Observation of Temperature Dependent Thicknesses in Ultrathin Polystyrene Films on Silicon

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The temperature dependent thicknesses of ultrathin polystyrene films under vacuum on Si(111) substrates were investigated via x-ray reflectivity *in situ*. The contraction of ultrathin polymer films was directly observed for the first time to the authors' knowledge. The degree of contraction depends on the initial thickness of the ultrathin polystyrene film, with the magnitude of contraction increasing with decreasing initial film thickness. This contraction ranged from 0%–17% and occurred at temperatures well below the reported bulk polystyrene glass transition temperature.

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The morphological behavior of thin polymer films at solid interfaces is of great technological importance to a wide variety of applications such as dielectric layers, coatings, composites, electronic packaging, lubrication, and biocompatible materials. Smooth and stable surfaces and interfaces are essential for many of these applications, especially considering that many devices require even thinner films. Understanding the temperature dependence of morphological changes of thin films is pertinent since many of these devices are used under conditions of thermal variation.

Over the years there has been considerable theoretical work on describing polymer molecules in contact with a solid or vacuum, including predictions about the glass transition temperature as a function of film thickness [1–3], but there have been fewer experimental studies showing the effect of temperature on film properties. Reiter has recently reported that spin-coated polystyrene ultrathin films (<100 nm) on silicon will dewet and break up if they are annealed at temperatures $\sim 25\,^\circ$C below the bulk T_g. Such chain mobility implies that the T_g of thin films is significantly reduced. The observed dewetting process consists of the formation of pinhole defects which grow into cellular structures, eventually resulting in polystyrene droplets on the silicon wafer surface [4]. Reiter has also observed that the dewetting temperature of polystyrene films increases with increasing film thickness and polymer molecular weight [5]. Stange *et al.* used atomic force microscopy to confirm the presence of pinholes and two-dimensional networks during the dewetting of ultrathin polystyrene films on silicon wafers and observed that film quality is dependent on the polymer concentration during spin coating [6]. It should be noted that in the work mentioned above, the films were annealed at a set temperature and subsequently cooled to room temperature before observation [4–6]. There are little or no experimental data on the *in situ* properties of thin films which have been maintained at elevated temperatures during observation.

In this Letter we consider the thickness changes of ultrathin polystyrene films on silicon substrates as a function of temperature. Initial film thicknesses (h_0 at $\sim 30\,^\circ$C) were varied from 45 to 835 Å. In films of these thicknesses, van der Waals forces should be relevant, thus it is likely that the observed morphology is very sensitive to the initial film thickness [7].

Polystyrene (Aldrich Chemical, Milwaukee, WI) [8] of molecular weights 184000, 573000, and 1447000 were spin coated from toluene onto clean Si(111) wafers (Semiconductor Processing Co., Boston, MA) which had been pretreated with a sulfuric acid solution. Previous work by us has established that there is a 15–25 Å thick oxide layer on Si surfaces prepared in this fashion, regardless of its crystal orientation. During modeling of the reflectivity data by a matrix multilayer method [9], the resulting "best" fits were insensitive to the thickness of the oxide for such a thin oxide film, so samples were modeled as two phases, Si/polymer, with diffuse interfaces. The polystyrene film thickness and interfacial width were determined at each temperature. Polymer film thicknesses were controlled by varying the polymer concentration in solution (1–3 mg/ML) (ML denotes monolayer). Films were annealed under vacuum at $90\,^\circ$C for approximately 1 h to ensure that the solvent (toluene) was removed from the spin-coated polymer films and then allowed to cool under vacuum to approximately $30\,^\circ$C. Films were then maintained under vacuum and investigated by x-ray reflectivity at each given temperature using nickel filtered Cu $K_{1\alpha}$ radiation with a wavelength of 1.54 Å. The temperature was electronically controlled within $0.2\,^\circ$C of the desired set point and the polystyrene films were maintained at the desired temperature for approximately 1 h before the x-ray reflectivity measurements were performed. The x-ray reflectivity measurements were made with a modified x-ray diffractometer (Scintag, Santa Clara, CA).

