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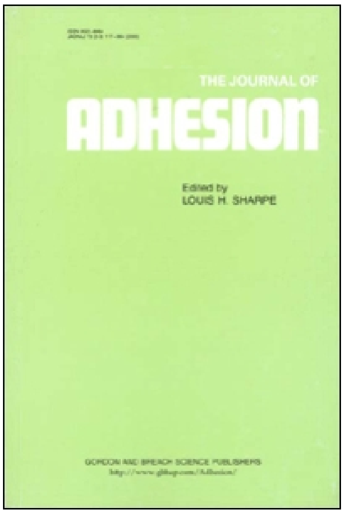

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Metalizable Polymer Thin Films in Supercritical Carbon Dioxide

Tadanori Koga[a]; J. L. Jerome[a]; M. H. Rafailovich[a]; J. C. Sokolov[a]; C. Gordon[b]
[a] Department of Materials Science & Engineering, State University of New York at Stony Brook, Stony Brook, New York, USA [b] Half Hollow Hills High School, New York, USA

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Metalizable Polymer Thin Films in Supercritical Carbon Dioxide

Tadanori Koga
J. L. Jerome
M. H. Rafailovich
J. C. Sokolov
Department of Materials Science & Engineering, State University of New York at Stony Brook, Stony Brook, New York, USA

C. Gordon
Half Hollow Hills High School, New York, USA

We report an environmentally "green" method to improve adhesion at a polymer/metal interface by using supercritical carbon dioxide ($scCO_2$). Spun-cast polystyrene (PS) and poly(methyl methacrylate) (PMMA) thin films on cleaned Si wafers were used for this study. Film thicknesses of both polymer films were prepared in the range of 100Å to 1600Å. We exposed the films to $scCO_2$ in the pressure-temperature (P–T) range corresponding to the density-fluctuation ridge, where the excess swelling of both polymer films occurred, and then froze the swollen structures by quick evaporation of CO_2. A chromium (Cr) layer with film thickness of 300–400Å was deposited onto the exposed film by using an E-beam evaporator. X-ray reflectivity (XR) measurements showed that the interfacial width between the Cr and exposed polymer layers increased by a factor of about two compared with that without exposure to $scCO_2$. In addition, the large interfacial broadening was found to occur irrespective of the thickness of both polymer films. After the XR measurements, the dewetting structures of the PS/Cr films induced by additional annealing were characterized by using atomic force microscopy, showing improved surface morphology in the exposed films. Contact angle measurements showed that a decrease in interfacial tension with exposure to $scCO_2$ accompanied the increase in interfacial width.

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Address correspondence to Tadanori Koga, Department of Materials Science and Engineering, State University of New York at Stony Brook, Stony Brook, NY 11794-2275, USA. E-mail: tkoga@notes.cc.sunysb.edu

Keywords: Atomic force microscopy; Contact angle; Interfacial width; Polymer thin films; Supercritical carbon dioxide; Vapor metal deposition; X-ray reflectivity

1. INTRODUCTION

Metallized polymer surfaces are used in numerous applications such as nonstick cooking utensils, printer jets, and microelectronics. In each case, the interface between the metal and polymer determines the adhesion of the metal layer, the thermal conductivity, and the electronic-conduction properties [1]. Dewetting of the metal surface by the polymer is often a serious problem, causing delamination and degradation of the mechanical or electronic properties, Therefore, a method of polymer coating that promotes wetting and maintains a uniform film coating is of great interest. Recently, it was shown that deposition of metals on porous structures, such as anodic porous alumina [2, 3], can be used to achieve strong electronic contacts because of the increase in surface area. However, the porosity required to produce these contacts is on the order of 1 micron. This is much larger than the thickness of polymer coatings and, hence, this techniques is not applicable for the metallization of thin polymer films, such as those used in microelectronics, where tight tolerances require submicron flatness of the polymer-film surfaces.

