

Confinement Induced Deviation in Ultra-thin Photoresist Films

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Abstract

With the advent of shorter wavelengths in deep UV lithography, the thickness of the photoactive polymeric films must decrease significantly. In this work we address the issue of confinement induced deviations of the physical properties for thin films of poly(hydroxystyrene) (PHS), a common lithographic polymer. Using specular X-ray reflectivity to measure a thin film thermal expansion coefficient, we report that significant confinement induced deviations in the glass transition temperature are not observed, irrespective of substrate surface energy. However, it is likely that the PHS films were thermally cross-linked and it remains to be seen if this overshadows any subtle confinement effects. Despite the possibility of cross-links, we demonstrate that the substrate surface energy can have a profound effect on the polymer's dynamics within films as thick as 100 nm, which may have relevance for the transport mechanisms requisite for photolithography. We also evidence a curious negative coefficient of thermal expansion deep within the glassy PHS films and *speculate* that this may be a signature kinetically hindered or arrested spinodal dewetting.

Introduction

In the field of lithography, there is a persistent push to write smaller devices features. Current optical lithography, using 248 nm UV radiation, is capable of writing features on the order of 0.180 μm , smaller than the wavelength of the radiation. Unfortunately, these dimensions appear to be at the limit for the 248 nm processes and to further reducing the feature size necessitates a shift to shorter wavelength radiation. However, at wavelengths of 193 nm or 157 nm, most polymers become strongly absorbing and the very deep UV radiation is not able to completely penetrate the lithographic film. One solution to this transparency problem is to create a bilayer resist where only a thin top layer is photoactive while the bulk of the underlayer is amenable to reactive ion etching. If the thickness of the thin photoactive top layer is reduced to approximately 100 nm or less, deep UV transparency is no longer an issue.

However, a sub-100 nm resist can introduce new class of problems related to the integrity or stability of the polymer film. These length scales approach the unperturbed dimensions (i.e., radius of gyration or rms end-to-end length) of a single polymer molecule and confinements induced deviations in the polymer properties must be considered. For example, it is well documented that the glass transition temperature can decrease [1-9], increase [8-12], or remain constant [13,14] when the thickness of a supported film approaches a few multiples of the polymer's radius of gyration, and these deviations can be as great as ± 50 °C. Another common effect of thin film confinement is spinodal dewetting of the film [15,16]. Clearly these issues are of extreme importance to the lithographic community. It is unacceptable to have the photoactive polymer film dewet because it is too thin. Furthermore, the post-apply and post-exposure bake stages of image development are typically within 20 °C to 30 °C of the bulk polymer's T_g . In addition to the possibility of enhanced dewetting, a significant shift of the glass transition temperature could lead to diffusion between the exposed and unexposed regions, and thus image blur. It is of

paramount importance for the bilayer resist technology to understand how confinement affects lithographic films and identify what factors influence the limits on film thickness before confinement induced deviations become an issue.

In this paper, we begin to address this problem by studying the thermal stability of poly(hydroxystyrene) (PHS) films on various substrates using specular X-ray reflectivity (SXR). PHS is almost a ubiquitous polymer used in optical lithography and thus a suitable novel material to begin this study. The SXR technique can be used to monitor the thickness of a polymer film as a function of temperature, and thus useful to determine a thin film coefficient of thermal expansion (CTE). Typically, when the glass transition temperature is encountered, the CTE exhibits a discontinuity, leading to a much stronger thermal dependence. This provides a useful tool to ascertain how the glass transition temperature is influenced by the thickness of the film.

