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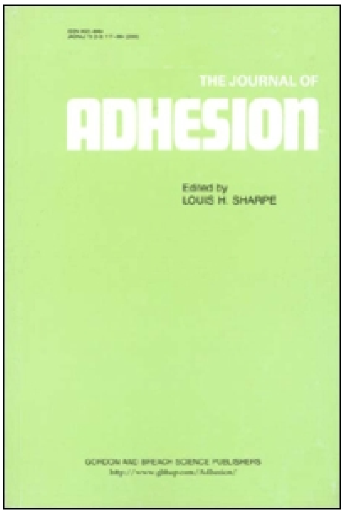

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Diffusion of Copper in Polymer During the Metallization of PET*

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Thin Cu metal layers were deposited on semicrystalline poly(ethylene terephthalate) PET films by thermal evaporation. RBS measurements revealed that, under our metallization conditions, the Cu layers are buried into the polymer bulk. This has also been confirmed by ToF-SIMS measurements which reveal that some PET remain at the top surface. Since the formation of a diffuse interface has important consequences on the adhesive properties, the Cu diffusion was investigated systematically by means of RBS. After metallization, the samples were annealed under vacuum for times varying between 0 and 120 hours at 80, 90, 100, 120 and 140°C, slightly above the glass transition of the PET (67°C). Since the diffusion profiles exhibit a behavior in accordance with Fick's laws, the diffusion coefficients were evaluted. The results are in agreement with a diffusion model based on the Brownian motion of particles in a viscous fluid.

KEY WORDS: Metallization; polymer; interface; diffusion; metal cluster; RBS; PET; copper.

INTRODUCTION

Metallized polymers are used more and more frequently for an increasing number of industrial applications such as automotive, dielectric layers in microelectronics, information support, flexible printed circuit boards and packaging. In most situations, strong adhesion and good thermal stability are required. The microscopic mechanisms governing adhesion are complex and may include various contributions: interfacial specific interactions, mechanical interlocking, intermixing, etc. The formation of an interphase by diffusion may be in some cases beneficial to adhesion. Indeed, the production of a diffuse interface may produce a microscopic interlocking. But it may also be detrimental if it leads to formation of a weak boundary layer. In our case, it seems that atomic metal diffusion tends to increase the adhesion while cluster segregation within the PET skin decreases the metal/PET adhesion.[1] Therefore, the characterization of the interphase composition and extent is very important to understand the adhesive properties of a given interface. In our previous work, we studied the "in situ" formation of the metal-polymer interface by means of static SIMS.[2-4] In the case of Cu deposited at RT on PET in the submonolayer and monolayer regime, we found that the

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interactions of Cu atoms with the polymer surface functional groups are very weak. This was also confirmed by other authors by means of XPS studies.[5,6] This low interfacial reactivity leads to a very low sticking coefficient at the early stage of Cu atom deposition on PET. The low sticking coefficient can either be due to the backscattering of the metal atom in the gas phase[7] and/or to diffusion into the polymer bulk. The interface growth is governed by the competition between ad-atom/ad-atom and ad-atom/substrate interactions. For Cu on PET and on PMMA, the first contribution dominates and metal clustering was observed on PMMA by ToF-SIMS molecular imaging.[4] Moreover, ISS and SIMS data showed that the first Cu atoms diffuse underneath the surface.[2-4] In this work, the diffusion process of Cu in the polymer bulk and the formation of the interphase are studied. To enhance the diffusion, the Cu-metallized PET samples are submitted to annealing treatments of different times and temperatures above the glass transition temperature. In order to have access to the buried metal-polymer interface, RBS is mainly used. This technique indeed allows one to obtain non-destructive, quantitative depth composition profiles with enough depth resolution.[9]

