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Metallization on Polyimide Film by Ion and Vapor Deposition (IVD) Method†

Akinori EBE*, Yuicji SETSUHARA and Shoji MIYAKE*****

Abstract

A study was performed to investigate the effect of argon ion bombardment for improvement of copper film adhesion on polyimide film substrates. The thin copper films were prepared on polyimide films by evaporation of copper metal and simultaneous irradiation by argon ions with energies in the range of 0.5 to 10.0keV. The argon ion density irradiated at the interface between the copper thin film and the substrate was changed from $5X10^{14}$ to $5X10^{16}$ ions/cm^2 in each ion energy range. The adhesion of copper films was evaluated by means of peel strength. The copper films prepared with 0.5keV argon ions have strong adhesion, but the adhesion of copper films with 5.0keV and 10.0keV argon ions was lower than that of copper films prepared without argon ion bombardment. The chemical states of the polyimide film surface and the chemical binding states at the interlayer were evaluated by X-ray photoelectron spectrometry. The structure of the interface between the copper film and the polyimide substrate was analyzed by transmission electron microscopy. The argon ion bombardment carbonized the film surface, and the increase of the carbonization caused the decrease of the adhesion. The increase of the adhesion did not depend on the change of chemical binding states at the interlayer. The interface structures prepared by ion bombardment have a mixed layer consisting of the copper atoms diffused into the substrate and the carbon atoms from the polyimide. The formation of the mixed layer by ion bombardment contributed to improve the copper film adhesion.

KEY WORDS: (Ion beam and Vapor deposition)(Copper)(Polyimide) (Adhesion)(Interface)

1. Introduction

Adhesion of copper films on polyimide substrates is becoming important for microelectronic applications, such as multilayer packaging and flexible circuit boards. The adhesion is determined by the nature and structure of the interface region between the copper film and the polyimide substrate. Therefore, the techniques of enhancement of the copper film adhesion have been investigated, and used to control the chemistry and structure of the metal/polymer interfaces by using plasma treatment processes and deposition of reactive metal layers on the polyimide surface (such as titanium and chromium)[1-4].

Recently, many investigations of the improvement of metal film adhesion on polymers by means of ion beam irradiation of the metal/polymer interface have been reported[5-8]. Ion bombardment of the interface can be expected to change the interface structure, enhancing film adhesion at near room-temperatures, through interfacial mixing and the production of new chemical bonding at the interlayer.

In this paper, copper films were prepared on polyimide film substrates by evaporation of copper metal and simultaneous argon ion bombardment at 0.5-10.0keV (IVD method). The adhesion of the samples was measured by using a 90° peel test method. The surface chemical states of the substrates and the chemical binding states at the interlayer were evaluated by X-ray photoelectron spectrometry. The structure of the interface was observed by using cross-sectional transmission electron microscopy. The effect of argon ion bombardment on the adhesion was examined.

2. Experimental

A IVD system developed in Nissin Electric Co. was used for the preparation of copper film. The details of the system have been described elsewhere[9]. The polyimide films (kapton) with 50μm thickness were used for the substrates, and the substrate temperature was kept below 100°C by a

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water cooling system during film formation. Firstly, copper was evaporated on the substrate which has simultaneously bombarded with argon ion . The thickness of the copper films was 100Å. The energy range of argon ions was varied from 0.5 to 10.0keV and the argon ion dose density was varied from $5X10^{14}$ to $5X10^{16}$ ions/cm^2. The ion current density was held constant at 0.32mA/cm^2. In order to change the transport ratio of copper atoms to argon ions, the evaporation rate of copper metals was changed in the range of 0.5 to 40.0Å/sec. Next, copper was deposited without ion bombardment. The total copper film thickness was 1μm.

In order to measure the adhesion of the samples by a 90° peel test method, 30μm thick copper film was electroplated and strips of 2X50mm were marked on the samples by chemical etching. These striped copper films were peeled off with a peeling speed of 5cm/min.

The chemical states of the polyimide film surfaces and the chemical binding states in the interlayer were analyzed by X-ray photoelectron spectrometry (XPS). An investigation of the chemical binding states at the Cu/PI interface was performed by XPS analysis of the 40Å copper film on the PI substrate without ion beam etching to avoid the effect of the ion beam etching on the chemical binding states.