Experimental

Two grades of PHS, with $M_{w,s}$ of 2.5 kg/mol and 8.0 kg/mol [17], were dissolved in poly glycol ether methyl acetate (PGEMA) at mass fractions of 0.2 %, 0.5 %, 1.0 % and 5.0 %. These solutions were filtered through a 0.2 μm Teflon filter and spun coat onto silicon wafers with three different surface treatments. The silicon substrates were hydrophilic (native oxide of silicon, SiO_x), intermediate (silicon nitride, SiN), or hydrophobic (hydrogen passivated silicon, SiH) with respect to their surface energy. The SXR experiments were performed on a modified Scintag (Santa Clara, CA) [18] diffractometer under a vacuum of approximately 10^{-4} to 10^{-5} Pa. While the SiO_x and SiN substrates are stable under atmospheric conditions, the SiH surface is unstable and readily reverts to an oxide within hours of the passivation with ammonium fluoride. To prevent oxide regrowth, the SiH substrate supported films were spun coat immediately after passivation and transferred to the high vacuum chamber of the reflectometer within 5 min of spin coating. Prior to all reflectivity experiments, the films were annealed for ≈ 12 h at 200 $^\circ\text{C}$ (and 10^{-4} to 10^{-5} Pa) to remove residual solvent. The subsequent thermal expansion curves were obtained by collecting reflectivity curves as a function of temperature between 20 $^\circ\text{C}$ and 200 $^\circ\text{C}$ in increments of 10 $^\circ\text{C}$. After each temperature increment, 45 min were allowed for thermal equilibration with 1 h required to collect the reflectivity data. The results from multiple heating and cooling runs, with 6 h equilibration allowed between each heating and cooling cycle, are then fit with non-linear least-squares recursive multi-layer algorithm [19] to extract the film thickness.

Results

Figure 1 displays a series of SXR curves obtained at 150 $^\circ\text{C}$ for the 2.5 kg/mol PHS spun coat onto the SiO_x surfaces. The film thickness is inversely proportional ($D \approx 2\pi/\Delta Q$) to the periodicity of the interference fringes, with fits [19] indicated by the solid lines.

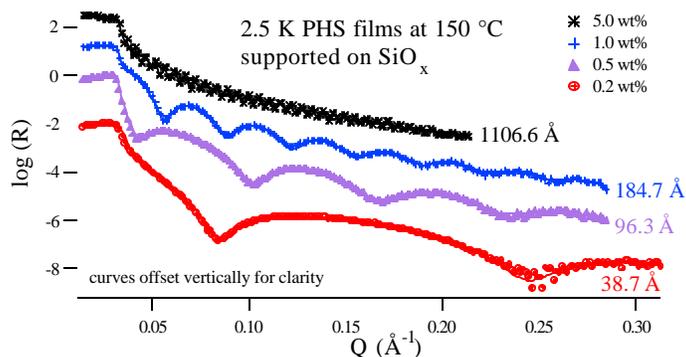


Figure 1. Specular X-ray reflectivity curves at 150 $^\circ\text{C}$ for the 2.5 kg/mol PHS films supported on the SiO_x substrate. Fits to the experimental data are indicated with the solid line, as described in the text. The fringe periodicity is inversely proportional to the film thickness with $D \approx 2\pi/\Delta Q$.

Clearly there is excellent agreement between the fits and experimental data. In this work, a satisfactory fit is obtained if the PHS film is modeled as single polymer layer of uniform density. Figure 1 demonstrates that by changing the mass fraction of PHS in PGEMA from 0.2 % to 5.0 % the film thickness can be varied from roughly 40 \AA to 1100 \AA . This is precisely the

thickness range (sub-100 nm) where deviations in the polymer properties are anticipated to be an issue with the bilayer resist technology.

Figure 2 displays a series of thermal expansion curves for the 2.5 kg/mol PHS films supported on the SiO_x substrate. In this figure, the expansion data is presented in terms of a thermal strain, or percent change in thickness (arbitrarily chosen relative to the thickness at 180 °C). For the sake of clarity, the curves are offset vertically. The isothermal error bars are obtained from two heating and cooling cycles, resulting in 4 thickness determinations per temperature. At each temperature the spread in the data points is recorded with the average spread over all temperature reported as the isothermal error in thickness. In terms of a thermal strain, this average spread is typically $\pm 0.25\%$.

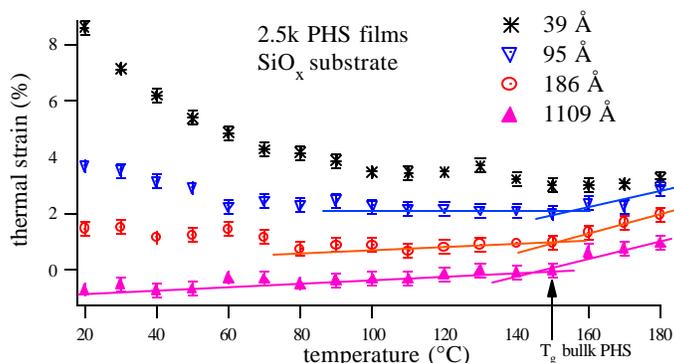


Figure 2. Thin film thermal expansion curves (in terms of a percent change in thickness) for the 2.5 kg/mol PHS films supported on the SiO_x substrates. For clarity, the curves are offset vertically for clarity. As indicated, the DSC T_g of high molecular mass PHS is approximately 150 °C.

