FIB Sample Preparation of Polymer Thin Films on Hard Substrates Using the Shadow-FIB Method

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Introduction

Focused ion beam (FIB) instrumentation has proven to be extremely useful for preparing cross-sectional samples for transmission electron microscopy (TEM) investigations. The two most widely used methods involve milling a trench on either side of an electron-transparent window: the "H-bar" and the "lift-out" methods [1]. Although these two methods are very powerful in their versatility and ability to make site-specific TEM samples, they rely on using a sacrificial layer to protect the surface of the sample as well as the removal of a relatively large amount of material, depending on the size of the initial sample. In this article we describe a technique for making thin film cross-sections with the FIB, known as Shadow FIBing, that does not require the use of a sacrificial layer or long milling times [2]. In this technique, the corner of a sample is positioned at an angle of incidence between the ion and electron beams in a dual-beam FIB, but not normal to either beam. As seen in Figure 1, the thin film is positioned such that it is in the "shadow" of the ion beam so the substrate is milled before the film. Thus, by changing the geometry of the sample, a hard substrate itself acts as a protective layer for the polymer film.

Understanding the microstructure of polymer thin films on hard substrates is important for many organic electronic applications. Because polymers are easily damaged by the incident ion beam [3], strategies for limiting FIB damage to the polymer thin film are particularly important. One of the main advantages of FIB preparation for thin film analysis is the ability to readily cross-section dissimilar materials. Traditional TEM sample preparation techniques such as microtomy or broad-beam ion milling are not ideal for cross-sectioning all of the device components in a manner that retains the structure of all components equally.

Characterization of these complex systems requires investigation of the internal polymer structure as well as the interface between the polymer film and the substrate [4]. To understand the thinned microstructure, a systematic investigation of ion beam damage to polymers is required. In

