Minimization of focused ion beam damage in nanostructured polymer thin films

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A B S T R A C T

Focused ion beam (FIB) instruments have proven to be an invaluable tool for transmission electron microscopy (TEM) sample preparation. FIBs enable relatively easy and site-specific cross-sectioning of different classes of materials. However, damage mechanisms due to ion bombardment and possible beam heating effects in materials limit the usefulness of FIBs. Materials with adequate heat conductivity do not suffer from beam heating during FIB preparation, and artifacts in materials such as metals and ceramics are primarily limited to defect generation and Ga implantation. However, in materials such as polymers or biological structures, where heat conductivity is low, beam heating can also be a problem. In order to examine FIB damage in polymers we have undertaken a systematic study by exposing sections of a PS-b-PNMA block copolymer to the ion beam at varying beam currents and sample temperatures. The sections were then examined by TEM and scanning electron microscopy (SEM) and analyzed using electron energy loss spectroscopy (EELS). Our empirical results show beam heating in polymers due to FIB preparation can be limited by maintaining a low beam current (<100 pA) during milling.

1. Introduction

Polymer thin films serve as important elements for a number of technological applications such as solar cells\textsuperscript{1}, organic light emitting diodes (OLED)\textsuperscript{2}, organic thin film transistors (OTFT)\textsuperscript{3}, and etch masks\textsuperscript{4,5}. Structural investigations of the polymer nanostructure are critical since, the nanostructure itself is closely related to the functionality of the polymers. However, when the sample of interest involves polymer thin films on hard substrates, as is often the case in organic electronic devices, preparation methods for electron microscopy can be particularly challenging. For TEM analysis of polymer structure, ultra-microtomy is most commonly used. However, this method is not practical for polymer thin film devices because microtomy cannot easily section hard substrates such as silicon or glass. Methods such as peeling-off the polymer from the substrate\textsuperscript{6} or even using a polymer substrate\textsuperscript{7} have been used to prepare TEM samples, but this inhibits the ability to investigate the interface between a polymer film and a hard substrate. Therefore, focused ion beam cross-sectioning is a very promising method for the preparation of cross-sectional TEM samples of polymer films on hard substrates. However, most FIB TEM sample preparation to-date has been used for inorganic samples such as metals or ceramics. Materials with adequate heat conductivity suffer FIB preparation artifacts such as defect generation and Ga implantation, although this damage can be either confined to the outer layers of a sample or mostly removed\textsuperscript{8}. However, in materials such as polymers or biological structures, where heat conductivity is low, beam heating can also be a problem. A primary concern in FIB preparation of polymer samples is that the FIB can cause local heating, resulting in damage or even removal of the polymer structure. Theoretically, the maximum temperature rise caused by local heating from an ion beam can be estimated by following equation\textsuperscript{9}:

\[ T = \frac{P}{\pi \alpha k} \]  

(1)

where \( P \) is the power of the ion beam, \( \alpha \) is the radius of the circular ion beam profile on the sample surface, and \( k \) is the thermal conductivity of the sample. In this equation, thermal conductivity plays a very important role in local heating of samples. Typical polymers have relatively low thermal conductivity compared with metals or ceramics. For example, the thermal conductivity of polystyrene, silicon and aluminum are 0.13, 149 and 247 W/mK, respectively. Thus, local heating of polymers by ion beam can therefore be a thousand times...
higher than that of metals. For typical $P/a$ ratios found in modern FIBs (1–1000 W/m) the temperature rise given by Eq. (1) is negligible for metals and ceramics, but can be thousands of degrees at the extreme power densities for polymers. From this perspective, the beam current is not a particularly important parameter when FIB milling metals and ceramics (other than to define pattern resolution), but with polymer samples the beam current becomes a critical parameter that controls damage caused by the FIB for TEM sample preparation. In addition to beam heating, direct ion bombardment damage to the polymer molecules can also be a problem. As is the case with metals and ceramics, this direct damage is contained within the near-penetration depth of the incoming ions [10]. However, since polymers are typically less-dense and also have lower elastic moduli than metals or ceramics, this interaction volume can be larger than for harder and denser materials.