Recently, we have shown that exposure of a polymer surface to supercritical carbon dioxide (scCO_2) in the pressure–temperature (P–T) portion of the phase diagram known as the “density fluctuation ridge” can be an easy and efficient means for introducing molecular-level porosity in the polymer [4]. Along the ridge, a large enhancement in the solvent quality was observed to occur for all polymer films used, even when the bulk miscibility with CO_2 was very poor [5–10]. To dampen the density fluctuations, scCO_2 is driven into the polymer where plasticization occurs in a region several hundred angstroms thick. Neutron-reflectivity results clarified that when the gas was released rapidly, the polymer was vitrified and preserved the internal structure present with scCO_2 [7]. Furthermore, a combined use of X-ray reflectivity (XR) and atomic force microscopy (AFM) measurements proved that the formation of additional voids did not occur during the evaporation process, and a lower-density layer was formed at the polymer/air interface regardless of the film thickness [4].

In this article, by using XR and AFM measurements, we show that this low-density polymer layer can be exploited to enhance metallization of the polymer surface by diffusion of metallic vapors into the molecular-scale voids.

2. EXPERIMENTAL

2.1. Samples

Two polymers were used in this study: polystyrene (PS, $M_w = 2.0 \times 10^5$, $M_w/M_n = 1.05$, Polymer Laboratories, Inc., Amherst, MA, USA) and poly(methyl methacrylate) (PMMA, $M_w = 1.0 \times 10^5$, $M_w/M_n = 1.05$, Polymer Source, Montreal, Quebec, Canada). Thin films of PS and PMMA with the thickness ranging from 100 Å to 1600 Å were spun-cast on HF-etched Si substrates and then preannealed for 5 h in a vacuum of 10^{-4} Torr at 150°C. The $scCO_2$ treatment was as follows: The polymer films were first placed in a high-pressure chamber [9] and immersed in $scCO_2$ at the density fluctuation ridge condition ($T = 36°C$ and $P = 8.2\,MPa$) for 24 h. The chamber was depressurized to atmospheric pressure within 10 s. The time was faster than the relaxation time of the glassy polymer and, hence, the molecular-level porous structure was preserved. These T and P conditions were chosen because they correspond to the density fluctuation ridge in the vicinity of the critical point and can be fine-tuned within the experimental resolution. A chromium (Cr) layer was deposited onto the vitrified polymer films using an E-beam evaporator (model 9320026, Varian Vacuum System, Palo Aeto, CA, USA). The thickness of the Cr layer, as measured with a quartz-crystal oscillator, was 300–400 Å.

2.2. X-Ray Reflectivity

To characterize the frozen films, x-ray specular reflectivity (XR), which is sensitive to the vertical concentration profiles (*i.e.*, thickness, density, and roughness), was conducted at the X10B beamline of the National Synchrontron Light Source (NSLS), Brookhaven National Laboratory (BNL), using photon energy of 14 keV, *i.e.*, x-ray wavelength (λ) of 0.87 Å. As is shown later, the roughness between the Cr and air layers was relatively large. We also measured the off-specular scattering from the samples and subtracted it from the specular-reflectivity profiles as background scattering. As is discussed later, the exposed polymer films after the Cr deposition had a homogenous density distribution in the direction normal to the surface, whereas the exposed PS films before the Cr deposition showed a density gradient [4]. Therefore, a four-layer model (*i.e.*, a silicon substrate, a native oxide, a PS or PMMA layer, and a Cr layer), was used to fit the corrected XR data for all the polymer/metal films.

