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Communications to the Editor

Film Thickness Dependent Thermal Expansion in Ultrathin Poly(methyl methacrylate) Films on Silicon

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The morphological behavior of ultrathin polymer films at solid interfaces is of fundamental importance to a large number of technological applications such as electronic packaging, dielectric layers, coatings, composites, lubrication, and biocompatible materials. Thermal stability is a major issue in many of these technologies since many applications involve large degrees of thermal variation and cycling. The importance of providing stable surfaces and interfaces will only increase as films become ever thinner with the concurrent miniaturization of devices. In most cases the minimum requirements are to achieve near homogeneity, uniform film thickness, and high durability.

Recently, considerable theoretical and experimental progress has been made in describing polymer molecules in contact with surfaces and interfaces.[1–4] Much of the experimental work has involved polymer–polymer interfaces.[2,3] Despite much theoretical attention over the years to polymer molecules in contact with solid nonpolymeric substrates,[4] experimental results on single-component polymer thin films have been obtained only fairly recently.[5–13] Fernandez *et. al.*[5] studied spun-cast deuterated poly(methyl methacrylate) (d-PMMA) thin films by neutron reflectometry and observed an increase in the density of ultrathin (<1000 Å) films of 6% above the bulk value. This observation of an increased thin film density is in contrast with the observations of the current authors, who have only observed a decrease in density for thin d-PMMA films. Much of the previous experimental work has been reviewed fairly recently by Stamm and co-workers.[6]

Recently many efforts have focused on ultrathin polystyrene films on solid substrates and their subsequent dewetting behavior.[7–11] Dewetting studies of polystyrene by optical phase microscopy,[7,8] X-ray reflectivity,[9,10] and atomic force microscopy[11] have shown the influence of both the surface treatment and the film thickness on the observed dewetting behavior. These authors have observed dewetting to occur for film thicknesses which are both smaller and larger than the unperturbed dimension of the constituent polystyrene molecules. Reiter[7–10] interprets dewetting which occurs below the bulk glass transition temperature to be evidence of a reduced glass transition temperature for polystyrene confined to thin films. The authors of the current report have performed an extensive study of the behavior of polystyrene ultrathin films on sulfuric acid cleaned Si(111) substrates at various temperatures *in vacuo*.[12] The surface of the acid-cleaned Si substrates is most likely covered with SiOH. The most interesting observation during this study was a decrease in the polystyrene film thickness, *h*, with increasing temperature for the case of very thin films (on the order of the polymer radius of gyration or less). This decrease in thickness occurred even at temperatures of ~30 °C, which is an indication that the glass transition temperature of these ultrathin polystyrene films is greatly reduced. Dewetting was observed only for very thin films (<60 Å) at elevated temperatures (*i.e.*, above the bulk glass transition temperature). Films which did not dewet displayed a thermal expansivity above the glass transition temperature which was ~20% less than that for the polymer in bulk. The observed thermal expansivity for polystyrene was *independent* of film thickness. Keddie and co-workers[13] have recently carried out an ellipsometric study of polystyrene ultrathin films on hydrogen-passivated silicon substrates. They have also noted a decrease in glass transition temperature with decreasing film thickness, however, contrary to the observations of the current authors, only increases in film thickness with increasing temperature were observed. In addition to the differing substrate surface composition, another significant difference between these two studies was the fact that one involved measurements conducted *in vacuo*,[12] while the other was conducted on open-air samples.[13] Indeed one of the current authors has observed that ultrathin polystyrene films display thermal contraction only under high-vacuum conditions ($<5 \times 10^{-6}$ Torr).[14] The same films when exposed to the ambient atmosphere only expand with increasing temperature. This phenomenon could be due to dissolved gases or low volatility contaminants. The origin of this observation is currently an area of intense research by the authors and other co-workers.