Despite these issues, the usefulness of FIB instrumentation has led to a number of electron microscopy investigations of FIB-prepared polymer samples. Kato et al. [11] tried FIB-milling for etching of block copolymers and investigated polymer structure using scanning electron microscopy (SEM). FIB-based preparation of polymer samples for TEM investigations has been used for cross-sectional TEM samples of solar cells [12], polymer light emitting diodes (PLED) [2], and block copolymer thin films [13,14]. Niihara et al. [15] successfully applied FIB to prepare TEM samples from bulk polymers by using a cryogenic holder, while Brostow et al. [16] investigated FIB damage to bulk polymer-metal hybrids. Kochumalayil et al. [17] investigated an effect of focused ion irradiation on bulk PMMA depending on FIB parameters such as dwell time and beam overlap as well as chamber environment. To our knowledge, however, there have been no systematic investigations of focused ion beam damage specifically on thin polymer films.

Here, we report on systematic studies of FIB damage and methods to limit this damage in polymer thin films. We have analyzed ion beam damage in polymer thin films depending on ion beam current, exposure time and temperature. We prepared thin polymer sheets of 100 nm thickness and milled holes under the different current conditions and times. The size of the holes and the polymer morphology around the holes were examined using a SEM and TEM. Based on our empirical results, we found an optimum condition to prepare cross-sectional TEM samples of polymer films. Finally, we demonstrate that it is possible to prepare cross-sectional TEM samples of polymer films without significant damage to the polymer films using these optimal low current conditions.

2. Experimental procedures

2.1. Preparation of polymer sheets

Poly(styrene(50,500 g mol$^{-1}$)-b-methyl methacrylate(20,900 g mol$^{-1}$)) (PS-b-PMMA, $M_w/M_n=1.06$) diblock copolymer was purchased from Polymer Source Inc. PS-b-PMMA polymer was annealed at 180°C under vacuum for 1 day. Annealed polymers were sectioned to approximately 100 nm thickness using an ultramicrotome (Power Tome XI, RMC Products) and the sectioned polymer sheets were placed on a Cu grid as shown in Fig. 1(a). The polymer sections were then stained by ruthenium tetroxide (RuO$_4$) for 2 h. The prepared PS-b-PMMA had cylindrical nanostructures and could be observed after the selective staining of PS with RuO$_4$ as shown in Fig. 1(b). PS-b-PMMA sheets were then coated with amorphous carbon of about 3 nm thickness to reduce charging during ion beam exposure.

2.2. Milling holes in polymer sheets

Holes were milled into the microtomed polymer sheets with a FEI Strata 235 Dual Beam FIB using a 30 keV Ga$^+$ ion beam at room temperature with nominal current conditions of 10, 100, 300 and 1000 pA. The actual measured currents were typically closer to 10, 113, 317 and 1065 pA, respectively, but for the purposes of this paper we will use the nominal current values to discuss the results. To drill the holes, the polymer sheets were placed on a Cu grid and tilted to be normal to the ion beam. At each current, 5 holes were milled into the polymer sheets. In order to avoid exposing the patterned region to the ion beam before drilling the holes, the beam was focused on the nearby Cu grid. After focusing, the polymer region to be patterned was moved under the ion beam with the beam blanked. For all of our experiments we fixed the FIB parameters dwell time to be 1 μs and the overlap percentage to be 50%, and the beam was rastered serially from the left to the right of the patterned region (with respect to the orientation shown in the SEM images). All of the patterned holes discussed in this work
used a fixed radius of 500 nm. SEM imaging of the holes after FIB milling was performed at 5 kV.

In order to cool down the stage, a custom-built cryostage was used. The cryostage consists of a metal braid inside the FIB chamber connecting the sample stage and a liquid nitrogen dewar outside the chamber. After filling the liquid nitrogen dewar, the temperature of the sample stage was cooled to approximately $-100\degree C$ over 2 h and allowed to stabilize at that temperature for an additional 2 h. The temperature was monitored and the fluctuation was less than $\pm 5\degree C$ during this stabilization period. Holes were then milled into the PS-b-PMMA sheet at $-100\degree C$ using beam currents of 300–1000 pA.

