# Interface Characteristics of Ion Beam Mixed Cu/polyimide system

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## ABSTRACT

Cu(400Å)/Polyimide has been mixed with 80 keV $Ar^+$ and $N_2^+$ from $1.0\times10^{15}$ ions/cm$^2$ to $2.0\times10^{16}$ ions/cm$^2$. The changes of chemical bond and internal properties of sample are investigated by X-ray photoelectron spectroscopy(XPS). The quantitative adhesion strength is measured by using scratch test. The optimized mixing condition is that Cu/PI is irradiated with 80 keV $N_2^+$ at a dose of $1.0\times10^{15}$ ions/cm$^2$, because $N_2^+$ ions can product more pyridine-like moiety, amide group, and tertiary amine moiety which are known as adesion promoters than $Ar^+$.

## I. INTRODUCTION

Cu/polyimide(PI) system is known to be the best candidate for the multilevel interconnection system, since Cu is a lower resistance metal(1.67 μΩ · cm) and polyimide is a lower dielectric material(ε = 2.9). The technical concern for the Cu/polyimide system is the enhancement of interface adhesion because Cu reacts weakly with polyimide(PI), resulting in poor adhesion[1].

The adhesion of two materials depends on the morphological and chemical properties of the interface. Ion beam technology has been found to provide a versatile and powerful mean for modifing the interface , at the atomic scale, both during the interface formation and after the film has been deposited, that is (i) ion beam mixing process is able to break the atomic bonding terminating the substrate surface and disorder or mobilize the atoms near the interface, which results in forming complex chemical bonding structure linking film and substrate. (ii) reactive ion implantation technique is able to enhance the formation of chemically bonded complexes involving both substrate and film species plus the implanted

species by implanting a chemically active ion species in the interface region. (iii) low energy inert ions may be used to pre-sputtering the substrate in situ, prior to vacuum deposition of the thin film. In this case, the contaminated surface layer can be sputtered off or microscopic surface morphology may be altered, which affects strongly the adhesion enhancement.

Ion beam techniques are widely used to enhance the adhesion between metal and polymer, however only a few reports[3-5] mention about the chemical complexies induced by ion bombardment. In this study, we have investigated the mechanism for the adhesion enhancement in Cu/PI system induced by ion beam mixing.

## II. EXPERIMENTAL PROCEDURES

The commercially available polyimide(Kapton) substrates were polished by 0.2 micron abrasive powder prior to electron beam evaporation of Cu. The thickness of Cu layer was chosen to match with the mean projected range of 80 keV $Ar^+$ and $N_2^+$ in Cu layer(40 nm for $Ar^+$ and 80 nm for $N_2^+$). Ion beam mixing was carried out at room temperature with $Ar^+$ and $N_2^+$. The incident energy of ions was fixed at 80 keV and the ion dose ranged from $1.0\times10^{15}$ to $2.0\times10^{16}$ ions/cm$^2$ at a typical flux of 1.5 μA/cm$^2$.

The adhesion of the Cu films was measured using a standard scratch test[6]. The scratch tester is equiped with a 120 ° Rockwell C diamond indenter with a tip radius of 200 μm. This instrument is coupled with an acoustic emission detector. The surface chemical properties of ion irradiated PI substrate were investigated with X-ray photoelectron spectroscopy(XPS). Photoelectrons were excited by monochromatized Al Kα(1486.6 keV). The pass energy of the hemispherical analyzer is 17.5 eV for high resolution studies of core level. The formation of chemical complexes by ion irradiation was studied from the XPS core level lines of C1s, N1s, and O1s. The electron beam shower method was employed to avoid the charging effect during XPS measurement.