EXPERIMENTAL SETUP

Twelve μm thick, biaxially-stretched, semicrystalline poly(ethylene terephthalate) (PET) films from Du Pont de Nemours-Luxembourg (Mylar®) were used for substrates. Before metallization, the PET samples were pumped down to 10^{-6} mBar and maintained at this pressure for at least half an hour in order to outgas O_2 and H_2O. The copper was deposited by thermal evaporation in a coating system (Veeco VES770) with an e-gun source (Varian 989-0003), uisng a tungsten basket. The thickness of the layer was measured by a quartz microbalance (Sloan DTM 200), calibrated with RBS measurements. Two sets of Cu metallization were made with the same total Cu deposited amount of 1.80×10^{17} at/cm^2. If a uniform coverage is assumed, this corresponds to a thickness of 21.3 nm, assuming a Cu atomic density of 8.45×10^{22} at/cm^3. The deposition time was 40 s for the first set of samples (0.5 nm/s deposition rate) and 14 s for the second (1.4 nm/s deposition rate). After metallization, the samples were maintained in air at room temperature for times varying between 1 h and few days before being introduced in the vacuum oven. It has been checked that this time has no influence on the results. During this delay, the formation of a native oxide of 3 nm is expected.[8] The samples were then annealed under vacuum during times varying from 0 to 120 h at temperatures from 80 to 120°C. (See Table I).

The RBS measurements were performed with a 1 MeV He beam generated by a Van der Graaf accelerator (High Voltage), using the standard RBS technique.[9] The scattered He was detected at a 165° scattering angle with a 11 keV resolution (FWHM) silicon surface barrier detector. In order to enhance the depth resolution, the beam was incident at 60° with respect to the surface normal. With this geometry, the resolution in terms of FWHM is about 14 nm for Cu in PET and 25 nm for C in the same medium. To obtain the composition depth profiles, the experimental spectra are reconstructed by simulation, using an iterative algorithm[10] and the stopping powers from Ref. 11. To convert the x scale into thickness (nm), the same density of 9.45×10^{22} at/cm^3

TABLE I
Thermal treatments for the different samples

Annealing time	As deposited	6h	24h	48h	72h	96h	120h
Annealing temperature		Sample metallized at 0.5 nm/s					
80°C	X		X		X		X
90°C	X		X	X	X	X	
100°C	X		X	X	X		
120°C	X	X	X	X			
140°C	X	X	X	X			
		Sample metallized at 1.4 nm/s					
100°C	X	X	X	X			
120°C	X	X	X	X			

corresponding to that of bi-stretched PET films[12] is used. This approximation, usually accepted,[13] neglects, however, the density difference between Cu and PET.

Time-of-flight SIMS spectra were obtained with a Charles-Evans spectrometer (TFS4000-MMI) in the following conditions. A primary 15 keV-Ga$^+$ ion beam with 530 pA DC current is pulsed at a 5 kHz repetition rate and 4 ns pulse width and the 500 nm beam spot is rastered on a 100 × 100 μm^2 surface area. The secondary ions are extracted at 10.5 kV acceleration voltage then 270° deflected by three electrostatic hemispherical condensers in order to compensate for the initial energy distribution of ions with the same mass. They are mass analyzed by measuring their time-of-flight from the sample surface to the position-sensitive detector.[14] The acquisition time is 300 s per spectrum and corresponds to a total ion fluence of less than 10^{12} ions/cm^2.

Contact AFM images were obtained using an Autoprobe CP from Park Scientific Instruments (Sunnyvale, CA). Pyramidal silicon nitride tips mounted on microlevers with a force constant equal to 0.5 Nm^{-1} were used for these observations. Typical scan speeds ranged between 1 and 2 μm s^{-1} and typical contact forces ranged between 40 and 150 nN.

