X-radiation damage of polymer thin films

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Introduction

Despite the obvious occurrence of synchrotron x-ray damage to organic thin films, few attempts have been made to qualitatively determine their *morphological* changes during x-ray exposure. Frydman *et al.* [1] used x-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) to study several different selfassembled monolayers (SAMs) on varying substrates. They found that the majority of the damage seems to occur at the surface of the film, especially if labile groups are present, rather than by removal of large amounts of film material. Despite the obvious surface changes, atomic force microscopy (AFM) pictures did not show any large scale increase in surface roughness, but rather indicated the formation of "diamond-like" carbonaceous material with only a modest (< 4 Å) surface roughness.

We have used x-ray reflectivity (XRR) to study x-ray damage of a polymer thin film. There are three main differences between polymer thin films and SAMs: first, the polymer films are not chemically bound to the substrate; second, the films are substantially thicker; and third, the molecules are not arranged to expose any particular component at the surface. These differences are important, since some reported x-ray damage in SAMs occurs by scission of the head group and removal of the tail group, and typical polymer films are thicker than the escape depth of photoelectrons, which are presumed to be responsible for some radiation damage [2–5].

Reflectivity probes the electron density profile of a film perpendicular to the surface and therefore allows us to obtain some of the important structural parameters necessary to quantify x-ray damage, such as the interfacial morphology, which cannot be obtained from spectroscopic techniques.

Methods and Materials

Ultrathin films of poly(*tert*-butyl acrylate) (PtBA) were spun cast onto silicon wafers and exposed to x-rays with an energy of 9.654 keV at beamline 1-BM-C of the Advanced Photon Source (APS). The beam was measured to be 0.7 mm (H) x 0.3 mm (V) and to contain 4.3 x 10^{10} photons/s at 100 mA storage ring current. Ten reflectivity scans were taken. Each scan took approximately ten minutes, three minutes of which were with full exposure (zero attenuation). Between scans, the sample was positioned so that the length of the footprint was slightly smaller than the sample and the unattenuated beam was allowed to impinge on the sample for specified amounts of time. The exposure time was therefore the sum of the waiting time and the three minutes of scanning time. We have purposely neglected the exposure with nonzero attenuation, as we assumed that it does not contribute significantly to the damage.

Results and Discussion

From the reflectivity curves, we can directly conclude that the polymer film thickness is approximately constant at 140 Å until late in the damage cycle, when it decreases in thickness (see Figure 1). Also, the magnitude of the oscillations decreases while the overall drop-off in the reflectivity does not increase with exposure time. This indicates that only one of the film interfaces increases in width.

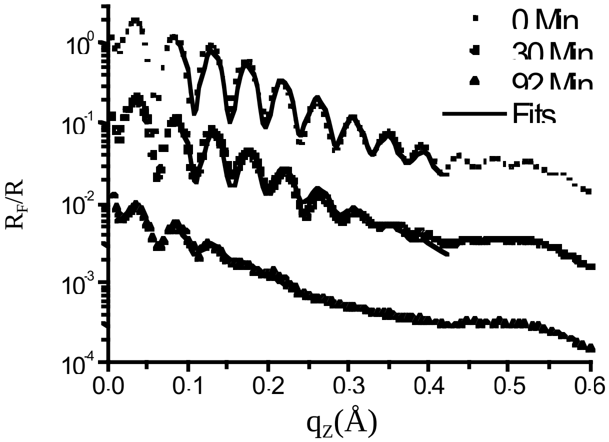

Figure 1: Normalized reflectivity curves after three exposure times, including the two-layer fits. Curves are displaced for clarity.

To more precisely quantify the film density and interface widths, a model has to be assumed for the electron density as a function of distance from the substrate. We have used a typical Gaussian-step model, in which the interfaces between regions of differing electron density are modeled as error-function smeared steps [6]. The simplest model for a film on a silicon substrate is a two-layer model: the silicon oxide layer and the film layer. Clearly from the complex shape of the reflectivity curves the film is not a simple, single layer. At this point we have accepted the limitations of a two-layer fit to gauge the way the two most prominent features change during x-irradiation: the film-oxide interface width $\sigma_{\text{oxide-film}}$ and the film-air interface width $\sigma_{\text{film-air}}$. Because these two parameters greatly influence the general features of the reflectivity curves, we are able to quantitatively track the changes in these parameters as the film becomes damaged even though the fitting does not adequately describe the entire curve.