## III. RESULTS AND DISCUSSION

Fig. 1 shows the change of adhesion strength for the $Ar^+$ and $N_2^+$ irradiated sample as a function of ion dose. The as-deposited sample shows negligible adhesion. After ion beam mixing, the adhesion strength increased drastically below an ion dose of $5.0\times10^{15}$ cm$^{-2}$, while it reaches a saturated value or decreases slightly above the ion dose of $5.0\times10^{15}$ cm$^{-2}$. And the $N_2^+$ irradiated sample has higher adhesion strength than $Ar^+$ irradiated sample.

In order to clarify the mechanism for the adhesion enhancement due to the ion beam mixing. We have investigated the surface chemical change induced by ion irradiation as a preliminary study. We have estimated the energy of incident ions at the interface after

passing through the overlayer of Cu using dynamic Monte Carlo simulation[7]. We found that the energy of $Ar^+$ and $N_2^+$ at the interface is around 20 keV. Thus 20 keV $Ar^+$ or $N_2^+$ are irradiated onto the PI substrate, and the surface chemical change of PI due to the ion irradiation has been investigated from the XPS observations.

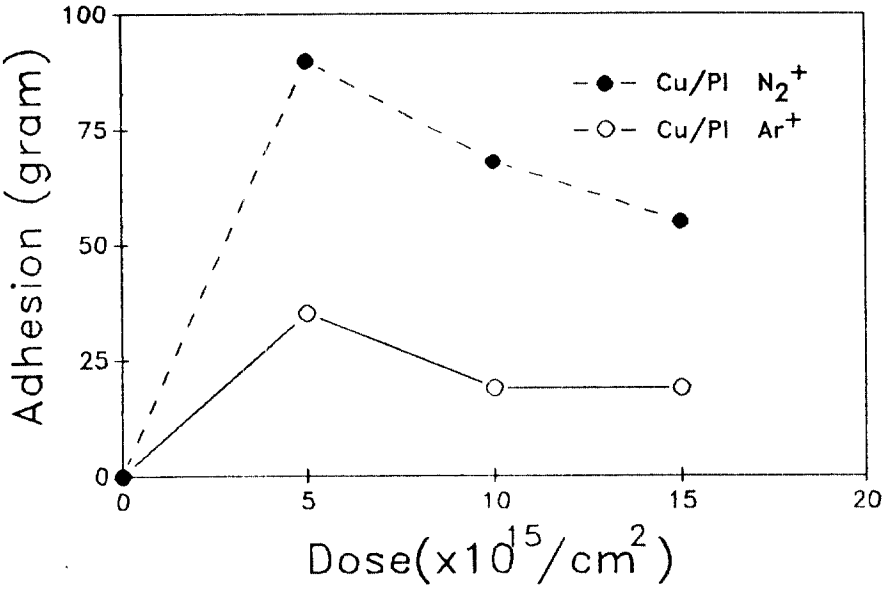


Fig. 1 Adhesion strength by scratch test plotted as a function of doses for $N_2^+$(●) and $Ar^+$(○) irradiated Cu/PI.

Fig. 2 shows the C1s core level spectra for (a) unirradiated sample (b) $N_2^+$ irradiated sample with a dose of $1\times10^{15}$ ions/cm$^2$ and (c) $N_2^+$ irradiated sample with a dose of $1\times10^{16}$ ions/cm$^2$. The C1s spectrum from unirradiated sample has three major peaks : the 285.2 eV peak is associated with aromatic carbons ; the 286.0 eV peak is assigned to the aromatic carbons bonded to oxygen and nitrogen ; and 288.5 eV peak is assigned to the carbonyl carbons. After $N_2^+$ irradiation, 288.8 eV peak due to the carbonyl carbon and 286.0 eV peak decrease, which suggests that the carbonyl oxygen is being sputtered from the surface. While two new peaks at 284.2 eV and assigned[8] to the amorphous carbons and the 287.2 eV is assigned[9] to the amide formation. These new peaks increase with increasing ion dose.