2.3. AFM Experiments

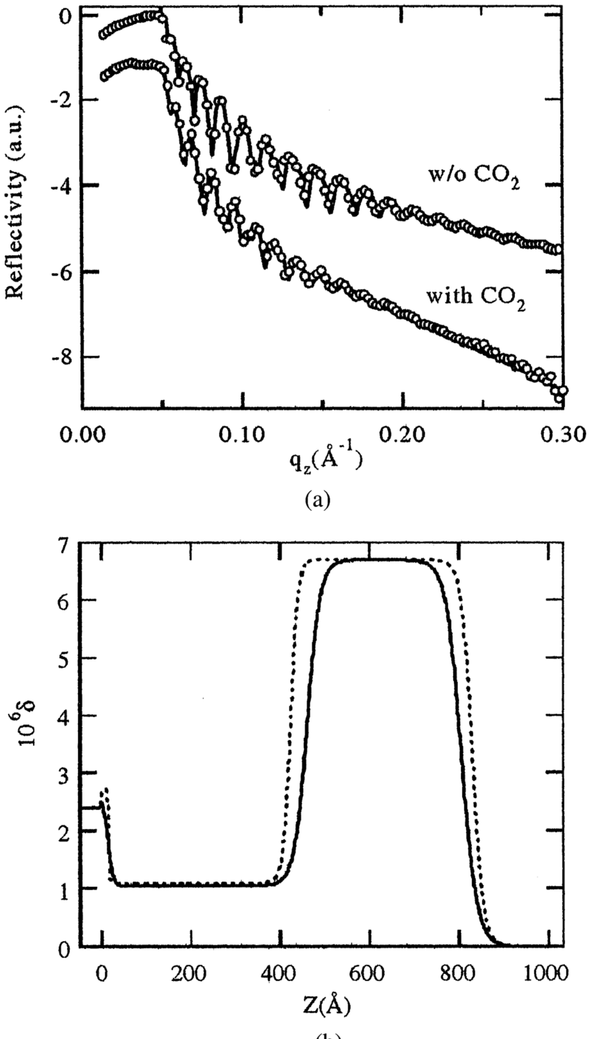
The surface morphology was analyzed with a Digital Nanoscope III AFM (Veeco Instruments, Inc., wood beeref, NY, USA) in the contact mode using an Si_3N_4 tip. As is discussed later, all the films used in this study had a flat Cr surface at room temperature. However, once polymer chains gain mobility at high temperature, the strong metallic bonding of metals and the weak intermolecular van der Waals interaction between polymers render the polymer/metal system unstable; *i.e.*, dewetting between the metal and polymer occurs. In the present work, to study the metal/polymer compatibility, we annealed the PS/Cr films at 80°C in a vacuum over for 1 h after the XR experiments, resulting in the surface dewetting. The annealing temperature, which was 20°C below the glass transition temperature of PS ($T_g = 100°C$), was chosen to keep the effect of the swollen PS structures as long as possible. We measured the contact angle between the Cr and polymer films to determine the interfacial tension between the polymer and metal layers through the classical Young's relationship:

$$\gamma_{AB} = \gamma_A - \gamma_B \cos\theta_c \qquad (1)$$

where θ_c is the contact angle, γ_A is the surface tension of metal, γ_B is the surface tension of polymer, and γ_{AB} is the interfacial tension between the two layers and depends on polymer/metal compatibility. For the purpose of this study, the surface tension of PS and PMMA was taken to be $\gamma_{PS} = 34.5 \times 10^{-3}$ J/m and $\gamma_{PMMA} = 36.5 \times 10^{-3}$ J/m, respectively [11], and we assumed the surface tension of Cr as $\gamma_{cr} = 41.5 \times 10^{-3}$ J/m.

3. RESULTS AND DISCUSSION

Figure 1a shows the representative XR profiles for the PS/Cr films with and without exposure to CO_2. In the figure we plot the scattering intensity, $I(p_z)$, as a function of the momentum transfer normal to the surface, $q_z = 4\pi\sin\theta/\lambda$, where θ is the glancing angle of incidence. The XR data were fitted by using a standard multilayer fitting routine for the dispersion value (δ) in the x-ray refractive index. The δ values of the Si, SiO_2, and Cr layers were calculated to be 2.39×10^{-6}, 2.25×10^{-6}, and 6.7×10^{-6}, respectively. It should be noted that the observed δ value of a SiO_2 layer is often different from the calculated value [12]. In principle, the roughness and thickness of each interface and the δ value of the PS layer were obtained from the fit. The roughness between the layers was assumed to be given by a Gaussian



