ENHANCED ADHESION STRENGTH OF Cu/polyimide AND Cu/Al/polyimide BY ION BEAM MIXING

G. S. Chang,* T. G. Kim,* K. H. Chae,* C. N. Whang,* D. S. Zatsepin,**
E. Z. Kurmaev,** H. S. Choe,*** and Y. P. Lee,****
*Department of Physics, ASSRC, Yonsei University, Seoul 120-749, Korea
**Institute of Metal Physics, Russian Academy of Science, Ekaterinburg, Russia
***Department of Physics Education, Kyungsang University, Jinju 660-701, Korea
****Department of Physics, Sunmoon University, Asan 336-840, Korea

ABSTRACT

The Cu/polyimide system is known to be the best candidate for a multilevel interconnection system due to the low resistance of Cu and the low dielectric constant of polyimide, respectively. Ion beam mixing of Cu(40 nm)/polyimide and Cu(40 nm)/Al(5 nm)/polyimide was carried out at room temperature with 80 keV Ar^+ and N_2^+ from 1.5 x 10^{15} to 15 x 10^{15} ions/cm^2. The quantitative adhesion strength was measured by a standard scratch test. X-ray photoelectron spectroscopy and x-ray emission spectrocopy are employed to investigate the chemical bonds and the interlayer compound formation of the films. Cu/Al/polyimide showed more adhesion strength than Cu/polyimide after ion beam mixing, and N_2^+ ions are more effective in the adhesion enhancement than Ar^+ with the same sample geometry. The XES results shows the formation of interlayer compound of $CuAl_2O_4$ which can reflect more adhesive Cu/Al/polyimide than Cu/polyimide which has not been reported previously. The latter results is understood by the fact that N_2^+ ions produce more pyridinelike moiety, amide group and tertiary amine moiety which are known as adhesion promotors.

1. INTRODUCTION

As the development of electronics industry, the need of the enhancement of interfacial adhesion has been increased for the sake of very large scale integrated (VLSI) and highly miniaturized electronic devices. Cu/polyimide(PI) system is known to be the best candidate for this purpose, since Cu is a low resistance metal (1.67 $\mu\Omega\cdot$m) and PI is a low dielectric material (ε = 2.9). The technical concern for the Cu/PI system lies in the enhancement of the interface adhesion because Cu reacts weakly with PI, resulting in a poor adhesion [1].

The adhesion between 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 modifying the interface at the atomic scale. It works during the interface formation and after the overlayer deposition as well. In other words, (i) ion beam mixing process is able to break the atomic bonding terminated at the substrate surface or to mobilize atoms near the interface, which results in forming a complex chemical bonding structure linking the film and substrate. (ii) reactive ion implantation technique can enhance the formation of chemically bonded complexes involving both the substrate and film species plus a chemically active ion species in the interface region. (iii) low energy inert ions may be used in presputtering the substrate in situ, prior the film deposition. In this case, a contaminated surface layer can be sputtered off or a microscopic surface morphology may be altered, which affects strongly the adhesion.

Ion beam techniques are widely used to enhance the adhesion between metal and polymer, but only a few reports mention about the chemical complexes induced by ion bombardment [2-4]. In this study, we are concerned with two mechanisms for the adhesion enhancement in the Cu/PI system by ion beam mixing: (i) changes in the chemical bond producing the reactive adhesion promoters, and (ii) a compound formed by introducing a thin buffer layer between Cu and PI.

2. EXPERIMENTAL PROCEDURES

Cu(20 nm)/PI and Cu(20 nm)/Al(5 nm)/PI films were prepared by e-beam evaporation after commercial PI (Kapton) substrates were polished with 0.2 μm abrasive powders. In addition, Cu(20 nm)/PI(120 nm)/Si and Cu(20 nm)/Al(5 nm)/PI(120 nm)/Si films were also prepared for x-ray emission spectroscopy (XES). The thickness of the Cu layer was chosen to match the calculated mean projected range of 80 keV Ar^+ and N_2^+ in Cu by using TRIM code simulation [5]. 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 was ranged from 1.0×10^{15} to 1.5×10^{16} ions/cm^2.

