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# Effects of heat treatment at 350°C on the adhesion of Cu-Cr alloy films to polyimide

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CuCr alloys with varying Cr content were sputter deposited on polyimide films, and the metal/polyimide films were maintained under 350°C/$N_2$ environment up to 10 hours for the reliability measurements. The Cr contents of the alloy layer prepared were 0, 8.5, 17, 25, 34, and 100 atomic %, respectively. Before exposures to 350°C, the peel strength increased proportionally with the Cr content in the alloy layer up to 17 atomic % and saturated. The failure occurred inside polyimide near the metal/polyimide interface by the cohesive failure mode except for the specimen with no Cr. After exposures to 350°C, the peel strength dropped for all the specimens, but most drastically for the specimens with 8.5% Cr which failed along the Cr-oxide/polyimide interface by the interfacial failure mode. Through AES and XPS analyses, it was shown that the decrease of the peel strength during the heat treatment was primarily caused by the formation of brittle $Cr_2O_3$ at the metal/polyimide interface, which was accompanied by the reduction of carbidic bonds responsible for the good adhesion. *© 2000 Kluwer Academic Publishers*

## 1. Introduction

In microelectronics packaging, good adhesion between Cu and polyimide is desired, nonetheless the two materials show inherently poor adhesion strength. Thus, polyimide surfaces are pretreated by rf plasma before the sputter deposition of Cu and a thin layer of Cr is often predeposited as an interlayer to enhance the adhesion strength [1]. In that regard, a typical structure of the two layer films used in the flexible circuit can be written as Cu/Cr/polyimide. Recently, efforts to replace the Cu/Cr double metal layer with a single CuCr alloy layer were made to reduce the number of processing steps [2].

In the present work, CuCr alloy films of varying Cr content were sputter deposited on polyimide before the subsequent thickening of metal films by electroplating Cu, and the reliability of these CuCr alloy/polyimide interfaces against the exposure to 350°C was investigated. The temperature was chosen to simulate tape automated bonding (TAB) inner lead bonding process which involves a thermocompression by a hot thermode (300–600°C) [1]. The adhesion strengths were measured by peel tests, and the mechanisms of the peel strength degradation were investigated through the analysis of peeled metal and polyimide surfaces with Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS).

## 2. Experimental procedure

The polyimide substrates used here were fully cured 50 $\mu$m thick Kapton-H films which is the PMDA-ODA type. Before the deposition of a metal layer, polyimide surfaces were *in situ* rf Ar plasma treated for 3 minutes under the energy density of 1900 W/$m^2$ and deposition Ar pressure ($P_{Ar}$) of 1.33 Pa. The CuCr alloy layers were deposited on pre-treated polyimide surfaces using pure Cu and Cr chips by d.c. magnetron sputtering under the initial vacuum level of $1.33 \times 10^{-4}$ Pa and $P_{Ar} = 0.93$ Pa. The CuCr layer was thickened by depositing Cu by sputtering (950 nm) and electoplating (20 $\mu$m). Thus, the specimen structure can be described as; electroplated Cu (20 $\mu$m)/sputtered Cu (950 nm)/sputtered CuCr alloy (50 nm)/PMDA-ODA (50 $\mu$m). The Cr content in the CuCr alloy layer ($x$) was $0, 2.5, 8.5, 17, 25, 34$ and 100 atomic%, and the

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peel strength was measured in air by the T-peel test at the grip displacement rate of 2 mm/min [2].

The metal/polyimide samples were exposed to 350°C in $N_2$ atmosphere up to 10 hours for the reliability measurements, and peeled metal and polyimide surfaces were analyzed using AES and XPS. The AES operating conditions were: incident beam energy = 3 keV, electron beam current = 50–100 nA, and the AES depth profiling was conducted under Ar ion beam energy = 2 keV and ion current density = 0.5 $\mu$A/cm$^2$. Similarly, operating conditions of XPS were; incident beam energy = 12.5 kV, electron current = 20 mA and the X-ray source = Al $K_\alpha$ (1486.6 eV).

## 3. Results and discussion

### 3.1. Peel strength of metal/polyimide films

The peel strengths of the metal/polyimide films before the 350°C treatment are shown in Fig. 1 as a function of the Cr content in the CuCr alloy layer ($x$, in atomic %). The peel strength was very low for pure Cu but increased almost linearly with Cr up to 17 atomic %. The trend is essentially similar to what was found in the CuCr alloy/$Al_2O_3$ system by Chan *et al.* [3] and Lee *et al.* [4]. The principal role of the Cr in the alloy layer is thought to form carbidic and oxide bonds with the C and O atoms of polyimide, respectively, and raise the peel strength [5, 6]. The peel strength increase at the low Cr content ($x \leq 17$), therefore, can be explained by the formation of the Cr—C bond, and to a minor degree by the formation of Cr—O bonds [7]. The saturation of the peel strength near 17% Cr is not fully understood at the present moment. One possibility is that the interface chemistry does not change much with the addition of Cr over 17%, presumably due to the saturation of the Cr-polyimide bonding sites at the metal/polymer interface. Other posssibilities include the nucleation of the Cr-rich bcc phase around that composition [8], increases of the Young's modulus or hardness of the alloy layer with Cr [9].