The measured thicknesses of polystyrene ultrathin films with varying temperature are strongly dependent on the initial polystyrene film thickness h_0, as can be observed in Fig. 1, a plot of the relative change in film thickness with temperature for a polymer with a molecular weight of 573000. Over the temperature range 25–150 °C, the polystyrene thin films show three different behaviors, depending on their initial thicknesses. One should note that

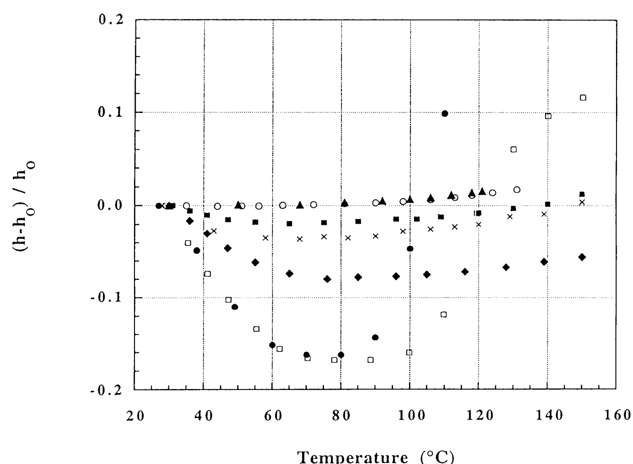

FIG. 1. The relative change in thickness of polystyrene ($M_v = 573000$) ultrathin films on Si as a function of temperature. Here h is the thickness at the given temperature and h_0 is the initial thickness. The initial thicknesses of the ultrathin films are denoted as follows: (●) 47.4 Å, (□) 49.9 Å, (◆) 100.4 Å, (×) 155.1 Å, (■) 216.6 Å, (○) 264.3 Å, and (▲) 833 Å.

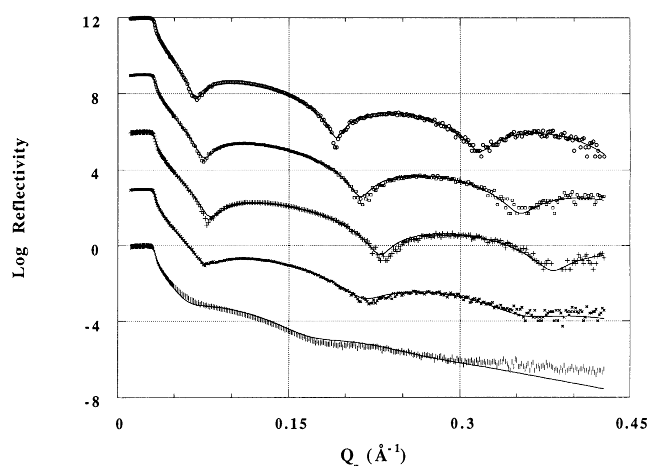

FIG. 2. Specular reflectivity profiles and their corresponding modeled fits (solid lines) measured for an ultrathin polystyrene film ($h_0 = 49.9$ Å) with varying temperature. The thickness and interfacial diffuseness changes are readily apparent here. The temperatures and measured thicknesses are denoted as follows: (○) 29 °C and 49.9 Å, (□) 47 °C and 44.8 Å, (+) 78 °C and 41.5 Å, (×) 110 °C and 44.0 Å, and (|) 140 °C and 54.7 Å.

the radius of gyration R_G for polystyrene ($M_v = 573000$) in the melt is 212 Å [10] and the persistence length is approximately 9 Å [10,11].

Very thin films (i.e., 100 Å or less) display film contraction at temperatures which are less than the glass transition temperature measured for polystyrene in the bulk, 104 °C [11]. The change in the morphology with temperature of one of the ultrathin films, $h_0 = 49.9$ Å, is shown in Fig. 2. Here the x-ray reflectivity profiles, along with their theoretical fits (solid lines; single polystyrene layer on a silicon substrate), are displayed at five different temperatures, with each respective profile offset three decades for clarity. The initial decrease in thickness over the range 29 to 78 °C is readily apparent by the shift of the second minima to higher Q_z for the three uppermost reflectivity profiles in Fig. 2. Further increasing the temperature to 110 °C results in an increase in film thickness with a concurrent increase in the diffuseness of the vacuum/polymer interface. The increase in this diffuseness is readily apparent if one observes the decrease in the depth of the minima. Damping of the reflected intensity at higher Q_z is the specular reflectivity signature of diffuse interfaces [12]. Increasing the temperature further to 140 °C results in the lowermost reflectivity profile, where the diffuseness of the vacuum/polymer interface is apparent from an almost complete loss of the interference fringes. Such an increase in interfacial diffuseness is most likely an indication of the dewetting of the polystyrene film from the silicon surface. Preliminary investigations of ultrathin films of polystyrene (i.e., $h_0 < 100$ Å) of molecular weights 184000 and 1447000 also display the same contraction and expansion behavior (i.e., approximately 10 Å of contraction followed by expansion). Additionally a commercially available broad molecular weight distribution polystyrene sample also produced thin films in which the same contraction/expansion behavior was observed [13].

