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# RBS, ERDA and XPS study of Ag and Cu diffusion in PET and PI polymer foils

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**Abstract**

Diffusion of Ag and Cu atoms in polyethyleneterephtalate (PET) and polyimide (PI) was studied using Rutherford Backscattering Spectroscopy (RBS) and Elastic Recoil Detection Analysis (ERDA). The samples were prepared by deposition of Ag and Cu thin layers on polymer surface using CVD and diode sputtering techniques. Samples were annealed at temperatures up to 240°C. X-ray Photoelectron Spectroscopy (XPS) was used for determination of metal-polymer interaction and chemical state of atoms on metal- polymer interface. Faster diffusion of Ag atoms was observed from non-compact Ag layers prepared by diode sputtering than from those prepared by CVD technique. Ag atoms show higher mobility in PET in comparison with PI. XPS measurement gives an evidence of Ag

clustering in Ag-PET samples prepared by cathode sputtering. In PI the Cu atoms exhibit higher diffusivity than Ag atoms due to their lower atomic radius.

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**Introduction**

Wide range of applications of metallized polymers [1] in microelectronics has stimulated research of metal-polymer interaction. Polyimide encompassing low dielectric constant, high temperature and radiation stability is one of the best candidates for fabrication of multilayer metallization structures on the chip level and for packaging. In these structures, comprising alternate metal and insulating layers, high-temperature polymers are increasingly used and aluminum is replaced by the lower resistance copper. It has been observed that the microstructure and hence the mechanical and dielectric properties of the metal- polymer interface is strongly affected by the degree of metal-polymer diffusion and intermixing [3]. Thus there is a basic need to understand the mechanism of metal diffusion in polymers and its effects on the structure and formation of metal-polymer interface. The diffusion depends on the physical and chemical properties of metal and the structure of the polymer as well. Cu and Ag for example exhibit higher mobility in polymers in comparison with that of more reactive metals such as Cr or Ti [2]. In this study the diffusion of Cu and

Ag in polyethyleneterephtalate (PET) and polyimide (PI) is examined using different methods with the aim to shed more light onto the diffusion mechanism.

**Experimental**

The samples were prepared by deposition of thin Cu and Ag layers on polypyromellitimide (PI, $C_{22}H_{10}N_2O_5$, ρ=1,43 g.cm$^{-3}$) and PET is the polyethyleneterephtalate (PET, $C_{10}H_8O_4$, ρ=1,397 g.cm$^{-3}$.). Cu and Ag layers with typical thickness less than 10 nm were deposited using CVD or diode sputtering (BAL-TEC, SCD 050 system) techniques on polymer substrates. The deposition was performed at room temperature and temperatures close to polymer glassy transition temperatures ($T_g$= 360°C and 76°C for PI and PET, respectively). In the case of diode sputtering (RT, total argon pressure about 4 Pa, the electrode distance 50 mm and current 20 mA), deposition times were 50 and 80 s. Annealing conditions are summarized in the Table 1. The annealing was performed on air atmosphere in small annealing furnace.

Metal concentration depth profiles we obtained from RBS spectra (2.2 MeV He ions, 170° laboratory scattering angle) using computer code GISA 3 [5]. ERDA measurement was performed with 2.7 MeV He ions and the protons recoiled under the angle of 30$^0$ were registered. Measurements of photoelectron spectra were carried out on an angular-resolved X-ray induced photoelectron spectrometer ADES-400 (VG Scientific) using Mg Kα radiation (1253.6 eV) and a rotable hemispherical energy analyser. The spectra were recorded at normal emission angle except those recorded for quantitative analysis where both normal and 60° emission angles were used. The energy positions were referenced to the Cu 2p peak at 932.6 eV and Au 4f peak at 84.0 eV binding energy. Atomic concentrations were determined from XPS peak areas corrected for photoelectron cross-

sections [6], the inelastic mean free paths [7], and experimentally determined transmission function of the energy analyzer . In a control experiment the Ag continuous surface layer was removed by 96% ethylalcohole solution and, after this treatment, the XPS measurement was performed again.