2.3. Preparation of polymer thin film TEM samples

A 4 weight % polymer solution was prepared by dissolving Poly(styrene $(20,000\,\text{gmol}^{-1})$-b-isoprene$(5000\,\text{gmol}^{-1})$) $(\text{PS-b-PI}, \quad M_\text{w}/M_\text{n}=1.02)$ into toluene. The prepared polymer solution was spin-cast onto a 300 $\mu m$ thick silicon wafer at 3000 rpm for 30 s. The prepared PS-b-PI polymer films were annealed at 120 $\degree C$ for 1 day. The PS-b-PI films were stained by osmium tetroxide (OsO$_4$) for 8 h, and then prepared for TEM analysis using the FIB as described later.

2.4. TEM analysis

All TEM imaging was performed with a Zeiss 200 kV Libra TEM. Ga elemental maps and sample thickness maps were obtained using the in-column energy filter. Ga elemental maps were obtained using the three-window method at the Ga L peak of 1115 eV using a 32 eV slit. Thickness maps were obtained with a 15 eV slit.

3. Results and discussion

3.1. FIB damage at room temperature

In Figs. 2–10 we show data from our experiments consisting of nominally 1 $\mu m$ diameter holes milled into the PS-b-PMMA sheet with varying beam currents and exposure times. In order to generate representative statistics, 5 holes were milled for each condition. For example, Fig. 2 is an SEM image of a series of 1 $\mu m$ holes milled with a 10 pA 30 kV Ga$^+$ ion beam for exposure times of 6, 18, 36 and 72 s, where each row of holes shows 5 identical conditions.

As can be seen from Fig. 2, when the PS-b-PMMA sheet was exposed with the 10 pA beam for 6 s, the Ga$^+$ ion beam could not mill through the PS-b-PMMA sheet. This condition set the baseline from which we then milled through-holes at higher doses (or higher currents at the same dose), where dose is the product of current and exposure time, to examine the width of the holes and morphology of the surrounding structure by TEM analysis. Fig. 3(a) shows a bright field (BF) TEM image of the PS-b-PMMA exposed to the 10 pA Ga$^+$ ion beam for 6 s. From this image, we can see the effect of Ga$^+$ ion beam exposure on the polymer. The lighter areas are thinner, and had been sputtered by the Ga$^+$ ion beam. In this sample the middle of the circle seems to be slightly thicker (dark contrast in the BF image), presumably due to non-uniform thinning across the circle at this low dose. At the edge of the circle, a dark contrast results from the implantation of Ga, confirmed by the Ga elemental map shown in Fig. 3(b). Fig. 3(c) is a BF TEM image of the hole milled by the 10 pA beam when exposed for 18 s. With this dose the Ga$^+$ ion beam made a through-hole. An even longer exposure of 36 s is shown in Fig. 3(d), where the hole has been more cleanly cut. The most interesting feature of Fig. 3 is the fact that the nanostructured morphology of the PS-b-PMMA film can still be seen in the middle of the thinned region in (a) and the edge of the holes in (c) and (d). As will be seen later, this is not the case for the larger beam currents used.

Fig. 4 shows a series of holes milled through the PS-b-PMMA membrane using a 100 pA ion beam for 9, 18 and 30 s. Fig. 5 details the morphology of one of the holes that was exposed at 100 pA for 9 s. As can be seen from these images, the results for the 100 pA holes are similar to the 10 pA holes. The Ga elemental map shown in Fig. 5(b) confirms that Ga$^+$ ion was implanted into PS-b-PMMA at the edge of hole, and the thickness map shown in Fig. 5(c) demonstrates no appreciable thickness change outside of the hole area. Similar to the 10 pA holes, the nanostructured morphology of the PS-b-PMMA structure can be clearly seen at the edge of the holes in Fig. 5(a).

