Interfacial Reaction of Cu/Polyimide using XPS

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We investigated the initial states of Cu film growth on polyimide at room temperature using x-ray photoelectron spectroscopy(XPS). The interfaces formed by deposited Cu layer on polyimide have been studied by XPS as a function of Cu coverage. From the C *1s*, N *1s*, and O *1s* spectra, we find that Cu atoms react to elements of PMDA(pyromellic-dianhybride) part in polyimide such as oxygen and nitrogen. Especially, by Cu LMM Auger spectra, we can summarize the initial growth mode of Cu on polyimide as follows ; at first Cu-N-O complex is formed, and sequentially Cu-O-C complex by the weak interaction is formed, simultaneously metallic Cu starts to grow.

1. Introduction

In very large scale integrated(VLSI) and highly miniaturized electronic devices, the Cu/polyimide(PI) system is known to be the best candidate for a multilevel interconnection system. The Cu has a lower electrical resistivity(1.7 $\mu\Omega$cm) and higher resistance to electromaigration than Al. Polyimide is a low dielectric material(ε=2.9) with high temperature stability[1,2]. Technical concern over the Cu/PI system lies in the enhancement of interface adhesion [2,3]. The adhesion between two materials strongly depends on chemical bonding at the interface. In the past few years, a number of photoemission studies[4-7] have been performed to investigate the chemical bonding on polymer surfaces and metal-polymer interfaces. However, the details of surface and interface bonding in Cu/PI system are still not adequately known.

In order to understand Cu/PI interface formation at room temperature, we studied the reaction of Cu in the context of different PI functional groups.

2. Experiments

Thin samples of pyromellic-dianhybride -oxydianiline polyimide (PMDA-ODA PI : Kapton) commercially available were prepared from DuPont.

Cu deposition were carried out by Ar^+ ion sputtered deposition. The deposition rates for Cu were ~1 Å/min. as determined by RBS and the pressure of this system was maintained in the low 10^{-8} Torr range during the Cu film deposition. The chemical reactions between Cu and PI were measured by *in-situ* XPS without changing the sample position.

X-ray photoemission experiments were performed in a UHV system at a base pressure of $\sim 1\times10^{-10}$ Torr. The UHV chamber was equipped with a PHI model 5700 x-ray photoelectron spectrometer. Photoelectrons were excited by monochromatized Al Kα (1486.6 eV) irradiation. The pass energy of PHI hemispherical electron energy analyser was 23.5 eV, giving an energy resolution of 0.7 eV to the FWHM of Ag $3d_{5/2}$ line for high resolution studies of core level. The electron beam shower method was employed to avoid the charging effect.

We measured C *1s*, N *1s*, O *1s*, Cu *2p* core level spectra, and Cu LMM Auger spectra for Cu/PI system by XPS. Binding energies were calibrated to the carbonyl O *1s* at 532.3 eV for pure PI and to Cu $2p_{3/2}$ at 932.7 eV for surfaces after the Cu deposition.