A standard scratch test was employed to measure the adhesion of the Cu films [6]. The scratch tester was equipped with a 120° Rockwell C diamond indenter with a tip radius of 200 mm. This instrument was coupled with an acoustic emission detector. The surface chemical states of the ion beam mixed PI substrate in the Cu/Al/PI system were investigated by x-ray photoelectron spectroscopy (XPS). Photoelectrons were excited by monochromatized Al Kα (1486.6 keV). The pass energy of the hemispherical analyzer was set at 17.5 eV for high resolution studies of the core levels such as C 1s, N 1s and O 1s. An electron flood gun was used to avoid charging effects during the XPS measurements. The formation of a interlayer compound in Cu/Al/PI was confirmed by using x-ray emission spectroscopy. Cu $L_{2,3}$ XES were obtained with a JCXA-733 (JEOL) instrument with a fully-focused Johan-type spectrometer and TAP crystal-analyzer (2d=2.576 nm) curved to R = 280 mm and electron excitation. The energy resolution was about 1.8 eV. A very soft regime of operation of the X-ray tube at V = 5 keV and I = 100 nA. The position of samples studied was changed in respect to the focused electron beam for every scanning to avoid sample decomposition during measurements.

3. RESULTS AND DISCUSSION

Figure 1 shows the change in adhesion strength of the Ar^+ and N_2^+ irradiated samples as a function of ion dose. An unmodified PI is known to have a critical load of 2.5 g/mm, and the as-deposited samples shows another negligible adhesion. The critical load of the Cu/PI after the conventional plasma etching is reported to be as small as 70 g/mm [7]. After ion beam mixing, the adhesion strength increases drastically below an ion dose of 5.0×10^{15} cm^{-2}, while it reaches at a saturated value or decreases less rapidly above the ion dose. Two distinct tendencies are also observed; (i) N_2^+ irradiation is more effective in the adhesion enhancement than Ar^+ for the both systems, and (ii) Cu/Al/PI shows higher adhesion strength than Cu/PI for the same ion type and dose.

The point (i) drives us to ask how the chemical state of PI is changed after ion beam mixing. In order to separate the effects due to overlayers, we calculated the energy of incident ions at the interface after passing through the overlayers using dynamic Monte Carlo simulation [8]. The energy of Ar^+ and N_2^+ at the interface was around 20 keV. Thus bare PI substrates were irradiated with 20 keV Ar^+ and N_2^+ from 1.0×10^{14} ions/cm^2 to 1.0×10^{16} ions/cm^2, and the changes in the

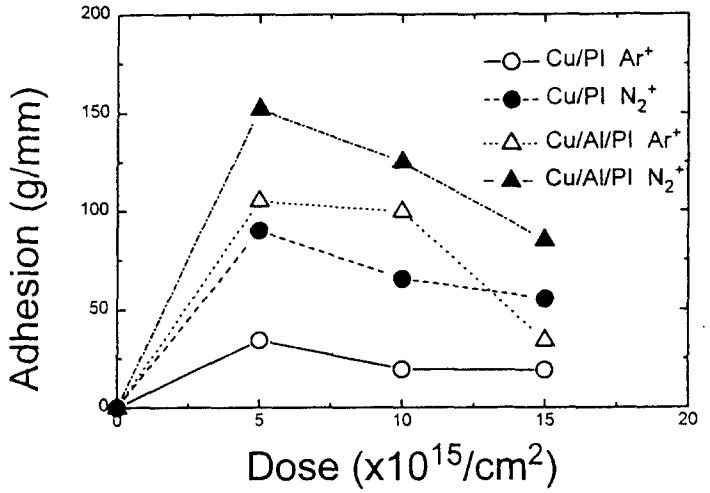

Fig. 1 Adhesion strength by a scratch test plotted as a function of ion dose of the Cu/PI and Cu/Al/PI systems.

surface chemical state of PI due to the ion irradiation have been investigated by XPS.