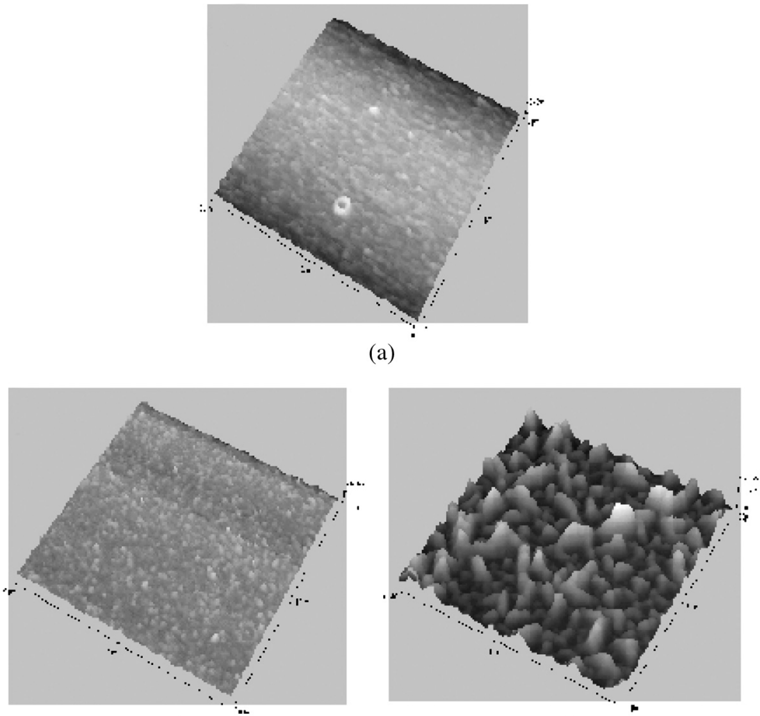
(a)

(b)

FIGURE 1 a) Observed (symbols) and calculated XR profiles (solid lines) of PS/Cr systems: unexposed (top) and exposed PS films (bottom). Note that the data points for the observed XR profile are reduced for clarity. b) Dispersion profiles for the fitting: unexposed (dotted line) and exposed films (solid line).

smoothing function with standard deviation σ, and the dispersion profiles across the interface between the layers were expressed as a convolution of a step function having the given film thickness and the Gaussian function. The solid lines in Figure 1a are the best fits to the data based on the corresponding dispersion profiles shown in Figure 1b, where we can see that the initial thickness, $L_0 = 408\,\text{Å}$, has increased to $L = 446\,\text{Å}$. This increase in thickness corresponds to a linear dilation, $S_f = (L - L_0)/L_0 = 0.09$, which is slightly larger than the bulk (0.07) [9] but is smaller than that of the exposed PS before the Cr deposition ($S_f = 0.13$) [4]. Additionally, the density (ρ) of the exposed PS layer, which is proportional to the δ value, was almost the same as the bulk or without exposure to $scCO_2$, whereas the density of the exposed PS film before the Cr deposition showed a 10% reduction [4]. Thus, it is clear that the deposition of the Cr layer altered the swollen structures of the bottom exposed PS layer. The root-mean-squre (rms) roughness (σ) at the air/Cr interface was almost constant ($21.5 \pm 0.7\,\text{Å}$) with and without exposure, indicating that dewetting did not take place. This is further confirmed by the AFM measurements shown in Figures 2a and b where the surface remains flat and the σ value of the surface was unchanged ($\sigma_{AFM} = 20\,\text{Å}$) even after the exposure. Conversely, it is obvious that exposure to $scCO_2$ after the Cr deposition causes the dewetting of the system (Figure 2c) because of the significant plasticization effect of density fluctuating $scCO_2$ [7]. It should be noted that the thickness of the Cr layers is slightly different in each case, because we prepared the Cr layers on the exposed and unexposed PS films separately.