Fig. 3 shows the N1s spectra for (a) unirradiated sample (b) $N_2^+$ irradiated sample with a dose of $1.0\times10^{16}$ ions/cm$^2$ and (c) $Ar^+$ irradiated sample with a dose of $1\times10^{16}$ ions/cm$^2$. The N1s spectrum from the unirradiated sample has two major peaks : the peak of 400.8 eV is due to the imide structure and the 399.3 eV peak is assigned[10] to the isoimide structure. After ion irradiation, the imide peak decrease drastically, while the isoimide peak increases, which means that the imide structure degrades by ion irradiation. In addition to this phenomena, three new peaks are observed at 398.8 eV, 400.3 eV and 401.4 eV, which are

assigned to pyridine-like moiety[8], amide group[10], and tertiary amine moiety, for the new peaks is dependent on the incident ion species.

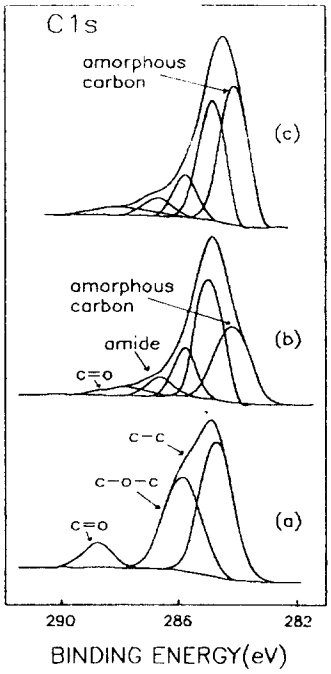


Fig. 2 The C1s signal region of XPS spectra for polyimide (a) unirradiated and irradiated with doses of (b) $1.0\times10^{15}$ $N_2^+/cm^2$ and (c) $1.0\times10^{16}$ $N_2^+/cm^2$, respectively.

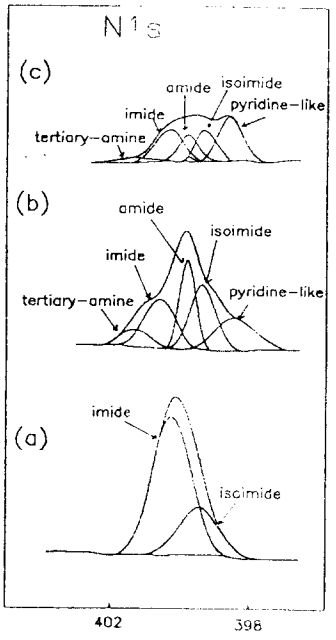


Fig. 3 The N1s signal region of XPS spectra for polyimide (a) unirradiated and irradiated with doses (b) $1.0\times10^{16}$ $N_2^+/cm^2$ and (c) $1.0\times10^{16}$ $Ar^+/cm^2$, respectively.

Greenblatt et al[12] reported that the tertiary amine and amide acts as a good adhesion promotors for polyimide and other materials and Khor and Taylor13) reported that the pyridine in PI acts as a strong coordinating ligand towards metallic species. Thus Fig. 3 indicates that the ion irradiation induces adhesion promotors such as amide, tertiary amine, and pyridine-like moiety in polyimide. We compare the production of promotors between $N_2^+$ irradiated sample

