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Initial Stages of Cu Growth on Polyimide Deposited by Ionized Cluster Beam

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1. Introduction

Polyimide(PI) has a low dielectric constant along with a low dissipation factor, high thermal resistance and high chemical resistance.[1] Hence it is a very good candidate for an interlevel dielectric and the passivation coating in high density interconnection systems. Cu is a promising materials in the multilevel metallization and interconnection for low resistivity, relatively low electromigration properties and high melting point.[2] However some problems are there in the use of Cu/PI system in the metallization, such as poor adhesion and diffusion of Cu into PI. Ionized cluster beam deposition (ICBD) is a very useful film fabrication technique that enables flexible control of film properties such as molecular orientation, film crystallinity and film-substrate interfacial state. In this technique, ionized clusters are accelerated by the attractive potential applied between crucibles and the substrate. It is known that there are interface smoothing effect and surface migration effect due to the bombardment by accelerated energetic clusters. So we expect high packing density and low surface roughness. Two Cu/PI systems were compared. One PI film was fabricated by ICBD and the other PI was spin coated. In this study, we focused on the interface properties of Cu on PI system deeply related with the adhesion and diffusion properties.

2. Experimental

We prepared PI films (PMDA-ODA type) by ICBD and spin-coating and compared the interface properties. PI films were deposited on the Si(100) substrate by ICBD technique at optimum deposition conditions[3] and by spin coating. Then Cu were deposited on these films by Ar^+ ion sputtering of Cu target at 250°C in UHV(low 10^{-9} Torr). We measured C 1s, N 1s, O 1s, Cu 2p core-level spectra and Cu LMM Auger spectra for Cu/ PI systems by X-ray photoelectron spectroscopy(XPS). We used PHI 5700 X-ray photoelectron system with hemispherical energy analyzer and its pass energy was 23.5 eV. And we used monochromatized Al-Kα line (1486.6 eV) as a X-ray source.

3. Results and Discussion

Figure 1 shows the packing density variation with the acceleration voltage by ellipsometry. It shows the highest packing density at the optimum condition (the acceleration voltage V_a=800 V). The dotted line in Fig. 1 is for spin coated PI. In ICBD process, ionized clusters have kinetic energy by acceleration voltage in addition to thermal energy by heating of the clucible. By this residual energy the molecules migrated on the substrate. Thus PI by ICB has high packing density than spin coated PI. Since at V_a = 1200 V the sputterig effects of the accelerated cluster are larger than the surface migration effect, the packing density of PI fabricated at V_a = 1200 V is lower than that at V_a = 800 V.

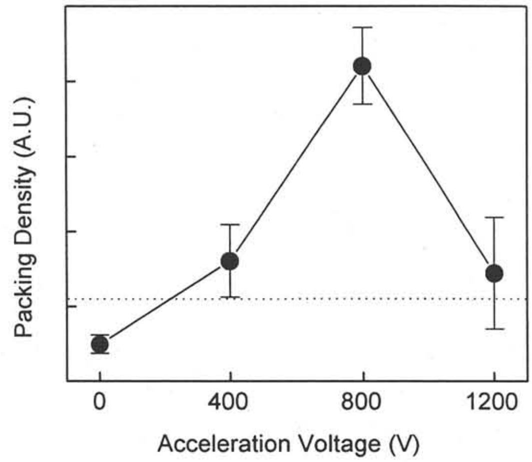

Fig. 1. Packing Density Variation with Acceleration Voltage. The dotted line is for spin coated PI.

Figure 2 (a) and (b) show Cu LMM Auger spectra for ICB-PI and spin coated PI, respectively. The Cu LMM Auger spectra show direct the initial stages of formation for Cu. In Fig. 2 (a), at Cu/C=0.024, the initial stage of deposition, the Cu-C-N complex (~572 eV)[4] are strongly shown and Cu-N-O complex (~571 eV) [4] and Cu_2O phase (~570 eV) [4] are shown, but pure Cu peak are not appeared. At Cu/C=0.041, metallic Cu peak start to grow. At Cu/C=0.051, the height of metallic Cu peak is almost same as those of other peaks. And at Cu/C=0.060, the intensity of the pure Cu is the largest. These results show the initial stages of Cu deposition on PI. Firstly, the Cu-C-N complex and Cu-N-O complex were formed on PI from broken C=O and C-N bonds. Secondly, the Cu_2O phase were grown and then metallic Cu was grown. In case of spin coated PI, the initial stage of deposition is similar with the ICB PI(Fig 2 (b)). By comparison of the spectrum of Cu/C=0.065 in ICB PI and Cu/C=0.1275 of spin coated PI, the shapes are same but the thickness of spin coated PI is double of that of ICB-PI. This result means that the interface of ICB-PI is sharper than that of spin coated PI, i.e., the surface of ICB-PI is more flat. This facts are coincident with the AFM results in the previous reported paper[3] and Ellipsometry results of Fig. 1.