The effect of beam heating on the polymer structure is evident when we examine the series of holes milled in the polymer film at 300 pA. Fig. 6 shows the series of holes milled at 300 pA for 3, 6 and 10 s, resulting in a similar total dose to the series of holes milled at 100 pA. While the resulting hole sizes are similar, there is a qualitative difference in the holes in Figs. 4 and 6. As Fig. 6 shows, at 300 pA distinctive wrinkling of the polymer membrane can be seen surrounding the holes, regardless of exposure time. Fig. 7 details one of the 300 pA 10 s holes. In the BF TEM image shown in Fig. 7(a), the structural change of PS-b-PMMA membrane can clearly be seen. In addition to local distortions and an uneven hole shape, the spacing between the PS and PMMA blocks has been expanded as compared to the unexposed area of PS-b-PMMA. The Ga elemental and thickness maps from the hole shown in Fig. 7(a) are shown in Fig. 7(b) and (c), respectively. While Ga was distributed around the edge of the hole, the thickness differences extend hundreds of nanometers from the edge. The wrinkles seen in Fig. 6 surrounding the 300 pA holes were confirmed by the intensity profile shown in Fig. 7(d) taken from the thickness map. It should also be noted that debris can be seen at the right edge of the hole (circled), but this debris is not Ga (confirmed by the Ga map). Presumably this debris is accumulated polymer material damaged by local heating.

As would be expected given the results found for 300 pA, an even higher current of 1000 pA resulted in severe damage to the polymer film. Holes milled at 1000 pA for 1 and 3 s are shown in Figs. 8 and 9. These holes have the same total dose as the holes milled for 3 and 10 s at 300 pA, but the damage is noticeably more severe. In comparison with Fig. 6, the 1000 pA holes shown in Fig. 8...
have more pronounced wrinkling and the wrinkles extend farther from the hole. TEM images of a hole milled at 1000 pA for 3 s are shown in Fig. 9. Similar to the 300 pA holes, Ga implantation is only found at the edge of the hole. The damage, however, is clearly more severe surrounding the 1000 pA hole, where the nanostructured morphology of the PS-b-PMMA is grossly distorted and the thickness variations are pronounced. Clearly, for a similar dose a higher current causes more damage and further from the actual hole and milled region, consistent with the hypothesis that higher currents cause more heating in the polymer film.

3.2. FIB damage at \(-100 \, ^\circ C\)

In order to verify the correlation between current and a temperature rise in the polymer sample, we used a custom-built cryo-stage to cool down the samples to \(-100 \, ^\circ C\). Holes were milled into the polymer film with beam currents of 300–1000 pA. Fig. 10 shows an SEM image of the holes milled at 300 pA for 3 and 10 s. Even after the temperature of the stage had been stabilized for 4 h, there was a large amount of specimen drift, causing the hole shape to be elongated in the drift direction. In addition, surrounding each hole there is a distinct layer of redeposition, presumably due to condensation of milled material. Despite this, it became immediately evident that the effect of beam heating seen at room temperature with the 300 pA beam had been dramatically reduced. As Fig. 10 shows, there is no wrinkling around holes. This is confirmed by the TEM image and thickness map in Fig. 11, which also confirm the redeposition of milled material.

In an even more dramatic confirmation of the beam heating hypothesis, the results from the holes milled with 1000 pA at \(-100 \, ^\circ C\) are shown in Figs. 12 and 13. Fig. 12 shows an SEM image of the holes milled with 1000 pA for 1 and 3 s. Similarly to the 300 pA holes, the drift of the specimen elongated the holes and caused local redeposition surrounding the milled region. Also similar to the 300 pA holes milled at \(-100 \, ^\circ C\), the sample milled at 1000 pA at \(-100 \, ^\circ C\) did not show any wrinkling around the holes. Fig. 13(a and b) shows BF TEM images of a 3 s 1000 pA hole,
where clearly the nanostructured morphology of the PS-b-PMMA remains unchanged, especially in comparison to the results found for the 1000 pA holes milled at room temperature (Figs. 8 and 9). When comparing Figs. 9 and 13, cooling the sample down to $-$100 °C has clearly decreased the damage from beam heating due to the ion beam at this high current. While Eq. (1) can only be used as an estimate for our thin film system, where the beam is rastered and not stationary, it is interesting to note that using the temperature rise for a 300 pA beam would be $45^\circ$ and for a 1000 pA beam $150^\circ$. Thus, it is reasonable to expect cooling our sample by $120^\circ$ would result in less beam damage at these higher currents.