Let us turn to the interfacial width (w) between the PS and Cr layers. The w value of the exposed film, which is expressed as $w = \sqrt{2\pi}\sigma$, increased by a factor of about 2 ($w = 52 \pm 4\,\text{Å}$), compared with that of the unexposed film ($w = 29 \pm 4\,\text{Å}$). We expect that exposure to $scCO_2$ introduces more free volume at the surface region of the film, which could allow easy penetration of metallic vapors and subsequent deposition of a well-adhered metallic layer. As we have previously reported, the low-density layer formation occurs at the polymer/air interface irrespective of the film thickness [4]. This would offer a potential benefit, *i.e.*, that the $scCO_2$-based adhesion-enhancing treatment is applicable for bulk polymers as well. To explore this hypothesis, we prepared PS films with a film thickness ranging from $100\,\text{Å}$ to $1300\,\text{Å}$, all of which were within the resolution of the XR technique. Figure 3a summarizes the effect of $scCO_2$ on the interfacial width of the PS/Cr interface as a function of the initial film thickness (L_0). From the figure we can see that the enhancement of the interface caused by $scCO_2$ is independent of film thickness. This is consistent with a low-density region at the film surface, which ultimately determines the interfacial structure. Hence, it is reasonable to conclude that the exposure to $scCO_2$ along the density fluctuation ridge



(a)

(b)

(c)

FIGURE 2 AFM images (20 µm × 20 µm) of PS/Cr films: a) without CO_2 exposure, b) CO_2 exposure before Cr deposition, and c) CO_2 exposure after Cr deposition. Height scales are 0–40 nm for a) and b) and 0–800 nm for c), respectively.

is a promising method to improve adhesion at the polymer/metal interface, even in bulk films.

It is important to quantitatively compare the swollen structure of the exposed PS films before and after the Cr deposition. Figure 3b summaries the S_f and ρ values of the exposed PS films as a function of the original film thickness. In a previous publication [4], we have shown that exposure to $scCO_2$ at the ridge produces uniform low-density films of approximately 2 R_g or less, where R_g is the radius of polymer gyration. For films $L_0 \gg 2R_g$, a region of low density, about 3 R_g in thickness, is produced at the surface that then decays into the bulk. Compared with the reported data, we can see that the exposed PS films collapse slightly after the deposition. In fact, the reduction in the density of the thinner exposed films (less than 2 R_g or 200 Å in thick), which could still maintain the homogeneous low-density formation even after the Cr