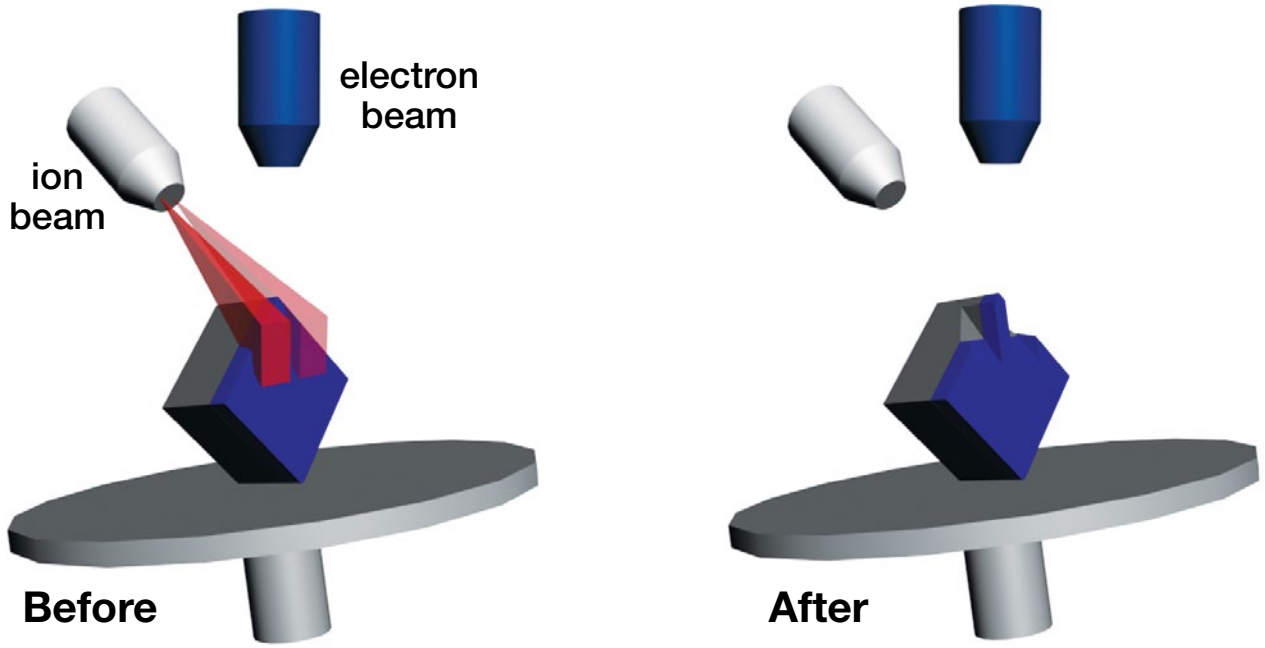

Figure 1: Schematic of the Shadow-FIB technique for cross-sectional TEM sample preparation. In this case, a thin film (blue) is tilted so that the surface is in the "shadow" of the ion beam, as seen in the "Before" image at left. This geometry allows for the ability to cross-section a sample without using a sacrificial layer or long milling times. The ion beam is rastered on either side of a corner of the sample, resulting in an electron-transparent wedge ending on the film surface, shown in the "After" image on the right. The angle of incidence of the ion beam can be varied depending on the circumstances, as long as it is directed from the back, substrate-side.

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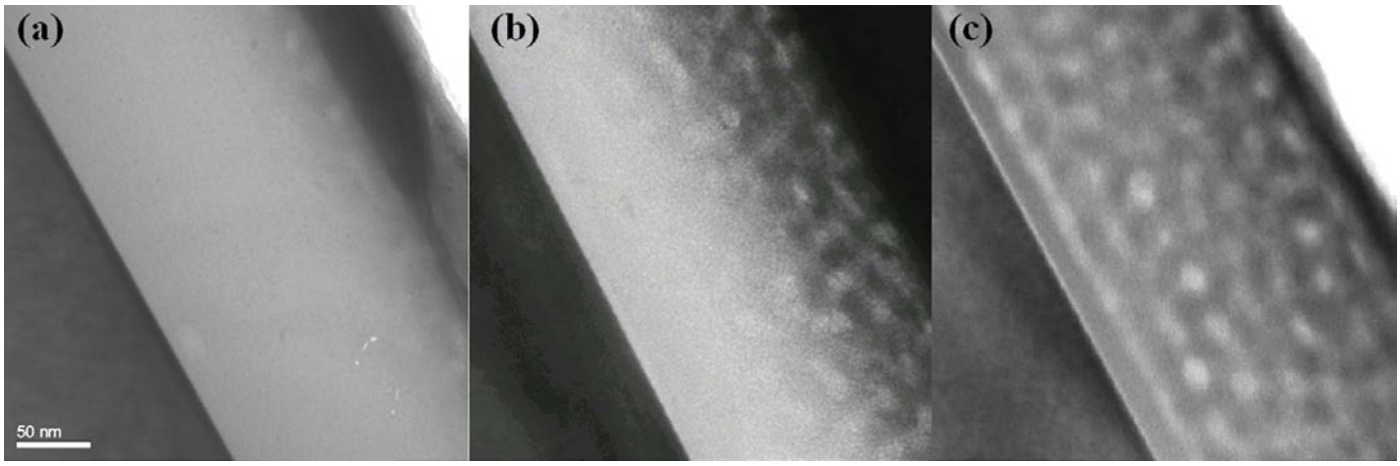

Figure 2: TEM images of stained polymer prepared by the Shadow FIB method at 30 pA for final thinning. Cross-sections of PS-b-PMMA diblock copolymer stained for (a) 2 hours, (b) 1 day, and (c) 4 days.

addition to direct damage from the incident beam, the low thermal conductivity of polymers as compared to metals and ceramics can lead to significant beam heating. We performed a systematic investigation on polymer films using a poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) diblock copolymer as a reference material.

Ion Beam Damage

First, we examined ion beam damage in microtomed block copolymer sheets with a thickness of 100 nm by milling holes with a diameter of 1 μm at 30 keV. We then documented the morphological changes of the microtomed polymer sheets as a function of ion beam current and dose. As shown in Figure 2, at an ion beam current of 100 pA, the polymer sheet remained flat around the holes after ion beam milling. However, at currents above 300 pA, the polymer film displayed wrinkles around the holes. Presumably, the wrinkling is a result thermal cross-linking of the polymers caused by local heating of the polymer. This thermal damage was proportional to an increase in the ion beam current even in the thin polymer sheet. Based on these studies, we concluded that thermal damage to the polymers can