Cross-sectional transmission electron microscopy (XTEM) analysis was performed to observe the change at the Cu/PI interface structure following ion bombardment. The XTEM observations were made in a HITACHI H9000 electron microscope operated at 300keV. To analyze the

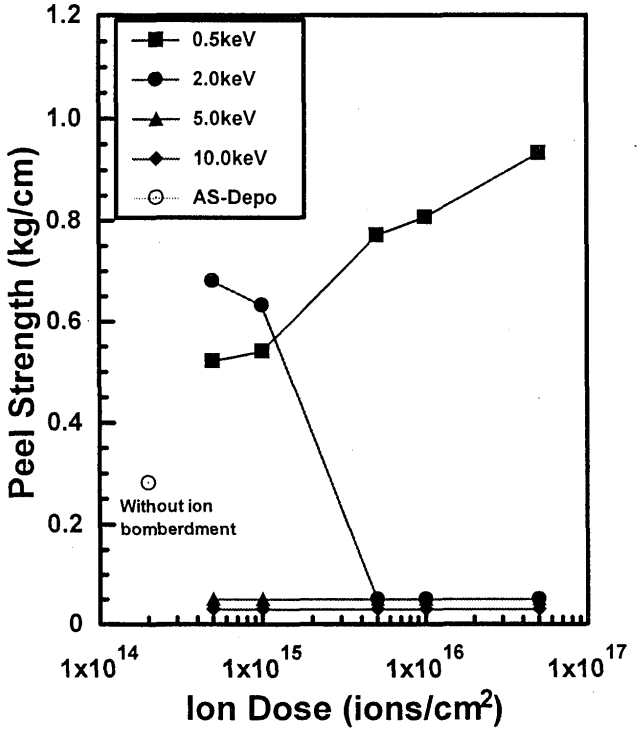

Fig. 1. The relationship between argon ion density at the interlayer and the peel strength of copper films prepared with various argon ion energy.

elements of the interlayer, energy dispersive X-ray spectroscopy (EDXS) analysis was performed in a VG HB501 system.

3.Results and Discussion

The relationship between argon ion dose density at the interlayer and the peel strength of copper films prepared with various argon ion energies is shown in **Fig.1**. Double circle in Fig.1 means the adhesion of copper film without argon ion bombardment. The peel strength of the Cu films prepared with 0.5keV argon ion increases with increasing ion dose density. However, at 2.0keV argon ions, the peel strength of the films decreases remarkably with increasing ion dose density and the peel strength at $5X10^{15}$-$5X10^{16}$ions/cm^2 ion dose density became lower than the films without argon ion bombardment. The peel strengths at 5.0keV and 10.0keV are lower than that of Cu film without argon ion irradiation in spite of the change of ion dose density. These results show that the ion irradiation to the interface between Cu film and polyimide film has a large effect on the adhesion of Cu film. It seems that the change of the adhesion was attubuted to the change of the Cu-PI interface structure cuesed by the ion bomberdment, such as a change in the surface chemical state of the polyimide, the chemical binding states at the interlayer and the diffusion of Cu atoms into the substrate. Therefore, we studied the relationship between the change of interface states by the argon ion bombardment and the adhesion of Cu films.

To study the variation of the chemical binding states in the polyimide surface following argon ion bombardment, surfaces bombarded with 2.0keV argon ions were examined using XPS analysis. XPS spectra of C_{1s}, N1s and O_{1s} photoelectrons for the polyimide surface are shown in **Fig.2**(a),(b) and (c). The C_{1s} spectrum of polyimide film without ion bombardment in Fig.2(a) shows a clear peak at about 285eV with a shoulder peak at 288eV due to the C=O bond.[5)]