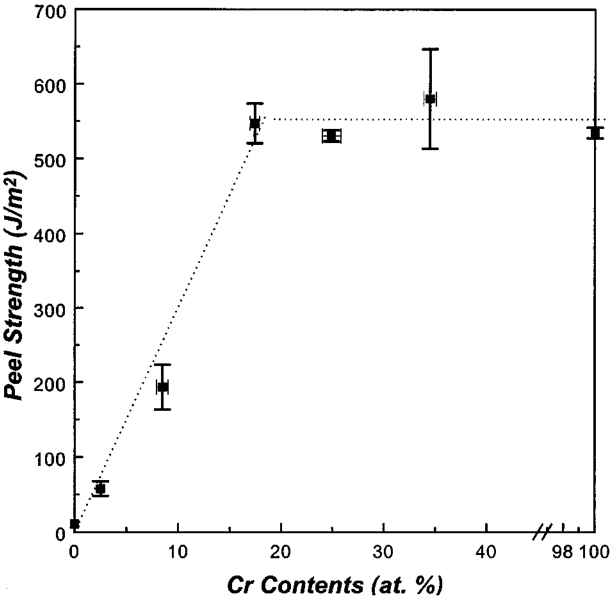


*Figure 1* Peel strengths of CuCr/polyimide films as a function of the Cr content in the alloy layer ($x$).

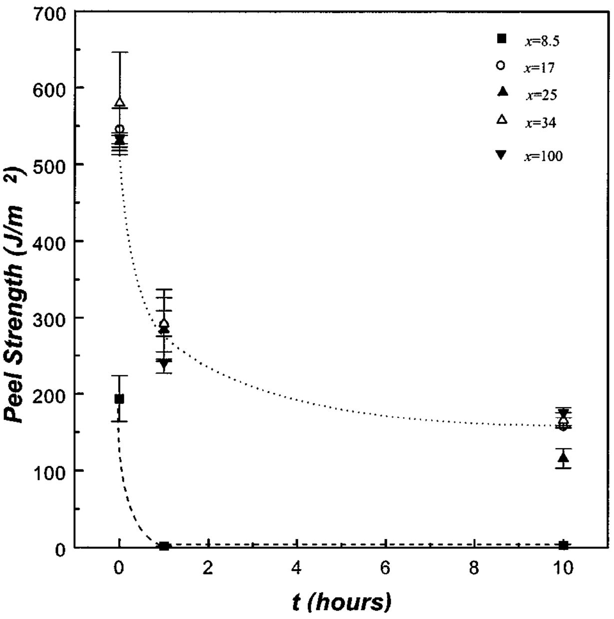


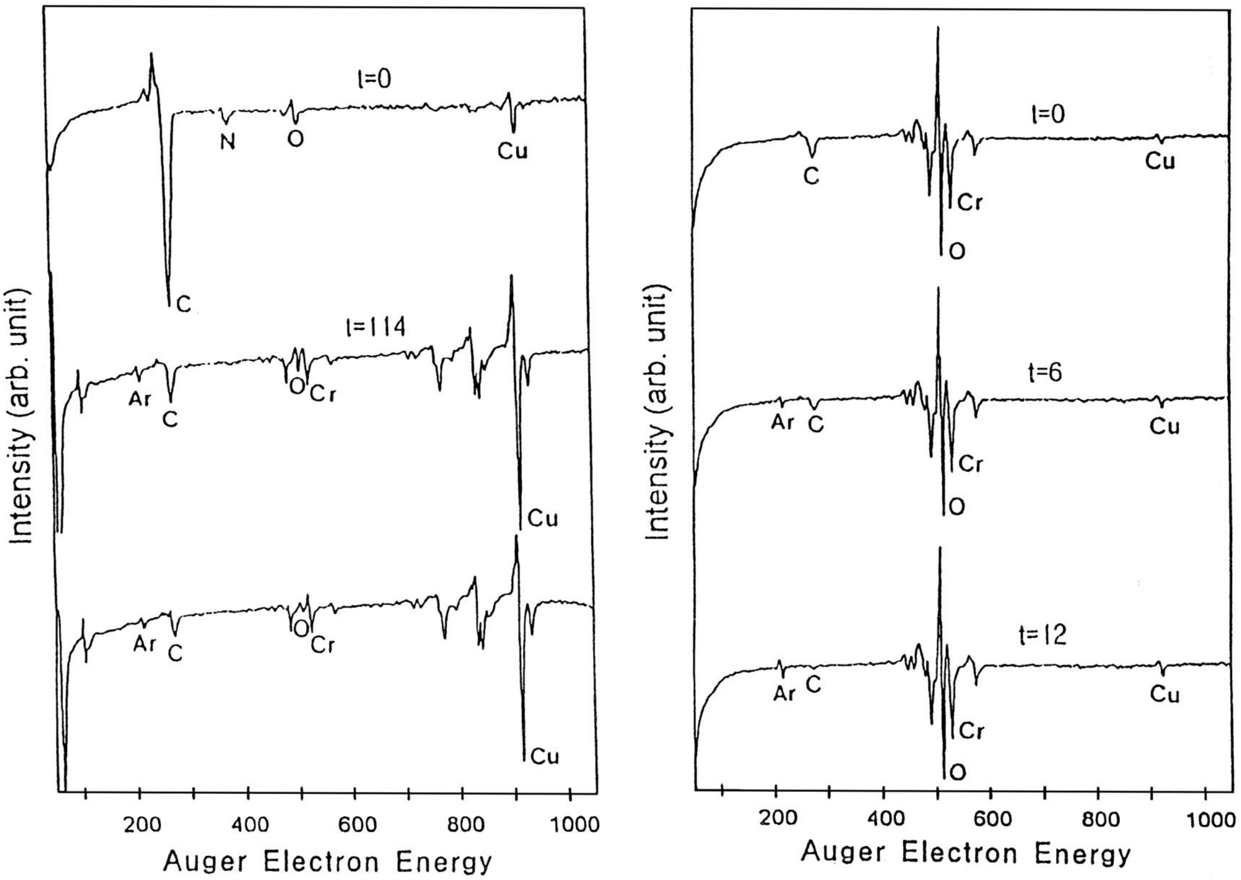
*Figure 2* Degradation of peel strengths in CuCr/polyimide specimens with the exposure time at 350°C.