In this paper the thickness and density changes of ultrathin, deuterated poly(methyl methacrylate), PMMA, films on silicon substrates are considered as a function of temperature. All of the samples were prepared in a consistent and reproducible manner. Initial PMMA film thicknesses of 75–570 Å (at 30–60 °C) are considered in this report. In films of these thicknesses, van der Waals forces should be relevant; thus, it is likely that any observed thermal behavior will be very sensitive to the initial film thicknesses as well as the interaction energies associated with the polymer interfaces.[15]

Deuterated poly(methyl methacrylate) with a polydispersity of 1.10 and a number-average molecular weight of 135 000 was synthesized via a group-transfer polymerization method. The polymer is ~57% syndiotactic, 37% atactic, and 6% isotactic. The d-PMMA was spin-cast from redistilled *o*-xylene onto clean Si(111) wafers (Semiconductor Processing Co., Boston, MA)[16] which had been pretreated with a sulfuric acid–No-Chromix solution for at least 12 h, followed by a thorough distilled water rinse. After drying with metha-

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nol and acetone, the wafer was rinsed with *o*-xylene several times prior to spin-casting the d-PMMA film at 2000 rpm. Polymer film thicknesses were controlled by varying the polymer concentration in solution (1–10 mg/mL). Spin-cast d-PMMA films were then annealed at ~90 °C in a vacuum oven to remove any residual *o*-xylene which may have been present. The d-PMMA films were further annealed above the bulk glass transition temperature under high vacuum for several hours to ensure that films were of uniform density and then allowed to slowly cool over several hours under high vacuum to approximately 30–60 °C. The annealing procedure is critical, considering that spin-coating under the conditions used here leads to the formation of a layer approximately 45 Å thick of reduced density at the polymer–vacuum interface.[17] After vacuum annealing at temperatures of 110 °C or above, this "fluffy" layer disappeared, resulting in an ultrathin d-PMMA film without surface structure.[17]

Following the annealing procedures, the ultrathin d-PMMA films were characterized in high vacuum by neutron reflectrometry[18] (BT-7 and NG-7 reflectometers, Research Reactor and Cold Neutron Research Facility, NIST) *in situ*. The temperature was electronically controlled within 0.2 °C of the desired setpoint and the d-PMMA films were maintained at the desired temperature for approximately 1 h before the neutron reflectometry measurements were performed. Modeling and fitting of the neutron reflectivity data were performed by nonlinear least-squares fitting of profiles generated using a recursive multilayer method.[19] Previous work has established that there is a 15–25 Å thick oxide layer on the as-prepared Si surfaces, regardless of their crystal orientation. However, during data modeling the resulting "best" fits were insensitive to the thickness of this thin oxide film, so samples were modeled as two phases, silicon and polymer, with diffuse interfaces. Specular reflection of neutrons allows one to measure the neutron scattering length profile perpendicular to a surface. Under the assumption of a single, homogeneous polymer film on a silicon substrate, neutron reflectometry allows the determination of the polymer film thickness, the polymer neutron scattering length density, and the diffuseness of the profile at the polymer–vacuum and polymer–silicon interfaces.[18] The authors chose to utilize a single film model as it is the simplest applicable model for the system under consideration here. No other density profile models have been considered by the authors in this report. In this paper the emphasis is on the temperature dependence of film thickness and density. The interfacial widths of the density profiles observed here are essentially independent of film thickness and temperature for all of the samples considered in this report. Typical neutron reflectivity scans of one film taken at several temperatures are shown in Figure 1. The film thickness is *inversely* proportional to the distance between minima (maxima), while the film density is derived from fitting the magnitude of these peaks, since peak height varies with the neutron scattering length contrast between the film and substrate.[18]

