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THIN FILM ADHESION IN Cu/Cr/POLYIMIDE AND Cu/Cu-Cr/POLYIMIDE SYSTEMS

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ABSTRACT

Adhesion of Cu/Cr and Cu/Cu_xCr_{1-x} thin films onto polyimide substrates has been studied. For an adhesion layer, Cr or Cu-Cr alloy films were deposited onto polyimide using DC magnetron sputtering machine. Then Cu was sputter-deposited and finally, Cu was electroplated. Adhesion was evaluated using 90° peel test or T-peel test. Plastic deformation of the peeled metal layer was qualitatively measured using XRD technique.

It is confirmed that high interfacial fracture energy and large plastic deformation are important to enhance the peel adhesion strength. High peel strength is obtained when the interface is strongly bonded. More ductile film has higher peel strength. In Cu-Cr alloy films, opposite effects of the Cr addition in the alloy film on the peel strength are operative: a beneficial effect of strong interfacial bonding and a negative effect of smaller plastic deformation.

INTRODUCTION

Cu/polyimide systems are frequently used in the electronic components such as metallized tapes for TAB (Tape Automated Bonding), flexible PCB, and thin film multichip module[1, 2]. For high performance, Cu thin films are deposited onto polyimides. However, adhesion between Cu and polyimide is very weak and an adhesion layer is deposited on polyimide prior to Cu deposition. Thin film of Cr or Ti is commonly used as an adhesion promoting layer[3, 4].

The peel test has been popularly used to characterize the strength of adhesion[5, 6]. Strong interfacial bond formation and large plastic deformation occurred during peel test are known to be important to obtain high peel strength value[7, 8]. Interfacial bond strength between thin films and polyimide substrates and the amount of plastic deformation depend on the process conditions such as substrate cleaning, thin film deposition, and electroplating. We investigated the effects of the process variables on the adhesion of Cu/Cr films by varying the conditions of plasma treatment on polyimide surface and mechanical properties of metal layers which affect the interfacial bond strength and the amount of plastic deformation. Also we applied Cu-Cr alloy film for an adhesion layer and studied the effect of Cr content in the alloy film on the adhesion strength.

EXPERIMENTAL PROCEDURE

Two types of polyimides were used in the experiment. First type was Kapton (Du Pont, PMDA-ODA types, 50μm thick) and Upilex-s(Ube Industries, BPDA-PDA type, 40μm) thick polyimide films obtained from manufacturers as completely cured state. Second type was Pyralin LX (Du Pont PI-2611D) and PIQ (Hitachi Chemical Co.) polyimides where the precursors were spin coated onto Cr coated alumina substrates and thermally cured in our laboratory.

DC magnetron sputtering was used for thin film deposition. Cr thin films or Cu-Cr alloy films were deposited onto polyimides as adhesion layers and Cu thin films were deposited successively. The metal films were thickened by electroplating Cu in a CuSO$_4$ solution to perform the peel test. 90° peel test[9] and modified T-peel test[10] were used to evaluate the adhesion. The XRD (X-Ray Diffraction) technique was used to measure qualitatively the amount of plastic deformation on the peeled metal strips[11,12]. The FWHM (Full Width at Half Maximum Intensity) of the deconvoluted Cu(331) kα_1 peak was measured.

RESULTS AND DISCUSSION

Effects of RF plasma treatment conditions

Fig. 1 represents 90° peel test results showing Cu/Cr adhesion to BPDA-PDA type polyimide (Du Pont Pyralyn LX PI-2611D) substrate as a function of RF plasma treatment time prior to metal deposition. The peel adhesion strength of Cr film to untreated polyimide is low (3 g/㎜), but that is drastically increased by plasma treatment of polyimide surface. The peel strength reaches the saturation value within 5 minutes and remains more or less constant with further etching. The AES analyses show that the carbide-like phase formed at the Cr/polyimide interface, indicating Cr reaction with polyimide. One example of AES is shown in Fig. 2. RF plasma treatment increases peel strength by activating the C or O of polyimide to form carbide or oxide with Cr[13] mainly through the polyimide surface modification.

