

Green thin polymer film metallization using supercritical carbon dioxide

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It is shown that low-density polymer layers created by supercritical carbon dioxide (scCO₂) processing can be exploited to enhance metallization of thin polymer films. Spun-cast thin films were exposed to scCO₂ within the narrow temperature and pressure regime known as the 'density fluctuation ridge', where excess swelling of the polymer thin films was induced, and the swollen structures could be subsequently preserved by quick evaporation of CO₂. X-ray reflectivity (XR) measurements proved that the 'expanded' films had a broader interfacial width between the polymer and deposited metal layers, regardless of the polymer film thickness or choice of polymers. Furthermore, standard peel test showed a drastic enhancement in adhesion between the polymer and metal layers, which correlates with the XR result: the broader interfacial width indicates increased adhesion.

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1. Introduction

Controlled adhesion of metals to polymers is crucial in many applications, particularly in the formation of circuitry in microelectronics, printing metal valves on polymer films for inkjet printers, forming metal–polymer multilayer films commonly used in packaging, and in patterning magnetic storage (Antesberger, 1989). Proper metal to polymer adhesion is also required to engineer biomedical devices and drug delivery systems that are implanted *in vivo*. In all these applications, reliability of the instrument is of fundamental importance. Since the surface energy of polymers has a large non-polar component, the adhesion of metals to polymers is known to be problematic. 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 (Carrier & Randolph, 1993; Masuda *et al.*, 1998), could be used to achieve strong electronic contacts due to the increase in the surface area. However, the porosity required to produce these contacts is of the order of a few microns. This is much larger than the thickness of polymer coatings, and hence this technique is not applicable for metallization of thin polymer films, such as those used in microelectronics, where tight tolerances require submicron flatness of the polymer film surface. In this paper, we use supercritical carbon dioxide to introduce molecular scale porosity in order to control metal adhesion.

Recently, supercritical carbon dioxide (scCO₂) as a 'green' solvent has been intensively used for polymer surface modifications (Li *et al.*, 2004; Meli *et al.*, 2004; Harton *et al.*, 2005; Li *et al.*, 2006). Specifically, we have found that, along the pressure–temperature portion of the phase diagram known as the 'density fluctuation ridge', excess swelling of ultrathin polymer films occurs (Koga *et al.*, 2002; Koga, Seo, Shin *et al.*, 2003; Koga *et al.*, 2004). It was also found that, when the gas was released rapidly, the polymer was quickly vitrified and the swollen structure could be preserved as it was (Koga *et al.*, 2002).

Furthermore, a combined use of X-ray reflectivity (XR) and atomic force microscopy (AFM) proved that the formation of additional large 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 (Koga, Seo, Jerome *et al.*, 2003). Recent grazing-incidence small-angle X-ray scattering results also indicated that the size of the porosity in the expanded film should be the same as that in the unexposed polymer film. Hence, scCO₂ processing can be an easy and efficient means for introducing molecular level porosity in polymer thin films.

Here, we show that this low-density polymer layer can be exploited to enhance metallization of the polymer surface. We hypothesize that more molecular scale porosity at the surface region of the film could allow easy penetration of metallic vapors and subsequent deposition of a well adhered metallic layer. This scCO₂-based technology is typically operated near room temperature, offering potential benefits for polymer thin-film processing as not only an 'environmentally friendly' but also a 'polymer-friendly' technique.

2. Experimental details

Monodisperse polystyrene (PS, molecular weight $M_w = 2.9 \times 10^5$, polydispersity $M_w/M_n = 1.05$; Polymer Laboratories) and polymethyl methacrylate (PMMA, $M_w = 2.5 \times 10^5$, $M_w/M_n = 1.05$; Polymer Laboratories) were used in this study. Both PS and PMMA thin films were prepared by spin-casting onto HF-etched Si substrates and annealed in a vacuum oven at $T = 423$ K for 5 h. The films were then placed in a high pressure chamber containing scCO₂ at $T = 309$ K and $P = 8.2$ MPa, corresponding to the ridge where anomalous sorption of CO₂ molecules into polymer thin films occurs, for 3 h. In order to preserve the swollen structures, the films were quickly depressurized to atmospheric pressure at a constant temperature, typically within 10 s. After CO₂ processing, either a chromium or a copper layer was