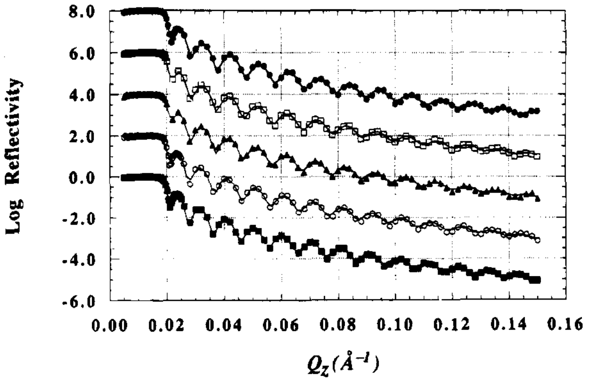

Figure 1. Specular reflectivity profiles and their corresponding modeled fits (solid lines) measured for an ultrathin deuterated poly(methyl methacrylate) (d-PMMA) film at various temperatures. The thickness changes are readily apparent here. The temperatures and measured thicknesses are denoted as follows: (●) 30 °C and 571.5 Å; (□) 90 °C and 577.5 Å; (▲) 120 °C and 580.5 Å; (○) 145 °C and 589.6 Å; (■) 170 °C and 596.8 Å.

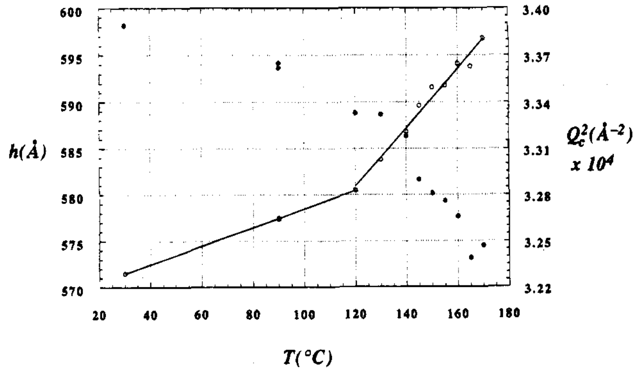

Figure 2. Film thickness, h, and the square of the film critical wavevector (*i.e.*, neutron scattering length density, see text), Q_c^2, measured for an ultrathin deuterated PMMA (d-PMMA) film with varying temperature. The solid curves are the best fit of $h = h(T_0)\exp\{\beta_h(T - T_0)\}$ in the two observed thermal expansivity regimes. The corroboration of the thickness and density changes is apparent for the d-PMMA film considered here.

The increase in film thickness with increasing temperature is readily apparent in Figure 1 where one can observe a decrease in distance between the interference fringes (*i.e.*, the consecutive minima) with increasing temperature. As for the case of bulk polymer samples, the rate of the magnitude of PMMA thin film thermal expansion depends on the temperature range under consideration, that is whether the observations are made below or above the glass transition temperature. This can be observed in Figure 2, where the film thickness, h, is plotted as a function of temperature for a film which is 580.5 Å in thickness at 120 °C. Above the bulk glass transition temperature (which is ~115 °C for this polymer sample), there is an increase in the rate of expansion.

A clear indication of the efficacy of this measurement procedure is that the mass is conserved during the expansion of the d-PMMA ultrathin films. To illustrate this, film densities were determined by fitting the reflectivity data and are also plotted as a function of temperature in Figure 2. By the convention utilized here, density is described by the square of the critical wavevector magnitude, Q_c, which is proportional to the neutron scattering length density by $Q_c^2 = 16\pi\rho_s$. As the d-PMMA film thickness increases, its neutron scattering length density, and therefore its mass density, decreases. The most rapid changes take place when the temperature exceeds 120 °C, which is near the measured PMMA bulk glass transition temperature of 115 °C determined by differential scanning calorimetry. Mass conservation holds for all of the film thicknesses studied. A good indicator of this is the product of the film thickness and the density. In Figure 3 the

