ti oxidizes when deposited on SiO_2 or Al_2O_3 surfaces. Kim *et al.* [10] proposed that the mechanical properties of the substrate are important in determining the peel strength, i.e. the substrate with a higher elastic modulus (E) has a higher peel strength, as shown in Table 1. Black [11] shows that Al adheres well to the SiO_2 surface, which is explained by the chemical interaction between Al and SiO_2 as well as Al penetration into SiO_2.

Chemical interaction at the interface is important for strong interfacial or fundamental adhesion [9–15] but may not be sufficient to yield a high peel strength [10]. The peel strength, which is a measure of practical adhesion [16], is affected by many factors in addition to the fundamental adhesion [12, 16–18] including: film mechanical properties, film thickness, substrate mechanical properties, peel rate, and peel ambient.

Fundamental adhesion is dictated only by interfacial interactions such as chemical bonding and mechanical interlocking. Mattox [9] suggests that metals with high heats of oxide formation be used as the bonding layers between a substrate oxide and another metal with low heat oxide formation. A comparison of the heats of oxide formation of selected metals is compiled in Table 2 [9]. From the heats of formation, Ta should have the best, while Cu should have the worst, adhesion to oxide, if oxide

Table 2.
Heat of oxide formation for selected metals

Metal	Oxide	Heat of formation (kJ/mol)
Ta	Ta_2O_5	−2046
Al	Al_2O_3	−1661
Cr	Cr_2O_3	−1140
Ti	TiO_2	− 941
Si	SiO_2	− 908
Mg	MgO	− 598
Cu	Cu_2O	− 169

formation is used as the sole criterion for good interfacial bonding. Ti should adhere better to SiO_2 than Cu, which is supported by data of Baglin [8] and Kim *et al.* [10].

This paper focuses on Ta and Cr adhesion to plasma-enhanced chemical vapor deposited (PECVD) SiO_2 and SiN. Metal adhesion to these insulator surfaces is studied after their exposure to CF_4–RIE and Ar-sputter treatments. The effects on the SiO_2 and SiN surfaces of CF_4–RIE with and without follow on Ar-sputter cleaning is discussed in some detail. Only initial adhesion of Ta and Cr to these surfaces is considered, as these interfaces are not part of the final structure as explained earlier. After the surface characterization and peel analysis, the locus of failure studies of the samples will be discussed as they relate to the data interpretation.

2. EXPERIMENTAL

The 200 nm thick SiO_2 films were deposited at a temperature of 390°C on clean Si-wafers using the PECVD technique. The reactants were tetraethoxysilane (TEOS) and O_2. The 100 nm thick SiN films were deposited onto clean Si-wafers using the PECVD technique at a temperature of 350°C from SiH_4 and NH_3 [19].

A 10–20 nm thick copper layer was deposited to cover about 10–20% of the 5″ diameter wafer surface area to initiate release of the peel strip for adhesion testing. The wafers were CF_4–RIE exposed in a parallel plate single wafer RIE tool for 12 s to avoid complete removal of the films. The samples were then heated to ≈140°C prior to Ar-sputtering in the metal deposition chamber. The surfaces were characterized *ex-situ* using a Surface Science Laboratories small spot XPS unit with monochromatized AlK_α X-ray radiation. A flood gun neutralized charging at film surfaces. The binding energies (BE) were referred to C1s at 285.0 eV due to surface adsorption of ambient organic contamination [20].

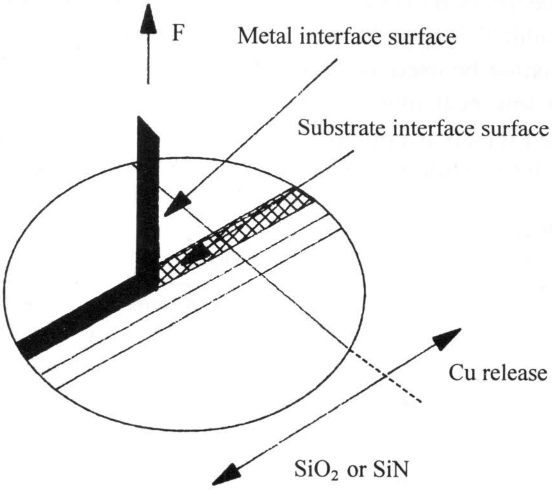

Figure 2. Peel sample configuration and locus of failure (LOF) analysis areas.

The metal-insulator interfaces were prepared by Ar-sputter deposition of 20–30 nm thick Ta or Cr films onto the treated SiO_2 or SiN surfaces. Cu films of 10 μm thickness were deposited onto the Ta or Cr surfaces to facilitate the peel adhesion measurement process. The 2 mm wide peel strips were delineated by cutting the Cu film with a Disco Dicer using DI water as coolant. Peel adhesion was measured with an Instron Tester using a 90° peel angle and a 5 mm/min peel rate in a N_2-flushed ambient. The locus of failure (LOF) between the metal and the underlying insulator was characterized using XPS analyses of both the metal peel and the substrate interface surfaces as indicated in Fig. 2.

3. RESULTS AND DISCUSSION

3.1. XPS analysis of untreated and treated surfaces

3.1.1. Elemental composition of PECVD SiN and SiO_2 surfaces. Since exposure to CF_4–RIE and Ar-sputtering are an integral part of all interface preparations, the insulator surfaces near the center of the 5″ wafers were analyzed by XPS after the insulators were exposed to these treatments but prior to deposition of Ta or Cr films.

The elemental compositions of the SiN and SiO_2 surfaces are summarized in Table 3. The metal deposition chamber used for Ar-sputter cleaning is precoated with Ta or Cr metal, some precoated metal is re-deposited onto the sample surfaces during the sputter cleaning process (Table 3). The Cu detected on the surface is attributed to contamination from the Cu peel release layer (Fig. 2). A major difference between the treated SiN and SiO_2 surfaces is that the relative carbon and fluorine concentrations on the SiO_2 surface are about one-half of that on the SiN surface.

High resolution scans of the elements listed in Table 3 were collected. A comparison of C1s XPS data shown in Fig. 3 illustrates differences between the two surfaces after treatment. For this study the chamber was precoated with Ta; C1s data for Cr precoating were qualitatively similar. The higher binding energy (BE) C1s peaks (Fig. 3A) are evidence of CF_4 polymerization on the surface. Carbon found at a C1s BE of 285.0 eV on the other surfaces is due to ambient contamination. Spectra B, C, and D do not have any evidence of C-F_x species.

Table 3.
SiO_2 and SiN surface characterization

Surface/precoating	Surface treatment	C%	O%	N%	Si%	F%	Ta%	Cr%	Cu%
SiN	CF_4	24	26	15	19	15	—	—	< 1
SiN/Ta	CF_4 + Ar	14	38	18	25	—	4	—	< 1
SiN/Cr	CF_4 + Ar	17	39	15	21	—	—	8	—
SiO_2	CF_4	10	58	—	25	6	—	—	—
SiO_2/Ta	CF_4 + Ar	20	55	—	21	—	4	—	< 1
SiO_2/Cr	CF_4 + Ar	20	54	—	17	—	—	9	—