### 3.2. Effects of heat treatments at 350°C

The peel strengths of the specimens are presented as a function of the hold time at 350°C in Fig. 2 where the specimen with 2.5% Cr was not studied because of the poor peel strength in the as-deposited condition (cf Fig. 1). All the specimens studied showed peel strength degradations, but among them the specimen with 8.5% Cr in the CuCr alloy layer was the most susceptible. After an hour at 350°C, the peel strength of that specimen dropped from 196 J/m$^2$ to almost nil, while the other specimens with higher Cr content showed more or less the same trend; i.e., the initial peel strength (548.8 ± 49 J/m$^2$) dropped to 277.3 ± 33.3 J/m$^2$ after an hour, and to 153.9 ± 24.5 J/m$^2$ after 10 hours. Therefore, it can be said that the peel adhesion strengths of the specimens with Cr content equal to or larger than 17% were resonably good even after the 10 hours exposure to 350°C. During the heat treatment, the metal/polymer interface chemistry may change due to the reactions among Cr, C and O atoms of polyimide, and adsorbed water in polyimide. Furthermore, mechanical properties of the metal layer change due to the annealing treatment. However, the peel strength is mostly affected by the amount of plastic deformation of the metal layer during the peeling process, which increases with the hardness drop [10–12]. Thus, the softening of the metal layers during the heat treatment is not expected to be a primary reason for the peel strength degradation observed here. Instead, in what follows, we show that the peel strength degradation is a direct consequence of the change in interface chemistry caused by Cr-oxide formation and reduction of Cr—C bonds at the metal/polyimide interface.