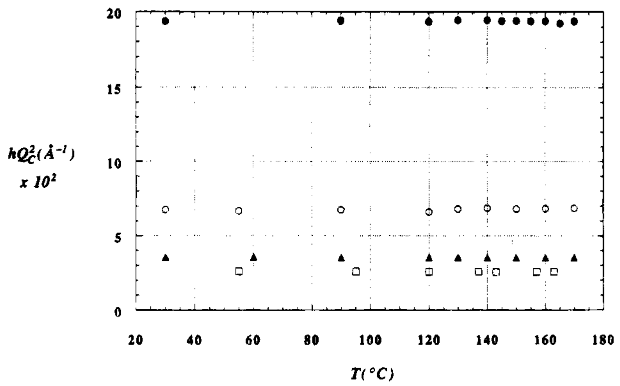

Figure 3. Product of the film thickness and the square of the film critical wavevector measured with varying temperature for all four ultrathin deuterated PMMA films considered in this report. The conservation of mass in all four d-PMMA ultrathin films is indicated by the essentially constant value of the considered product. This is also indicative of negligible in-plane expansion (*i.e.*, parallel to the solid substrate), since $hQ_c^2\ \partial A/\partial T + A\ \partial(hQ_c^2)/\partial T = 0$ (where A is the area of the film) and this figure indicates that $\partial(hQ_c^2)/\partial T = 0$. Therefore, $\partial A/\partial T = 0$.

Table 1. Calculated Thermal Expansivity Values below and above the Glass Transition Temperature (~120 °C) Given for Four Ultrathin d-PMMA Films of Varying Thickness on Silicon Substrates[a]

$h\|_{T=120\ °C}$	$1/h\ \partial h/\partial T\|_{T<120\ °C}$ ($\times 10^{-4}$ K^{-1})	$1/h\ \partial h/\partial T\|_{T>120\ °C}$ ($\times 10^{-4}$ K^{-1})
75.7	1.09	4.44
105.9	1.33	4.58
212.4	1.26	5.21
580.5	1.73	5.40
bulk PMMA	2.225–2.70	5.6–5.8

[a] The thermal expansivity values were determined from linear least-squares fits to the two regimes of data in Figure 2. Note the trend of decreasing thermal expansivity with decreasing film thickness, both below and above the glass transition temperature.

product (hQ_c^2) for films with thicknesses of 76, 106, 212, and 581 Å at 120 °C is essentially independent of temperature. Therefore, the measured film expansion is self-consistent with the density determination. Perhaps more interestingly, this formulation of mass conservation implies that there is no detectable expansion parallel to the solid substrate. This observation confirms what one would expect for the system under consideration. Below the glass transition temperature in-plane thermal expansion is excluded due to mechanical considerations, while above the glass transition temperature this is a result of fluid flow phenomena.

As noted above, the thermal expansion behavior of d-PMMA thin films consists of two regimes; one below the glass transition temperature of ~115 °C and the other above it. By assuming that the volume expansion is in the thickness direction (*i.e.*, perpendicular to the Si substrate) the film thickness expansivity, β_h, is defined as $\beta_h = 1/h\ \partial h/\partial T$ where T is the temperature. The excellent agreement between the data and the fits of β_h is obvious in Figure 2. The calculated thickness expansivities for all the d-PMMA ultrathin films considered here are listed in Table 1. Clearly there is a trend of decreasing expansivity with decreasing film thickness, both below and above 120 °C. A continuum mechanics analysis of these data reveals that the Poisson's ratios for the 580.5 Å film are 0.35 and 0.48 below and above the glass transition temperature, respectively, which indicates that at this thickness the thin film displays the same mechanical properties as the bulk material. The thinner films display deviations from the bulk material behavior. This observation makes sense considering that PMMA should interact favorably with the silicon substrate, and it may corroborate an earlier observation about the possible influence of van der Waals forces on the behavior of ultrathin polymer films on solid substrates. It is interesting to conjecture about the role of the surface interactions and geometric confinement on the film thermal expansivity, considering that the values of β_h listed in Table 1 for PMMA thin films are less than the (3D) bulk value reported in the literature. However, for ultrathin polystyrene films on silicon substrates conflicting behavior has been observed. For polystyrene films *in vacuo* the current authors[12] found that thermal expansion above the glass transition temperature was also less than the bulk value; however, it was found to be independent of the film thickness. Keddie *et al.*[13] have observed an increase in thermal expansion with decreasing film thickness for polystyrene films on hydrogen-passivated silicon substrates. They also measured a decrease in glass transition temperature for decreasing film thickness, which is in agreement with observations of enhanced chain mobility in ultrathin polystyrene films.[7–12] Recently, Keddie and co-workers[20] have reported an increase in PMMA glass transition temperature with decreasing film thickness for thin films on silicon substrates similar to those considered here. There are indications that an increase in glass transition temperature with decreasing PMMA film thickness is also occurring in the films studied here. However, due to a lack of detailed data in the glass transition region this result cannot be definitively confirmed at this time.

