X-ray Surface Diffuse Scattering from Polymer Films

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Introduction

Proximity to an interface modifies the microscopic configuration within a polymer melt. Thin supported polymer films contain two interfaces: the vacuum-polymer interface and the polymer-substrate interface. At each of these interfaces, different factors determine the local structure. Near the substrate, short-range van der Waals forces pin the polymer to the surface. At the vacuum side, thermally excited capillary waves roughen it. In thin films, the presence of the substrate modifies the capillary-induced roughness. The long-range van der Waals forces suppress long-wavelength capillary modes, and short-range forces pin the polymer motion at the substrate, consequently modifying the capillary spectrum.

In the present measurements, we have employed surface diffuse x-ray scattering to study the structure of the free interface of thin films of liquid polystyrene (PS) spun-cast onto oxide-terminated silicon substrates. The scattering is analyzed to extract the surface roughness as a function of length scale. This information allows the surface tension of the thin films to be extracted and possible modifications of the interfacial properties at short-length scales to be probed.

Methods and Materials

Films were prepared by dissolving PS with a Mw of 123000 g/mol and Mw/Mn of 1.08 in toluene and then spin-casting it onto optically flat silicon substrates. The samples were then annealed in vacuum for 12 h at 150°C to ensure complete solvent removal. The thicknesses of the PS films investigated ranged from 84 to 359 nm. The experiments employed monochromatic radiation with an x-ray energy of 7.66 keV. The sample surface was oriented so that specular reflection deflected the beam horizontally. Films were thin and viscous enough to be unaffected by the wafer orientation. By arranging for the x-ray incidence angle (0.14°) to lie below the critical angle for total external reflection (0.16°), we were able to restrict the x-ray penetration into the film to a depth of 9 nm. Consequently, scattering from the film-substrate interface was negligible, and only fluctuations of the vacuum-polymer interface were probed. The off-specular diffuse scattering of the rough polymer surface was recorded with either a direct-illumination charge-coupled device (CCD) camera or a CCD coupled via tapered optical fibers to a fluorescent screen.

Results and Discussion

Figure 1 shows a cross section of the 2-D scattering pattern obtained from a 359-nm film held in vacuum at 160°C. This temperature is 60°C above the bulk glass transition temperature, so the PS should behave as a liquid melt. Similar measurements were obtained for other film thicknesses and temperatures. Each point represents the intensity from several pixels of the CCD, which were binned together to improve statistics. The amplitude of the measured data was normalized by comparison with an amorphous carbon intensity standard.

The solid red line shown along with the data depicts the scattering that would be predicted on the basis of only the expected spectrum of thermally activated capillary modes and a wave-vector-independent surface tension [1]. Comparison of the measured scattering intensity with the capillary wave prediction near $q_x = 0$ yields the surface tension. The surface tension extracted in this manner agrees with the bulk value to within the precision of the normalization (~5%). The measured scattering does not agree with the capillary wave model for larger in-plane wave vectors. An estimation of the contribution from bulk density fluctuations, based on the compressibility of PS and the penetration depth of the x-rays, is shown for comparison as a solid green line [2]. While the scattering from bulk fluctuations is non-negligible, it does not account for the deviations of the diffuse scattering from the capillary wave model. Further analysis of the scattering profile at a large in-plane wave vector is currently underway.

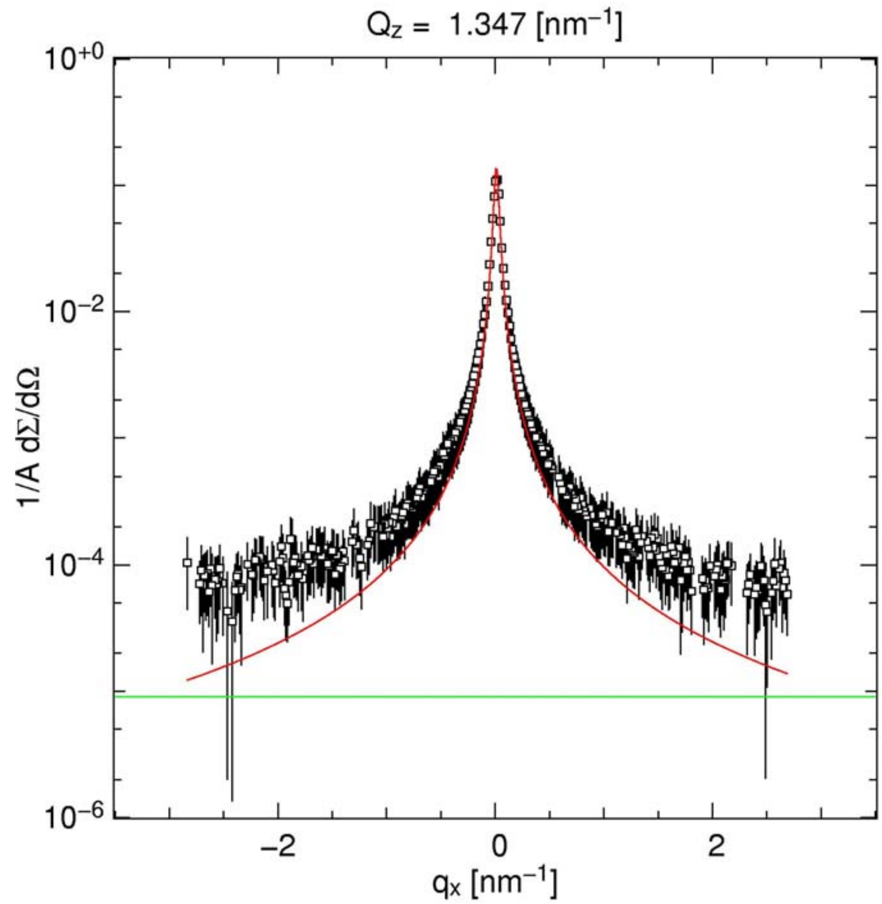

FIG. 1. Cross section from a 2-D scattering pattern obtained from a 359-nm-thick PS film on a Si substrate at 160℃. Squares are measured data. The red line depicts the prediction of capillary wave theory, and the green line is an estimate of the scattering from bulk density fluctuations.

Acknowledgments

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