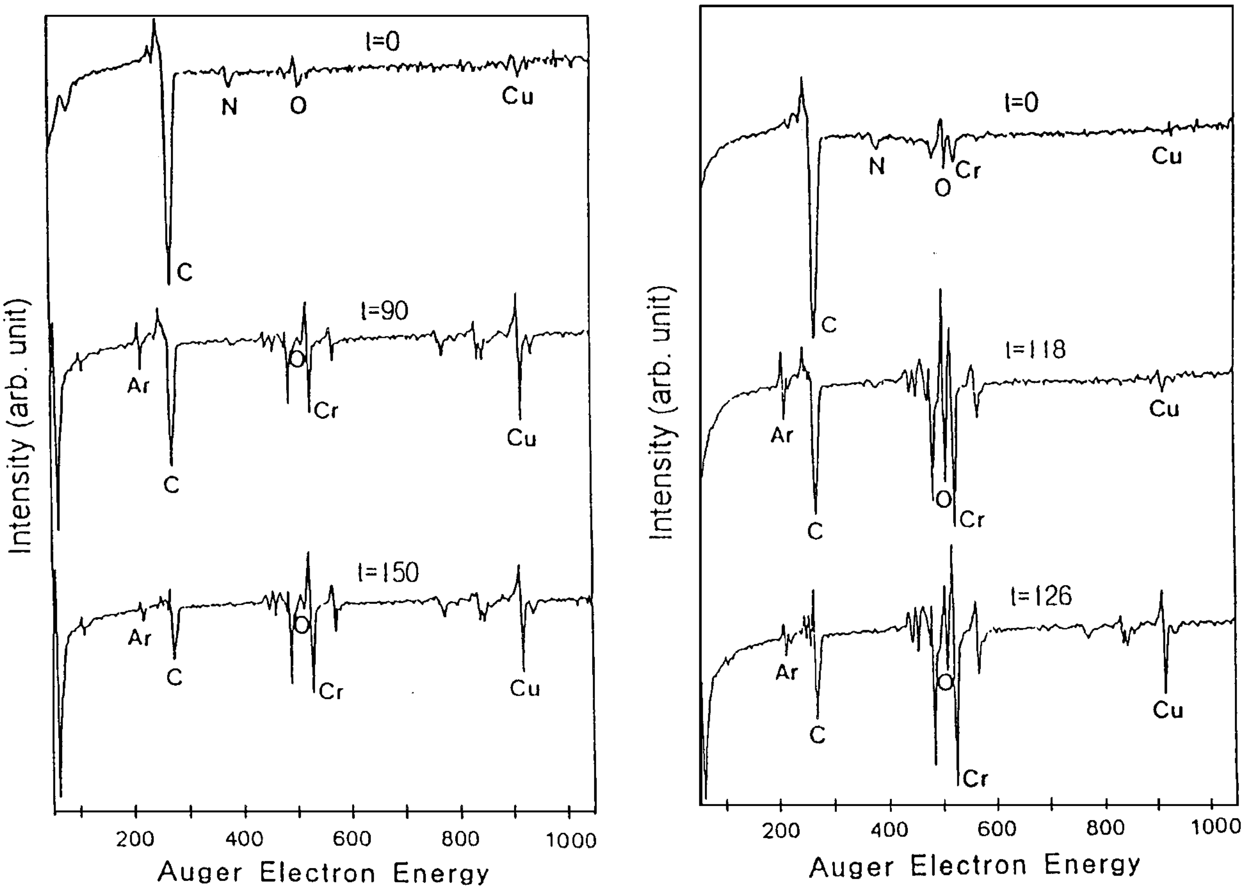
#### 3.2.1. AES analysis

In Fig. 3, peeled metal surfaces of the specimen with 8.5% Cr, before and after a heat treatment (1 hour at 350°C), were studied with AES, and the Auger spectra



(a) (b)

*Figure 3* Variations of Auger spectra during the *in situ* depth monitoring of peeled metal surfaces of the specimen with 8.5% Cr (a) before and (b) after heat treatment of 1 hour at 350°C. The sputtering time is given in seconds in this figure.



(a) (b)

*Figure 4* Variations of Auger spectra during the *in situ* depth profiling of the specimen with 34% Cr (a) before and (b) after heat treatment of 1 hour at 350°C. The sputtering time is given in seconds.

before and after the Ar ion sputtering are presented for both cases. The specimen without the heat treatment showed a typical Auger spectrum of polyimide on Cu before the Ar sputtering ($t = 0$), which can be seen from the N and large C peaks coming from the polyimide and the Cu peak coming from the metal layer beneath (or around) polyimide. With the Ar ion sputtering, the C and N peaks were greatly diminished, and a small fine-structured C peak coming from the carbide-like bond [13, 14] was noticed, which indicates the formation of Cr—C bonds between C atoms of polyimide and Cr atoms in the alloy layer. The presence of Cr—C bonds was consistent with the reasonable peel strength of the untreated 8.5% Cr specimen (cf Fig. 3a).

After the heat treatment of 1 hour at 350°C, the Auger spectrum from the same specimen showed large O and Cr peaks coming from the Cr-oxide at the metal/polyimide interface (cf Fig. 3b) [13]. Since an XPS study of the peeled polyimide film did not show any Cr or Cu peaks, it was thought that the peeling took place along the Cr-oxide/polyimide interface. In the literature, the interfacial failure caused by oxides at the interface has been reported in Cr/polyimide [13], Ti/polyimide [15], and Ta/polyimide [16] systems. When the heat treated specimen was sputtered by Ar ion for 12 seconds, the O and Cr peaks coming from the Cr-oxide remained undiminished, but the C peak coming from exposure to air after the peel test disappeared completely without showing any fine structured C peaks during the sputtering process (cf Fig. 3b). Thus, the formation of Cr oxide and depletion of Cr—C bonds at the metal/polyimide interface are thought to be two principal factors affecting the peel strength degradation. A subsequent selected area electron diffraction analysis of the same specimen identified the Cr-oxide as $Cr_2O_3$ (cf Fig. 6). The reason why the formation of $Cr_2O_3$ at the metal/polyimide interface lowers the peel strength is not so clear at the moment. One possibility is that the formation of $Cr_2O_3$ results in the complete bond separation from the polyimide. Thermodynamically, Cr reacts preferentially with O rather than with C, and forms a stable oxide, which tends to reduce the number of beneficial Cr—C or Cr—O bonds at the interface. The other possibility is the mechanical effect caused by the presence of brittle oxides at the metal/polyimide interface which tends to reduce the peel strength in a similar way as the presence of brittle carbides lowers the fracture toughness of tempered steels [17].

