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〈연구논문〉

Thermally-Induced Atomic Mixing at the Interface of Cu and Polyimide

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Abstract — Rate of mixing of Cu particles to polyimide substrate at interfaces under different thermal treatments was analyzed by Rutherford Backscattering Spectroscopy using 2.0 MeV He^+ ions. The mixing rate was a function of annealing temperature and time, and was constant at a fixed temperature. The amount of mixing increased linearly with time and the mixing rate increased with temperature. The activation energy for interface mixing between Cu and polyimide was 2.6 kcal/mol. The X-ray studies showed the Cu(111) plane peak changed with annealing time at fixed temperature. The mixing of Cu to polyimide was explained with segmental motion of PI chain and with interaction between functional group of the chain and metal electron donor. The comparisons were made bewteen the mixing induced by ion irradiation and by thermal treatment. The various factors affecting the interface mixing are discussed.

1. Introduction

Rutherford backscattering technique has been widely used to study in the area of metal, semiconductors, and the other inorganic materials. The usage of this technique to organic polymeric systems has been sparse. This analytical technique could be used to study various properties of metal-polymer system, because the mixing of heavier metal species in the light material, such as carbon, nitrogen, oxygen, and silicon compound, can be easily monitored. There were several diffusion studies in polymer-polymer and metal-polymer systems, and those systems have been investigated using only limited number of techniques. Refractive index techniques and Radiation absorption method have been used to study the concentration-distance relationships of polymer-polymer systems [1, 2]. Radiotracer method was applied for measurement of diffusion distance by C^{14}, P^{32} and S^{35} [3-5]. Tritium was used to label a polymer and to follow the diffusion process through the signature of the tritium β-decay radiation [6]. SEM has been used to measure the interdiffusion properties of the compatible polymers [7]. Polymerpolymer interdiffusion [8] and metal diffusion [9] in polymer were studied by selected absorption peak of IR selenium diffusion through a polystyrene hexamethacrylate copolymer film, and a Mylar substrate was also studied [10]. In this paper, the results of a study on thermally-induced mixing of copper and polyimide (PI) are presented. A comparison is made between the thermally-in duced mixing and the ion beam-induced mixing of the same system.

2. Experimental

A large block of polyimide (PI) (SP-1 du Pont Company) was cut into small rectangular bars of 1/2 cm×1/2 cm×1/5 cm. A flat surface (1/2×1/2 cm^2) was polished with a fine Emery paper (grade 600) and then with polishing compound (grade B, particle size less than 0.1 mm). Cu (99.99%) film

was deposited to yield 400 Å thickness on the polished surface of PI by thermal evaporation technique at a rate of 2 Å/s in vacuum (10^{-7} torr). Each set of ten Cu/PI samples were annealed in a vacuum isotemp. oven (10^{-3} torr) at 150℃, 200℃ and 250℃, respectively, for up to 20 hours. Samples were then removed from the vacuum oven, allowed to be cool down to room tempeature, and stored in a vacuum decicator until characterization was carried out. Rutherford backscattering spectroscopy (RBS), using He^+ ions at 2.0 MeV, was employed to determine the amount and the depth of mixing of Cu and PI. The X-ray study (CuK_α at 30 mA and 40 kV) was also made using a Philips diffractometer to see changes that might have occurred during annealing.

3. Results and Discussions

Fig. 1 shows RBS spectra of untreated Cu/PI system. Various peaks were identified as Cu at 379 channel and 1.55 MeV, oxygen at 169 channel and 0.72 MeV, nitrogen at 143 channel and 0.62 MeV, and carbon at 114 channel and 0.50 MeV. Extended RBS spectra between 300 and 400 channeals of Cu/PI composite samples, annealed at 150℃ for up to 20 hrs are shown in Fig. 2. RBS spectra for those annealed at 200℃ for up to 20 hrs and 15 hrs are shown in Fig. 3 and 4, respectively. The solid line spectra in all three figures represent unannealed 400 Å thick Cu film on PI. The shape of the peaks in the figures are related to the concentration profile of the Cu film on PI substrate and the shift of the left hand side of the peaks toward the lower channels indicates penetration of Cu particles into the PI substrate. Using these RBS spectra, the amount of Cu particles diffused into the substrate was determined by a computer program, "RUMP" [11]. The RBS spectrum of the virgin sample exhibits almost symmetric peaks, but the peaks gradually shifted to lower channel numbers, broadened asymmetrically, and diminished

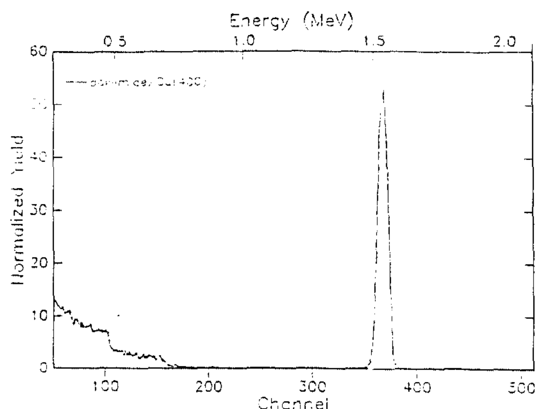

Fig. 1. RBS spectra of untreated Cu (400 Å)/PI system.

