Measurement of the x-ray dose-dependent glass transition temperature of structured polymer films by x-ray diffraction

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The glass transition temperature (T_g) of polymer nanostructures was measured using a technique based on synchrotron x-ray diffraction from periodic grating structures. Poly(methyl methacrylate) (PMMA) nanostructures consisting of 1:1 lines:spaces with a 100 nm period and 100 nm height were characterized to have a T_g of 118 °C, which is comparable to the T_g of PMMA in bulk systems. The T_g of the PMMA structures also was measured as a function of absorbed x-ray dose. Doses ranging from 0 to 2400 mJ/mm² were delivered to the PMMA structures prior to the T_g measurements; the T_g of the structures was found to decrease from 118 °C to 95 °C, respectively. The dose dependence of the PMMA glass transition temperature can be attributed to changes in the polymer molecular weight under exposure to x rays. © 2007 American Institute of Physics.
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I. INTRODUCTION

The glass transition temperature (T_g) is a key parameter for determining the suitability of thermoplastic polymers for applications at both the macro- and nanoscale.¹ Polymers are glasslike at temperatures below the T_g but become rubbery with drastically different rheological and mechanical properties at temperatures above the T_g . The widespread application of polymers in coatings, membranes, and nanocomposites has necessitated an improved understanding of the thermophysical properties of polymers in confined geometries and in close proximity to surfaces and interfaces. Consequently, the glass transition temperature of thin polymer films has been measured using techniques such as ellipsometry,^{2–6} Brillouin light scattering,^{3,7} x-ray reflectivity,⁸ local thermal analysis,^{5,6,9} ensemble fluorescence,^{10,11} and quartz crystal microbalance measurements.¹² Ultrathin polymer films with thicknesses less than ~50 nm have been observed to have glass transition temperatures that deviate from the T_g measured for the bulk polymer.^{2–12} These deviations often depend upon the film thickness,^{2–12} polymer molecular weight,⁴ the polymer-substrate and polymer-free surface interactions,^{3,5,13} and whether the film is supported or unsupported.³ Mechanical properties,^{14–17} diffusion coefficients,^{10,18,19} and the physical aging behavior^{20–22} of polymers have shown similar dimension-dependent behavior in thin films.

Characterization of the glass transition of polymers in three-dimensional nanoscale structures is of critical importance to many nanofabricated systems. For example, polymeric photoresists are used in advanced lithography to pattern semiconductor devices at dimensions of 65 nm and

smaller, and the fabricated photoresist structures must be stable, both thermally and mechanically, when subjected to a wide range of processing temperatures and conditions.^{23–25}

Three-dimensional nanostructures have substantially larger ratios of polymer-free surface to polymer-substrate interfacial areas than thin films and as a consequence have been measured to have T_g 's that differ by as much as 15 °C from thin films of the same thickness.²⁶ Furthermore, polymer nanostructures such as those lithographically patterned in complex layouts for integrated circuits may exhibit spatially varied glass transition temperatures as a function of the geometry, dimension, and local environment of the structures. The thermophysical behavior of polymers structured in three dimensions at the nanoscale must therefore be directly measured for the dimensions and geometries of interest. Many techniques used to determine the T_g of polymers in thin films, however, are difficult or impossible to employ on structured systems. Brillouin light scattering is an exception that has been used to measure the elastic constants of periodic grating structures in polymer thin films.^{27–29} X-ray-based methods for characterizing nanostructured polymers also are being pursued because of their high spatial resolution, the ability to operate in ambient conditions (i.e., vacuum conditions are not required, unlike electron microscopy), and the potential of probing buried structures. Small-angle x-ray scattering (SAXS) and x-ray crystallography methods for nanoscale structural analysis must be adapted for the requirements of polymer materials and three-dimensional structures. Recently, Jones *et al.*³⁰ have introduced a transmission SAXS approach and characterized the periodicity, linewidth, and sidewall angle geometry of polymer gratings with nanometer precision.