Since the specimens with Cr content higher than 17% showed more or less the same trend, only the specimen

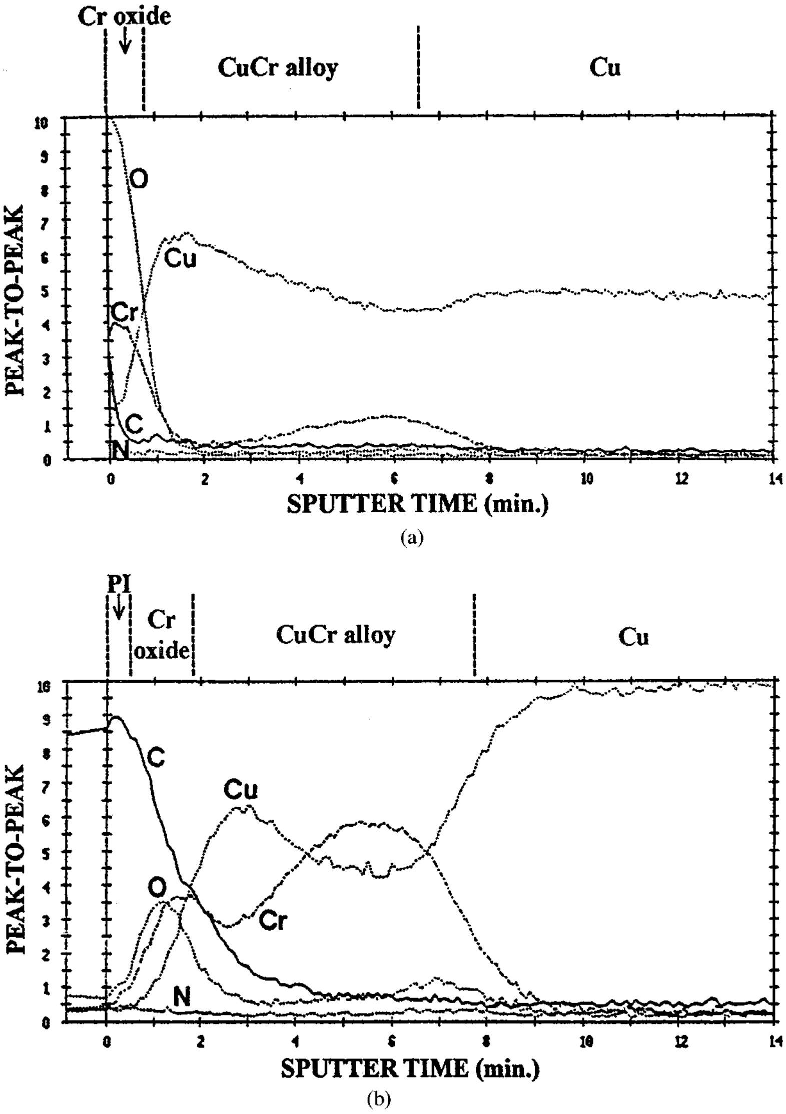
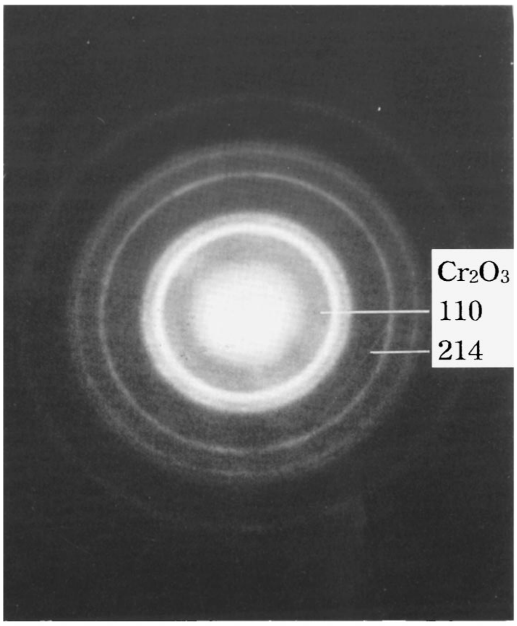


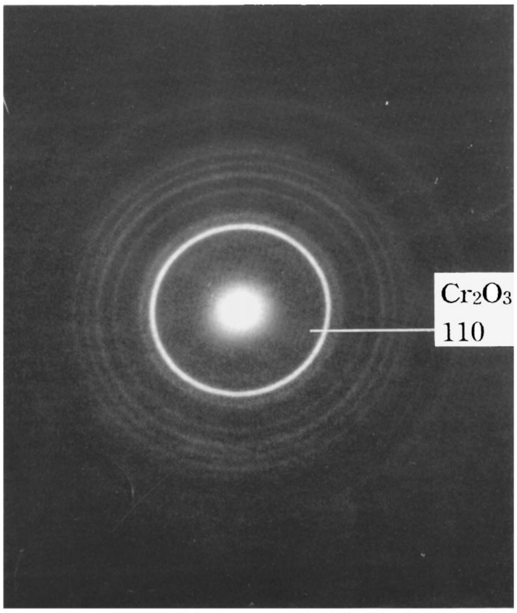
*Figure 5* AES depth profiles of peeled metal films of the specimens with (a) 8.5% Cr and (b) 34% Cr after the heat treatment of 1 hour at 350°C.

