Exceptional Thermal Stability of Thermoplastic Polymer Nanostructures Patterned by Nanoimprint

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In thermal nanoimprint, thermoplastic polymers are shaped into patterns by polymer flow under pressure at a temperature above the glass transition temperature (T_g) of the polymer. It is well known that nanoimprinted thermoplastic polymer micro- and nanostructures are not stable and pattern decay due to internal stress relaxation can occur at a temperature close to or even below the polymer's T_g[1] . Such thermo instability negatively impacts the applications of thermoplastic polymer micro- and nanostructures patterned by nanoimprint. In this work, we report that shallow nanostructures of thermoplastic polycarbonate have exceptional thermal stability on chromium layer even at temperatures well above the T_g of polycarbonate.

We experimentally examined the thermal stability of polycarbonate pillars of sub-50 nm in size. The sample was prepared by spin-coating of 50 nm polycarbonate (M_w 36,000) on 40 nm chromium layer, which was evaporated on Si wafer. Polycarbonate resist (T_g=154 ^oC) was imprinted by Si mold with holes of 50 nm in diameter and 100 nm in depth at 220 ^oC and 5 MPa. Oxygen RIE was applied to remove the residual layer and to control the final height of the pillar patterns (Fig. 1(a)). The height of the pillars was around 35 nm. The polycarbonate pillar patterns were annealed at 300 ^oC (Fig. 1(b)), which is well above its T_g, for various time periods. The pattern morphology was characterized by SEM and the corresponding statistical data of pillar diameters from a random area were shown in Fig. 2. It is clearly observed that the polycarbonate patterns exhibited unusual stability at temperatures well above its T_g. For the same polycarbonate pillars with a height greater than 50 nm, we observed significant diameter increase due to pattern relaxation. The drastic thermal behavior differences of the polycarbonate structures below and above 50 nm thick is ascribed to strong chain entanglement in sub-50 nm thick polycarbonate film, which results in very sluggish chain movement to maintain structural stability.

One application of the thermal stability of shallow polymer micro- and nanostructure is to determine the end point for polymer reflows. Polymer reflow is a simple technique to modify feature size and shape after initial patterning and to reduce surface roughness. Because polymer reflow process is nonlinear in time domain, it is difficult to control the final pattern size by polymer reflow. To demonstrate end point control through polymer pattern stability, polycarbonate resist was patterned by Si grating mold with 700 nm pitch and 57% duty cycle (Fig. 3(a)). Residual layer was removed by oxygen RIE and the final thickness of the grating patterns was controlled by RIE time. Thermal annealing was carried out at 200 ^oC for 30 min. It was observed that although the polycarbonate gratings spread on chromium surface at the early stage, they finally ended up with a film thickness of ~ 35 nm regardless the annealing time. The final pattern size after the reflow can be determined by the initial height of the polycarbonate gratings. The trench widths between the polycarbonate ridges are 120 nm (Fig. 3(c)) and 220 nm Fig. 3(d) with initial thickness of 110 nm and 70 nm, respectively. The details of the polycarbonate nanostructure stability and its applications will be discussed.

References

[1]R. L. Jones, T. Hu, C. L. Soles, E. K. Lin, R. M. Reano, S. W. Pang, and D. M. Casa, Nano Lett. **6**, 1723 (2006).

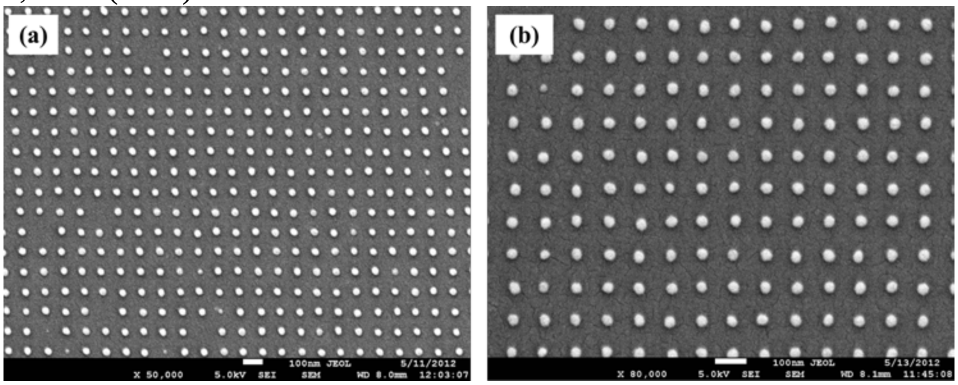

Figure 1. (a) polycarbonate pillars without thermal annealing and (b) polycarbonate pillars with 300 °C thermal annealing for 30 min.