**Results and Discussion**

Annealing at higher temperatures may leads to degradation of the polymer substrate accompanied with emission of volatile, hydrogen or oxygen rich degradation products. This effect was thoroughly examined by RBS and ERDA techniques and no compositional changes were observed. Concentration depth profiles of diffusing metal atoms were determined from RBS spectra. On PET-Ag samples surface concentration decrease and deeper Ag penetration with increasing annealing temperature is observed. Diffusion coefficients for deposition times 50s and 80s were determined using standard procedure from the plot of ln (concentration) vs. depth$^2$. Arrhenius plot for diffusion of Ag deposited by two deposition techniques and for different times are shown in Figs. 1a and 1b. Diffusion coefficients of Ag atoms on Ag-PET samples prepared using diode sputtering are by one order of magnitude higher than those on the samples prepared using CVD technique. Diode sputtering enables one to prepare metal layers with low thickness facilitating high inward mobility of metal atoms. Higher diffusion coefficients are also observed for Ag layers deposited for 50 s in comparison with those deposited for 80s (see Figure 1a).

In the XPS spectra shown in Figure 2 the main part of C1s peak C-C doesn't change its position; small uncertainty is connected with corrections on sample charging during XPS measurement. Most significant reduction of the C=O peak is observed for annealing

temperature 70°C for both deposition times 50s and 80s (see Figure 2). The data indicate that at the temperature 70°C a perturbation of C=O bond takes place . On the samples prepared by diode sputtering for 50 s, Ag fraction measured by XPS after removing a continuous Ag surface layer decreases significantly with annealing temperature. It indicates the higher depth incorporation of Ag atoms as is referred in [8]. Low difference between Ag fraction XPS measured under the angles 0° and 60° indicates higher compactness of Ag layer deposited for 80 s, in comparison with the layer deposited for 50s. The fact that XPS spectra of above mentioned Ag/PET samples showed the shift of the Ag binding energy of 0.5 eV relatively to the bulk Ag layer (368,4 eV) is another evidence of the presence of Ag clusters see Figure 2. Most significant shift of Ag binding energy is observed for annealing at the temperature of 70°C.

Arrhenius plots of Ag and Cu in PI deposited by CVD at RT and 250°C are presented in the Figs. 3a, b. Diffusion coefficients of Ag CVD deposited at RT on PET (Fig. 1b) are , at comparable annealing temperature, about twice higher than those for Ag deposited under the same conditions on PI (Fig. 3b). This is in accordance with expectation because of higher density of PI. Increase of the deposition temperature from RT to 250°C leads to significant decline of Ag diffusion coefficient in PI (Fig.3b).

Under the similar deposition conditions, diffusion coefficients of Cu in PI are nearly one order of magnitude higher than those of Ag. This can be due to a smaller diameter of Cu atoms and in turn to their higher mobility in comparison with Ag atoms. Present diffusion coefficients for Ag in PET and PI are comparable with those reported for Ag in BPA-PC (bisfenol-A-polycarbonate) in [9] or Ag in photoresist AZ1350-J ($C_{6,17}H_6O_1N_{0,14}S_{0,063}$) [10].

**Conclusions**

The study on diffusion activity of Ag and Cu atoms in PI, PET was done.

The samples were prepared by CVD and diode-sputtering techniques on polymer substrate and the diffusion was initiated by annealing to temperatures below polymer glassy transition temperatures. The diffusion coefficients of the order of $10^{-15}$ - $10^{-14}$ $cm^2 .s^{-1}$ were found in accord with the results reported earlier for other polymers. Under similar deposition and annealing conditions the higher diffusion coefficients are observed for Ag atoms in PET in comparison with those in PI. Faster diffusion of Ag atoms was observed on the samples prepared by diode-sputtering technique. This may be due to the fact that CVD technique produces thicker and more compact Ag films. In comparison with Ag the Cu atoms exhibit much higher diffusion coefficients in PI.