with 34% Cr was chosen for analysis and their Auger spectra are shown in Fig. 4. Before the heat treatment, the specimen failed in a cohesive mode as can be seen from C, N and O peaks coming from polyimide (cf Fig. 3a), and the fine structured C peak from the carbide-like Cr─C bonds was observed when sputtered for 150 seconds (peel strength = 578.2 J/m$^2$) (cf Fig. 4a). The large Cu and Cr peaks observed at the intermediate stage ($t = 90$ seconds) came from the alloy layer around or beneath the thin polyimide layer. Even after the heat treatment of 1 hour at 350°C, the failure mode is mostly cohesive as can be seen from the N, C, and O peaks of Fig. 4b. After sputtering, the specimen showed the fine structured C peak coming from the carbide-like bonds as well as the Cr and O peaks from the Cr oxide and the Cu and Cr peaks from the CuCr alloy as shown in Fig. 4b. Therefore, despite the formation of Cr-oxide, a substantial amount of Cr─C carbide-like bond persists at the metal/polyimide interface due to the high Cr content, and that was responsible for the reasonably high peel strength observed.

The AES depth profiles of peeled metal surfaces of the two specimens (8.5 and 34% Cr) which were heat treated for 1 hour at 350°C are presented in Fig. 5. High Cr and O Auger peaks were found on the failure surface for the 8.5% Cr specimen suggesting a failure along the Cr oxide/polyimide interface. However, N, O, and a large C peaks were observed on the failure surface, and the maximum O and concomitant Cr peak occurred after sputtering for one to two minutes. Also, a gradual decrease of the C peak with the sputtering time indicates that the C came from adhered polyimide and not from contamination during an exposure to air. Therefore, the failure occurred in the polyimide and not along the Cr-oxide/polyimide interface for the specimen with 34% Cr. Therefore, the interfacial failures were found in the 8.5% Cr specimens heat treated for 1 hour at 350 °C where Cr-oxide formation and Cr─C bond depletion occurred simultaneously at the metal/polyimide interface. Note from the heat treated 34% Cr specimen the Cr enrichment at the Cr-oxide and CuCr alloy/Cu interfaces, and the slight Cu enrichment at the Cr oxide/CuCr alloy interfaces. Effects of the Cu and Cr segregation on the peel strength remain unclear from this study.



(a)



(b)

*Figure 6* Selected area diffraction patterns out of Cr oxides at the CuCr alloy/polyimide interface of the specimens with (a) 8.5% Cr and (b) 34% Cr after the heat treatment of 1 hour at 350 °C.

### *3.2.2. TEM analysis*

In order to identify the Cr oxide present at the metal/polyimide interface, unpeeled specimens were heat treated for 1 hour at 350°C, and TEM specimens were prepared by preferential grinding from the metal side until the selected area diffraction pattern (SADP) from the Cr oxides at the CuCr alloy/polyimide interface were obtained. In this process, metal oxides existing on the surface of the metal layer were carefully excluded by ion milling. Fig. 6 illustrates ring patterns from the Cr oxide of the specimens with 8.5 and 34% Cr which were identified as $Cr_2O_3$ for both specimens. Note that $Cr_2O_3$ formed at the CuCr alloy/polyimide interfaces during the heat treatment for both cases, but only the specimen with 8.5% Cr showed interfacial failure due to the lack of sufficient Cr─C bonds.

### *3.2.3. XPS analysis*

In the XPS analysis of peeled metal surfaces, specimens were subjected to continuous *in situ* Ar ion sputtering, and XPS spectra were obtained at several stages of the sputtering process. Figs 7 and 8 show variations of the C 1s peak during the sputtering of the peeled metal surfaces of the specimen with 8.5 and 34% Cr, respectively. In the case of the 8.5% Cr specimen, a typical C 1s peak of polyimide which consists of carbonyl bond (near 289.4 eV) and aromatic or graphite carbon (near 285 eV) was observed before the sputtering due to the presence of polyimide on the metal surface [15]. However, most of the carbonyl peak disappeared after 60 seconds of Ar ion sputtering, and the C 1s peak showed a mixture of peaks coming from the aromatic or graphite carbon and the other coming from