The general form of the expansion curves in Figure 2 is typical for both PHS molecular weights and all substrates. Changing the molecular mass from 2.5 kg/mol to 8.0 kg/mol produces negligible differences in the expansion curves. The thicker films exhibit bulk-like expansion with a discontinuity observed close to the bulk T_g of high molecular weight PHS. However, as the film thickness drops below 100 nm (1000 Å), a curious negative CTE is observed below the bulk glass transition temperature; the films appear to increase in thickness upon cooling. The magnitude of the negative CTE effect increases as the film thickness decreases with the approximately 40 Å film showing a negative CTE over almost the entire temperature range. A similar negative CTE is observed on all three substrates as well as with both molecular weights.

Figure 3 compares the effect of substrate surface energy on the three thickest films (nominally 1100 Å to 1300 Å), again with the curves offset vertically for clarity. Within experimental error, there does not appear to be a significant shift of the apparent glass transition temperature when the substrate surface energy changes from hydrophilic to hydrophobic.

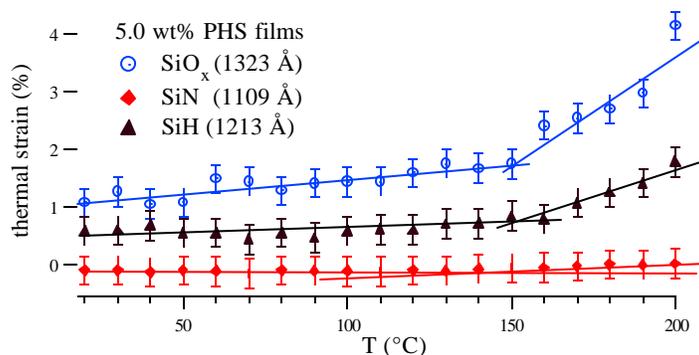


Figure 3. A comparison of the substrate effects on the thermal expansion of the thickest PHS films. Even at a thickness of approximately 1100 Å to 1300 Å, the substrate surface energy has a profound influence on the coefficient of thermal expansion. However, significant shifts in the apparent glass transition temperature are not observed.

However, it is observed that the intermediate surface energy substrate (SiN) exhibits a significantly reduced CTE in comparison to either the SiO_x or SiH surfaces. This suggests that the interactions between the substrate on the PHS are greater for the SiN surface.

A similar comparison of the thinnest films (approximately 40 Å to 50 Å thick) is provided in Figure 4, again with the curves vertically offset for clarity. The negative CTE is prominent on all three substrates, with the SiN substrate exhibiting the strongest effect. From these curves, it is no longer possible to ascertain how the glass transition is influenced by confinement or substrate interactions.

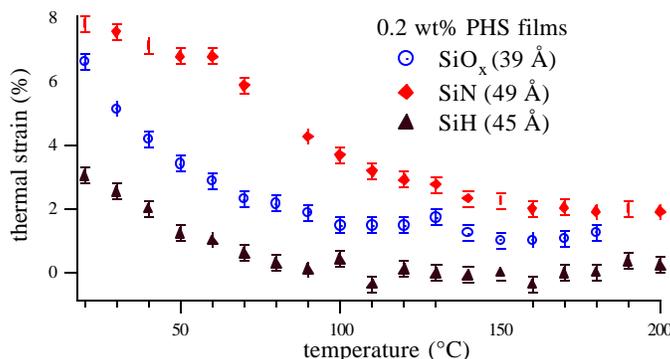


Figure 4. A comparison of the substrate effects on the thermal expansion curves of the thinnest PHS films (curves offset vertically for clarity). An apparent T_g is no longer visible in the thinnest films, obscured by a strongly negative coefficient of thermal expansion.

