

Substrate morphology repetition in “thick” polymer films

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Abstract

Using Grazing-incidence small-angle scattering (GISAXS) technique we investigated the surface morphology of polymer films spin-coated on different silicon substrates. As substrates we used either technologically smooth silicon wafers or the same silicon wafer coated with thin aluminium or gold films which show a granular structure at the surface. Although the polymer thickness exceeds 300 nm the GISAXS pattern of the film shows the same in-plane angle distribution $\Delta 2\theta$ as the underlying substrate. Annealing the polymer films at a temperature above its glass transition temperature $\Delta 2\theta$ changed from a broad to a narrow distribution as it is typically for films on pure silicon. The experiment can be interpreted by roughness replication and density fluctuation within the polymer film created while spin-coating at room temperature. Due to the low segment mobility there are density fluctuations which repeat the surface morphology of the substrate. Above the glass temperature the polymer density can be homogenized independently from the morphology of the substrate.

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1. Introduction

Grazing-incidence small-angle scattering (GISAXS) is a powerful tool for the investigation of the morphology of surface and subsurface

nanostructures [1,2]. The method combines the strength of X-ray reflectivity at very small angles with the possibility to probe a large in-plane momentum transfer. The latter is achieved by inspecting diffuse scattering in a non-coplanar scattering geometry. The information depth of this scattering can be tailored exploiting the effect of refraction of the X-ray beam at the air-sample interface. Changing the incident or exit angle, α_i , or α_f , respectively, from a value smaller than the

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critical angle of total external reflection, α_c , to a larger one, the penetration depth A varies from a few nanometres to several 100 nm. Using a CCD and setting $\alpha_i > \alpha_c$ one can measure a two-dimensional intensity mapping for a certain range of exit angles ($0 < \alpha_f < 2-3 \alpha_c$) and in-plane angles (2θ) simultaneously [3]. This pattern subsequently contains information from various depths below the surface and can be used to separate surface from subsurface information. This geometry [3] has the advantage that there are no strong beams hitting the detector (that could saturate it) and the overall intensity of the diffraction pattern can be adjusted over a wide range by the choice of α_i .

In this contribution we will demonstrate the capability of this method by investigating the influence of substrate morphology on the diffuse scattering of spin-coated polymer films. That the substrate influences the morphology of polymer films is well known [4]. Phase separation in polymer blends covering various metallic substrates was investigated by NEXAFS spectroscopy [5]. Micro-focus GISAXS was used to probe the roughness replication of polymer bi-layer films [6]. Here we will show that spin-coated homo-polymer films show the same morphology as the underlying substrate surface.

2. Experiment

The experiment was performed at beamline 34-ID-C of the advanced photon source using monochromatic radiation of 8.92 keV, as defined by a Si 111 double reflection monochromator. A beam size of $10 \mu\text{m} \times 25 \mu\text{m}$ was defined by slicing the incidence beam by roller-blade slits. The samples mounted horizontally on the principal axis of a hybrid Microcontrole-Huber goniometer were illuminated under an angle $\alpha_i \approx 2-3 \alpha_c$ and the scattering signal was detected by a direct illumination charge-coupled device (CCD) X-ray camera with pixel size of $22.5 \mu\text{m}$ placed on the detector arm at a distance of 2.5 m from the sample. By selecting a region of interest $\alpha_f < \alpha_i$, we ensured that the specularly reflected beam did not hit the CCD.

As samples we used the side-chain azobenzene polymer poly{(4-nitrophenyl)[4-[[2-(methacryloyloxy)ethyl]ethylamino]phenyl]diazene} (pDR1 M) spin-coated onto technologically smooth silicon wafers or onto the same silicon wafer after coating with thin aluminium or gold films. The polymer thickness was always thicker than 300 nm; the metallic films prepared by vacuum deposition (thermal evaporation) had a thickness of about 150 nm. For the annealing experiments the sample was mounted on a reverse biased Peltier heater. It was measured at a temperature of $143 \pm 3^\circ\text{C}$, which is above the glass transition temperature of the polymer ($T_g = 129^\circ\text{C}$).

3. Room temperature structural measurements

Fig. 1. shows two CCD frames recorded from a silicon wafer with a gold coating (a) and from the same sample after spin-coating with the polymer film (b). The exit angle α_f varies in the vertical direction and the in-plane angle 2θ in the horizontal direction. The centre of both frames is dominated by the specular scattering. The intensity along 2θ originates by the diffuse scattering which splits into sharp speckles due to the coherent illumination (see inserts). The understanding of these speckles is not essential for the present experiment. It is clearly seen that the diffuse component in Fig. 1b is enhanced in comparison to that shown in Fig. 1a. This is attributed to the microstructure of the polymer film mimicking the substrate.