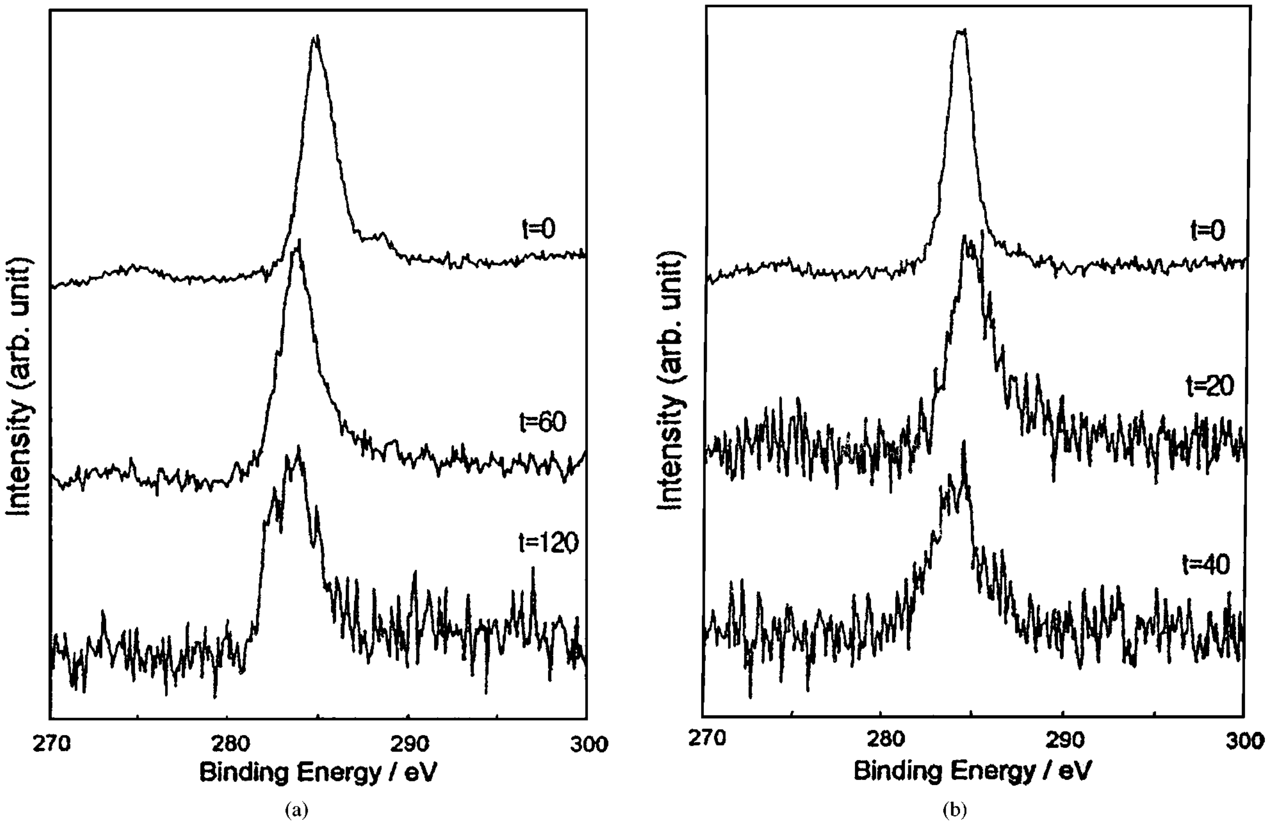


*Figure 7* Variations of the C 1s peak in XPS during the *in situ* sputtering of peel metal surfaces of the specimen with 8.5% Cr (a) before and (b) after the heat treatment of 1 hour at 350°C.