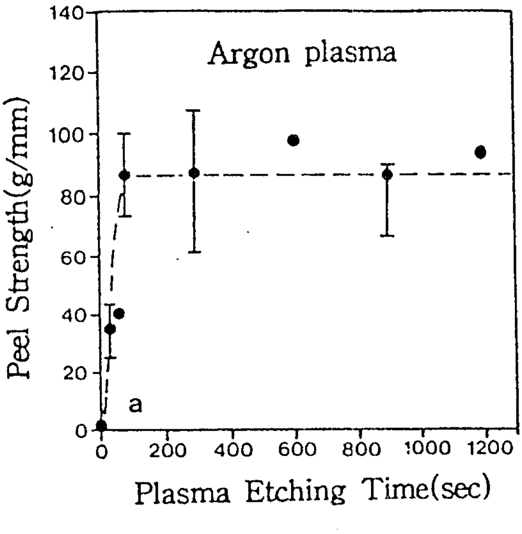

Fig. 1 Variation of peel adhesion strength of the Cr to polymide as a function of the RF plasma etching time.

Fig. 3 is 90° peel strength data of Cu/Cr thin films onto PIQ (Hitachi Chemical Co.) polyimide substrates as a function of the the electroplated Cu thickness at various RF plasma power densities. The plasma power density raises the peel strength value at the same thickness of electroplated Cu. This enhancement is due to the increased chemical reactivity in the Cr/polyimide interface, as similar to the plasma treatment time effect which was explained above. The peel strength increases with the thickness of electroplated Cu layer at small thickness, reaches maximum, and then decreases at large thickness. This trend is clear for specimens that were treated under the RF plasma density of 0.030 and 0.036 W/cm², but not quite so at higher plasma density because the thickness of maximum peel strength is larger than the largest film thickness studied in this experiment.

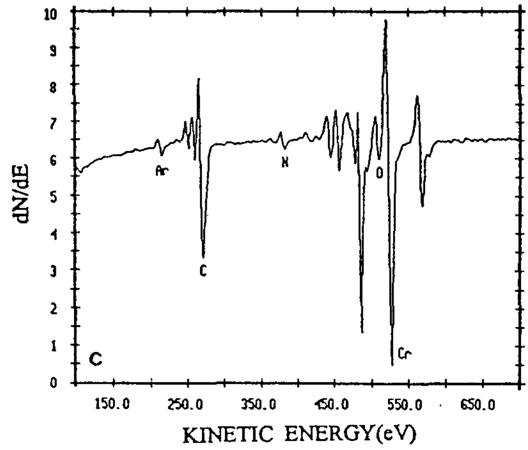

Fig. 2 Auger spectrum of the Cu/Cr strip peeled from polyimide substrate. Polyimide surface was RF plasma-treated for 300 secomds prior to metal deposition.

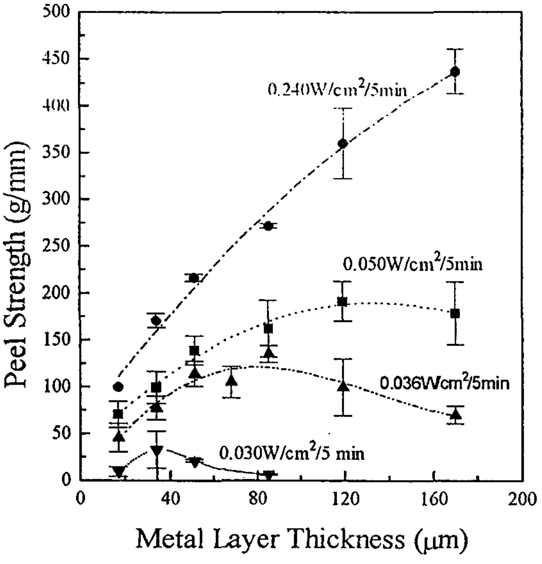

Fig. 3 Variation of peel strength as a function of electroplated Cu thickness at various RF power densities.

It becomes clear that the peel strength is very strongly affected by the electroplated Cu layer as well as interfacial bond strength between Cr and polyimide. Extensive plastic deformation occurs during the peel test and the peel strength does not truly represents the interface fracture energy, because the measured value includes the work needed to break the interfacial bond and other work expended in the plastic deformation in the thin film. At the very small thickness, the amount of plastic deformation is small and the measured peel strength is low. The amount of plastic deformation increases with increasing thickness. However, the peel strength decreases at very large thickness because it becomes more difficult to bend and thereby causing smaller amount of plastic bending deformation. It is expected that the interfacial fracture energy is large at high RF plasma density. The large amount of plastic deformation is needed to separate the metal layer from polyimide and the critical thickness having maximum peel strength becomes large.

