The Effects of Thin Films Confinement on Polymer Viscosity and Thermal Nanoimprint Lithography Patterning

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Nanoimprint lithography (NIL) is a next generation lithography (NGL) with the potential to realize many emerging technologies with smaller scales compared with conventional lithography. One of the primary differences from conventional lithography is that NIL utilizes a mechanical squeeze-flow mechanism to force the resist material to fill the mold. This requires inducing polymer flow in thin films and into nanoscale spaces. It is well known from the polymer thin film literature that many of the fundamental properties of polymeric materials begin to deviate from their bulk values when the film thickness drops below approximately 50 nm. These are precisely the same length scales that become relevant for NIL when trying to imprint features on the order of 20 nm or smaller. By necessity one needs to work with extremely thin resist films to minimize the ratio of the residual layer thickness to the pattern height to facilitate robust pattern transfer. However, there are many reports of how viscoelasticity, diffusion, and other transport properties slow down in thin polymer films. These results suggest that NIL mold filling process might become more difficult in thin polymer films and nanoscale mold cavities. In this presentation we present evidence in support of this notion.

At a previous EIPBN meeting, we presented initial results suggesting that the viscous flow processes can be significantly retarded in thin polymer films, making it more difficult to induce flow into the mold. These initial measurements provided quantitative evidence that polymer flow is impeded when the resist film thickness drops below 50 nm. In this presentation we explore this observation in greater detail. It is well known that the zero shear viscosity of an entangled polymer melt increases exponential with molecular mass. In this presentation we quantify the resistance of several thin polystyrene films, ranging from (10 to 160) nm in the initial film thickness, to fill the cavities of an NIL mold for several different molecular masses ranging from (100 to 1500) kg/mol using the thermal form of NIL. Concepts of time-temperature superposition are used to compare the known viscoelastic response of the polymer to its ability to fill the mold cavity by performing imprints at NIL temperatures of (Tg+20, Tg+30, Tg+40 and Tg+60) °C. We also provide evidence, as seen by inelastic neutron scattering, for the reduced molecular mobility in these thin polymer films. We quantify a strong reduction in the thermally induced mean square atomic fluctuations of hydrogen atoms in the polymer chain and relate this reduced molecular motion an increased viscosity in the thin film state.
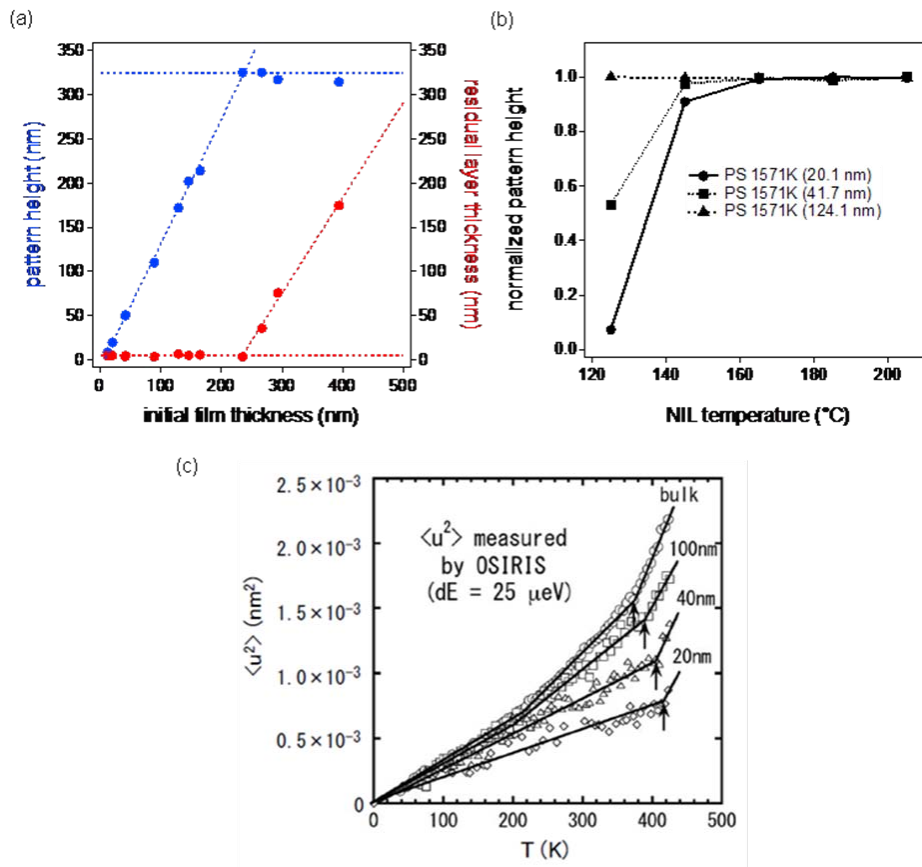
Figure 1. (a) Specular X-ray reflectivity is used to quantify pattern height and residual layer thickness for a series of line-space patterns imprinted into polystyrene films where the initial film thickness is varied. When the initial film thickness is insufficient for complete mold filling, a finite residual layer thickness of approximately 10 nm is still observed. (b) In this figure the evolution of the full pattern heights, taking into account both the incomplete and complete mold filling regimes, are shown as a function of temperature. The pattern heights have been normalized to one at their highest imprint temperatures for each film thickness. In this representation one can clearly see the evidence for reduced polymer flow at low temperatures in the films with the thinner initial thickness; the film must be heated to higher temperature to induce complete filling. (c) This figure shows a strong reduction in the mean-square displacement $<u^2>$, i.e., the thermal fluctuations of the atoms in the polymer, evaluated in inelastic neutron scattering measurement.[1] These reduce polymer dynamics with decreasing film thickness are quantitatively consistent with an increase in the effective viscosity of the thin polymer film.

[1] R. Inoue, T. Kanaya, K. Nishida, I. Tsukushi, M. T. F. Telling, B. J. Gabrys, M. Tyagi, C. Soles, W.-l. Wu, *Phys. Rev. E.* **80**, 031802 (2009)