With the increase of ion dose density at 2.0 keV, the peak position of C_{1s} spectrum of the polyimide film begins to shift to the position of the binding state due to the C-H bonded carbon (graphitic C),[5)] while the peak intensity of C=O bonded carbon has decreased. In Fig.2(b), the N1s spectrum obtained from the polyimide without ion bombardment is dominated by the imide peak at 400.4eV[5)]. After the ion bombardment, broad peaks are observed at 399eV and these peaks position correspond to C-NR^2 bonds[5)]. The O_{1s} peaks in Fig.2(c) are also changed into broad peaks by ion bombardment. **Fig.3** shows the relationship between the ion dose density and the composition ratios of nitrogen and oxygen on the polyimide surface. The composition ratios were calculated from the

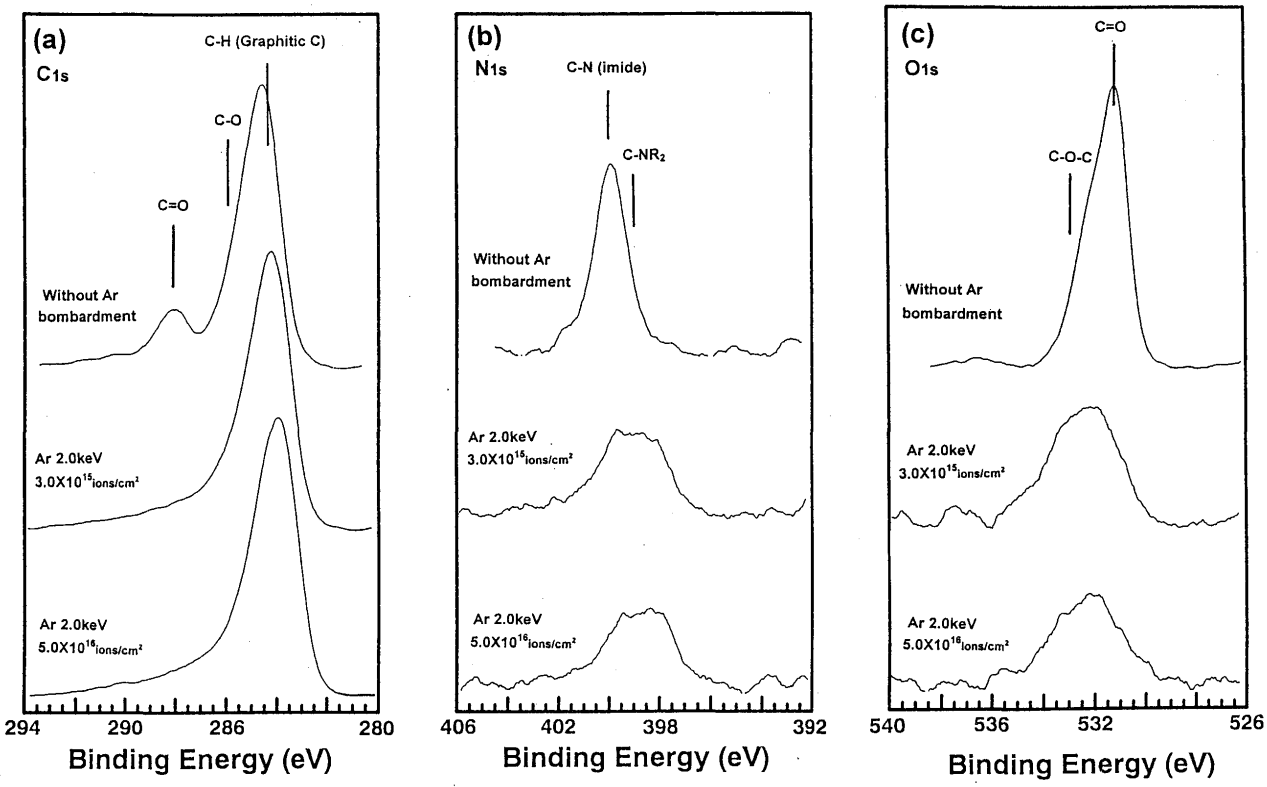

Fig. 2. XPS spectra of polyimide films bombarded by 2.0keV argon ions.