RESULTS AND DISCUSSION

Figure 1 presents a typical RBS spectrum obtained for Cu deposited on PET. The kinematic factors for C, O and Cu are indicated by arrows. The simulation of the RBS spectrum to be obtained with an unifom 21.3 nm copper layer deposited on PET is shown by the dotted line. In this simulation, a sharp Cu/PET interface is introduced and the surface of the Cu layer presents a 3 nm thick native oxide (Cu_3O_2). It is seen that, even before annealing, the high energy edge of the Cu peak is slightly shifted to an energy ratio lower than the kinematic factor. By comparison with experimental data (dots), it is seen that the presence of carbon and oxygen surface peaks cannot be explained by the surface oxide but should rather indicate that polymer is present at the surface. The presence of PET at the surface after Cu deposition has been confirmed by

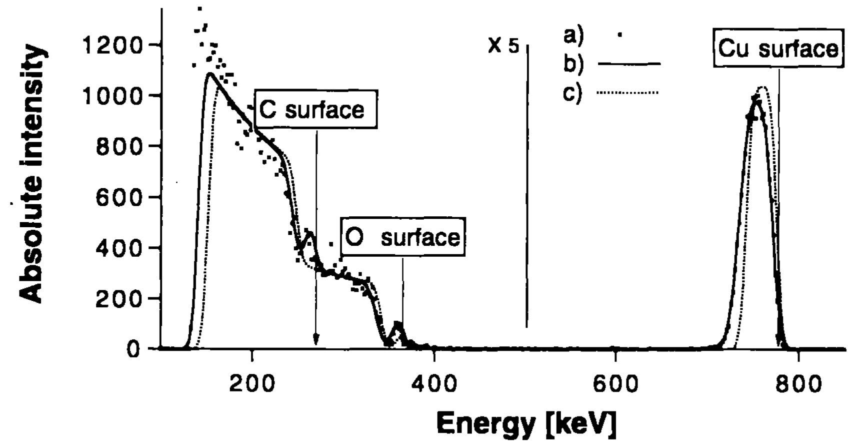

FIGURE 1 RBS spectrum of Cu (20 nm) deposited on PET; a) experimental spectrum; b) simulated spectrum with calculated concentration profile; c) simulated spectrum of 21.3 nm Cu on PET with sharp interface and a 3 nm thick surface native oxide layer (Cu_3O_2).

ToF-SIMS. After a Cu deposition of 21.3 nm the positive ToF-SIMS spectra are strongly dominated by the copper peaks at mass 63 and 65; however, some molecular ions coming from the PET are also present but with a lower intensity. The relative concentration cannot be deduced from the intensity ratios because of the higher secondary ion yield for metal atom as compared with organic fragments. The negative ToF-SIMS spectrum presented in Figure 2 confirms clearly that the characteristic peaks of the polymer are still present even after 21.3 nm Cu metallization. Indeed, static SIMS is extremely surface-sensitive when molecular ions are detected.[16] These results confirm that PET is still present at the surface and that Cu atoms penetrate at least partly into the polymer bulk.

From the RBS spectrum, the composition depth profiles are deduced by an iterative fitting procedure between the experimental and simulated spectra (full line in Fig. 1). In the simulation, only the PET composition ($C_{10}H_8O_4$) is introduced. The maximum Cu concentration is found below the surface and this supports the presence of metal clusters buried into the polymer.

Figure 3 shows AFM images of the PET film before and after 20 nm Cu deposition. It clearly shows that the Cu layer consists of small structures in the range of 40 nm. A similar effect has been also reported for Cu deposition at high temperatures on polyimide, and spherical buried Cu particles were evidenced by means of cross-sectional TEM.[15]

Similar formation of subsurface particulate film has been observed and studied for metal vacuum deposition on thermoplastic substrates above their glass transition temperature, T_g.[17,18] This subsurface structure is thermodynamically favored when the particle surface tension exceeds the sum of the substrate surface tension and interfacial tension. This is verified for metal on thermoplastics.[17] Of course, this equilibrium can be prevented by kinetic factors, such as a penetration rate lower than deposition rate