Discussion

It is interesting to note that there is not a significant molecular weight effect on the glass transition temperature of the thin films studied here. Differential scanning calorimetry studies on bulk PHS reveal a strong molecular mass dependence on T_g for lower M_w values [20], contradicting the results presented here. However, we note that all of our films are initially annealed at 200 ° for 12 h in a vacuum to remove residual solvent and stresses. Despite the fact the annealing is done *in vacuo*, it is highly likely that cross-linking occurs in the films. This is supported by the observation that after performing the reflectivity experiments, the films are not easily washed off of the wafer using the casting solvent (PGEMA). One must use a more aggressive solvent, such as acetone, and gentle rubbing action with a cotton swab to remove the film. At the outset of this work, we did not appreciate the possibility of cross-linking and the measurements are now being repeated without the high temperature pre-anneal. It is possible the lack of a molecular mass effect on T_g is due cross-linking in the films studied here.

Neglecting the negative CTE effect for now, our results do not support significant confinement induced deviations of the glass transition temperature. Within the error bars of Figure 2, the discontinuity at the bulk T_g is essentially the same for film thickness from 1100 Å to 95 Å. While Figure 2 is for the SiO_x substrate, similar behavior is observed with the SiH and SiN substrates. Confinement does not appear to shift the apparent T_g significantly in PHS for film nominally 100 Å to 1000 Å thick. However, this statement is made under the caveat of possible cross-linking. It remains to be seen if a similar conclusion can be made when the possibility of cross-linking is eliminated. A similar conclusion might be anticipated based on evanescent wave optic studies of PHS thin films supported on ester-terminated silanes [21] which demonstrate bulk-like T_g s regardless of the extent of confinement. Again, this issue will be readdressed once the measurements are completed on the non-cross-linked films.

Despite the lack of a confinement induced shift of the glass transition temperature and the possibility of cross-linking, it is important to note that the substrate has a profound influence on the dynamics of the PHS films. Even in the 1100 Å to 1300 Å films of Figure 3, the substrate surface energy can greatly affect the CTE, and thus the anharmonic vibrations or atomic motions within the film. It remains to be seen if a depressed magnitude of these high frequency motions will influence the lithographic process. Chemically amplified resists rely heavily upon the transport of small molecules, ions,

or acidic species to complete the photochemical process. If the atomic motions are depressed, it is quite likely that atomic and molecular diffusion will be hindered. Confinement-hindered diffusion has been observed in several polymeric thin film systems [12,22]. It is quite possible that similar confinement issues will affect the kinetics of the photochemistry in thin film resists and thus the ultimate image quality. This possibility is currently being explored in our laboratory.

Up to this point, we have not addressed the counter-intuitive negative CTE effect. Unfortunately exact molecular origins of this phenomenon are still not clear. In a separate publication, we observe a similar behavior in polycarbonate thin films [23]. In this work we demonstrate that the phenomenon is not an artifact due to the adsorption of small molecules at the film surface or interface. The effect is strongly time-dependent and shows a relaxation-like behavior. Thus far we can only *speculate* that the phenomenon is related an “unwillingness” of the film to be confined by the substrate in the thin film geometry. In high molecular mass polycarbonate, the negative CTE is completely reversible upon multiple heating and cooling cycles. However, in low molecular mass PC, the phenomena loses reversibility and coincides with an apparent overall decrease in film thickness. Figure 5(a) shows a sequence of consecutive heating/cooling expansion curves for a low molecular mass polycarbonate supported on a SiH substrate. On the initial heating and cooling between 20 °C to 200 °C, more or less normal expansion is observed. However, on the second heating (following a 12 h anneal under vacuum at 20 °C), a very strong negative CTE is encountered at low temperatures.