The critical angles between the polymers, $\alpha_{c,\text{polymer}} = 0.14^\circ$, and between substrates, $\alpha_{c,\text{subst}} = 0.48^\circ$, the width of diffuse scattering along 2θ becomes broad and increases with α_f . Considering the penetration depth $A(\alpha_{f,i}) = \text{Im}\{2\pi/\lambda [(\alpha_f^2 - \alpha_c^2) + (\alpha_i^2 - \alpha_c^2)]^{-1/2}\}$, the diffuse scattering in Fig. 1a stems from the surface region of the Au film only, whereas the feature in Fig. 1b reflects the morphology of the whole polymer film in addition, i.e. the region between the air-polymer and polymer-substrate interface. The angular distribution along 2θ taken at $\alpha_f \leq \alpha_{c,\text{subst}}$ can be approximated by a Gaussian with centre at $2\theta = 0$. For the Au film the full-widths of

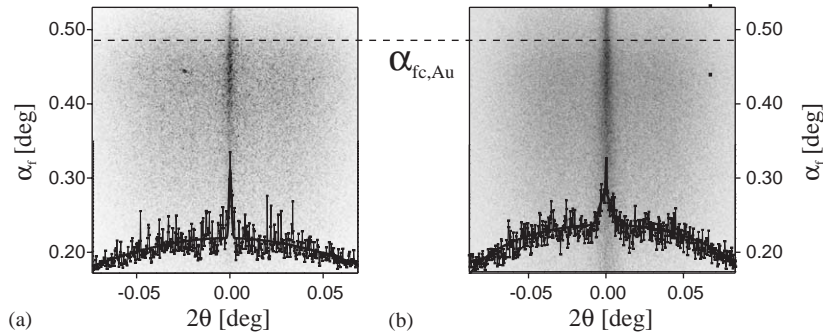


Fig. 1. Two-dimensional contour plot of the intensity recorded by the CCD taken from a silicon wafer after vacuum deposition with a gold film (a) and from a 350 nm thick polymer film (pDR1 m) spin-coated onto the Au/Si substrate (b). Overplotted at the bottom of the figures are line scans taken at an angle of incidence α_f smaller than $\alpha_{c,substrate}$ but larger than $\alpha_{c,polymer}$. The dotted line indicates the position of $\alpha_{c,substrate}$.

half-maximum (FWHM) correspond to an in-plane correlation length of about $L = 50$ nm. Using AFM inspection this length could be correlated with the surface morphology. Here the film appeared very rough with rms roughness of about 3 nm. This is caused by a granular substructure visible at the surface with an average lateral grain size of about 70 ± 20 nm.

Similar evaluation of the polymer film covered on the Au film shows the same in-plane correlation length L as the substrate independently from the α_f position taken. Additionally one finds a second correlation length of $L_2 > 1000$ nm. Along α_f , thickness fringes disappear due to the inhomogeneous film thickness after the spin-coating process. At the same time the rms roughness measured by AFM is reduced to 1 nm. Because L does not vary with $\Lambda(\alpha_f)$, the diffuse scattering must be originating mainly by conformal roughness of polymer surface and density fluctuations within the film. That means the granular surface morphology of the metallic films is translated into morphological fluctuations over the whole polymer film.

The main argument for the significant contribution of polymer scattering is that the 2θ distribution becomes narrow right after heating the film above the glass transition temperature (see the next paragraph). We have observed this effect on many samples including polymer films covering aluminium-coated silicon substrates. This is in contrast to polymer films on pure silicon where we found a three times narrower in-plane

distribution reflecting the smooth surface of the substrate.

4. Morphology changes while annealing

One of the polymer films spin-coated onto aluminium-coated silicon was investigated in situ while annealing at a temperature above T_g . Fig. 2 shows a series of CCD frames taken at time steps of 100 s just after reaching the annealing temperature. As found at room temperature (not shown), the diffuse scattering of the first frame is not centred at $2\theta = 0$ but displays pronounced correlation peaks at $2\theta = \pm 0.01^\circ$. Between the critical angles of the polymer and the substrate ($\alpha_{c,polymer} = 0.14^\circ$, $\alpha_{c,Alu} \approx \alpha_{c,Si} = 0.21^\circ$), one observes thickness oscillations measuring the polymer thickness of $d = 340 \pm 4$ nm. The layer thickness remains unchanged while annealing, but the angular position and the intensity of the side wings change. Line scans taken at $\alpha_{f1} = \alpha_{c,polymer}$ and $\alpha_{f2} = \alpha_{c,substrate}$ were used to determine the changes of the position and intensity of the correlation peaks. Both line scans differ in intensity but not in the position of correlation peaks, and show qualitatively similar behaviour. In general, one finds that the correlation peaks shift towards the centre accompanied by a decrease of intensity. The final in-plane angular distribution (Figs. 2g and h) equals that of polymer films spin-coated onto pure silicon