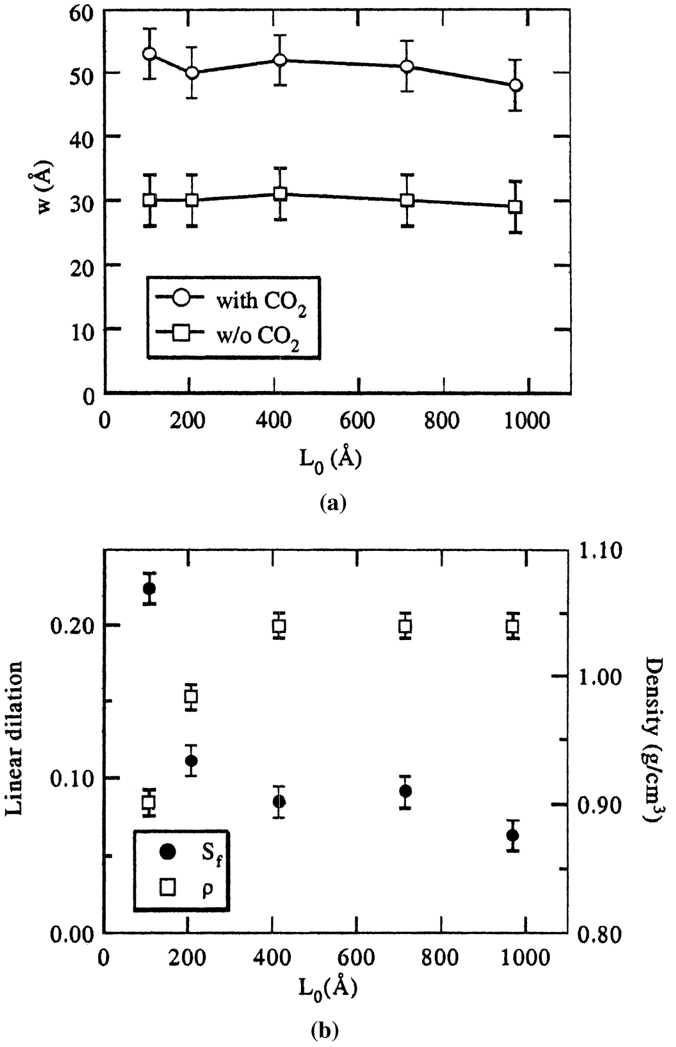


FIGURE 3 Effect of $scCO_2$ on interfacial width between PS and Cr layers as a function of the original PS thickness and b) linear dilation and density of the exposed PS films for PS/Cr as a function of the original PS thickness.

deposition, was only 5%. In addition, a Fourier transformation (FT) analysis [13], which is a useful tool to obtain details of the interfaces within the multilayers, proved that the exposed PS films after the deposition had a homogenous density distribution with the bulk density ($\rho = 1.04\,\mathrm{g/cm^3}$) when the thickness was more than 400 Å (the data

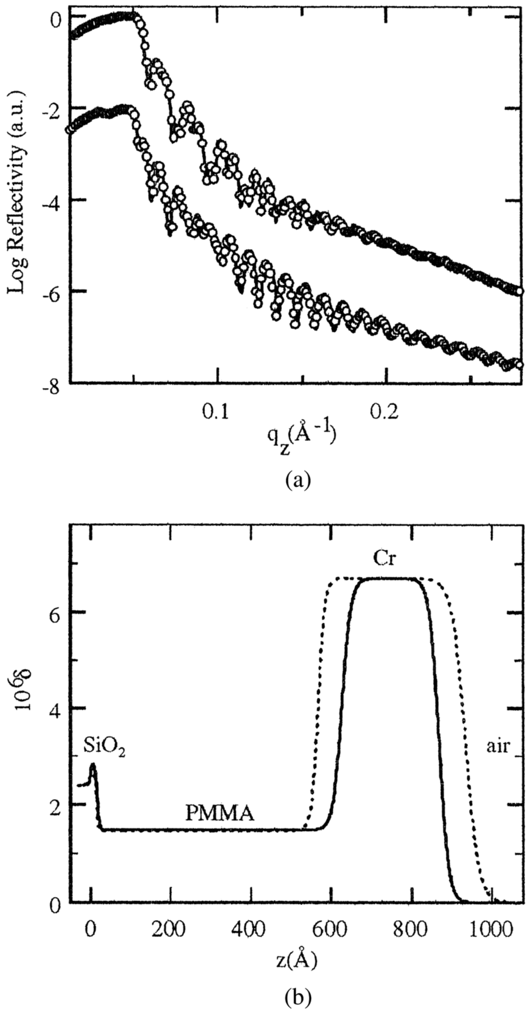


FIGURE 4 a) Observed (symbols) and calculated XR profiles (solid lines) of PMMA/Cr films: unexposed (top) and exposed PMMA films (bottom). Note that the data points for the observed XR profile are reduced for clarity. b) Dispersion profiles for the fitting: unexposed (dotted line) and exposed films (solid line).

are not shown here). Hence, the surface structures of the exposed PS films were found to be altered during the vapor-deposition process.

The XR measurements also detected similar scCO$_2$-induced adhesion enhancement at the PMMA/Cr interface. As we have previously shown, the anomalous swelling of the PMMA thin films occurred at the density fluctuation ridge and the isothermal swelling behavior was quite similar to the PS films, except for the high-pressure region where the S_f values of the PMMA films increased with increasing pressure [9]. Additionally, because PMMA has the CO_2-induced glass–liquid transition at low pressure (approximately 6 MPa) and room temperature [14], the *in situ* swollen structures could be preserved by the quench process mentioned previously. In the present study, the thickness of the PMMA films was prepared in the range from 400 Å to 1600 Å. Figure 4a shows the representative XR data for the PMMA/Cr films with and without exposure to $scCO_2$. The solid lines in Figure 4a are the best fits to the data based on the dispersion profiles shown in Figure 4b. After exposure to $scCO_2$, the film thickness of the PMMA layer changed from 555 Å to 610 Å, which corresponds to $S_f = 0.1$. As for the exposed thick PS films, the dispersion value of all the exposed PMMA layers used was identical to the bulk after the Cr deposition, and the σ value of 21 Å at the air/Cr Cr interface was unchanged with and without exposure to $scCO_2$. Figure 5 summarizes the effect of $scCO_2$ on the interfacial width between the PMMA and Cr layers. From the figure we can see that the interfacial width increases with exposure regardless of the film thickness of the PMMA layers, as for the exposed PS/Cr films. The *w* values of the exposed PMMA/Cr samples seem to be slightly smaller