Greenblatt et al. reported that the tertiary amine and amide act as good adhesion promoters for PI and other materials [9], and Khor and Taylor also reported that the pyridine in PI acts as a strong coordinating ligand towards metallic species [10]. Thus Fig. 2 indicates that the ion irradiation induces adhesion promoters such as amide, tertiary amine and pyridinelike moiety in PI and the promoters produced by the N_2^+ and Ar^+ irradiation are compared from C 1s, N1s, O 1s XPS spectra. The amount of promoters induced by ion beam irradiation increases before an ion dose of 1.0 x 10^{14} ions/cm^2, and saturates or decreases less rapidly after an ion dose of 1.0 x 10^{15} ions/cm^2. In addition, the N_2^+ irradiated sample has larger amount of promoters than the Ar^+ irradiated one. These results reveal a nearly same trend as the adhesion strength in Fig. 1, since the promoters are related with the nitrogen atoms.

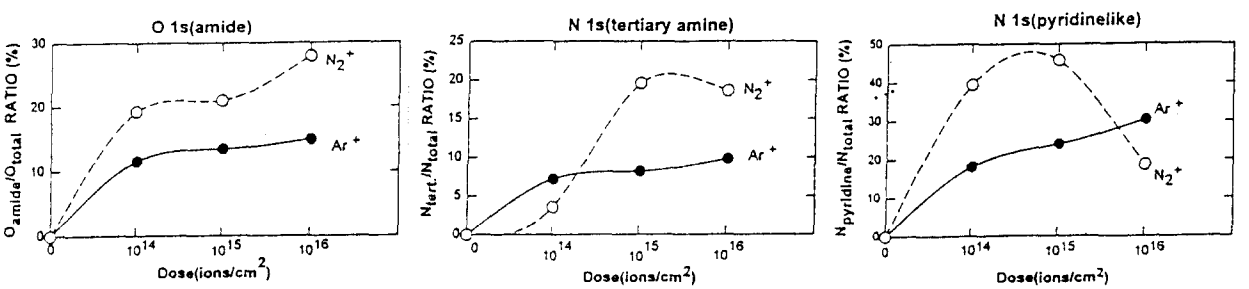

Fig. 2 (a) the ratio of amidic oxygen to total oxygen, (b) the ratio of tertiary nitrogen to total nitrogen, and (c) the ratio of pyridinelike nitrogen to total nitrogen as functions of doses of Ar^+ and N_2^+.

Flitsch and Shin found that an ion beam modification of the PI surface results in the formation of many new C-O and C-N species giving rise to a polar surface that has a higher surface energy

of Ar^+ and N_2^+.

Flitsch and Shin found that an ion beam modification of the PI surface results in the formation of many new C-O and C-N species giving rise to a polar surface that has a higher surface energy through breaking the imide and benzene rings [11]. Thus the formation of adhesion promoters by ion beam mixing increases the polar sites that can react with the deposited metal overlayer forming a more stable interface with enhanced bonding.

Now, we would like to focus on the second mechanism of the adhesion strength enhancement. mixing, which is thought to come from a bond broken PI. Figure 2 shows the Cu $L_{2,3}$ XES spectra of pure Cu, $CuAl_2O_4$ and Cu/Al/PI/Si with ion species and doses. The typical shape of $CuAl_2O_4$ spectrum shows higher L_2 peak than that of pure Cu. After Ar^+ and N_2^+ irradiation with a 5 x 10^{15} ions/cm^2, L_2 peak increases which reflects the formation of $CuAl_2O_4$ compound at interface region, and the height of L_2 peak by Ar^+ irradiation is larger than that by N_2^+ irradiation. This suggests that Ar ions are more effective than N_2 ions in the formation of $CuAl_2O_4$ due to the higher stopping power of Ar [5], and the effect of adhesion promoters plays more important role in adhesion enhancement than that of $CuAl_2O_4$ interlayer compound. In that sense, the difference of adhesion strength of Cu/Al/PI between N_2^+ and Ar^+ was smaller than that of Cu/PI without the effect of interlayer compound. The formation of $CuAl_2O_4$, which is closely related with the enhanced adhesion strength, is found experimentally for the first time.