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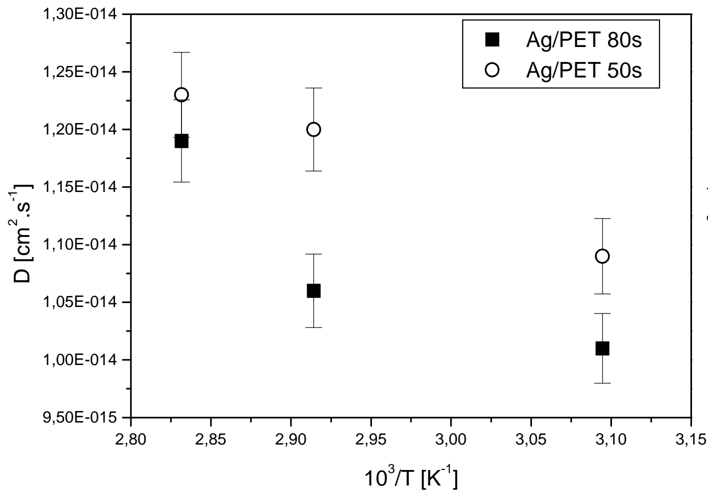
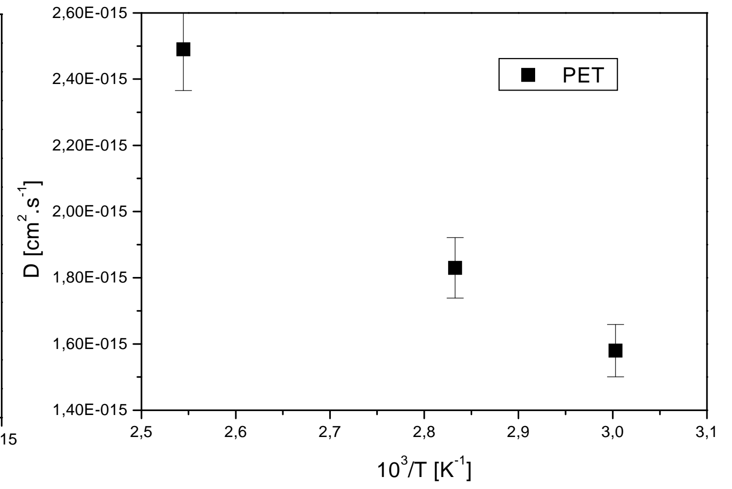
| **Polymer substrate—deposition-metal** | Deposition temperature [ºC] | Annealing temperature [ºC] |
|---|---|---|
| PI-CVD-Ag | 250 | 80 |
| | | 160 |
| | | 240 |
| PI-CVD-Ag | RT | 80 |
| | | 160 |
| | | 240 |
| PET-CVD-Ag/PET-Sputtering-Ag (50s, 80s) | RT/RT | 60/50 |
| | | 80/70 |
| | | 120/80 |
| PI-CVD-Cu | 230 | 80 |
| | | 160 |
| | | 240 |

Table 1 Deposition and annealing conditions for CVD and diode sputtering Ag and Cu films deposited on PI and PET substrates.




a)




b)

Figure 1 a) Arrhenius plot of Ag deposited by diode sputtering at RT on PET substrate – deposition time 50 s and 80 s . b) Arrhenius plot of Ag deposited by CVD at RT on PET substrate.