Here, we report the development of a grazing incidence x-ray diffraction technique for characterizing the glass tran-

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FIG. 1. Cross-sectional SEM image of a PMMA grating. The height of the grating lines is 100 nm and the gap between the grating lines is 50 nm. The period is 100 nm.

sition temperature of three-dimensional polymer nanostructures. A poly(methyl methacrylate) (PMMA) film structured with 100 nm period linear gratings was illuminated with a collimated x-ray beam and the diffracted intensity was measured as the temperature of the film was increased at a constant rate. The total diffracted intensity was found to be a useful parameter to determine the T_g of the polymer nanostructures. The T_g of the PMMA structures was measured to be 118 °C and corresponded well with values for PMMA measured in comparable bulk and thin-film systems. A linear decrease in the T_g of the nanostructures as a function of the absorbed x-ray dose also was observed and quantitatively explained in terms of a decrease in the molecular weight of the PMMA polymer.

II. EXPERIMENT

The PMMA nanostructures were fabricated by photolithography in 100 nm thick PMMA films with extreme-ultraviolet interference lithography (EUV-IL) exposures at the XIL beamline of the Swiss Light Source (SLS) at the Paul Scherrer Institut (PSI), Switzerland.^{31,32} Figure 1 shows a cross-sectional scanning electron microscope (SEM) image of such a PMMA grating. The grating nanostructures had a height H of 100 nm, a period T of 100 nm, and a channel width D of 50 nm, and were fabricated over an area of 0.5×1.0 mm². Poly(methyl methacrylate) with a molecular weight of $M_w=600$ kg/mol dissolved in chlorobenzene was purchased from Allresist GmbH, Germany. PMMA films with a thickness of 100 nm were prepared by spin-coating from solution on bare Si (100) wafers. No special cleaning or preparation steps were performed on the Si wafers prior to deposition. The films were annealed at 170 °C for 3 min on a hot plate after spin-coating. A linear grating structure was produced by coherently interfering two beams of 92 eV energy and exposing the PMMA photoresist on the wafer to the interference pattern.^{31,32} The final PMMA structures were formed after development for 30 s in a 3:7 solution of H₂O:IPA (isopropyl alcohol).

X-ray diffraction experiments on the gratings were performed at the materials science wiggler beamline X04SA of the SLS, using the reflection geometry shown in Fig. 2.³³ The photon energy of the collimated beam was 8.5 keV. The

FIG. 2. Experimental setup for x-ray diffraction from a grating made by EUV-IL. The distance L is 1.5 m. The wavelength λ of the incoming x-ray beam is 0.146 nm. Two pairs of slits define the beam. An ionization chamber counts the number of photons per second, I_{inc} , on the sample.

PMMA grating was oriented such that the grating lines were in the plane of incidence as shown in the figure. The 1.0 m long flight tube, filled with He, was needed to reduce scattering from the air (the $1/e$ attenuation length of x rays in air at this energy is 1.4 m). The 2D pixel detector consisted of 157×366 pixels, each 217×217 μm in size. The pixel detector used single-photon counting technology and provided unsurpassed signal-to-noise ratios.³⁴ The distance L from the sample to the detector was 1.5 m, implying a subtended resolution angle of 1.45×10^{-4} by 1.45×10^{-4} rad per pixel. A grazing incidence angle θ_i of 1.0°, significantly higher than the critical angles for PMMA and Si at this energy (0.156° and 0.211°, respectively) for total reflection, was used. The height H of the grating lines (100 nm) corresponds to an effective height H_{eff} of $2H/\theta_i=11.4$ μm for the total path length traveled by the x-ray beam within the PMMA layer. The phase shift through the grating, ϕ , is equal to $2\pi\delta_{PMMA}H_{eff}/\lambda=1.82$ rad. The fact that the phase shift is smaller than π is important in the interpretation of the data, as we will explain below.