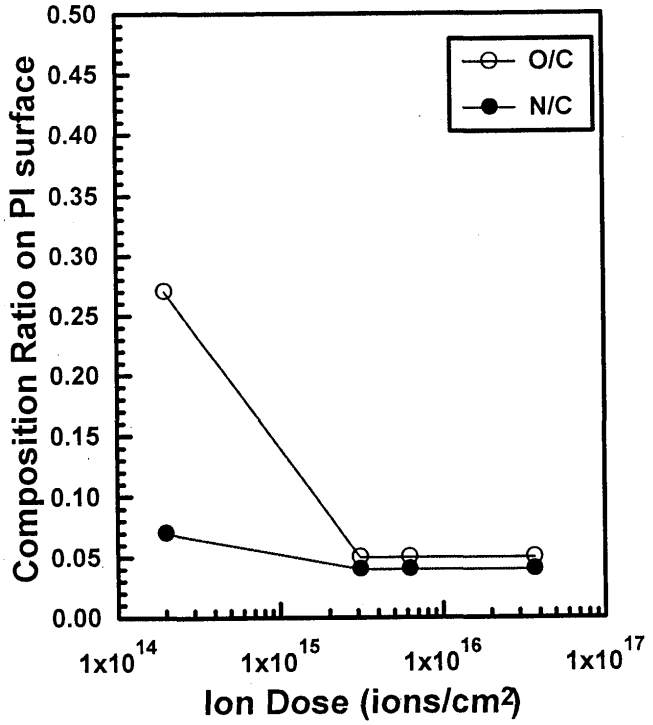

Fig. 3. The relationship between argon ion density and composition ratio for polyimide films bombarded by 2.0keV argon ions.

ratio of each peak intensity of O_{1s} and N_{1s} photoelectrons to those of C_{1s} ones by photo-cross section. The composition ratio of both nitrogen and oxygen were decreased with the increase of the ion dose density. From these results, it is conculuded that argon ion bombardment cuts off chemical bonds on the polyimide surface and the polyimide surface is hereby carbonized.

To investigate the effect of carbonization of the polyimide substrate on adhesion, copper films were prepare by the IVD method with 0.5keV, $5.0X10^{16}$ions/cm^2 argon ions on the polyimide surface bombarded with 1.0keV argon ions before the copper deposition. The ion dose density of the pre-ion bombardment was changed from $1X10^{15}$ to $5X10^{16}$ ions/cm^2 to increase the carbonization of the polyimide substrate. The adhesion of these samples was evaluated by using a pull test because these adhesion was too low to measure with a peel test. The relationship of the ion dose density of the pre-treatment and the pull strength of the copper films is shown in **Fig.4**. The pull strength in Fig.4 decreases with an increase in the pre-treatment ion dose density. This result indicates that increasing carbonization of the polyimide causes a decrease in the copper film adhesion. Therefore, it is thought that the decrease of the copper film adhesion with 5.0,10.0keV in Fig.1 is caused by the increase of the carbonization by high energy ion bombardment.

The chemical binding states at the film-substrate interlayer prepared with 0.5 keV argon ions are examined by using XPS, as shown in **Fig.5**. In Fig.5(a), the peak of C=O bonded carbon at 288eV decreases and the

