

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

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