III. RESULTS

Diffraction patterns were monitored as a function of temperature. Figure 3 plots several diffraction measurements at different temperatures from 65 °C to 117.6 °C. Two effects can be clearly seen: (i) from 65 °C to 116 °C the in-

FIG. 3. (Color online) Diffraction patterns of a PMMA grating with a period $T=100$ nm. The temperature was ramped from 65 °C to 117.6 °C. A clear enhancement of the intensities in the diffraction peaks is seen up to the temperature of about 115 °C. Above 116 °C the peaks disappear due to a glass transition. Note that the diffraction intensities have been offset for clarity.

tensity in the diffraction peaks shows small variations with some enhancement observed especially in the higher order peaks; (ii) above 116 °C the diffraction orders decrease quickly and disappear. The first effect can be qualitatively explained as being due to the annealing of the polymer gratings, i.e., the grating lines become smoother by the removal of defects such as surface roughness. The rapid disappearance of the diffraction pattern, however, was due to the glass transition, which causes the nanometer-scale PMMA grating to lose its structure and turn into a uniform film. Although the distribution of diffracted x rays into the different diffraction orders contains detailed information about the profile of the grating lines, the total diffracted intensity appears to be a useful measure that is directly related to a basic structural parameter, namely the standard deviation of the height of the grating pattern. The total diffracted intensity γ can be found from the experimental data by adding the intensity in all the peaks,

$$\gamma = \frac{1}{I_{\text{inc}}} \sum_{m=1}^N I_m, \quad (1)$$

where I_{inc} is the incident x-ray intensity and N is the number of the maximum order measured. The efficiency of diffraction into various orders by a grating can be obtained by expanding the field at the exit plane of the grating into a Fourier series. Using kinematical theory of diffraction for calculating the field distribution at the exit of a grating, we can calculate the quantity γ for a square grating with period T , gap size D , and height H by subtracting the zeroth-order efficiency from the total power, giving³⁵

$$\gamma = 1 - \frac{1}{T^2} \{ D^2 + (T-D)^2 + 2D(T-D)\cos\phi \}. \quad (2)$$

Equation (2) is valid for a pure phase grating, which is a reasonable approximation when hard x rays are used to illuminate thin polymer films. For example, the total absorption in the PMMA film in our case is less than 1%. With straightforward manipulation one can show that, if the phase shift ϕ is much smaller than π , the total diffracted intensity is approximately equal to the variance of the phase shift imparted by the grating lines to the beam, i.e.,

$$\gamma = \sigma_\phi^2, \quad (3)$$

where

$$\sigma_\phi^2 = \frac{(T-D)D}{T^2} \phi^2. \quad (4)$$

The relation between the diffracted power and the variance of the grating structure is akin to the well-known dependence of scattering on the root-mean-squared roughness of a surface.

We performed diffraction experiments on a number of identical gratings that were pre-exposed to x rays for certain durations of time. The pre-exposures were performed at the same x-ray diffraction setup just prior to the x-ray diffraction measurements. The total x-ray dose delivered to the sample in the pre-exposure step was always significantly larger than the dose delivered during the diffraction measurement so that

FIG. 4. (Color online) The total scattering power γ of the grating as a function of temperature. Curves are shown for gratings which have been pre-exposed to x rays so as to study the influence of x-ray radiation on the glass transition temperature T_g of PMMA.

modification of the polymer during the measurement itself is negligible. This was accomplished by the introduction of strong attenuators into the beam during the measurements. The irradiation of PMMA is known to cause chain-scission and cross-linking reactions in the polymer which should significantly modify the glass transition temperature. Figure 4 plots γ versus the temperature for several gratings pre-exposed with different x-ray doses. The doses were calculated from the measured flux of the x-ray beam. The number of photons hitting the sample was measured with an ionization chamber to be 2.3×10^{12} photons/s/mm². Considering the angle of incidence (5° during pre-exposures) and the absorption length of PMMA at this energy, we find absorbed doses, ϵ , of 240, 600, 1200, and 2400 mJ/mm³, for exposure times of 120, 300, 600, and 1200 s, respectively. The pre-exposures were performed at a constant temperature of 60 °C. The temperature ramp rate during x-ray diffraction measurements was 0.3 °C/s. The data acquisition time for a single diffraction spectra like the ones shown in Fig. 3 was 1 s.