3. Results and discussion

The formation of the Cu/PI interfaces

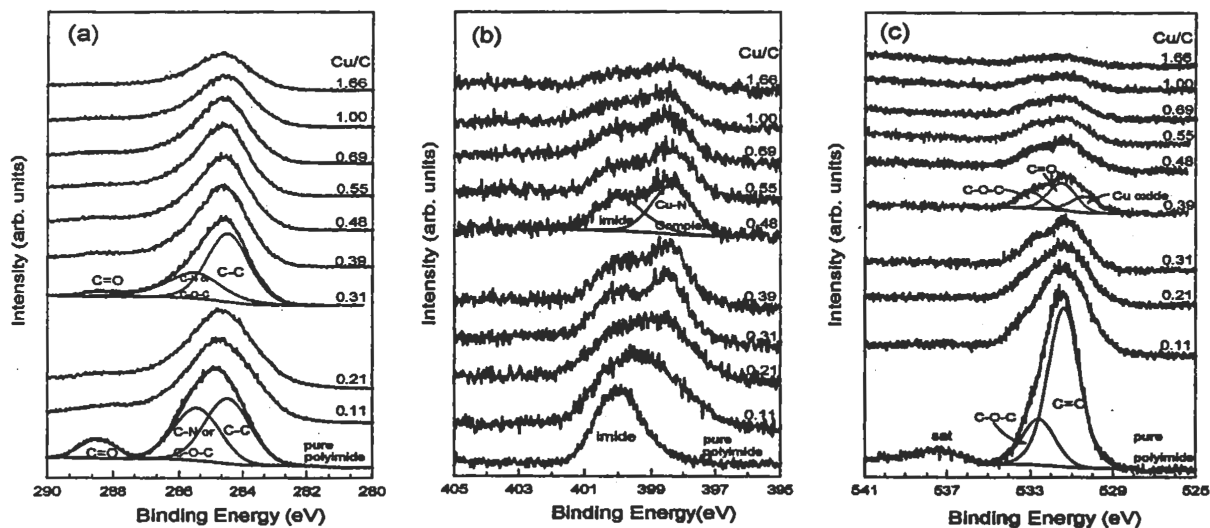

Figure 1. (a) C *1s*, (b) N *1s*, (c) O *1s* core-level XPS spectra measured during *in-situ* formation of the Cu/polyimide interface as a function of Cu coverage at room temperature.

was followed by monitoring the polyimide C *1s*, N *1s*, and O *1s* core level as well as the Cu *2p* core level and Cu LMM Auger peaks as a function of the Cu coverage. Figure 1(a), (b), and (c) show the chemical state changes of C *1s*, N *1s*, and O *1s* of PI by the deposition of Cu, respectively. The C *1s* spectrum for pure PI (Fig. 1(a)) is resolved into four components related to the C=O and C-N bonds in the PMDA part and the C-C and C-O-C bonds in the ODA part(Fig. 3(a)). The deconvolution of these XPS spectra in Fig. 1 was performed on the basis of the fitting results by Ref. 8 and 9. According to the increase of the coverages of Cu (i.e., Cu/C ratio), the carbonyl bonds (C=O) decrease abruptly but C-C bonds of ODA part nearly don't change as can be seen from Fig. 1(a). This result means that the PMDA part of PI change mainly by Cu deposition, that is, the deposited Cu atoms react with the PMDA part of PI. However, we cannot obtain any information of the reaction between the deposited Cu and carbon of PI from C *1s* spectra.

In Fig. 1(b), we can observe the reaction between Cu and nitrogen of PI. The imide bonds (C-N) exist in PMDA part of PI. As soon as the Cu deposits onto PI, at Cu/C=0.11, the peak width is broadening and a new peak appears in lower binding energy. The more Cu deposits, the smaller the imide peak height is and the clearer the new peak is. From this result, this new component can be assigned to Cu-N complex by interaction between Cu and nitrogen atoms.

In Fig. 1(c), with increasing of Cu coverage the peak intensity of the O *1s* spectra is decreasing abruptly due to the decrease of C=O bonds in PMDA part. In addition, with increase of Cu/C ratio the shapes of peak are broadening due to the formation of Cu oxide (~530 eV : Cu_2O phase[10]). From these results in Fig. 1, we can find that the deposited Cu reacts with the PMDA part in PI and the Cu-N complex and Cu oxide are formed by broken C=O and C-N bonds in the interface of Cu/PI.

In the Cu LMM Auger spectra of Fig. 2, we show the chemical state change of Cu site by the reaction between PI and Cu atoms. From the Cu LMM spectra we can see directly the initial states of Cu compound formation. As shown in Fig. 2, firstly, at Cu/C=0.11 the Cu-N-O complex (~

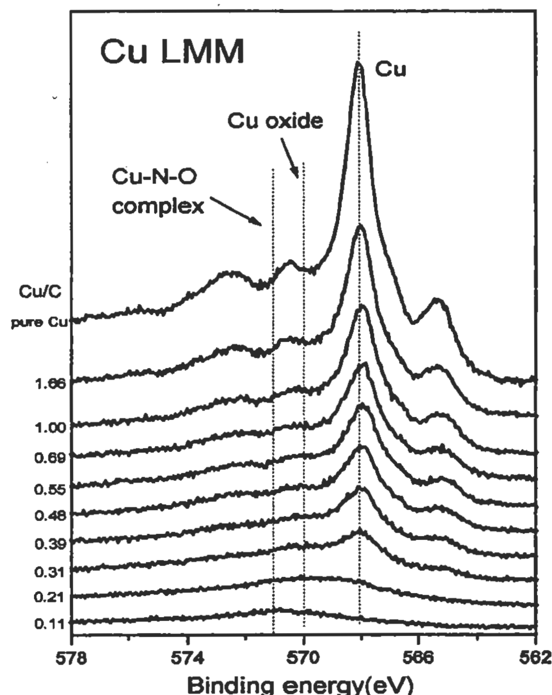

Figure 2. Cu LMM x-ray induced Auger peaks measured during *in-situ* formation of the Cu/polyimide interface as a function of Cu coverage at room temperature.