Effects of the structure of sputtered Cu films

To investigate the effects of the structure of Cu films on the adhesion, the following experiment was performed. 50 nm thick Cr films was sputter-deposited onto polyimide films (Upilex-s, Ube Co.) of which surface had been Ar^+ RF plasma treated. Then 500 nm or 1000 nm thick Cu films were sputter-deposited on Cr/polyimide films at the pressure of 5, 50, and 100 mtorr. Finally 20μm thick Cu layers were electroplated. All methods except Cu sputtering condition are the same. Peel strength of metal films was measured by using modified T-peel test. Adhesion test results in six different specimens are summarized in Table 1. Increasing sputtering pressure during Cu deposition generally increases the average peel strength value. The peel adhesion of the specimen in which Cu was deposited at 5 and 50 mtorr does not vary with Cu film thickness (specimen #1 vs. #4 or specimen #2 vs. #5).

Meanwhile, the peel adhesion of the specimen in which Cu was deposited at 100 mtorr increases with the thickness of Cu deposition layer (specimen #3 vs. #6).

Since interface between Cr and polyimide has the same character in all six specimens, interfacial bond strength should be identical and the difference in the T-peel strength values should be related to the amount of plastic deformation. Metal layer is deformed plastically during peeling. So non-uniform deformation of grains causes the line broadening of XRD peaks. Wider FWHM means larger deformation. The FWHMs of Cu (331) peaks measured in the peeled metal layers are also presented in Table 1. The relative amount of plastic deformation obtained from XRD data in Table 1 corresponds to the T-peel strength value. That is, high T-peel strength means large plastic deformation.

The Cu film deposited at low pressure has a very dense structure. Meanwhile, low density regions (open boundaries between columns) are formed in the film deposited at high sputtering pressure due to atomic shadowing effect. As the deposition pressure or the thickness increases, more open boundaries are observed[14]. Wide and long open boundaries in the Cu film assist the electroplated metal layer to be bent more easily during peeling. Easy bending in the metal film induces more extensive plastic deformation. During T-peel test, it was observed that metal layer was bent more in the specimen deposited at high pressure than in the specimen deposited at low pressure. Line broadening

Table 1. Peel strength and XRD results in plated Cu/deposited Cu/Cr/polyimide

Specimen Number	Cu Deposition Condition (pressure, thickness)	Peel strength (g/mm)	FWHM ($\Delta 2\theta$)
1	p=5 mtorr, t=500nm	52.1	0.496
2	p=50 mtorr, t=500nm	62.1	0.630
3	p=100 mtorr, t=500nm	62.2	0.636
4	p=5 mtorr, t=1000nm	51.6	0.494
5	p=50 mtorr, t=1000nm	60.8	0.660
6	p=100 mtorr, t=1000nm	73.2	0.694

in XRD peaks also supports this explanation (Table 1).

As a result, the specimen of which metal layer is bent more has higher peel strength even though the interface fracture energy is the same in all specimens.

Effects of electroplated Cu layer

50 nm thick Cr films and 500 nm thick Cu films were sputter deposited successively onto polyimide films (Kapton, 50㎛ thick, PMDA-ODA type and Upilex-s, 40㎛ thick, BPDA-PDA type). Then 20㎛ thick Cu was electroplated in various electroplating solutions shown in Table 2 to control the mechanical properties of metal layer. The measured mechanical properties of the layers by using tensile testing machine are summarized in Table 2.

The T-peel strength is measured in four specimens with different mechanical properties, and results are presented in Fig. 4 as a function of yield strength. Peel strength decreases as the yield strength of the metal layer increases. Adhesion behavior of metal layers onto two types of polyimide films has the same trend regardless of polyimide types.

As explained in the previous sections, the measured peel strength is the sum of the interface fracture energy and the amount of plastic deformation. When metal films(Cr adhesion layers) are deposited on the same polyimide film with identical deposition condition, the interfacial fracture energy is the same in all specimens. However, the mechanical properties of metal layers are different. The difference in peel strength is attributed to the change of mechanical properties; The metal layers which have lower strength will be bent more and the amount of plastic deformation will be heavier in more ductile specimens.