In Fig. 4 we notice that at temperatures below 100 °C, γ decreases slightly for the sample that was not pre-exposed and the one that received only a slight dose (240 mJ/mm³) as the temperature was ramped. In addition, the initial value of γ exhibits a significant dependence on the exposure dose, i.e., this value goes down from about 0.4 to 0.2 between the unexposed sample and the sample that received the highest dose. Both observations can be interpreted to be due to loss of mass by creation of volatile components during x-ray exposure. The mass loss is likely to be accelerated by the elevated temperature during the x-ray exposure. As the temperature is further increased, a sudden drop of the diffracted intensity is observed. The point at which this sudden transition starts can be estimated by the intersection points of lines that approximate the constant intensity and the falling edge as seen in Fig. 4. We interpret the onset of this transition as the glass transition temperature T_g , which is plotted as a function of the absorbed dose ϵ in Fig. 5.

IV. DISCUSSION

The experimental value of γ at a temperature well below T_g can be compared with the expected theoretical value

FIG. 5. (Color online) The glass temperature T_g as a function of the absorbed x-ray dose. The linear behavior can be explained with a theoretical model for the decrease in PMMA molecular weight as a function of x-ray dose.

given by Eq. (2). For the nonexposed grating γ is 0.4 at 65 °C, whereas the theoretical value is 0.62. In Fig. 4 we notice the large initial rate of decay of γ for the nonexposed sample, which we have already attributed to x-ray induced mass loss. Before the first measurement, the sample was exposed to x rays for a short (undetermined) time for alignment purposes. Therefore, it is likely that the grating had already degraded to some extent before the first measurement. This is a very likely reason for the small difference between the theoretical and experimentally measured values of γ . In addition, the difference may be due to inaccuracies in the measurement of structural parameters (i.e., height and width of PMMA lines) by SEM or loss of diffracted intensity due to roughness in the gratings.

The effect of heat treatment on the shape of polymer micro- and nanostructures is well appreciated in the lithography community and is sometimes used to anneal out surface roughness.³⁶ At temperatures just below the T_g the shape change can show considerable variation depending on the properties of the polymer and the surface energy of the substrate. As the glass transition is reached, however, it is expected that the structured polymer will lose its shape and eventually will spread over the substrate. This dramatic transformation is accompanied by a corresponding decrease and eventual disappearance of the variance of the grating height, which is directly related to σ_ϕ and thus the diffracted power γ . Therefore, the prominent decrease in γ observed in Fig. 4 at high temperatures can be attributed to the glass transition of the polymer.

The glass transition temperature T_g of a polymer as a function of its molecular weight can be expressed by the Fox-Flory form,

$$T_g = T_g^\infty - \frac{K}{M_n}, \quad (5)$$

where T_g^∞ is the glass transition temperature for a polymer of infinite molecular weight and K is the Fox-Flory constant. The latter is known from the literature to be $K = 4.9 \times 10^4 \text{ g mol}^{-1} \text{ °C}$ for PMMA.³⁷ M_n is the number averaged molecular weight, i.e., the weight of all the polymer molecules divided by the total number of polymer molecules.

TABLE I. Properties of PMMA (Refs. 37 and 39).

T_g^∞	$118.0 \pm 3.0 \text{ °C}$
K	$4.9 \times 10^4 \text{ g mol}^{-1} \text{ °C}$
M_0	$6.0 \times 10^5 \text{ g mol}^{-1}$
G	$1.9 \times 10^{-2} \text{ eV}^{-1}$
ρ	$1.19 \times 10^6 \text{ g m}^{-3}$