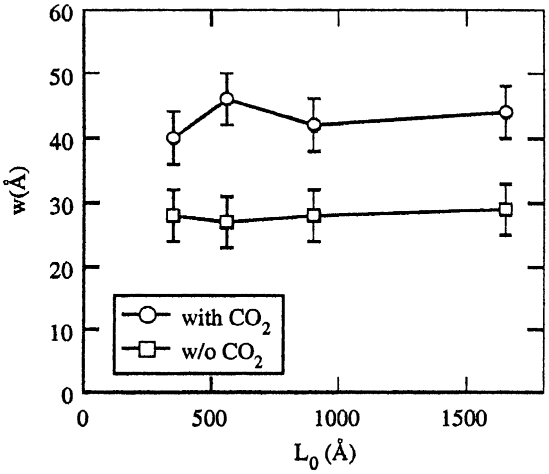


FIGURE 5 Effect of $scCO_2$ on interfacial width between PMMA and Cr layers.

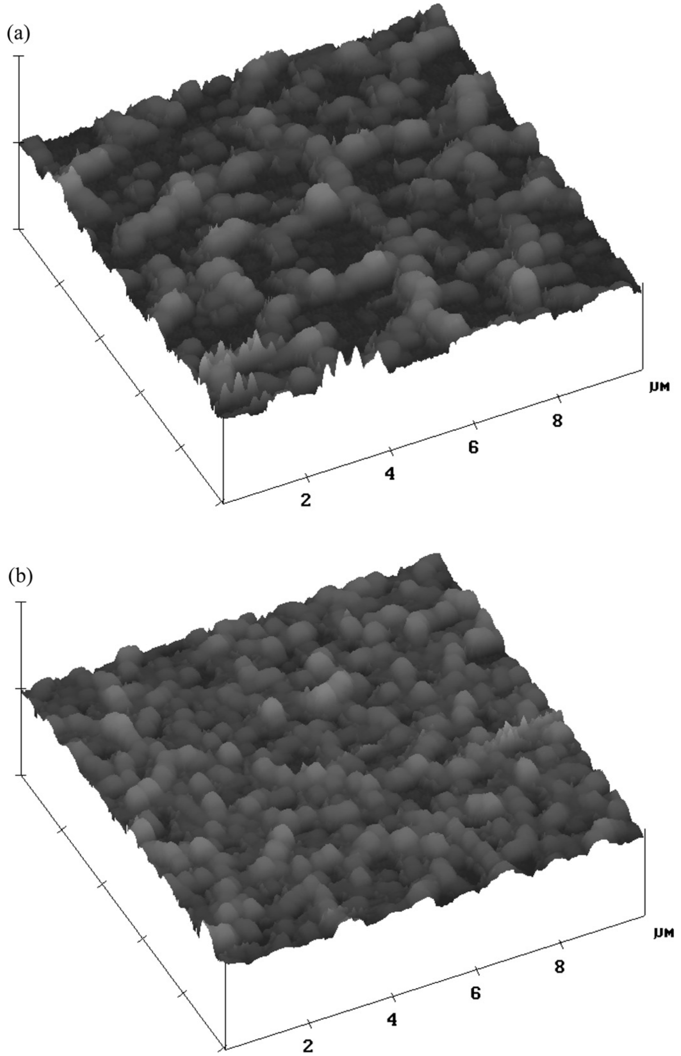


FIGURE 6 Three-dimensional AFM images ($10\,\mu m \times 10\,\mu m$): a) unexposed PS/Cr film and b) exposed PS/Cr film. Height scales are 0–300 nm for both images.