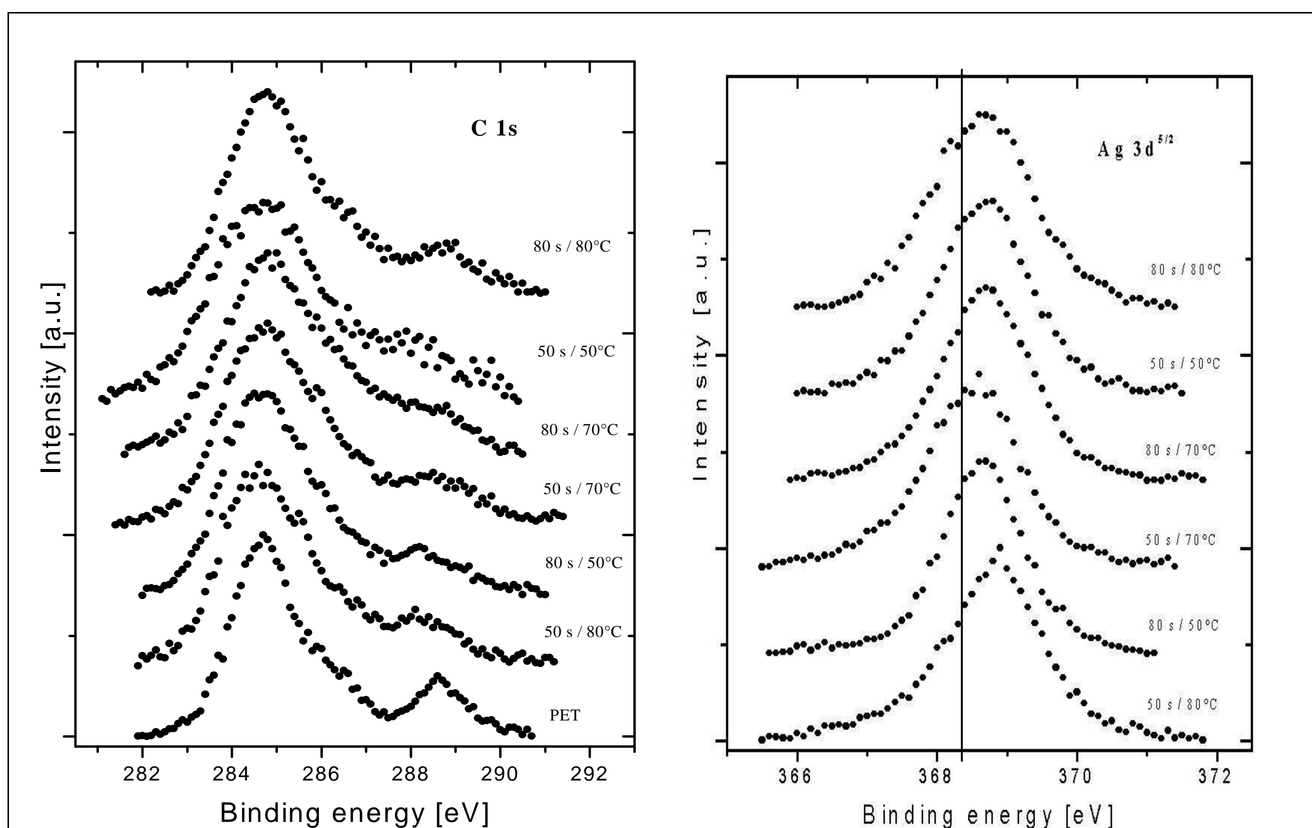
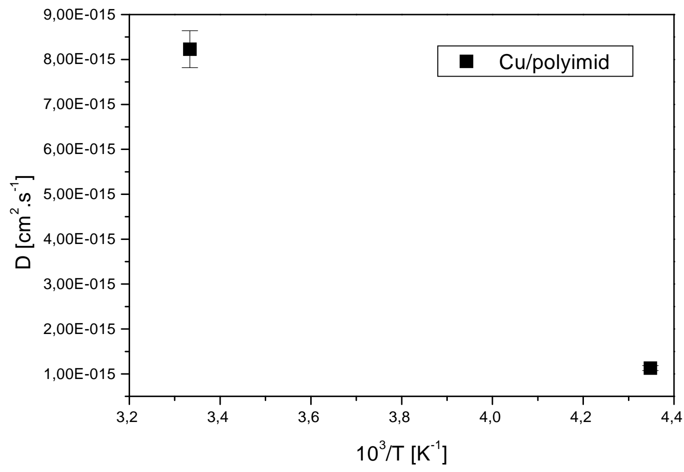
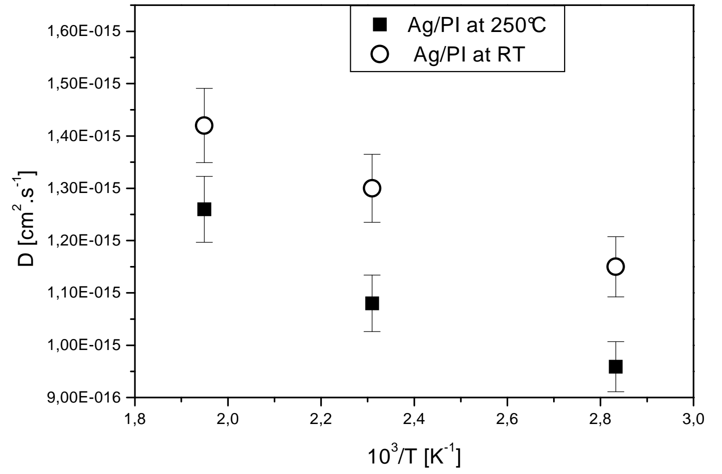



Figure 2 XPS C 1s and Ag 3d $^{5/2}$ spectrum recorded from Ag deposited by diode sputtering for 50s and 80s at RT on PET substrate . The vertical line follows the binding energy of bulk Ag layer (368,4 eV).




a) b)

Figure 3 a) Arrhenius plot of Cu deposited by CVD on PI substrate at 230°C b) Arrhenius plot of Ag deposited by CVD on PI substrate at RT and 250°C.