Table 2. Variation of yield strength of Cu/Cr metal layers as a function of the composition of electroplating solution

Solution No.	$CuSO_4$ (g)	H_2SO_4 (g)	Brightner (g)	Yield strength (MPa)
E1	295	75	0	156
E2	160	225	0	174
E3	295	75	0.25	284
E4	295	75	6	325

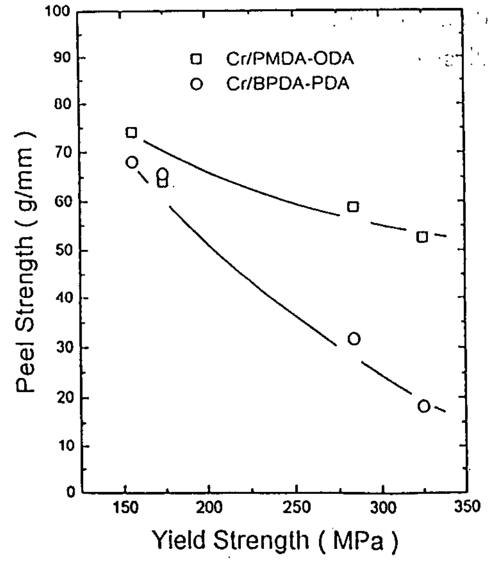

Fig. 4 Peel strength of Or/PMDA-ODA and Cr/BPDA-PDA interfaces vs. yield strength strength Cu/Cr films.

Effects of Cu-Cr alloy adhesion layers

200 nm or 50 nm thick Cu-Cr alloy films with various Cr content were sputter deposited onto RF treated polyimide films (Upilex-s, 40㎛ thick, BPDA-PDA type). 200 nm thick Cu thin films were sputter deposited on Cu-Cr alloy films and Cu was electroplated to the thickness of 20㎛. The conditions of

Cu deposition and electroplating are identical in all specimens. The peel adhesion strength of metal layers (plated Cu/deposited Cu/deposited Cu-Cr) onto polyimide films measured by using modified T-peel test and the results are shown in Fig. 5. The peel strength increases with Cr content in Cu-Cr alloy film and has maximum in the film containing 22-33 wt% Cr. The peel strength of pure Cr film is lower than the maximum.

Cr is more reactive than Cu. Peel strength increases with Cr concentration is expected since stronger interface is formed by adding Cr in the alloy films. However, Cu-Cr alloy film becomes more brittle as Cr concentration increases. Furthermore, the crystallographic structure of Cu-Cr alloy film changes from FCC at low Cr content to BCC at high Cr content[15]. BCC phase is less susceptible to plastic deformation. Metal layers with high Cr concentration are bent less easily during T-peel test and subjected to be deformed less. The FWHMs of Cu(331) peaks presented in Fig. 5 show that the specimen having highest peel strength is deformed most heavily. When the Cu-Cr alloy films are thinner, the mechanical effect is reduced. The peel strength values of 50 nm thick Cu-Cr alloy films were higher than those of 200 nm thick films especially at higher Cr concentration(Fig. 5).

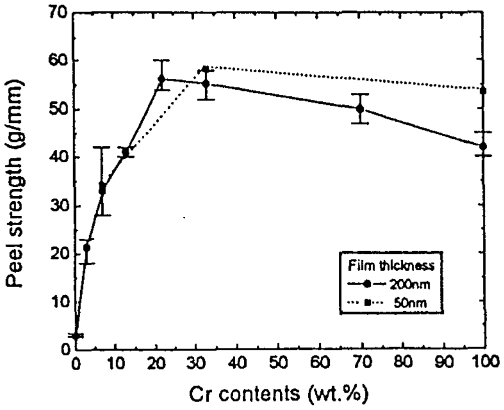

Fig. 5 Average peel adhesion strength between Cu-Cr alloy thin films and polyimide.

CONCLUSION

In Cu/Cr/polyimide system, the peel strength of Cu/Cr film increased significantly by applying in-situ RF plasma treatment on the polyimide surface prior to metal deposition. This enhancement was attributed to the increased Cr-polyimide reactivity. The peel strength of Cu/Cr film to polyimide increased with Cu sputtering pressure and open boundaries formed in the Cu film deposited at high pressure seem to play an important role in increasing the amount of plastic deformation in the metal film. The thickness and mechanical properties of electroplated Cu also influence the peel strength value. The more ductile film is, the higher peel strength it has.

In Cu-Cr alloy films, peel strength increased with increasing Cr content in the alloy film and has a maximum in the film containing 22-33 wt% Cr. The effect of Cr content on the peel strength is interpreted in terms of the interfacial bond strength between Cu-Cr alloy film and polyimide as well as mechanical properties of Cu-Cr alloy films.

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