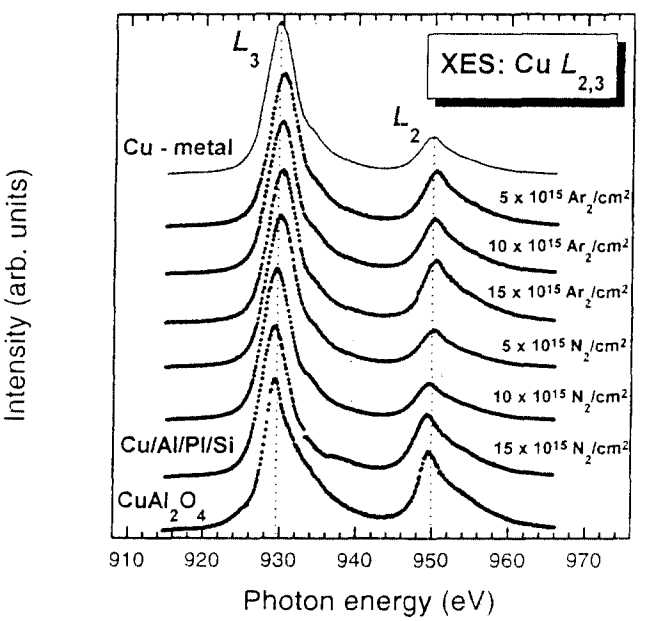

Fig. 3 Cu $L_{2,3}$ XES spectra of pure Cu, $CuAl_2O_4$ and Cu/Al/PI/Si with ion species and doses

4. CONCLUSIONS

Cu/PI which are mutually inert reveal a prominent adhesion enhancement after an ion beam mixing. N_2^+ ions are more effective in increasing the adhesion strength than Ar^+, since N_2^+ ions are incorporated as an active bond component. The adhesion enhancement are analyzed to be due to the induction of the adhesion promoters on PI by ion irradiation. A thin Al layer as a buffer layer makes a ternary compound of $CuAl_2O_4$ confirmed by using XES, which enhances the

are larger than that for the Cu/PI after the conventional plasma etching, and much larger than that for the unmodified PI.

ACKNOWLEDGMENT

This work was supported by the Basic Science Research Institute Program, Ministry of Education, Project No. BSRI-97-2426 and by the Electronics and Telecommunications Research Institute.

REFERENCES

1. J. Chou, D. W. Dong, K. Kim, and A. C. Liu, J. Electrochem. Soc., **131**, 2335 (1984).
2. A. A. Galuska, J. Vac. Sci. Technol., B **8**, 482 (1990).
3. C-A. Chang. J. E. E. Balgin, A. G. Schrott, and K. C. Lin, Appl. Phys. Lett., **51**, 103 (1987).
4. K. S. Kim, I. S. Choi, Y. S. Lee, Y. W. Kim, and C. N. Whang, Nucl. Instrum. Methods, **B80/81**, 1300 (1993).
5. J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and Range of Ions in Solids* (Pergamon, New York, 1985), p. 232.
6. C. Weaver, J. Vac. Sci. Technol., **12**, 18 (1975).
7. K. W. Paik and A. L. Ruoff, J. Adhesion Sci., **4**, 465 (1990).
8. K. H. Chae, J. H. Song, J. J. Woo, H. J. Kang, and C. N. Whang, Nucl. Instrum. Methods, **B71**, 271 (1992).
9. J. Greenblatt, C. J. Araps, and H. R. Anderson, *in Polyimides; Synthesis, Characterization andApplications,* edited by K. L. Mittal (Plenum Press, New York, 1984), p. 573.
10. E. Khor and L. T. Taylor, *ibid.*, p. 507.
11. R. Flitsch and D-Y. Shin, J. Vac. Sci. Technol., A **8**, 2376 (1990).