The other two observed regimes did not display a large increase in the interfacial diffuseness in the temperature range investigated. The films with initial film thicknesses of 264 and 833 Å display little change with temperature until approximately 60 °C, where they begin to expand. Once again this is well below the bulk glass transition temperature of 104 °C. In the last case, the films with initial thicknesses of 100, 155, and 216 Å exhibit a decrease in film thickness as the temperature is increased from 30 °C until a minimum thickness is reached at a temperature of 60–80 °C. The magnitude of the observed thickness contraction is smaller than in the case of the very thin films. The temperature of minimum thickness increases with decreasing initial film thickness. Further increasing the temperature beyond these thickness minima results in film expansion, eventually leading to thicknesses at high temperatures which are larger than the initial thickness. Interestingly, for both of these cases, the polystyrene films display nearly the same rate of thermal expansion at high temperature as the bulk polymer, as can be seen in Table I. The changes in dimensionless thickness with temperature for these five cases has an average value of 4.35×10^{-4} K^{-1}, which is of the same order of magnitude as the reported value of $(5\text{–}6) \times 10^{-4}$ K^{-1} reported for bulk polystyrene [11]. In both of these cases there does not appear to be any dewetting of the polystyrene film from the silicon surface, since the observed x-ray reflectivity profiles remain sharp over the full temperature range (data not shown).

TABLE I. The calculated thermal expansion coefficients are given for five ultrathin polystyrene films on Si. The temperature range in the second column was used to determine the thermal expansion, since plots of the dimensionless thickness versus temperature were linear over this regime. The thermal expansion coefficient was determined from the slope of these plots.

Initial film thickness (Å)	Temperature range (°C)	Thermal expansion coefficient (K^{-1})
833	100–121	4.21×10^{-4}
264.3	106–131	4.46×10^{-4}
216.6	102–140	4.30×10^{-4}
155.1	98–139	4.77×10^{-4}
100.4	105–150	4.32×10^{-4}

The contraction and expansion of the ultrathin polystyrene films is thermally reversible, as can be observed in Fig. 3. A very thin polystyrene film, $h_0=45.2$ Å, was heated from 30 to 80 °C in approximately 10 °C increments. The film contracted from 45.2 to 39.3 Å during this temperature cycle. After cooling the film back to 27 °C, the thickness returned to 47.4 Å. The film was again heated incrementally to 80 °C, and very similar contraction behavior was observed in the second cycle, with $h=39.7$ Å at 80 °C. It should be noted that films were first annealed at approximately 90 °C, which typically lies in the temperature minima for the thin films. The annealing process and the reproducibility of the contraction phenomena are indications that this is not an artifact of the spin-coating process.

In this work, density variations of the ultrathin polystyrene films have not been determined, since the density changes of thin films are best observed as variations in the critical angle. In our x-ray reflectivity data, however, there are no readily observable changes in the data at low Q_z near the critical edge. This behavior is not surprising since the x-ray scattering length density of Si, $Q_c^2=10.4\times10^{-4}$ Å^{-2}, is significantly larger than that of polystyrene, $Q_c^2=4.8\times10^{-4}$ Å^{-2}, and therefore dominates the reflectivity behavior at low Q_z. Neutron reflectivity is a more sensitive technique for determining density changes of polymer thin films with temperature since, if one uses deuterated polystyrene, the contrast between the polymer and silicon will favor the determination of the deuterated polystyrene density. Deuterated polystyrene has a Q_c^2 value of 3.25×10^{-4} Å^{-2} versus 1.06×10^{-4} Å^{-2} for Si.

Recent preliminary investigations of ultrathin deuterated polystyrene films on Si via neutron reflectivity reveal film contraction and a corresponding increase in film density upon contraction [13]. An ultrathin deuterated polystyrene film was determined to have a thickness of 51.0 Å at 30 °C and a neutron scattering length (Q_c^2) of 3.05×10^{-4} Å^{-2}. After heating the deuterated polystyrene film to 80 °C the thickness decreased to 45.3 Å while Q_c^2 increased to 3.37×10^{-4} Å^{-2}. A film contraction of 11.2% corresponded to an increase in density of 10.5%, which indicates mass is conserved.