For the PMMA gratings the pre-exposure to the x-ray radiation alters the molecular weight of the polymer through the equation^{38–40}

$$M_n = \frac{M_0}{1 + g\varepsilon M_0 / (\rho A_0)}, \quad (6)$$

where M_0 is the molecular weight of the unexposed PMMA, g is the scission efficiency factor which is proportional to the radiation chemical yield, ε is the absorbed energy density, ρ is the density of PMMA, and A_0 is Avogadro's number. The radiation chemical yield of a polymer is a measure of the chemical action produced by radiation energy (expressed in number of molecules reacted per 100 eV of absorbed energy). Combining Eqs. (5) and (6) yields

$$T_g = K_1 - K_2 \varepsilon, \quad (7)$$

where

$$K_1 = T_g^\infty - \frac{K}{M_0}, \quad (8)$$

and

$$K_2 = \frac{Kg}{\rho A_0}. \quad (9)$$

The linear decrease of T_g as a function of the absorbed dose ε , predicted by Eq. (7), explains the trend that we observe experimentally (Fig. 5). We can further expect the transition to become more gradual with increasing x-ray dose as the polydispersity of the polymer in the structures increases by the scissioning events that can be assumed to occur randomly along the length of the polymer backbones. Therefore, the broadening in the glass transition with increased pre-exposure dose observed in Fig. 4 can be interpreted as an increase in the polydispersity of the molecular weight of the PMMA.⁴

The theoretical formula for the linear decrease of T_g as a function of the absorbed dose ε [Eq. (7)] can be directly compared with the experimental findings by calculating the constants K_1 and K_2 using Eqs. (8) and (9) and inserting them in Eq. (7). Table I shows the properties of PMMA used in this calculation. The values for K , g , and ρ were taken from previously reported values.^{37,39} The value of 118.0 °C (with an error bar of $\pm 3.0 \text{ °C}$) for T_g^∞ is the estimated value of T_g for the sample that was not pre-exposed (see Fig. 4). The theoretically expected dependence of T_g on the dose is thus

$$T_g(^{\circ}\text{C}) = 118.0 - 8.2 \times 10^{-2} - 8.0 \times 10^{-3} \varepsilon \text{ (mJ/mm}^3\text{)}. \quad (10)$$

This dose dependence is plotted in Fig. 5. We conclude that, within the error bars, the theoretical values agree quite well with the experimental values.

In the above model we have assumed the molecular weight of the polymer forming the grating lines to be equal to that of the polymer that was spun from solution onto the Si wafer. The EUV-IL technique that was used to form the PMMA nanostructures, however, involved an exposure step which depends precisely on the same process, i.e., chain scission to alter the solubility of the exposed polymer in the developer solution. Therefore, the potential effect of the EUV exposure on the T_g of the grating needs to be considered. The image in the EUV-IL exposure had a sinusoidal intensity distribution and PMMA, which is a positive resist, was removed during the development from the areas that correspond to the region near the intensity maximum. The PMMA lines that remained on the surface consequently received a minimal dose as they corresponded to the broad minima of the sinusoidal intensity distribution. The exposure dose necessary for lithographic exposure of PMMA is around 1000 mJ/mm³,⁴¹ which is of the same order as the doses that were used in the pre-exposures (Fig. 5). Therefore, we can conclude that the T_g 's of the gratings considered in our experiments were not significantly modified by the EUV-IL fabrication process, which is also confirmed by the good agreement of the measurements with the theoretical model.

V. CONCLUSION

The x-ray diffraction method described here is an effective tool for measuring the glass transition temperature of nanostructured polymer films. The influence of radiation-induced damage and polymer molecular weight on the measured glass transition temperature was determined and found to be in agreement with a theoretical model. The sample that was not exposed to x rays prior to the diffraction measurements was found to have a T_g equal to the one expected for the bulk polymer of the same molecular weight. While the present experiments were performed at a synchrotron radiation facility, the developed method is applicable for use with laboratory x-ray sources. The method should be especially useful in studying the effects of film thickness, nanostructure size and dimensionality (one-dimensional for lines and zero-dimensional for dots), and polymer-substrate interfacial interactions on the glass transition. Nanoimprinting methods can be used to fabricate the necessary nanostructures for a large variety of polymers, such that the polymer does not have to be one that works as a photoresist like PMMA.

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