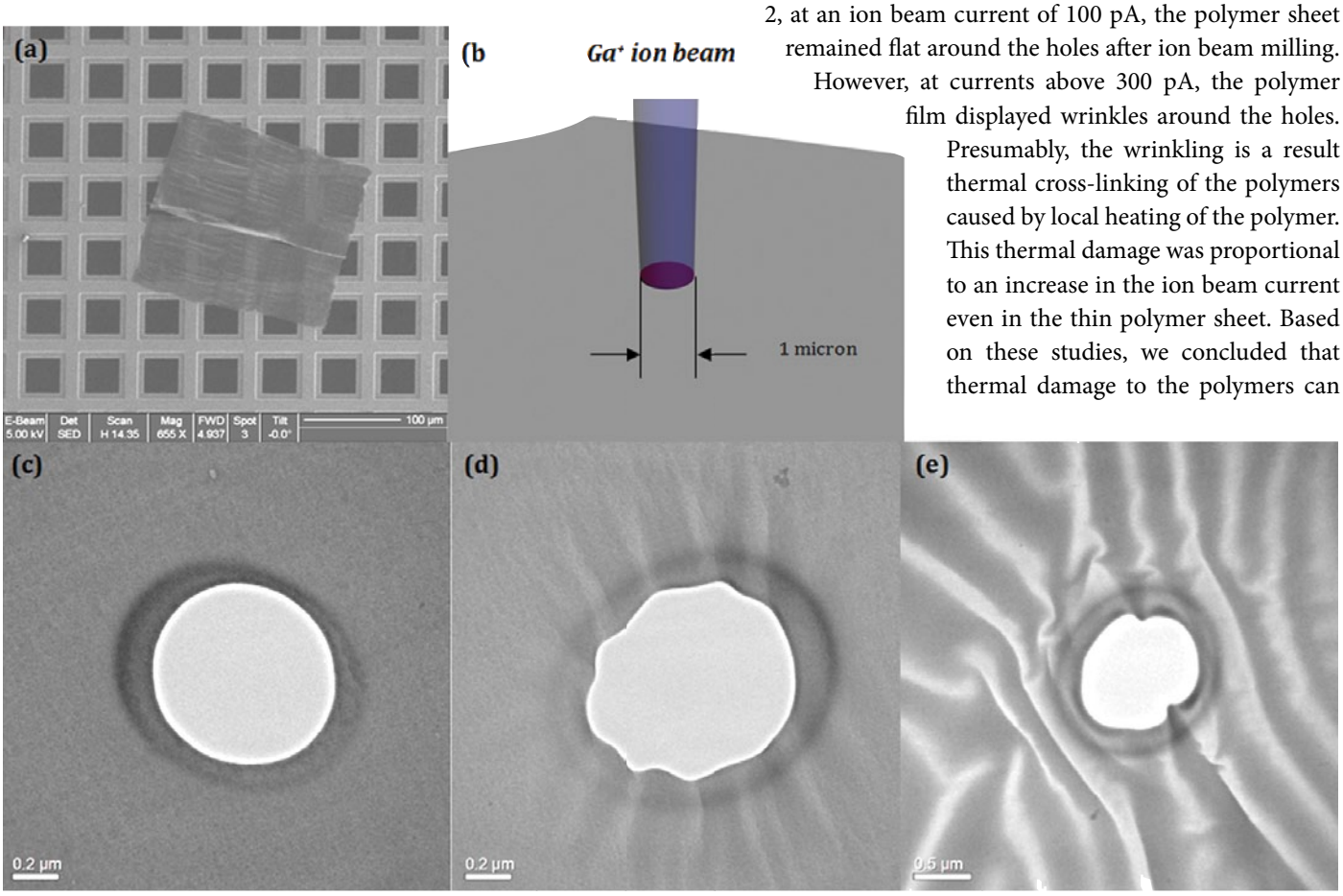

Figure 3: (a) Microtomed polymer sheets with thicknesses of about 100 nm on a Cu grid (b) schematic diagram of drawing holes on the samples. TEM images of polymer sheet after exposed at (c) 100 pA for 12 seconds, (d) 300 pA for 4 seconds and (e) 1000 pA for 1 second. Images (c)-(e) were acquired in a 300-kV TEM.