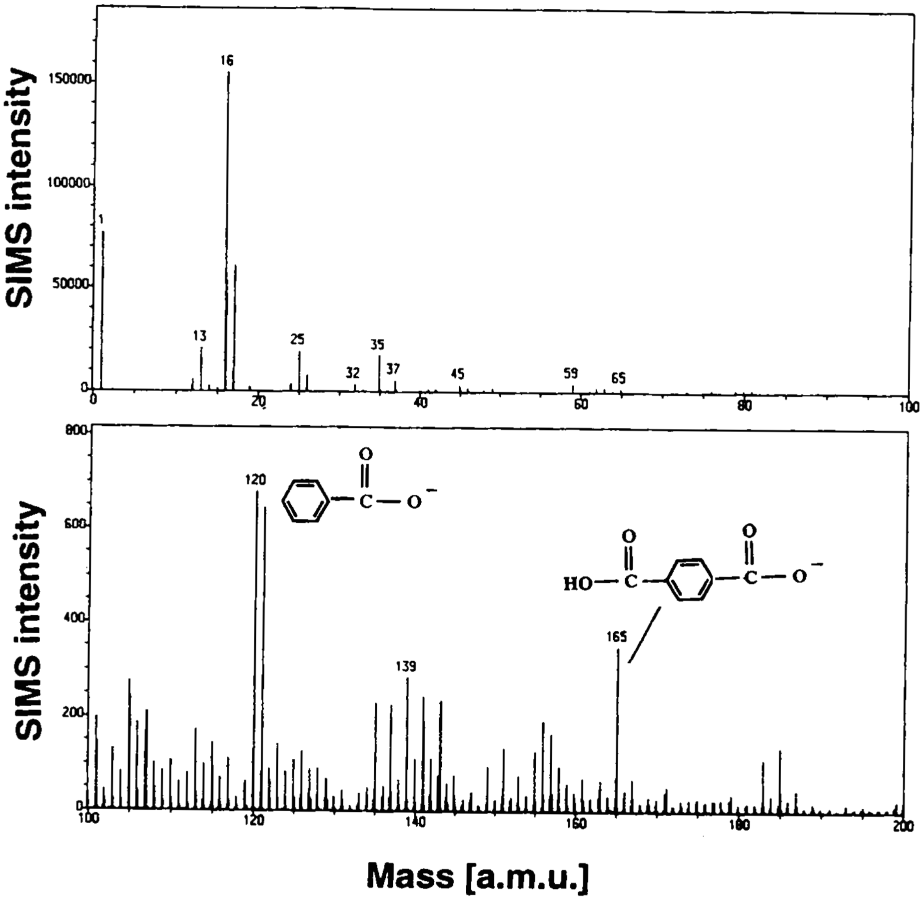

FIGURE 2 Negative ToF-SIMS spectrum of Cu (21.3 nm) deposited on PET.

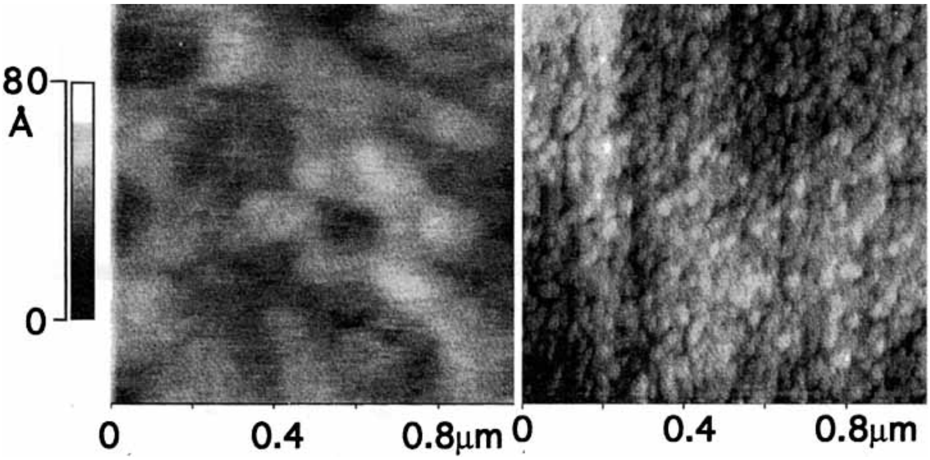

FIGURE 3 AFM images of PET before and after 21.3 nm Cu deposition at 1.4 nm s^{-1} rate.