($43 \pm 4\,\text{Å}$) than those of the PS/Cr films ($51 \pm 4\,\text{Å}$), whereas the w values of the unexposed films were almost identical to each other.

To further explore the polymer/metal compatibility, by using AFM, we characterized the dewetting structures that were induced by

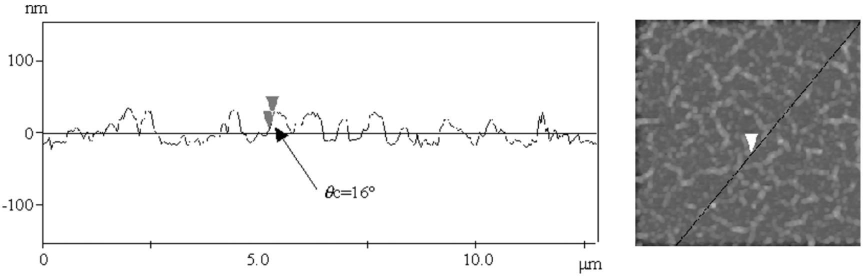


FIGURE 7 AFM image of exposed PMMA/Cr film.

TABLE 1 Summary of Contact-Angle Experimets

Samples	CO_2 Exposure	θ_c (deg)	γ_{AB} (mJ/m)
PS/Cr	NO	28 ± 3	11.0 ± 0.5
	Yes	17 ± 3	8.5 ± 0.5
PMMA/Cr	NO	21 ± 3	7.4 ± 0.5
	Yes	16 ± 3	6.4 ± 0.5

reannealing at 80°C in a vacuum oven after the XR runs. AFM images visually reveal the effects of $scCO_2$ on metallized polymers. Figure 6a shows the three-dimensional surface topology of the Cr layer plating the unexposed PS layer (970 Å in thick). The large domain structures indicate the dewetting of the system caused by the incompatibility between the Cr and PS films. Figure 6b shows the effect of $scCO_2$ on the PS/Cr film. Comparison of these figures clearly proves that $scCO_2$ has decreased the interfacial tension, as made evident by the more uniform surface and reduction in the domain size. It should be pointed out that the effect of $scCO_2$ precluding the dewetting was also seen in the PMMA/Cr films.

In addition, the AFM images allowed us to extract the contact angle between the layer adhering to the substrate and the core layer. Figure 7 shows the AFM image of the exposed PMMA/Cr film. The contact angle data and interfacial tension between the two layers calculated by Equation (1) are summarized in Table 1. These data show that exposure to $scCO_2$ before the Cr vapor deposition reduces the interfacial tension by 23% for PS and 14% for PMMA, respectively. Hence, it is clear that the enhancement in the polymer/metal compatibility is more significant for PS than for PMMA, which is consistent with the XR results. This may be due to the fact that the low-density formation of the exposed PMMA films is different from the exposed PS films. Further XR studies for the exposed PMMA films are currently in progress.

CONCLUSION

We showed that $scCO_2$ could potentially be used for improving adhesion at a polymer/metal interface during the vapor deposition process. X-ray reflectivity measurements showed that the interfacial width between the Cr and exposed polymer layers (PS and PMMA) increased by a factor of about two as compared with that without exposure to $scCO_2$ at the density fluctuation ridge. In addition to this, the large interfacial broadening occurred irrespective of the thickness of both polymer films after exposure to $scCO_2$. This effect was also confirmed by the AFM images, which provided direct evidence of not only a decrease in the surface dewetting but also a decrease in contact angle and, thus, the interfacial tension between the polymer and Cr layers. The contact angle data proved that the decrease of the interfacial tension accompanied the increase in the interfacial width. This new "green" technology could be employed in the fabrication of circuit boards, food packaging, and compact discs, and has the potential to produce a higher-quality, longer-lasting product.

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