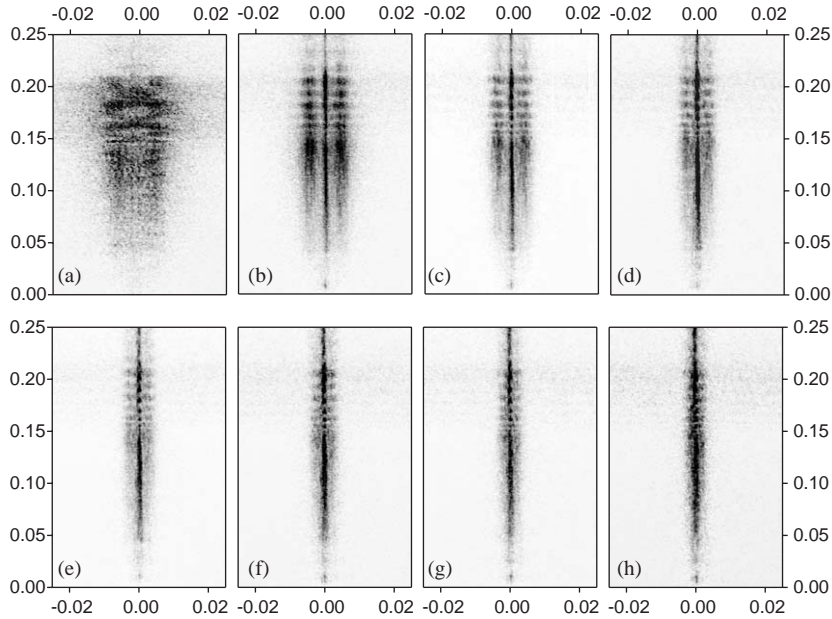


Fig. 2. Two-dimensional contour plot of the intensity recorded by the CCD taken from a 340 nm thick polymer film spin-coated onto silicon substrate covered with aluminium at $T = 143^\circ\text{C}$. The patterns (a–h) were recorded in time steps of 100 s and are plotted on the same scale.

substrate (see above). These changes do not affect the specular reflectivity. The results of a numerical evaluation are shown in Figs. 3a and b. The intensity of side wings can be correlated with the number of domains. It decreases within the first 400 s and remains unchanged after. The smaller slope of the initial decay evaluated from the data taken at the substrate edge might be caused by the much lower side wing intensity at this α_f position. The angular position of the correlation peaks can be interpreted by a domain size and their half-width by a size distribution. The points taken at α_{f2} scatter for $t > 500$ s, and again are caused by the low-intensities. Neglecting the change in size distribution, the average domain size increases continuously with time. The slope can be interpreted by a growth velocity of about 200 nm per min.

5. Discussion

The experiments demonstrate the capability of GISAXS for morphology investigation of confined

films. The investigated angular region reveals information of the surface and subsurface region of films simultaneously. Using a fast CCD, one is able to probe dynamical phenomena on a time scale of a few seconds. In the present case we found that the morphology of relatively thick polymer films is controlled by the surface morphology of the substrate. If the substrates are covered with a metallic film, the surface shows a granular structure. The appearance of small metal clusters after evaporation is known [7]. It is interesting that the polymer film can adopt structural features from such morphology. We hypothesize this is incorporated as density inhomogeneities during spin-coating. Apparently density fluctuations within the polymer conserve the granular surface morphology of the substrate throughout the film surface. Due to the low segment mobility at room temperature, denser polymer segments might be arranged between the grains but less dense segments onto the ridges of grains.

On pure silicon, the films appear homogeneous and flat as the substrate. Heating the polymer

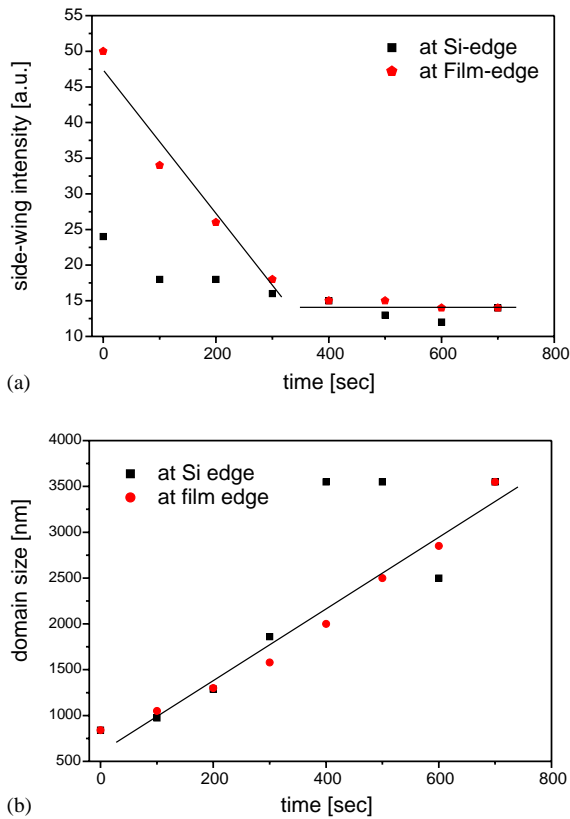


Fig. 3. Variation of the intensities (a) and domain size (b) plotted as a function of time. The lines should guide the eyes.

above T_g , the segment mobility is much increased and can homogenize the polymer density. The essential parameter of segment mobility could be

extracted from time-dependent GISAXS measurements.

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