### 3.3. Demonstration of polymer thin film TEM cross-section

Our results have shown that sample heating in the polymer sample due to the FIB preparation can be avoided by using either a low beam current or cooling the sample. For practical reasons, simply using a low beam current is a more desirable approach than using a cryostage. Thus, in order to demonstrate the effectiveness of using a low beam current, we have prepared cross-sectional TEM

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**Fig. 5.** (a) BF TEM image, (b) Ga elemental map, and (c) thickness map of polymer sheet milled by the 100 pA ion beam for 9 s.

**Fig. 6.** SEM image of 300 pA FIB-milled holes in the PS-b-PMMA polymer sheet.

**Fig. 7.** (a) BF TEM image, (b) Ga elemental map, (c) thickness map of polymer sheet milled by the 300 pA ion beam for 10 s, and (d) thickness profile of selected region.
samples of a polymer films on a hard substrate using the FIB. Since the ion beam can easily sputter a polymer thin film during preparation, either a sacrificial layer is required to protect the polymer film during milling, or one can use a FIB method developed specifically for rapid cross-sectional TEM sample preparation of thin films termed “shadow FIBing” [18,19].

To show the effectiveness of the shadow FIB technique, a PS-b-PI polymer film was selected because poly(isoprene) has relatively
low glass transition temperature and therefore can presumably be more easily damaged than PS-b-PMMA, for example. The prepared PS-b-PI film on Si was broken into small pieces and a piece with a sharp corner was attached to a Cu grid. The FIB was exposed from the back side of the Si substrate as shown in Fig. 14(a) and etched from the substrate through to the polymer film on two sides. As the name “shadow FIB method” implies, the polymer film is in the shadow of substrate and so is never directly exposed to the ion beam except for the side walls of the cross-section. A series of SEM images are shown in Fig. 14 describing the preparation steps of the PS-b-PI on Si TEM sample. During the preparation a high current of 1000 pA was used to make the gross cuts, but when the sample had been shaped so that the corner was only a few microns in width, the beam current was lowered. The final cross-section was thinned using an ion beam current of 100 pA. It should be noted that the heat transfer from a polymer thin film on a substrate such as Si is expected to be better than the simple case of a suspended polymer film as used in our hole milling studies; however, as a precaution the low beam current 100 pA was still used for final thinning. Fig. 15 is a BF TEM image of the cross-sectioned PS-b-PI on Si sample. As can be seen, the shadow FIB method using a low beam current for final thinning was successful in obtaining TEM images of the hexagonally packed cylindrical nanostructure in the PS-b-PI film.

4. Conclusion

In this paper we reported systematic studies of FIB damage and methods to limit this damage in polymers. We examined the direct ion beam damage in polymers depending on the ion beam current, exposure time and sample temperature. The PS-b-PMMA sheet showed damage from beam heating that distorted the nanostructured morphology and forming wrinkles in the polymer sheet at ion beam current above 100 pA. However at beam currents of 100 pA and below, ion beam heating damage was minimized and the polymer sheet still retained its nanostructured morphology even where it had been exposed to the Ga beam. Cryogenic studies demonstrated that damage to the polymer film resulting from larger currents could be suppressed by cooling the sample down to –100 °C, consistent with the observations that the damage seen above 100 pA at room temperature was heat related. While an unstained sample or a different polymer system might require a lower beam current, we found that the nanostructured morphology

![Fig. 12. SEM image of holes milled into the PS-b-PMMA polymer sheet by a 1000 pA focused ion beam at –100 °C.](image)

![Fig. 13. (a and b) BF TEM image, (c) Ga elemental map, and (d) thickness map of the PS-b-PMMA polymer sheet milled by the 1000 pA ion beam for 3 s at –100 °C.](image)
of our stained block copolymer thin films could be retained during FIB preparation of a cross-sectional sample by maintaining a beam current of \( \leq 100 \) pA during final thinning.

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