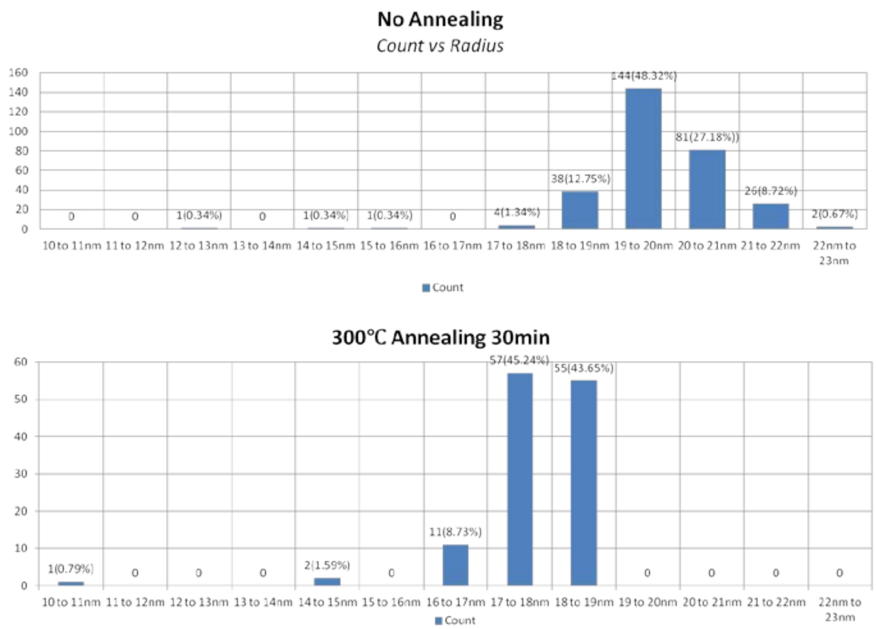

Figure 2. Statistical distribution of polycarbonate pillar diameters: no annealing on the top and 30 min 300 °C annealing on the bottom.

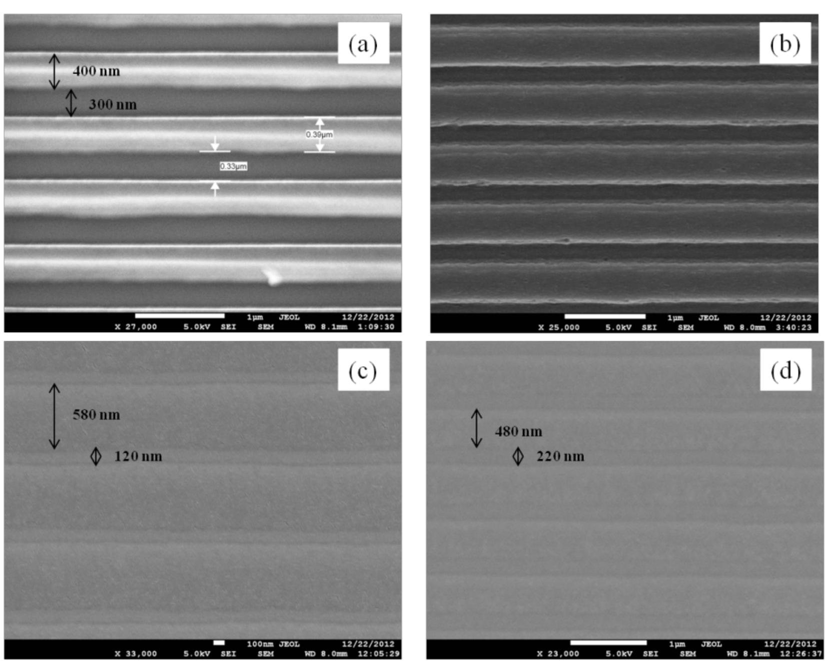

Figure 3. (a) Si grating mold with 700 nm pitch and 57% duty cycle; (b) polycarbonate gratings patterned by the Si grating mold in (a); (c) polycarbonate gratings after 200 °C annealing for 30 min, the initial thickness before annealing is 110 nm; and (d) polycarbonate gratings after 200 °C annealing for 30 min, the initial thickness before annealing is 70 nm.