and a layer-by-layer growth mode.[17,18] However, the observation of a subsurface structure indicates that, in our metallization conditions, the PET substrate temperature should exceed T_g (67°C[12]). Even if the substrate temperature is below the T_g at the beginning of the metallization (room temperature), it rises above T_g in our metallization conditions due to the thermal radiation flux and the condensation heat. The sample temperature during metallization was measured by means of a calibrated aluminum thin film resistor metallized on the back side of the PET film. The temperature is then deduced from the calibrated temperature dependence of the metal resistor. The measured value was between 90°C and 100°C in our experimental conditions.

Two sets of metallized samples were annealed under vacuum at different temperatures, from 80°C to 120°C, for times varying from 0 to 120 hours (see Table I). The effect of annealing on the RBS copper peak is shown in Figure 4a for the sample metallized at 0.5 nm/s and annealed at 90°C for 0, 24 and 72 hours, respectively. The corresponding Cu depth profiles are presented in Figure 4b. A broadening of the Cu profiles is observed with the annealing time and evidences the copper diffusion into the polymer bulk. This was confirmed by SIMS depth profiles showing a similar broadening of the Cu signal with the annealing time. In the case of a Fickian diffusion, the thin film solution for the concentration profile $c(x,t)$ is given by:[20]

$$c(x,t)=\frac{S_0}{(\pi Dt)^{1/2}}\exp\left(-\frac{x^2}{4Dt}\right)$$

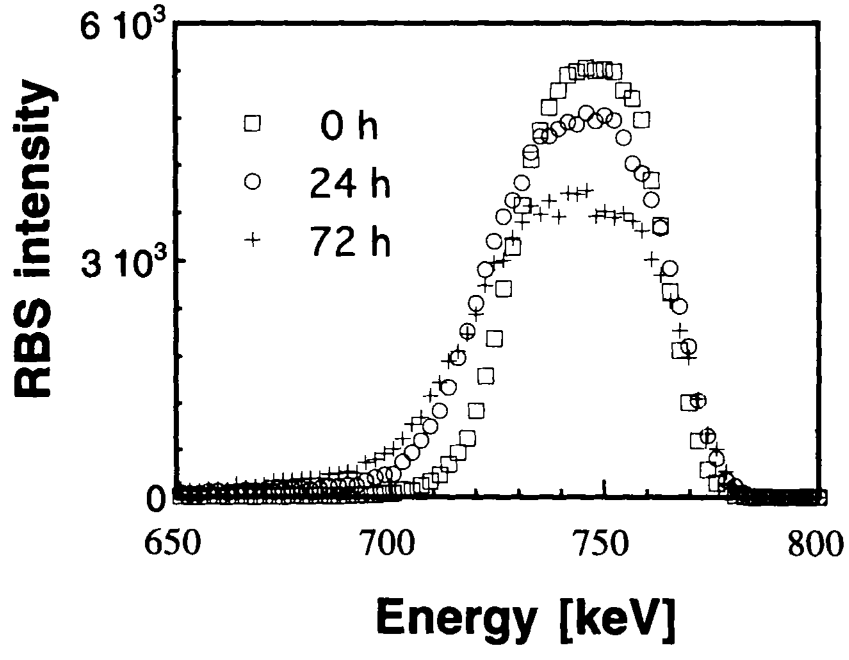

FIGURE 4 a) Evolution of Cu RBS peak as a function of the annealing time for $T = 90°C$. b) Cu concentration depth profiles corresponding to the Cu RBS peaks shown in a).