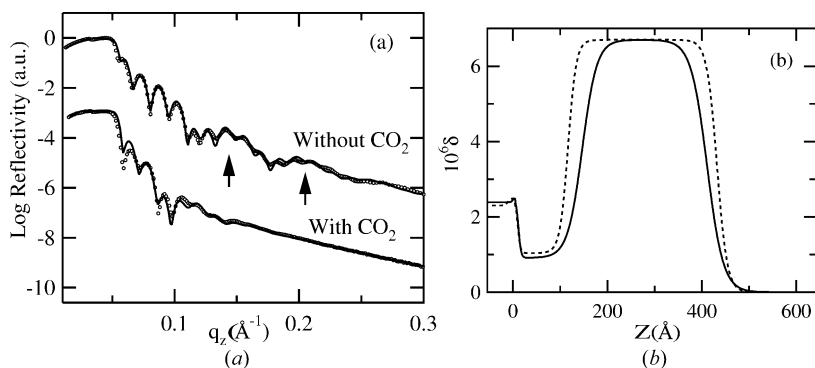


Figure 1
(a) Observed (symbols) and calculated XR profiles (solid lines) of the PS/Cr systems. The XR data were fitted using standard multilayer fitting routines for the dispersion profiles (δ) in the X-ray refractive index shown in (b): unexposed (dotted line) and exposed films (solid line).

deposited onto the vitrified films using an electron-beam evaporator (Model 9320026, Varian Vacuum Systems). The thickness of the metal layer was about 300 \AA .

X-ray reflectivity (XR), which is sensitive to vertical density profiles (*i.e.* thickness, density and roughness), was conducted at the X10B beamline of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), using a photon energy of 14 keV, *i.e.* an X-ray wavelength (λ) of 0.87 \AA . The total acquisition time was about 1 h, with the dwell time for each angle adjusted, depending on the scattering angle. The angular resolution $\Delta\theta = 0.02^\circ/0.3$ mrad, and the wavelength spread, $\Delta\lambda/\lambda$, was about 0.03%, so the instrument resolution, Δq_z , is ~ 0.04 nm^{-1} , where q_z is the scattering vector normal to the surface [$q_z = 4\pi \sin(\theta/2)/\lambda$, θ is the scattering angle]. A four-layer model, *i.e.* a silicon substrate, a native oxide, a polymer layer and a metal layer, was used to fit the XR data for all the polymer/metal films.

For peel test, transparent adhesive tape (half an inch wide; Scotch, 3M) was carefully applied onto the metallized sample and removed under D3359 standard. Viewed under magnification on an optical microscope (BH2-HLSH, Olympus), we qualitatively measured the amount of metal after peel testing on each sample.

3. Results and discussion

The films were first characterized by X-ray reflectivity. Fig. 1(a) shows the representative XR profiles for the PS (~ 100 \AA thick)/Cr (~ 300 \AA thick) films with and without CO₂ exposure. In the figure, the reflectivity is plotted as a function of q_z . The solid lines in Fig. 1(a) are the best fits to the data based on the dispersion profiles shown in Fig. 1(b). The δ values of the Si, SiO₂ and Cr layers were calculated to be 2.39×10^{-6} , 2.54×10^{-6} and 6.7×10^{-6} , respectively. The roughnesses between the layers were assumed to be given a Gaussian smoothing function with standard deviation σ , and the interfaces were expressed as a convolution of a step function having the given film thickness and the Gaussian function. From the best-fitting results, we found that the initial thickness, $L_0 = 107$ \AA , had increased to $L = 131$ \AA . This increase in thickness corresponds to the linear dilation, $S_f = (L - L_0)/L_0 = 0.22$, and the degree of dilation is much larger than in the bulk PS film (0.07) (Koga, Seo, Shin *et al.*, 2003). In addition, the density, ρ , of the exposed PS layer, which can be calculated by the δ value, decreased ($\rho = 910$ kg m^{-3}) by 15% compared with that of the bulk or without exposure ($\rho = 1040$ kg m^{-3}). Hence, we can say that the swollen structure was preserved even after complete depressurization. It should be noted that these S_f and ρ values of the

exposed PS film are slightly different from those before Cr deposition ($S_f = 0.3$ and $\rho = 850$ kg m^{-3}), suggesting that the deposition of the Cr layer alters the frozen structures of the bottom exposed PS layer. Further study to clarify the change in the structure will be conducted in future.

Let us focus on the surface and interfacial roughness, both of which can be obtained by the XR technique. The root-mean-square (r.m.s.) roughness, σ , at the air surface increased slightly with exposure ($\sigma = 19$ \AA) compared with that of the unexposed PS/Cr film ($\sigma = 16$ \AA). In order to see whether dewetting takes place, the surface morphology was analyzed with a Digital Nanoscope III atomic force microscope

(AFM) in contact mode using an Si₃N₄ tip. As a result, we found that the surface remained flat even after exposure, and the corresponding r.m.s. roughness was almost equivalent to that obtained by XR (the AFM data are not shown). Thus, we can conclude that the exposed PS/Cr film does not have any surface dewetting structures.