571 eV)[10] is strongly shown. At Cu/C=0.21, the main peak position changes into the Cu oxide position (~570 eV : Cu_2O or Cu-O-C complex[10]), but the peak shape is very broad due to the overlap with Cu-N-O complex(~571 eV) and metallic Cu peaks (568 eV)[10]. This means that metallic Cu started already to grow at very low coverage (i.e. Cu/C=0.21). Successively, at Cu/C=0.31, the pure Cu peak is dominant. From these results, we can see that Cu-N-O complex is formed at an early, and Cu oxide and metallic Cu are formed sequentially. However, this reaction between Cu and PI does occur at low coverages. The Cu-N-O complex forms earlier than Cu oxide in the interface of Cu/PI. It may be due to the value of heat of formation ($\triangle$H). The heat of formation value of Cu-N-O complex ($\triangle$H=-303 kJ/mole) is negatively larger than that of Cu oxide (Cu_2O) ($\triangle$H=-169 kJ/mole)[11].

From Cu LMM Auger spectra, we obtained more detail information than that in C *1s*, N *1s*, and O *1s* spectra. Consequently, we find that Cu-N complex in N *1s* spectra is Cu-N-O complex. However we can not find whether Cu oxide has Cu_2O phase or Cu-O-C complex although Cu_2O phase was observed in O *1s* spectra. On the basis of these results, the possible reaction models are shown in Fig. 3(b).

A process of Cu-N-O complex formation is as follows (the left of Fig. 3(b)). When Cu deposits with a few eV energy on PI with the structure of Fig. 3(a), firstly C=O bonds in PMDA part break, successively Cu-O ionic bond is formed by reaction between Cu atoms and the broken oxides, finally Cu-N covalent bond is formed between this ionic bonded Cu atoms and the dangling bonds of N part. Using this model, we can explain not only the appearance of Cu-N complex peak in N *1s* spectra and Cu-N-O complex peak in Cu LMM spectra but also the decrease of C=O bonds in C *1s* spectra.

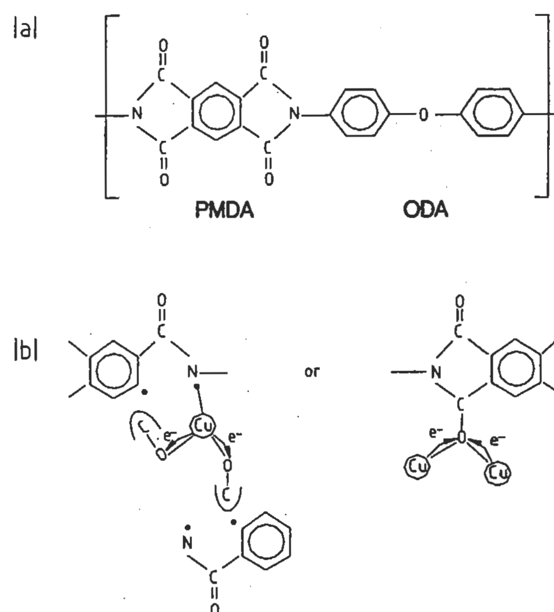

Figure 3. A proposed model for the interfacial interaction between PMDA-ODA polyimide and Cu during sputtered deposition of Cu on the polyimide. (a) Basic units of the molecular structure of polyimide. (b) Interactions between Cu atoms and polyimide.

In a viewpoint of Cu oxide, the possibility of Cu-O-C complex formation (the right of Fig. 3(b)) is more dominant than that Cu_2O formation. Since the existence of carbon with dangling bond by separation of Cu_2O group is impossible constructionally, Cu-O-C complex is chemically more stable than Cu_2O phase. However, the cohesion of Cu-O-C complex composed of Cu_2O and carbon atoms is very weak. This weak interaction may be the reason why the Cu-O-C complex has not been clearly detected in experiments. Also, A. Ringenbach *et al.*[12] had proposed the Cu-O-C complex formation without any experimental observation. From these results, finally, we can conclude Cu-N-O and Cu-O-C complexes are formed at the interface between Cu and PI.

4. Conclusion

In order to study of the initial growth state of Cu deposited on polyimide at room temperature, we investigated the interface of Cu/polyimide using x-ray photoelectron spectroscopy. Our results suggest that Cu atoms mainly interact with the PMDA part of PI and that Cu-N-O and Cu-O-C complexes are formed by chemical reaction between Cu and PI. However, this reaction range in the interface of Cu/PI is very narrow since metallic Cu started already to grow at very low coverage. Finally, we can summarize the initial stages of formation for Cu. At first Cu-N-O complex is formed, and sequentially Cu-O-C complex is formed by weak interaction, simultaneously metallic Cu starts to grow.

5. References

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