Step-and-Repeat Thermal Nanoimprint for Functional Polymers

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In recently years, the need for low-cost and high-throughput nanopatterning has stimulated the quick-paced development of the nanoimprint lithography (NIL) technique. According to the process schemes, NIL can be classified into two types: thermal NIL[1] and ultraviolet NIL (UV-NIL)[2]. UV-NIL has gained more attention, particularly for commercial nanofabrication, than thermal NIL because it can be implemented in a step-and-repeat fashion (e.g. Step-and-Flash Imprint Lithography) for nanopatterning over a large substrate with low-cost and high-throughput. Such step-and-repeat mechanism cannot be implemented in thermal NIL because subsequent NIL process will inevitably destroy the nanostructures formed in preceding nanoimprints by heating. Since thermal NIL is gaining increasing attention in direct patterning of functional polymers for novel applications[3], it is highly desirable to achieve the step-and-repeat capability in thermal NIL over large surface areas.

In this work, we demonstrate that step-and-repeat thermal NIL can be achieved in thermoplastic functional polymers with low yield stress. The principle is based on that a polymer with low yield stress can deform under a pressure before reaching its glass transition (T_g) temperature. It is thus possible to perform nanoimprint at a temperature below T_g on the same substrate many times in a step-and-repeat fashion without destroying the patterns formed in preceding nanoimprints. Regioregular poly(3-hexylthiophene) (P3HT), a widely used conjugated polymer for polymer electronics, is a polymer that has the mechanical property suitable for step-and-repeat thermal NIL. P3HT solution in dichlorobenzene (20mg/ml) was first spin-coated on a Si wafer to achieve a film thickness of 200 nm. A Si grating mold with 700 nm periodicity and 50% duty cycle was coated with 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FDTS) for easy mold releasing after NIL. The nanoimprint process was carried out at 120^{o}C with a pressure of 5 MPa. After separating the mold from the substrate, the mold was moved to an adjacent area on the same substrate to perform the next nanoimprint. Because the heating temperature is below the T_g of P3HT, it will not damage the pattern formed in the preceding steps. The P3HT gratings nanoimprinted in the first and second times are shown in Fig. 1. Polarized absorption spectra of the P3HT gratings shown very small differences (Fig. 2), indicating minimal structural change, in P3HT gratings formed in the 1st and the 2nd nanoimprints. Details on the step-and-repeat thermal NIL in polymers with low yield stress, such as the number of repeating steps that can be achieved, will be presented. The step-and-repeat thermal NIL is expected to have significant impacts on applications that require low-cost nanostructures over large surface areas, such as nanostructured polymer surfaces for superhydrophobic properties and nanoscale-ordered bulk heterojunction structures in polymer solar cells.

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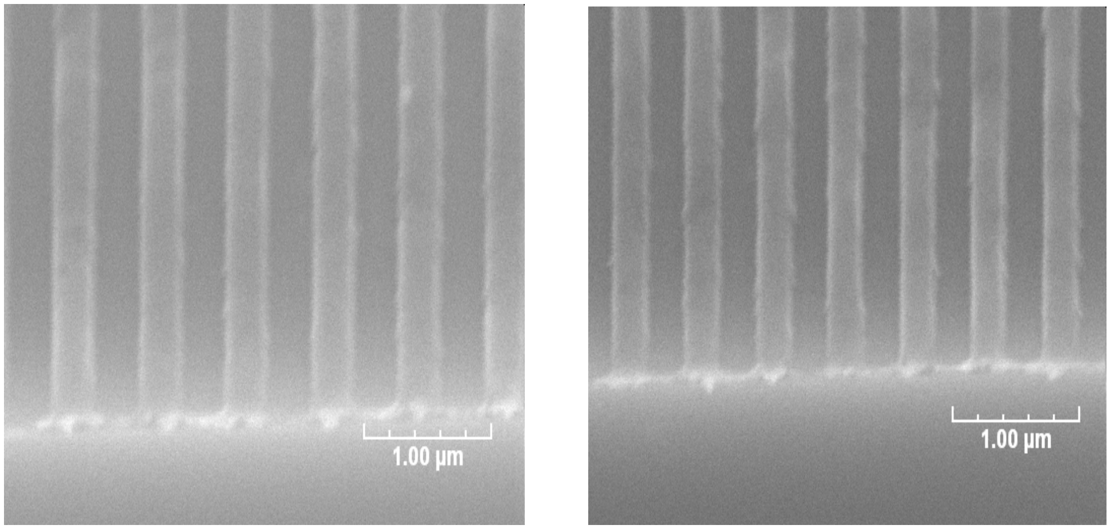

Figure 1. SEM pictures of P3HT gratings formed in (a) the first nanoimprint and (b) the second nanoimprint.

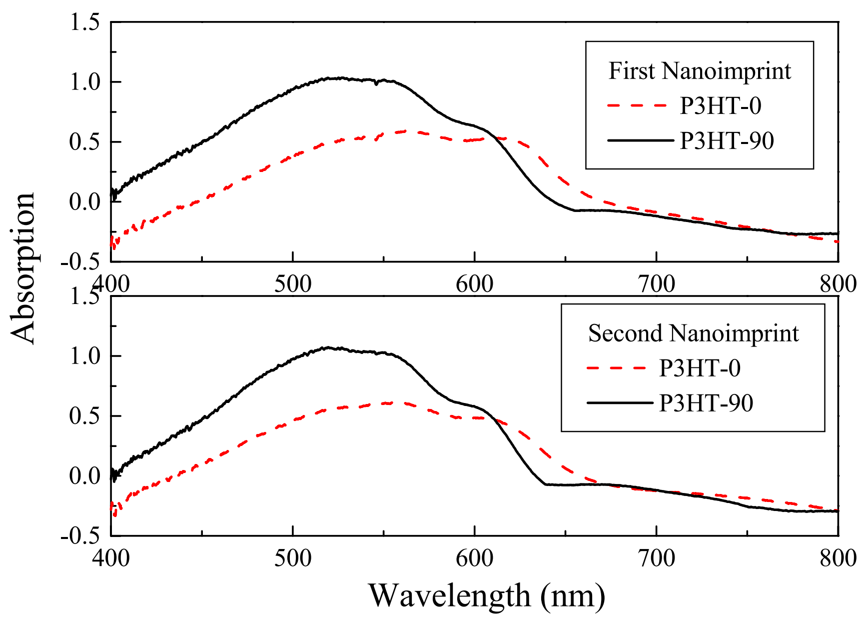

Figure 2. Polarized absorption spectra of P3HT gratings formed in the 1st and 2nd nanoimprints. Due to chain orientation in nanoimprinted P3HT structures, the pattern exhibit difference in absorption spectra when excited by light with different polarization directions. Dark solid lines are absorption spectra of P3HT gratings when incident light is polarized perpendicular (90^{o}) to grating lines, while red dashed lines correspond to the case when incident light is polarized parallel (0^{o}) to the grating lines.