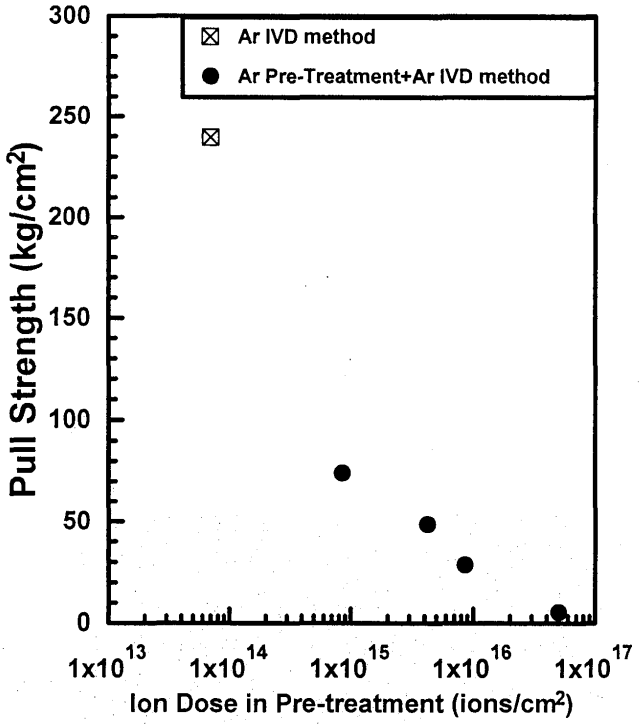

Fig. 4. The relationship between argon ion density in the pre-treatment process and the pull strength of copper films prepared with 0.5keV $5.0X10^{16}$ions/cm^2 argon ions.

carbonization at the interlayer increases with increasing argon ion dose density. In Fig. 5(b), the Cu_{LMM} spectrum of Cu films without ion irradiation shows a large broad peak at about 334.6eV with three shoulder peaks at about 322eV, 337eV and 338.8eV. The peak intensity at 337eV, which agrees with Cu-O bonded copper atoms, is changed with argon ion dose density. From these spectra, however, here is no evidence of large chemical peak shifts which would suggest the formation of new chemical bond at the Cu/PI interlayer, such as a C-Cu bond.

In order to study the effect of copper oxides on the adhesion, the relationship between the peel strength of Cu films and the composition ratio of copper oxide at the interlayer is shown in **Fig.6**. The composition ratio of copper oxide is calculated from the ratio of the peak intensity at 337eV of Cu_{LMM} photoelectrons to those of C_{1s} by photo-cross section. The peel strengths of Cu films evidently do not depend on the composition ratio of copper oxide. The increase in adhesion of Cu films by ion irradiation is not attributable to the formation of copper oxide at the film-substrate interlayer; therefore it is considered that the diffusion of Cu atoms into the substrate during argon ion bombardment causes the increase of the adhesion.