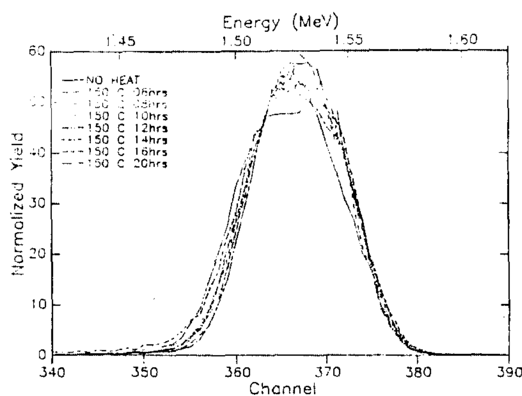

Fig. 2. Rutherford backscattered spectra (2.0 MeV He^+ ions) of samples with 400 Å thickness of Cu on polyimide. Samples were annealed at 150℃ temperature for indicated time.

in its normalized yield as annealing time becomes longer. The amount and the rate at which it dif fused into the substrate depended upon the annealing temperature and time as shown in Fig. 5. $x(=C/C_0)$ is the ratio of number of Cu particles (C) diffused into the PI substrate per unit area to the original number of Cu particles (C_0) on the PI substrate per unit area (C_0). The mixing or the diffusion thickness could not be calculated without knowing the atomic density of each layer of the interface where mixing occurs and stopping power of He^+ in PI. Although Cu diffusion was observed, it could not be characterized by complementary error function of Gaussian profiles [12]. The lo-

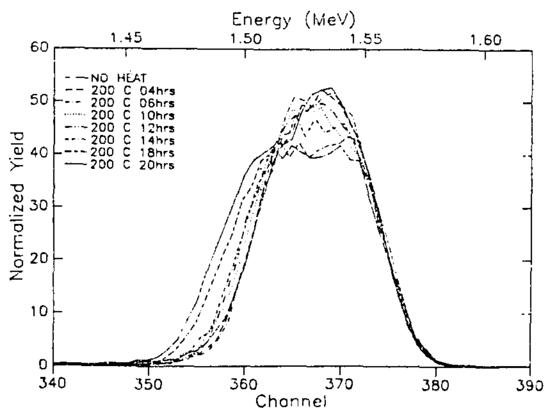

Fig. 3. Rutherford backscattered spectra (2.0 MeV He^+ ions) of samples with 400 Å thickness of Cu on polyimide. Samples were annealed at 200℃ temperature for indicated time.

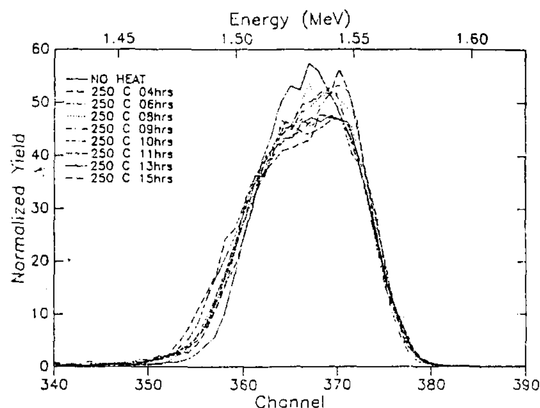

Fig. 4. Rutherford backscattered spectra (2.0 MeV He^+ ions) of samples with 400 Å thickness of Cu on polyimide. Samples were annealed at 250℃ temperature for indicated time.

nger the annealing time is, the more Cu particles penetrate into the PI substrate at a given annealing temperature, and the higher the annealing temperature is, the greater the amount of Cu pa rticles diffuse into the PI substrate for a given annealing time. It appears that the mixing rate was constant (dx/dt=k) at a fixed temperature (k= rate constant of mixing reaction ($hour^{-1}$), t=annealing time at fixed temperature) and the relationship between C/C_0 and t was linear for each temperature (T), that is