To these author's knowledge there are no existing models which predict the thermal properties, as well as the dewetting behavior, of ultrathin polymer films on solid substrates. Especially pertinent is the influence of the polymer–solid substrate interaction on these properties, considering the somewhat conflicting results found by several groups for the case of polystyrene films on silicon substrates which had undergone various surface treatments.[7–13] It is apparent that polystyrene thin films on silicon substrates display chain mobility well below the bulk glass transition temperature.[7–13] Presumably, van der Waals forces should dominate the solid–polymer interactions for ultrathin polystyrene films on silicon substrates, while for d-PMMA polar forces will predominate. The influence of the free surface and geometric confinement effects will also have to be considered in any theoretical treatment of ultrathin polymer films. The length scale over which these various processes influence the ultrathin film behavior should be particularly relevant in light of the fact that both the dewetting behavior and the thermal expansion of ultrathin polymer films are dependent on the film thickness.[7–13]

Keddie *et al.*[13] speculate that the thermal behavior they observed for ultrathin polystyrene films on hydrogen-passivated Si(111) substrates may be due to the existence of a region of enhanced mobility at the free surface of the film. Their positioning of this mobile layer at the free surface is based on molecular dynamics simulations[21] which indicate that the polymer–solid interface is on the order of only two chain segments in thickness. Therefore, it is assumed by Keddie and coworkers that polymer–substrate interactions do not strongly influence the behavior of thin polymer films.

This assumption of a more mobile region allows them to predict the thermal behavior they observed. The decrease in thermal expansion with decreasing d-PMMA film thickness observed here seems to suggest that some other mechanism is influencing the behavior of ultrathin d-PMMA films. If one were to assume that polymer–substrate interactions were important, and for PMMA–SiO_2 interfaces favorable polar interactions should be present, in a manner analogous to Keddie *et al.*, it could be hypothesized that a region with an elevated glass transition temperature exists near the PMMA–SiO_2 interface. This assumption would explain the decrease in the thermal expansion with decreasing thickness below the glass transition temperature. However, it should also lead to an elevation of the glass transition temperature with decreasing thickness which, while it has not been definitively observed here, has been observed by Keddie *et al.*[20] for a very similar PMMA–silicon system. Unfortunately, because of time constraints due to the use of neutron reflectrometry in this study, it was not feasible to obtain extensive data in the region of the glass transition temperature. A more thorough study of the glass transition region utilizing X-ray reflectivity is being conducted and will be reported upon in due time.

The temperature dependence of the thicknesses and densities of ultrathin deuterated PMMA films under high vacuum on Si(111) substrates was investigated via neutron reflectometry *in situ*. The increase in film thickness, and concurrent decrease in film density, with increasing temperature in such ultrathin d-PMMA films was observed directly for the first time to these author's knowledge. The degree of thermal expansion observed here differs below and above the approximate glass transition of the polymer, just as in the case of bulk polymer, with the degree of thermal expansion decreasing with decreasing film thickness both below and above the glass transition temperature. There also appears to be an increase in the glass transition temperature with decreasing film thickness. Unfortunately, due to inadequate data in the glass transition region this cannot be definitively demonstrated at the present time. These observations suggest that polymer–surface interactions have an influence on the thermal properties of ultrathin polymer films. Future work will focus on the effects of solid substrate surface treatments on these observed phenomena.

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