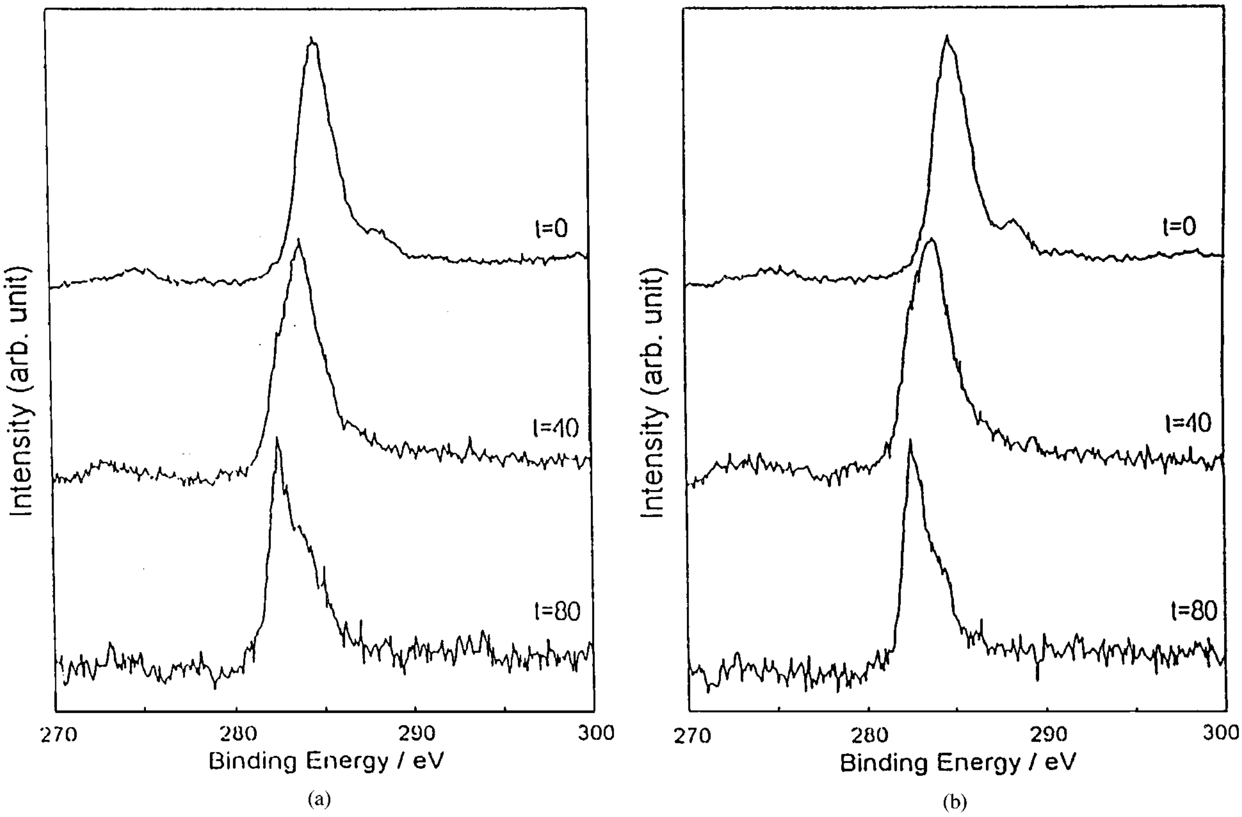


*Figure 8* Variations of the C 1s peak during the *in situ* sputtering of the specimen with 34% Cr (a) before and (b) after the heat treatment of 1 hour at 350°C.

the carbide like carbon (282.5 eV). It can be seen that the carbide-like peak became slightly more distinct with further sputtering. After the heat treatment of 1 hour at 350°C, the C 1s peak from the peeled metal surface before the Ar sputtering showed no peak coming from the carbonyl bonding of the polyimide but only the peak due to adsorbed carbon, which is consistent with the occurrence of the interfacial failure between CuCr alloy and polyimide. With sputtering, the absorbed carbon peak was diminished without showing the carbide-like carbon peak. Note that the overall binding energy of the C 1s peak is shifted toward higher energy due to the electron charging effect.

In the case of the specimen with 34% Cr without the heat treatment, the C 1s peak showed the carbonyl bond peak before the sputtering, but strong carbide-like carbon peak after sputtering of 80 seconds. Basically, the same was true of the same specimen after the heat treatment. Therefore, a substantial amount of the Cr—C carbide-like bond was thought to remain at the metal/polyimide interface even after the heat treatment of 1 hour at 350°C. The XPS results are completely consistent with the AES results.

Up to now, we have shown that the specimen with 8.5% Cr had a reasonable adhesion strength (peel strength = 196 $J/m^2$) before the heat treatment due to the presence of Cr—C (or Cr—O) bonds at the metal/polymer interface, but had no adhesion strength (peel strength ∼ 0 $J/m^2$) after 1 hour at 350°C due to the formation of $Cr_2O_3$ and the depletion of the Cr—C carbide-like bonds at the interface. In contrast, the specimen with 34% Cr showed high peel strength (peel strength = 578 $J/m^2$) before the heat treatment due to the abundant Cr—C carbide-like bonds (or Cr—O) at the interface. After 1 hour at 350°C, $Cr_2O_3$ formed at the interface, but a substantial amount of Cr—C carbide-like bonds remained, thereby giving reasonably high peel strength (peel strength = 294 $J/m^2$). Therefore, it can be concluded that the peel strength degradation is caused by the formation of $Cr_2O_3$ phase at the metal/polyimide interface, and that the effect is most devastating for the specimen with low Cr content where Cr—C carbide-like bonds are depleted.

## 4. Conclusions

1. The peel strength of the metal/polyimide film increased almost linearly with the Cr content in the CuCr alloy layer up to 17 atomic % Cr, but reached a saturation level with more Cr.

2. An exposure to 350°C decreased the peel strength at all Cr levels in the CuCr alloy layer mainly by the formation of $Cr_2O_3$ at the metal/polyimide interface. Among the specimens studied, the specimen with the lowest Cr (8.5%) was the most susceptible to the peel strength degradation by the 350°C heat treatment. Only after an hour at 350°C, the specimen was peeled along the $Cr_2O_3$/polyimide interface showing almost zero peel strength. Subsequent AES and XPS analyses showed that the carbide like Cr—C bonds at the metal/polyimide interface was almost depleted during the heat treatment. In contrast, specimens with higher Cr content had substantial amount of the carbide like Cr—C bonds at the metal/polyimide interface after 1 hour at 350°C despite the formation of Cr-oxide, and showed reasonably high peel strength.

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