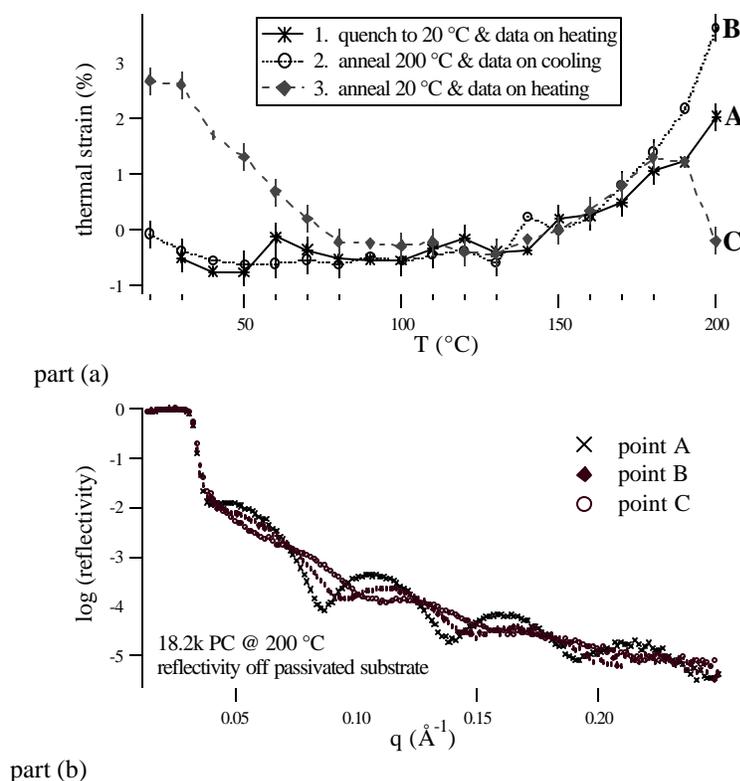


Figure 5. (a) Thermal expansion curves for nominally 100 Å PC film on the SiH substrate. Initially the film heated from 20 °C to 200 °C (stars), annealed at 200 °C for 12 h, cooled from 200 °C to 20 °C (open circles), annealed for 12 h at 20 °C, and finally heated back to 200 °C (filled diamonds). During the first 12 h anneal at 200 °C, the overall film thickness decreased by ≈ 10 Å (not evident in a percent change of thickness). Additionally, a pronounced negative coefficient of thermal expansion is observed after the 12 h anneal at 20 °C. (b) The reflectivity curves for points A, B, and C obtained at 200 °C. The interference fringes become less distinct as the sample spends more time at high temperatures possibly indicating hindered dewetting.

When the sample is then heated towards 200 °C, a significant drop in the overall thickness is observed. The first, second, and third data points collected at 200 °C in Figure 5(a) are labeled A, B, and C. What is not obvious in each of these points (presented in terms of a percent change in thickness) is that the overall thickness decreases by ≈ 10 Å each time the film is annealed at 200 °C. This is more obvious in Figure 5(b) where the reflectivity curves are presented for points A, B, and C.

The width between the interference fringes increases with each successive measurement at 200 °C. Also, the persistence of the fringes diminishes with time, a strong indication of dewetting.

From the coincidence of the apparent dewetting and the negative CTE on the second heating in Figure 5, we *speculate* that the negative CTE is an indication that the film wants to dewet. If the mobility is high enough, due to an elevated temperature, low molecular weight, or a lack of strong intermolecular or substrate/polymer interactions, dewetting can proceed. However, under kinetic hindrances, such as strong interactions, high molecular weight, or potentially intermolecular cross-linking, dewetting is prohibited. The resulting negative CTE might be a consequence of such a kinetic hindrance to dewetting. It should be mentioned that curves similar to Figure 5, with a loss of overall thickness and less distinct interference fringes, are obtained when the PHS thermal expansion curves are obtained in air (no vacuum). Under atmospheric conditions, it is likely the covalent bonds of PHS are degraded at temperatures near 200 °C, which could lead to regained mobility and thus the ability to dewet. However, we emphasize that this explanation for the negative CTE is speculation and additional experiments are needed to verify the correct mechanism.

Conclusions

In this paper we use specular X-ray reflectivity to measure the thickness of PHS films in the range of approximately 50 Å to 1300 Å as a function of temperature. This allows us to determine a coefficient of thermal expansion coefficient and evidence the apparent glass transition temperature of the PHS confined by the thin film geometry. For films ranging from 100 Å to 1300 Å thick, confinement induced deviations in the apparent glass transition temperature are not observed, regardless of substrate surface energy (ranging from hydrophilic to hydrophobic) or molecular mass (2.5 kg/mol and 8.0 kg/mol). However, it is likely that all of these PHS films were thermally cross-linked which could overshadow confinement, molecular mass, or substrate surface energy effects. Regardless of cross-linking, we demonstrate that the substrate surface energy can significantly influence the magnitude of the CTE and thus the atomic motions that should be relevant for small molecule/atomic diffusion. An interesting negative CTE is observed below the glass transition temperature in the sub-1000 Å films, with the magnitude of the effect increasing with decreasing film thickness. While the molecular origins of this negative CTE are not understood, we discuss the possibility that it is related to a kinetically hindered spinodal dewetting.

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