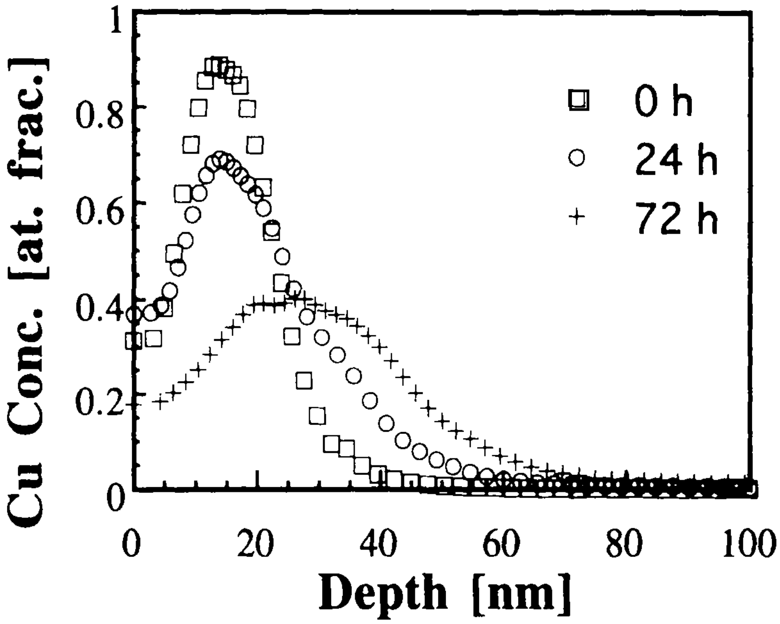

FIGURE 4 (*Continued*)

where S_0 is the total amount of diffusing species and t is the annealing time. The diffusion constant, D, can be determined by the slope-1/4 Dt of the log(c) *versus* x^2 plot. Such graphs, corresponding to the Cu concentration profiles shown in Figure 4, are presented in Figure 5. A linear behavior is observed for thicknesses deeper than the maximum so that Dt can be extracted from the slope. Since the so-determined values of Dt were found to be proportional to t, the diffusion coefficient D was evaluated. However, this treatment is a first approximation as the Cu clusters in PET require a more complex treatment than a diffusion process described by Fick's models. For example, the total free energy of the copper clusters is probably dependent on the distance of the cluster from the surface.[19] Nevertheless, the values of D are shown on a Arrhenius plot (ln D *versus* $1/T$) in Figure 6 for the two sets of samples. The observed non-linearity excludes the classical thermally-activated diffusion process. A similar trend was also reported for Cu diffusion in polyimide.[20] Our results are better fitted with a diffusion model proposed for aggregate spheres in a softenable substrate (thermoplastics above T_g)[21] and it is based on a Brownian motion of particles of radius r in a fluid of viscosity η at a temperature T. D is then given by the Stokes–Einstein relation:[21]

$$D = \frac{k_B T}{6\pi\eta r}$$

For polymers above T_g, the temperature dependence of the viscosity is given by:[22]