$$x=k(T)t \quad (1)$$

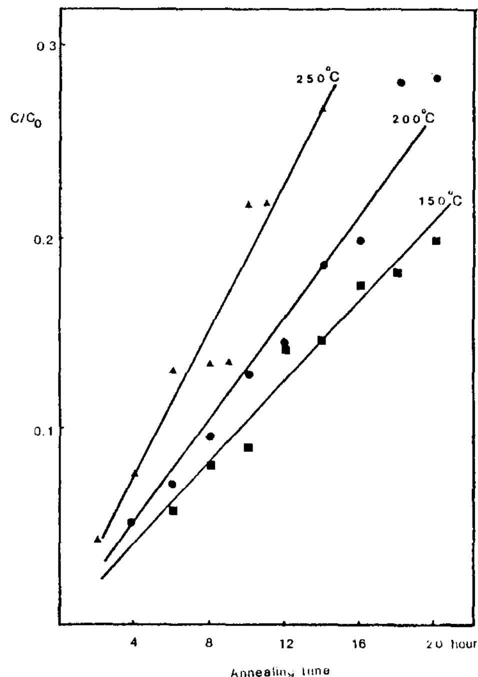

Fig. 5. The fraction of amount of mixing at fixed temperature vs. annealing time (hour): 150℃ (filled square), 200℃ (filled circle) and 250℃ (filled triangle).

The values of k for each annealing temperature are 1.05×10^{-2} at 150℃, 1.34×10^{-2} at 200℃ and 1.92×10^{-2} at 250℃ as listed in Table 1, and are found to be compatible with the Arrhenius equation,

$$k=A\exp(-E_a/RT) \quad (2)$$

where A=pre-exponent factor, E_a=activation energy of interface mixing between Cu and PI, R=gas constant (8.314 cal/mol), and T=annealing temperature (K). Fig. 6 shows the logarithm of the rate constant plotted against the reciprocal of the absolute temperature. The slope of the line is 2.6 kcal/mol and represents the activation energy.

Table 1. Temperature dependence of mixing rate constant of Cu/PI system

T(℃)	1/T(K)	k($hour^{-1}$)
150	2.36×10^{-3}	1.05×10^{-2}
200	2.11×10^{-3}	1.34×10^{-2}
250	1.91×10^{-3}	1.92×10^{-2}

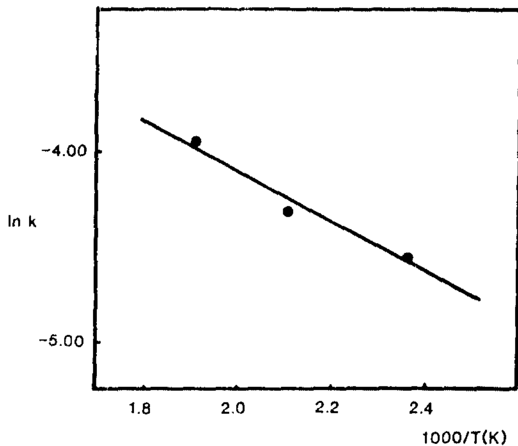

Fig. 6. Arrhenius plot on the mixing reaction rate of Cu/PI system.

The rate of thermally-induced mixing depends on the free volume of PI substrate and the motion of segments of PI molecules. The motion of PI molecules depends on the degree of packing of the chains and is also correlated to the coefficient of thermal expansion and the glass transition temperature. The increase of the rate constant with temperature may be interpreted as due to the increase of free volume and consequently also in the segmental mobility, provided that the metal has no chemical interaction with the polymer.

From X-ray diffraction study (Fig. 7), the strong peak from Cu(111) plane increased with time at 150℃ up to 6 hrs annealing, and then slowly decreased with further increase in annealing time. The Cu film was almost in an amorphous state because the Cu atoms were deposited on the amorphous PI. This unstable amorphous Cu film on the PI substrate transformed to a more stable crystalline state during the thermal treatment. After 6 hrs annealing at 150℃, the crystalline Cu surface began to degrade due to a large amount of diffusion of the Cu particles into the PI sub-