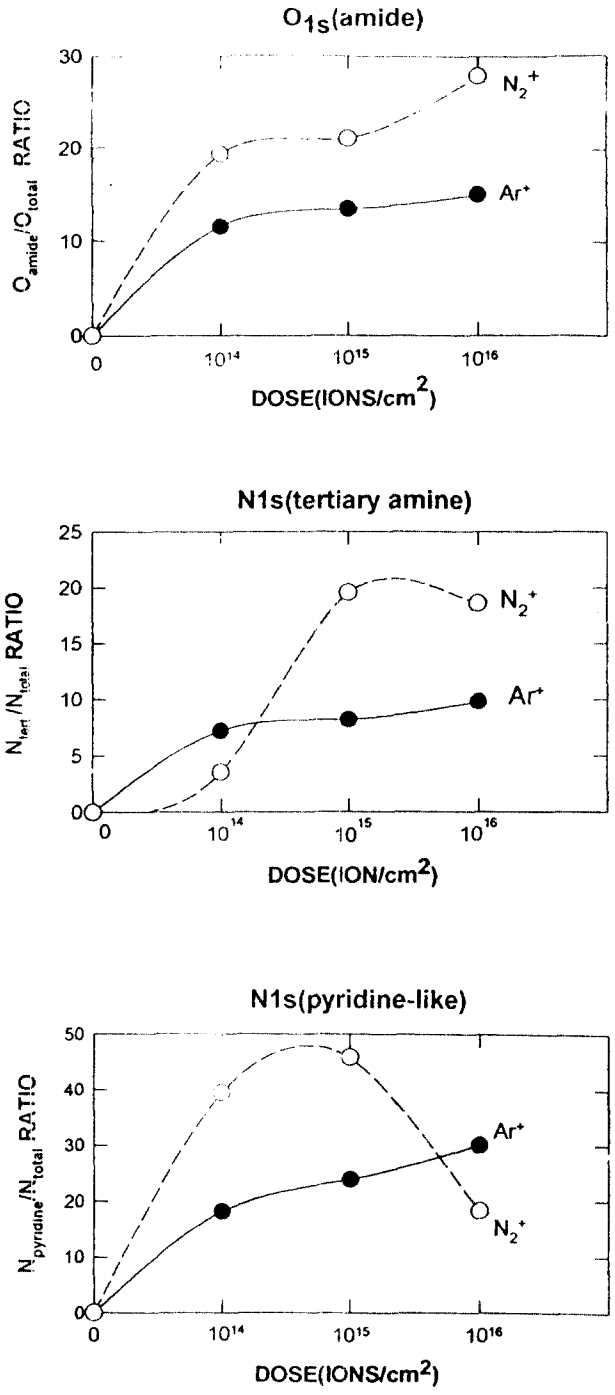


Fig. 4 (a) the ratio of amidic oxygen to total oxygen, (b) the ratio of tertiary nitrogen to total nitrogen (c) the ratio of pyridine-like nitrogen to total nitrogen plotted as a function of doses of $Ar^+$ and $N_2^+$.

and $Ar^+$ irradiated sample as shown in Fig. 4. The amount of promotors induced by ion irradiation increases below the ion dose of $1.0\times10^{14}$ ions/cm$^2$, and it saturates or decreases slightly above the ion dose of $1\times10^{15}$ ions/cm$^2$. And $N_2^+$ irradiated sample has larger amount of promotors than $Ar^+$ irradiated one. These results reveal nearly same trend with the results of adhesion strength as shown in Fig. 1. We suggest that $N_2^+$ is more effective than $Ar^+$ to induce the adhesion promotors, since the promotors are related with the nitrogen atoms.

Flitsch and Shin[14] found that ion beam modification of PI surface results in breaking of

the imide and benzene rings with the formation of many new C-O and C-N species giving rise to a polar surface having higher surface energy. Thus we suggest that the formation of adhesion promotors by ion irradiation increases the polar sites which can react with the deposited metal overlayer forming a more stable interface with enhanced bonding.

## IV. CONCLUSION

Cu/PI which are mutually inertive show the prominent adhesion enhancement after ion beam mixing. $N_2^+$ ion which incorporates as active bond component shows more increased adhesion strength than $Ar^+$. The critical load of ion beam mixed Cu/PI under the optimized condition, 85 g/mm is larger than that of Cu/PI after convetional plasma etching, 70 g/mm and that of unmodified PI, 2.5 g/mm[15].

## Acknowledgement

This study was supported in part by Electonics and Telecommunications Research Institute, by the Ministry of Education, Project No. BSRI-94-2425, and by the KOSEF on through the Science Research Center of Excellence Program (1995).

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