$$\eta = A \cdot \exp\left(\frac{B}{T - T_x}\right)$$

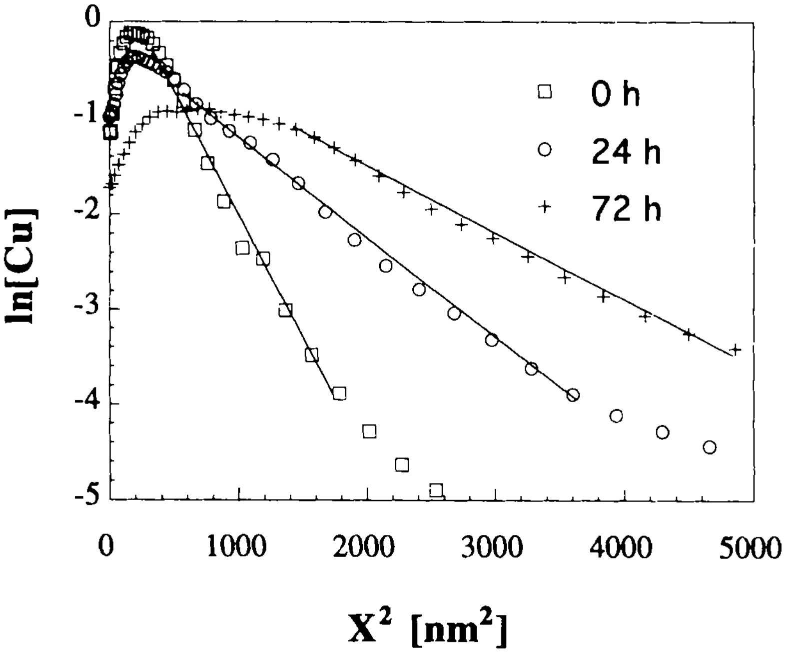

FIGURE 5 Evolution of the Cu concentration profiles as a function of x^2 for different annealing times at 90°C.

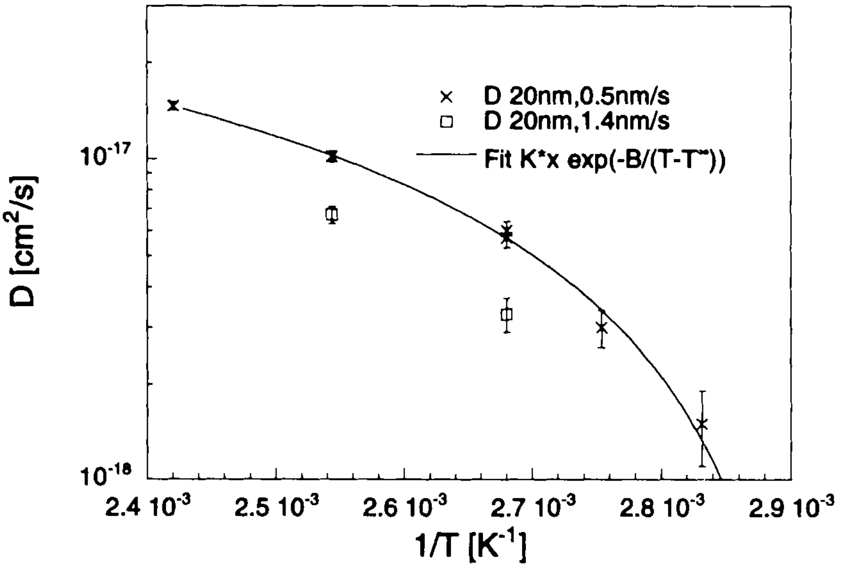

FIGURE 6 Arrhenius plot of the diffusion constant, D, as a function of the inverse temperature, $1/T$.

where A and B are experimental parameters and T_x is the temperature for which the viscoelastic relaxation time becomes infinite.

The temperature dependence of D should have the form:

$$D = \frac{k_B T}{6\pi r A} \exp\left(-\frac{B}{T - T_x}\right).$$

This model correctly fits our experimental data if T_x is taken equal to 50°C for samples metallized at 0.5 nm/s deposition rate, as shown by the solid line in Figure 6. This value is realistic[22] and, in agreement with the model, lower diffusion constants are found when increasing the deposition rate.

CONCLUSION

The RBS results on Cu metallized PET showed that, under our deposition conditions, the metal layer is buried in the polymer substrate. This reveals that the glass transition temperature is exceeded during the metallization. Annealing above T_g allows the copper to diffuse more deeply. The variation of the Cu diffusion constant with the temperature agrees with a diffusion model based on the Brownian motion of particles in a viscous fluid. More work is, however, needed to understand the influence of the metallization conditions (deposition rate, substrate surface temperature) on the metal layer microstructure and to determine the exact nature of the diffusing particles (oxidation state, aggregate size and shape, etc.). The influence of the polymer crystallinity on the diffusion process has also to be investigated in detail.

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