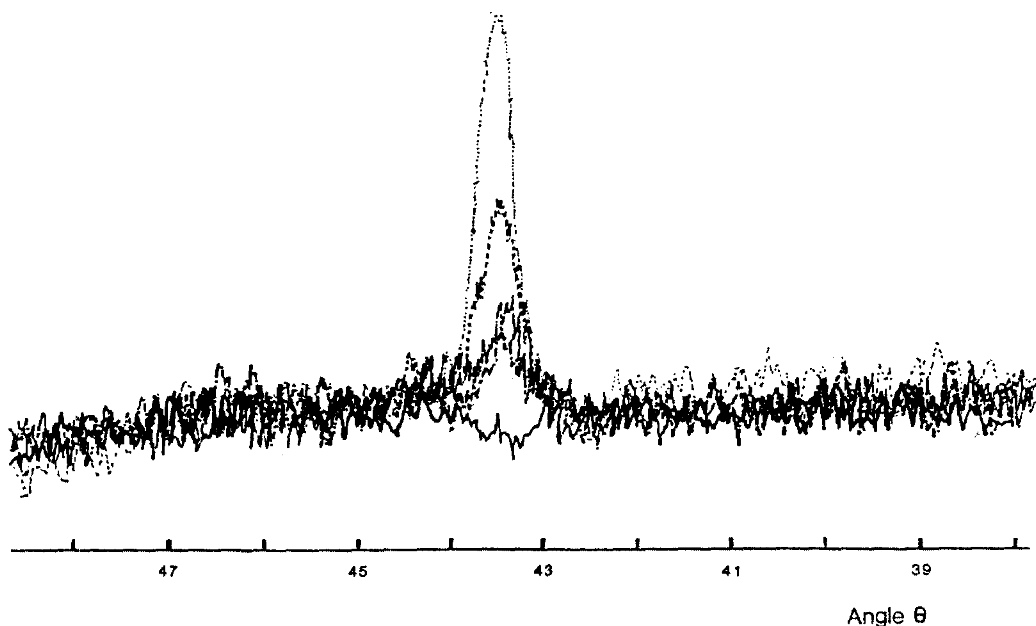

Fig. 7. X-ray peaks of Cu(111) surface on polyimide with various annealing time at 150℃: 4×10^{16} ion dosage with 200 KeV Ar^+ (dotted line), pure polyimide (solid line), Cu film without heat treatment (dash-and-dotted line), for 6 hrs annealed Cu film (broken line), and for 12 hrs annealed Cu film (dash-and-dotted-dotted line).

strate. But the Cu particles on a few top layers of the surface would not have diffused into the substrate at this temperature. Rothman *et. al.* [13] suggested the self diffusion equation in copper to be $D=0.78\ \exp(-50.5\,kcal\cdot mol^{-1}/RT) cm^2/sec$ in the temperature range 700 to 1060℃. Their experiments were done on copper single crystals mainly with purified copper 67 tracer. They suggested that the self diffusion in copper arise partly from vacancies and partly from a temperature dependence in the enthalpy and entropy of activation became more important at the higher temperatures. However, the activation energy of 2.6 kcal/mol obtained in the Cu/PI system is so low that the copper particles on the surface can not diffused into the interface area by vacancy of self diffusion at low temperature. Therefore the local motion of the Cu particles should be due to the segmental motion of PI. Those Cu particles would be trapped by functional groups of the PI chain at the beginning step, and then moved into the low Cu concentration area with increasing the entropy following the path of large free volume site. The Cu particles that passed through the boundary of PI, number of mixed Cu particle (C), were just measured at fixed temperature with various annealing time in disregard of the diffusion distance. Roughly the diffusion distance of Cu particle could be seen by RBS spectra (Fig. 2~4) comparing with the peak of unannealed sample. Mixing at the interface by heat treatment probably occurred by diffusion but the mixing rate is not the same as the diffusion rate. The value of activation energy of the interface mixing between Cu and PI is the same order of magnitude as the diffusion activation energy of polymer-gas (usually intert gas) system [12]. The reason for the low activation energy of 2.6 kcal/mol is probably due to formation of organic-metallic bonds between electron donor and acceptor.

Generally, the chelating ligands which come from nitrogen and oxygen in polyimide attract the Cu atom to make complex bonds between metal *d* oribital and the lone pair electron in polyimide [14]. Recently, some investigators suggested that the principal interaction occur with carbonyl oxygens of PMDA (pyromellitic dianhydride) portion of the polyimide and Cu atom initially occupied energetically favorable site of high coordination above the aromatic ring of the PMDA portion [15]. These kinds of interaction should decrease the activation energy of the mixing. The formation of the organo-metallic bonds make it easier for Cu atoms to diffuse into the PI substrate.

Comparing the thermally-induced mixing with the radiation-enhanced mixing of Cu/PI systems, one distinctly different feature is that the Cu film received a great deal of energy from Ar^+ irradiation in the radiation-enhanced mixing [16]. Therefore Cu atoms located at every layer of the film could have been moved into the polyimide substrate at the same time by kinetic collisional and radiation enhanced diffusion with breaking the bonds of PI. The number of Cu particles that diffused into PI depended on the Ar^+ ion energy and the fluence [16]. These Cu particles with high energy are so unstable that they might have bonded with nitrogen in PI. The amorphous Cu film was transformed into a higher ordered and preferentially oriented phase than that of the thermal treatment (dotted line in Fig. 7). However, for the thermally-induced mixing, the amount of mixing is a function of annealed time, temperature, free volume, and chain mobility of PI without breaking the bonds of PI. Therefore, mechanism of the thermally-induced mixing of Cu/PI system should be the interfacial diffusion and the mixing rate depends on chain mobility of polymer, temperature, and time.

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