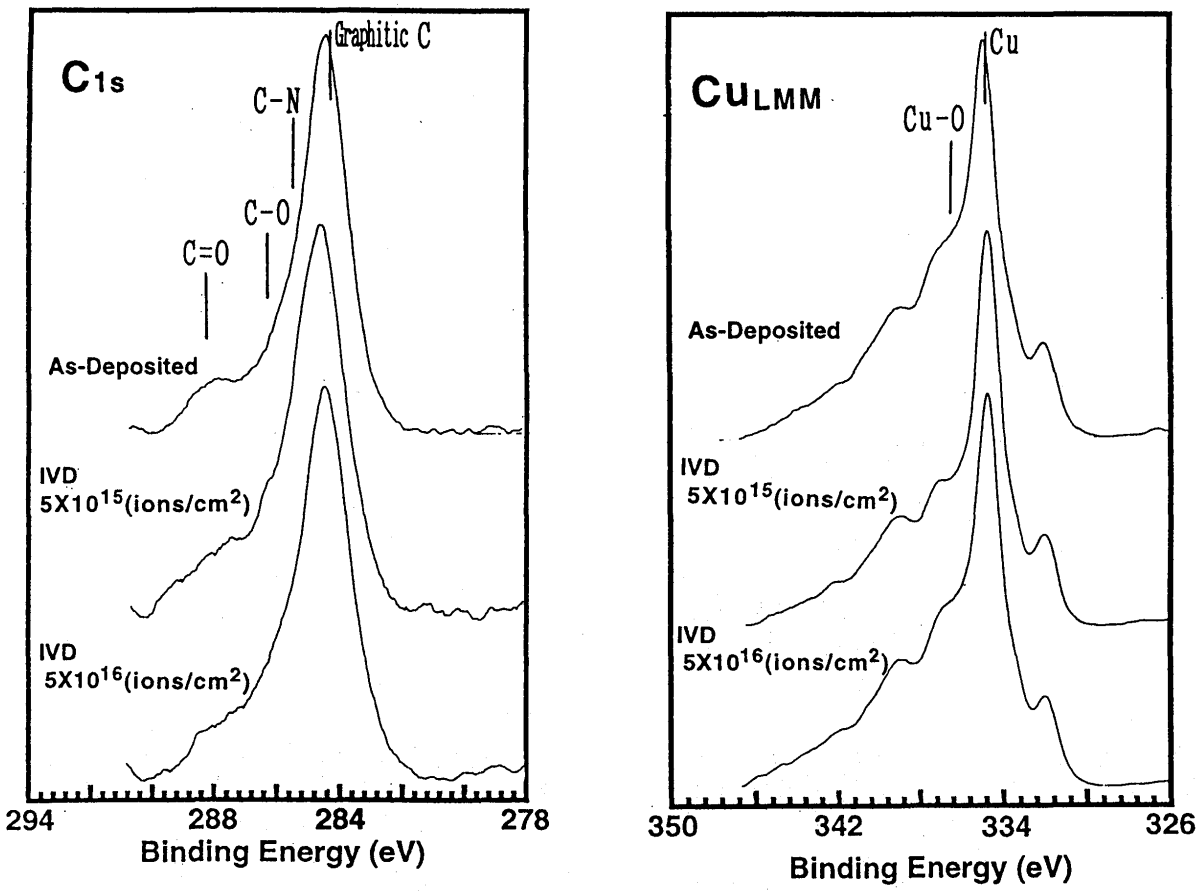

Fig. 5. XPS spectra of interface between copper film and PI film prepared with 0.5keV argon ions.

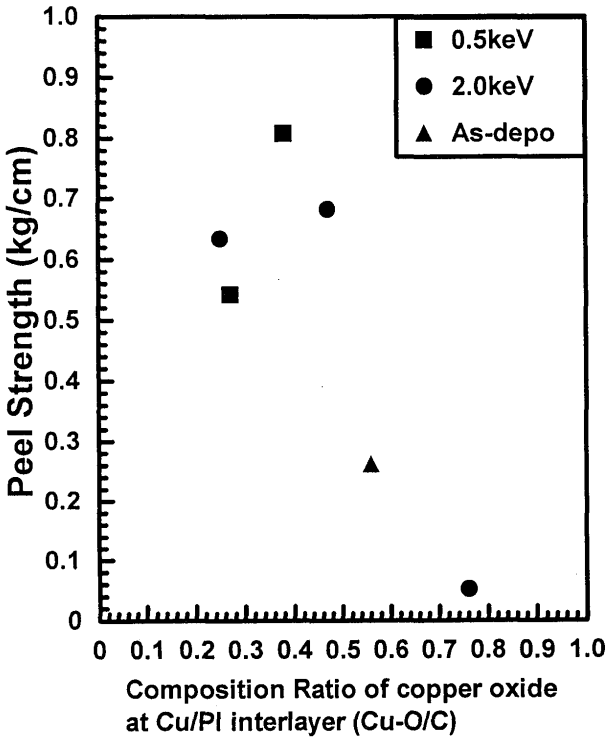

Fig. 6. The relationship between the peel strength and composition ratio of copper oxide at the interface.

Fig.7 shows the XTEM micrographs that illustrate the interface structure between the polyimide substrate and the copper films. The Cu/PI interface prepared without the ion bombardment in Fig.7(a) has a clear and flat interlayer. In fig.7(b), spotted dark areas appear at the interface prepared with 0.5keV $5X10^{16}$ions/cm^{15} argon ion density. EDXS analysis was performed to reveal the elements in these dark areas. The EDXS spectra of the dark area marked with a black dot in Fig.7(b) is shown in fig.8. It is found that the dark area contain Cu atoms and the carbon atoms of the polyimide. These results indicate that the argon ion bombardment has caused the formation of an intermixed layer between the copper film and the polyimide substrate. Therefore, it is considered that the increase of the adhesion is attributable to an anchor effect caused by the formation of the intermixed layer following argon ion bombardment. However, argon ion bombardment causes not only the formation of the intermixed layer but also carbonization which results in a decrease of adhesion at the interlayer. Therefore, it is important to control ion bombardment conditions to minimize carbonization at the interlayer in order to improve the adhesion.