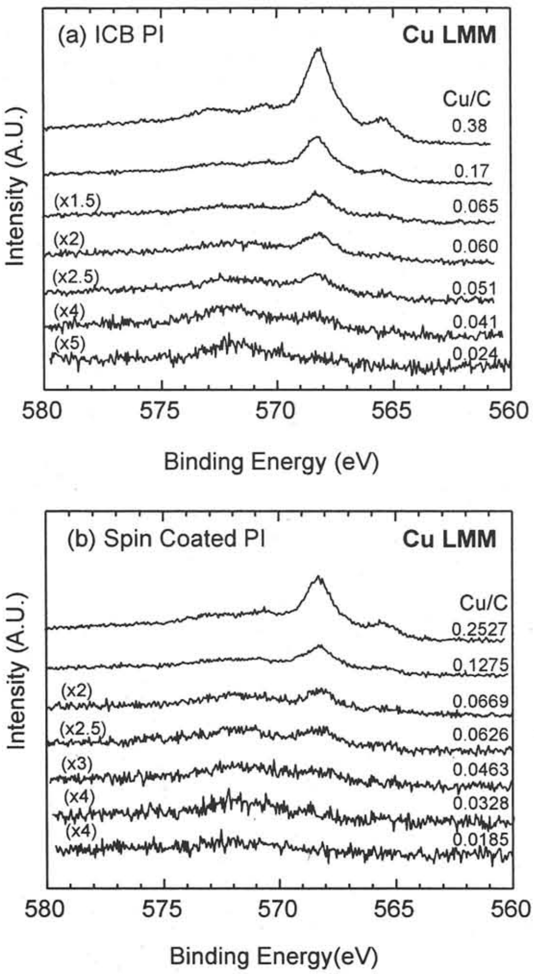

Fig. 2. Cu LMM X-ray induced Auger peaks measured during *in-situ* formation of the Cu/PI interface as a function of Cu coverage at 250°C for (a) ICB PI and (b) Spin Coated PI

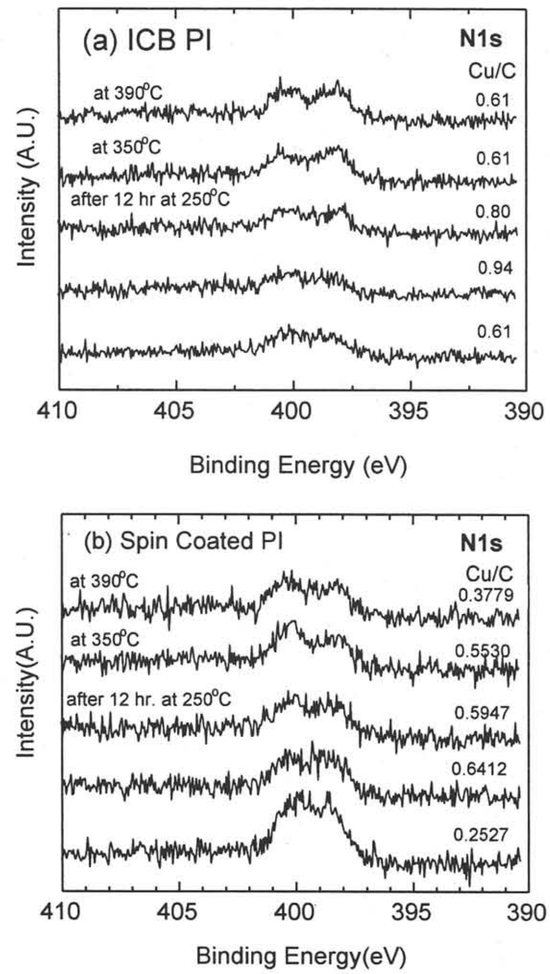

Fig. 3. N 1s core-level spectra measured during *in-situ* formation of the Cu/PI interface as a function of Cu coverage at 250°C for (a) ICB PI and (b) Spin Coated PI

Figure 3 (a) and (b) show the photoemission core level results of nitrogen (N 1s) for ICB-PI and spin coated PI, repectively. In the case of pure PI, N 1s spectrum has only one peak from C-N band (400.1 eV) [4] in the imide ring. But Cu deposited PI film has another peak in about 398 eV from Cu-N-O complex.[4] In fig 3 (a), at Cu/C=0.94, the intensity of C-N (imide nitrogen) peak is almost same with that of Cu-N-O complex. In addition, as the temperature increase, the changes of spectra were not found. But in the case of spin coated PI, after 12 hr at 250°C the imide nitrogen peak is higher than that of Cu-N-O complex (Fig. 3 (b)). At Cu/C=0.5530, at 350°C the imide nitrogen peak is more higher. This means that Cu diffused into spin coated PI film. Thus the imide structure was found on the top of Cu/PI. However in case of ICB PI, Cu atoms were little diffused into PI. These results are coincide with Ellipsometry results. Thus ICB PI has more flat surface and higher packing density than those of spin coated PI.

4. Conclusions

We have fabricated two kinds of PI. One is by ICBD and the other is by spin coating. And we investigated two Cu/PI systems by XPS. According to XPS study of the Cu/PI systems, we have concluded that ICB-PI films have more flat surface, larger packing density and little diffusion of Cu than spin-coated PI films.

Acknowledgments

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