The crucial parameter to control adhesion is the interfacial roughness between the PS and Cr layers. As indicated by the arrows shown in Fig. 1(a), the low-frequency component of the Kiessig fringes (which arise from the bottom PS film) for the unexposed PS/Cr film were damped with exposure. This indicates that the interface between the PS and Cr layers increases. From the best fits to the data, we found that the σ value of the exposed PS/Cr film increased by a factor of about 2 ($\sigma = 22 \pm 2$ \AA) compared with that of the unexposed film ($\sigma = 12 \pm 2$ \AA). It should be noted that the thicknesses of the Cr layers are slightly different, since we prepared the Cr layers plating the exposed and unexposed PS films separately. Further experiments varying the film thickness of the PS films up to 1300 \AA , all of which were within the spatial resolution of the XR technique, showed that the excess enhancement in the interfacial roughness was independent of the initial film thickness (L_0) (Fig. 2). This is consistent with our previous XR results, which showed that low-density layer formation occurs at the polymer/air interface irrespective of the film thickness (Koga, Seo, Jerome *et al.*, 2003). We hypothesize that scCO₂ exposure introduces more free volume into the film, which could allow easy penetration of metallic vapors and subsequent deposition of a well adhered metallic layer. It is important to emphasize that similar excess enhancement in the interfacial roughness was observed in PMMA/Cr films with scCO₂ processing (Koga *et al.*, 2005), indicating

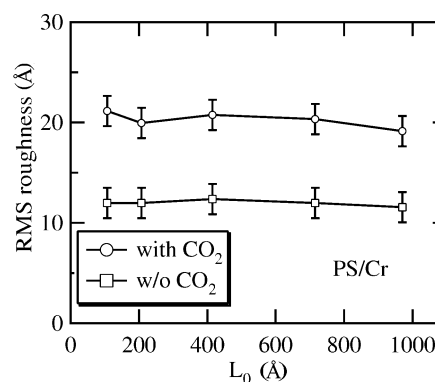


Figure 2
Effect of scCO₂ on the interfacial roughness as a function of the original PS thickness (L_0).

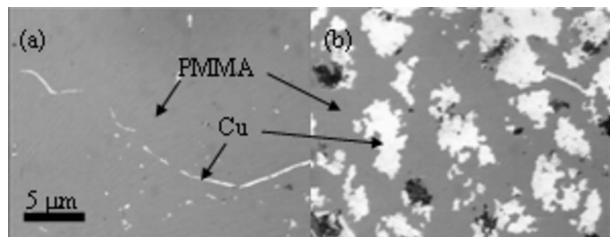


Figure 3
Peel test results. (a) The unexposed PMMA/Cu film and (b) the exposed PMMA/Cu film. The bright areas correspond to the Cu film.

that $scCO_2$ -based adhesion enhancement appears to be a general phenomenon that is non-specific to particular polymers. Thus, exposure to $scCO_2$ along the density fluctuation ridge could be a promising method to improve adhesion at the polymer/metal interface and could be applied to bulk films.

In order to explore our hypothesis further, we directly measured the adhesion between PMMA and copper (Cu) layers by peel test. We utilized Cu as a model since replacing aluminium by copper is the main approach for reducing the resistance of metal wires in integrated circuits. Under the D3359 standard, a piece of adhesive tape was applied to the surface of the metal. The tape was then removed in order to test adhesion. Fig. 3 shows optical microscope images of both unexposed and exposed PMMA films ($\sim 600 \text{ \AA}$ thick) where a Cu layer of about 300 \AA thick was deposited. The Cu layer on the unexposed PMMA layer was peeled off completely, as shown in Fig. 3(a). In contrast, approximately 30% of the Cu layer on the exposed sample remained on the PMMA film (Fig. 3b). Hence, we can see that the adhesion of the Cu layer with the exposed PMMA film is strengthened. This supports our XR results: increased interfacial roughness correlates with increased adhesion. We are currently studying the effect of $scCO_2$ on the adhesion of semi-crystalline polymer and metal layers, which behave differently from amorphous

polymers such as PS and PMMA; $scCO_2$ weakens metal adhesion to crystalline polymers. Details will be described elsewhere.

In summary, we have reported that low-density polymer layers created by $scCO_2$ processing can be used to improve polymer metallization. The combination of XR and the peel test has clearly proved that the broader interfacial width between the exposed polymer and the deposited metal layers has resulted in increased adhesion.

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