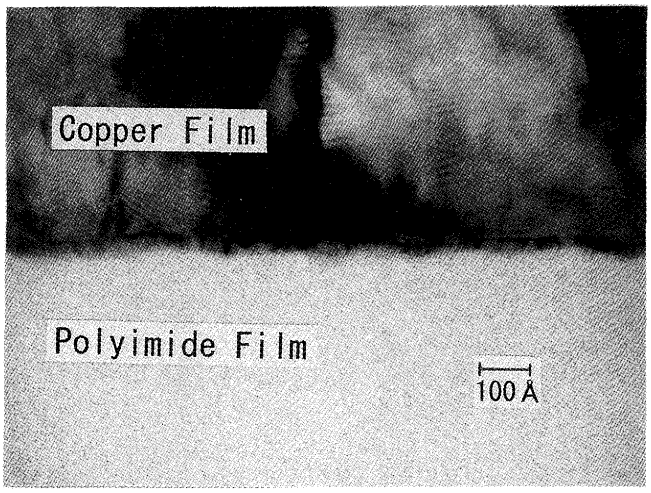

Fig. 7. (a) TEM micrograph of the interface betwen the copper film and the polyimide film prepared without argon ion bomberdment.

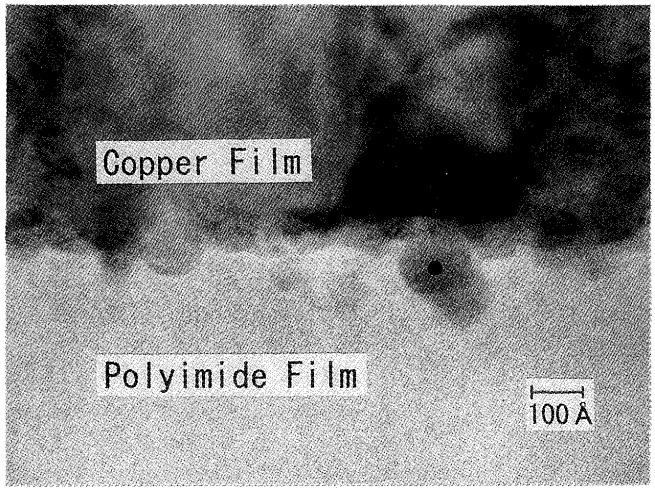

Fig. 7. (b) TEM micrograph of the interface betwen the copper film and the polyimide film prepared with 0.5keV, $5.0X10^{16}$ions/cm^2 argon ion.

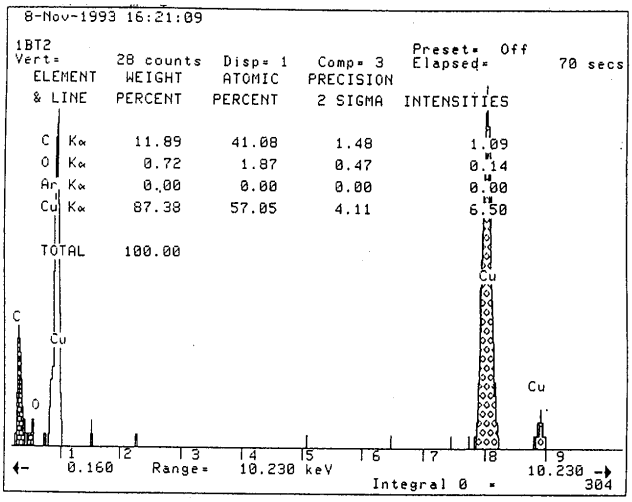

Fig. 8. EDXS spectra of the dark area at the interface betwen the copper film and the polyimide film prepared with 0.5keV, $5.0X10^{16}$ions/cm^2 argon ion.

4.Summary

We have prepared copper films on polyimide films by evaporation of copper metal and simultaneous irradiation with argon ions with 0.5keV-10keV energies (IVD method). The copper films prepared with 0.5 KeV argon ion irradiation show strong adhesion. However, the adhesion of copper films prepared with 5.0keV and 10.0keV argon ions were lower than those without argon ion irradiation. The decrease of the copper film adhesion can be caused by carbonization at the film-substrate interlayer. It is considered that the formation of an intermixed layer between the copper film and the polyimide substrate following the ion bombardment promotes the improvement of the adhesion.

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