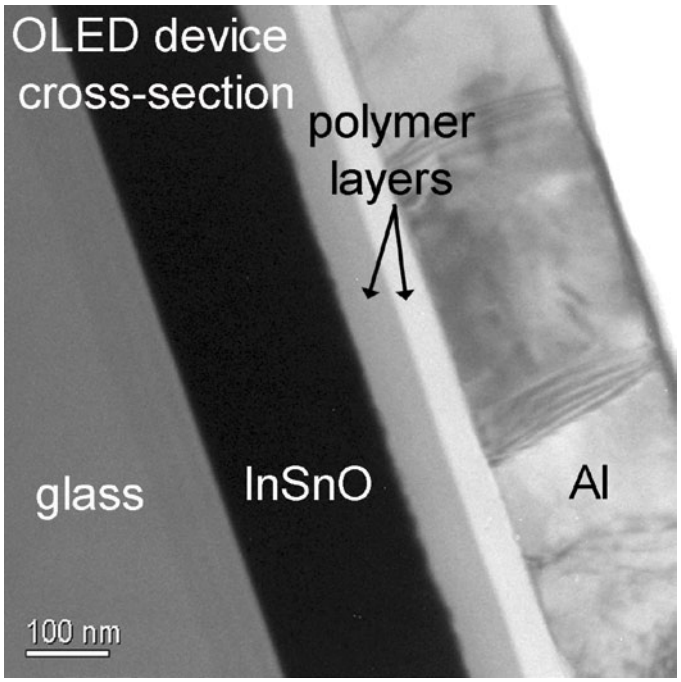

Figure. 4: TEM image (300kV) of an Organic Light Emitting Diode (OLED) device cross-sectioned with the Shadow-FIB method. In this case, the method was used to section through multiple dissimilar materials without the use of a sacrificial protection layer: glass substrate, Indium Tin Oxide (ITO) anode, polymer active layers (PEDOT:PSS and PFO), and the Al cathode.

be minimized by restricting the ion beam current to below 100 pA for the 30-keV Ga ion beam.

Shadow-FIB Effectiveness

Now we were ready to test the effectiveness of the Shadow-FIB method for making cross-sectional samples of soft thin films on hard substrates. First, we prepared cross-sectional TEM samples of block copolymer thin films on a Si substrate using low ion-beam-current (below 100 pA) milling. To see the nanostructure of block copolymer, PS was selectively stained by ruthenium tetroxide (RuO_4) before FIB milling. To successfully image the microstructure of the PS-b-PMMA films, optimization of the staining condition was necessary. A normal staining condition for the microtomed polymer was found to be unsuitable in this case because the staining agents can only diffuse into the films from the top exposed surface. As shown in Figure 3, we varied the staining conditions from 2 hours to 4 days and took TEM images of the cross-sectioned sample. Our results demonstrated that the stain only diffused through the entire film after 4 days of stain diffusion in an air-tight sealed jar. Thus, the Shadow-FIB method was able to produce comparable images that revealed features in the polymer up to the polymer-Si interface (Figure 2c).

The Shadow-FIB method was then applied to a practical microelectronic device. To investigate the degradation of organic materials within a device via TEM, a cross-section revealing all layers is required. Organic electronic thin film systems are particularly difficult to section with other sample preparation methods because they often contain ceramic, polymer, and metallic thin films stacked together. Through the Shadow-FIB technique, it is possible to cross-section whole devices, including the polymer layers, with minimal FIB-time. Figure 4 shows the cross section of an as-prepared organic light emitting diode (OLED) device sectioned using the Shadow-FIB technique.

Discussion

In the case of the block copolymer, the orientation of the two polymer phases with respect to the Si substrate can be clearly seen (Figure 2c). In the case of the OLED we were able to clearly image the different polymer phases, without staining, using mass-thickness contrast in the TEM (Figure 4). Although it is difficult to prepare site-specific samples with the Shadow-FIB method, the Shadow-FIB method has significant advantages for cross-sectioning soft films on hard substrates as opposed to the alternative FIB milling strategies (for example, "H" bar or "liftout"). The Shadow-FIB method requires no sacrificial layer to protect the soft film because the hard substrate provides this protection. Moreover, by mechanically thinning an organic electronic device prior to FIB sectioning, a TEM sample can be prepared in a matter of hours, and it is possible to generate a cross-sectional TEM image of specimens like the OLED in under a day, start to finish.

Conclusion

We have shown a highly effective procedure for cross-sectioning soft thin films on hard substrates. By using the shadow-FIB method and limiting the current of the FIB during preparation to below 100 pA, damage to the polymer thin film by heating was minimized, and cross-sectioning could be readily achieved. This method allowed us to cross-section directly the thin film and the hard substrate in a few hours and still retain useful information about the polymer microstructure.

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