As the film becomes more damaged, the oscillations become damped out sooner, so fitting of later data sets was truncated at a lower momentum transfer. After finding the silicon oxide thickness using the first reflectivity curve, its value along with the silicon oxide density and the silicon-silicon oxide interface width were held constant for the later fits. We allowed all of the film parameters to vary. The thickness and density of the film did not change appreciably over time. The parameter that changed the most during irradiation was the film-air interface width, starting at 6.14 ± 0.21 Å and ending at 15.64 ± 0.61 Å after 92 minutes of exposure. Figure 2 shows the film-air interface width as a function of exposure time. The variation is fit well by a quadratic function. We also found that a model in which the oxide-film interface changes instead of the film-air interface did not give good fits to the data.

More information can be obtained by calculating the Patterson function. The Patterson function is essentially the Fourier transform of the reflectivity data. Peaks in the Patterson function are located at Z values that correspond to the distances between the various interfaces in the film; the peak at the largest Z value gives the total thickness of the film. The widths of the peaks are convolutions of the widths of the two interfaces that give rise to the peaks. The Patterson function of our reflectivity curves shows only one major peak at 142 ± 1 Å. Over exposure time, the peak grows in width and decreases in amplitude, indicating a broadening of one or both of the interfaces is occurring (see Figure 3).

Conclusions

The data indicate that most of the damage that leads to a change in the reflectivity occurs at or near the film interfaces that are furthest apart. This can be deduced by the obvious disappearance of the oscillations during x-irradiation and by examining the Patterson function as a function of time.

We will perform further experiments, using both XRR and AFM, to further elucidate this important process. Especially of interest is whether AFM images will also show a pronounced increase in the top surface roughness. We will also examine the effect of x-ray photon energy and intensity on the damage of the polymer thin films.

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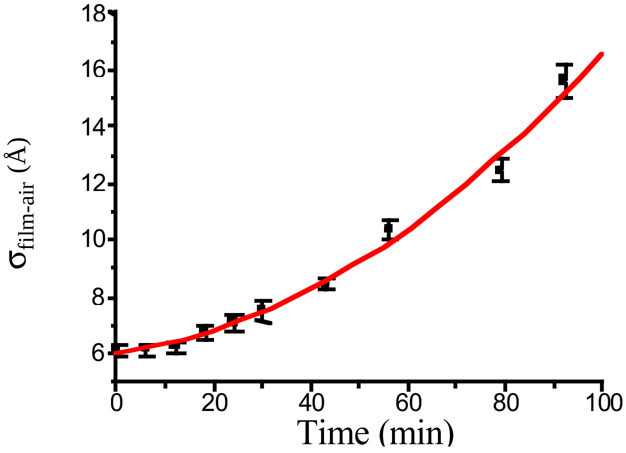

Figure 2: The film-air interface width as a function of exposure time. The line is a fit to a quadratic.

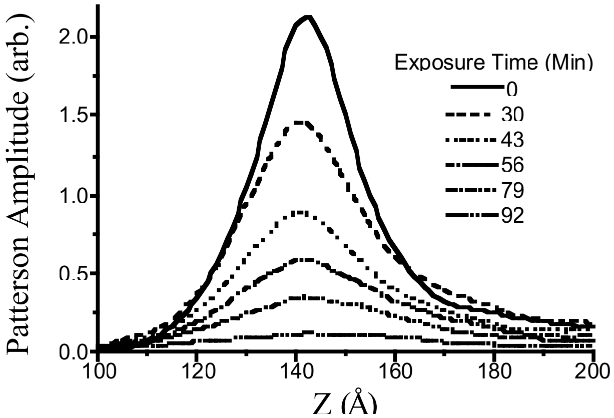

Figure 3: Change of the single peak at Z~140 Å in the Patterson function as a function of exposure time.

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