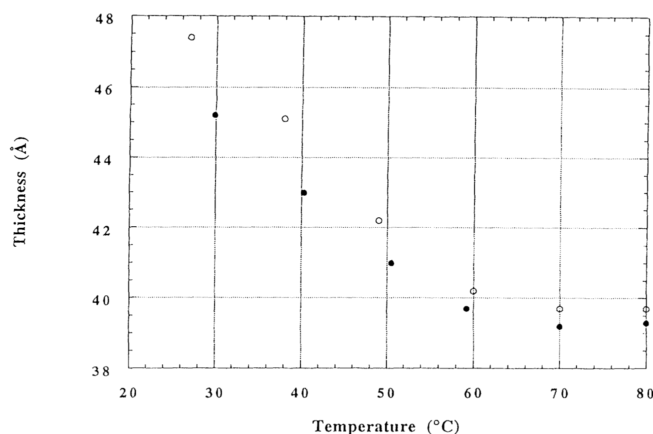

FIG. 3. The reproducibility of the observed contraction or "shrinking" phenomena. An ultrathin polystyrene film was annealed and then subsequently heated incrementally to 80 °C, cooled, and reheated to 80 °C. The two heating cycles are denoted as follows: (●) the first heating cycle and (○) the second heating cycle.

The initial value of Q_c^2 is less than that found for deuterated polystyrene in the bulk. For very thin films of deuterated polystyrene and polymethylmethacrylate the densities determined by neutron reflectivity measurements (at 30 °C) are typically less than those of the bulk polymer with the film density decreasing with decreasing film thickness [13]. The low density of the thin films relative to the bulk polystyrene density may account for their ability to display such significant contraction with increasing temperature. This reduced density should also lead to a decrease in the observed glass transition temperature. The observed conservation of mass in these preliminary neutron reflectivity measurements indicates that the x-ray reflectivity measurements, which highlight changes in film thickness, most likely correspond to appropriate changes in density as well.

The complex nature of the contraction/expansion phenomena is apparent in light of the following two observations. First we have seen that the relative decrease in polymer film thickness increases with decreasing initial thickness. Second, the temperature of minimum thickness increases with decreasing initial film thickness. These trends are indicative of a coupled phenomenon: the densification of the interfaces and the expansion of any "bulklike" polymer which may be present in the ultrathin film. Most likely it is the interfacial properties which dominate the observed contraction or "shrinking" behavior, especially in the ultrathin films which are 100 Å or less in their initial thicknesses. Ultrathin films should be very anisotropic in their structure, bordered as

they are by a solid surface and a free vacuum surface. This anisotropic structure is most likely responsible for the unusual temperature dependent morphology observed here.

No existing models for either the polymer-vacuum or polymer-solid interface predict contraction of polymer thin films with increasing temperature. One possible way to account for this decrease in thickness may be with a variable density polymer melt modeling approach similar to that used by Theodorou [3]. The variable density model allows for the existence of voids within the polymer melt. It should be noted, however, that this modeling approach does not account for the effect of the bond constraints on the polymer conformations near a surface. The addition of bond constraints may lead to a temperature dependent interfacial density profile thickness. One can envision a scenario in which, as the temperature increases, the rotation about the monomer-monomer bonds also increases with at least an initial increase in the polymer density near the interfaces (and a concurrent decrease in the film thickness) due to chain access to an increased number of conformations, therefore reducing the concentration of voids near the interface. Eventually the increased monomer-monomer interactions dominate the energetics, leading to a decrease in the polymer density and a subsequent increase in the polymer film thickness. The two competing effects would be especially prevalent for the thinnest films, which have an initial thickness which is less than the unperturbed dimension of the polymer chain in the bulk. If this segment rearrangement is the cause of the observed contraction, the phenomena should be independent of the polymer molecular weight. The observation of essentially the same contraction phenomena in ultrathin polystyrene films comprised of different polymer molecular weights indicates that the observed behavior is independent of molecular weight. Therefore the relevant length scale may be the persistence or statistical segment length. Further investigations of ultrathin films comprised of other polymers should prove relevant to discerning the influence of the persistence length on the observed contraction phenomena.

The temperature dependent thickness of ultrathin polystyrene films on Si substrates was investigated. The contraction of ultrathin polymer films (i.e., initial film thicknesses less than or equal to the unperturbed radius of gyration of the chains in the bulk) was observed for the first time to the authors' knowledge. This contraction ranged from 0%–17% depending on the initial film thickness, and occurred at temperatures well below the reported bulk polystyrene glass transition temperature. At higher temperatures, the contraction of the polymer films was followed by expansion at a rate similar to that reported for bulk polystyrene.

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