Effect of Nanoimprint on Crystallization in Polymer Thin Film

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Though nanoimprint on amorphous thermoplastic polymers such as poly(methyl methacrylate) and polycarbonate has been well studied, the effect of nanoimprint on the properties of crystalline and semi-crystalline polymer thin films remains unexplored. It is well known that crystalline and semi-crystalline polymers experience flow-induced crystallization during thermal processing. When patterning those polymer thin films into micro- and nanostructures by nanoimprint, chain ordering is expected due to pressure-driven polymer melt flow. In this work, we examine the polymer chain crystallization during nanoimprint and its effect on the physical, particularly optical, properties of the patterned structures.

Polyvinylidene fluoride (PVDF) is a piezoelectric polymer that can form chain-ordered structures. PVDF thin film on silicon substrate is prepared by spin-coating from solutions in hexamethylphosphoramide solvent. After soft-baking, the PVDF thin film is amorphous. The mold for nanoimprint was fabricated by photolithography and reactive ion etching from thermally grown silicon oxide. Nanoimprint on PVDF thin film was carried out at 200^{o}C and 5 MPa. Patterns of various sizes were created in PVDF thin film by forced polymer melt flow during nanoimprint. PVDF chain ordering gives rise to optical birefringence in patterned structures, while amorphous PVDF structures remain optically isotropic. Polarized microscopy, a well-studied and widely used technique for studying birefringence in mineral crystals, is used to directly observe crystallization in PVDF patterns after nanoimprint. Micrographs were taken with Zeiss Axiophot microscope under polarized-light illumination. Images of nanoimprinted structures with analyzer inserted show characteristic interference patterns that result from birefringence in structures (figure 1). Detailed observation on different patterns and patterns of different sizes show distinctive optical properties (figure 2). Those differences are linked to the polymer flow in the formation of each structure during nanoimprint. It is thus possible to control the chain ordering by carefully designing the geometry of the patterns.

The ordering of polymer chains during nanoimprint has significant impact on the application of polymers in micro- and nanofabricated devices and systems, particularly functional polymers such as organic semiconductors, optically non-linear and piezoelectric polymers. Chain ordering can induce or enhance desired properties of the functional polymers. Nanoimprint is a much easier and simpler way than other actively pursued methods to achieve chain-ordering. Coupled with its inherent advantages such as high resolution, low-cost and high-throughput, nanoimprint can open the door towards wide-spread incorporation of functional polymers into micro- and nanofabricated devices and systems. The phenomena observed in this work also have important implications on passive components made from crystalline or semi-crystalline polymers by embossing because of the induced optical birefringence. It is the purpose of this work to shed some light into polymer chain ordering in nanoimprint and outline its potential applications.

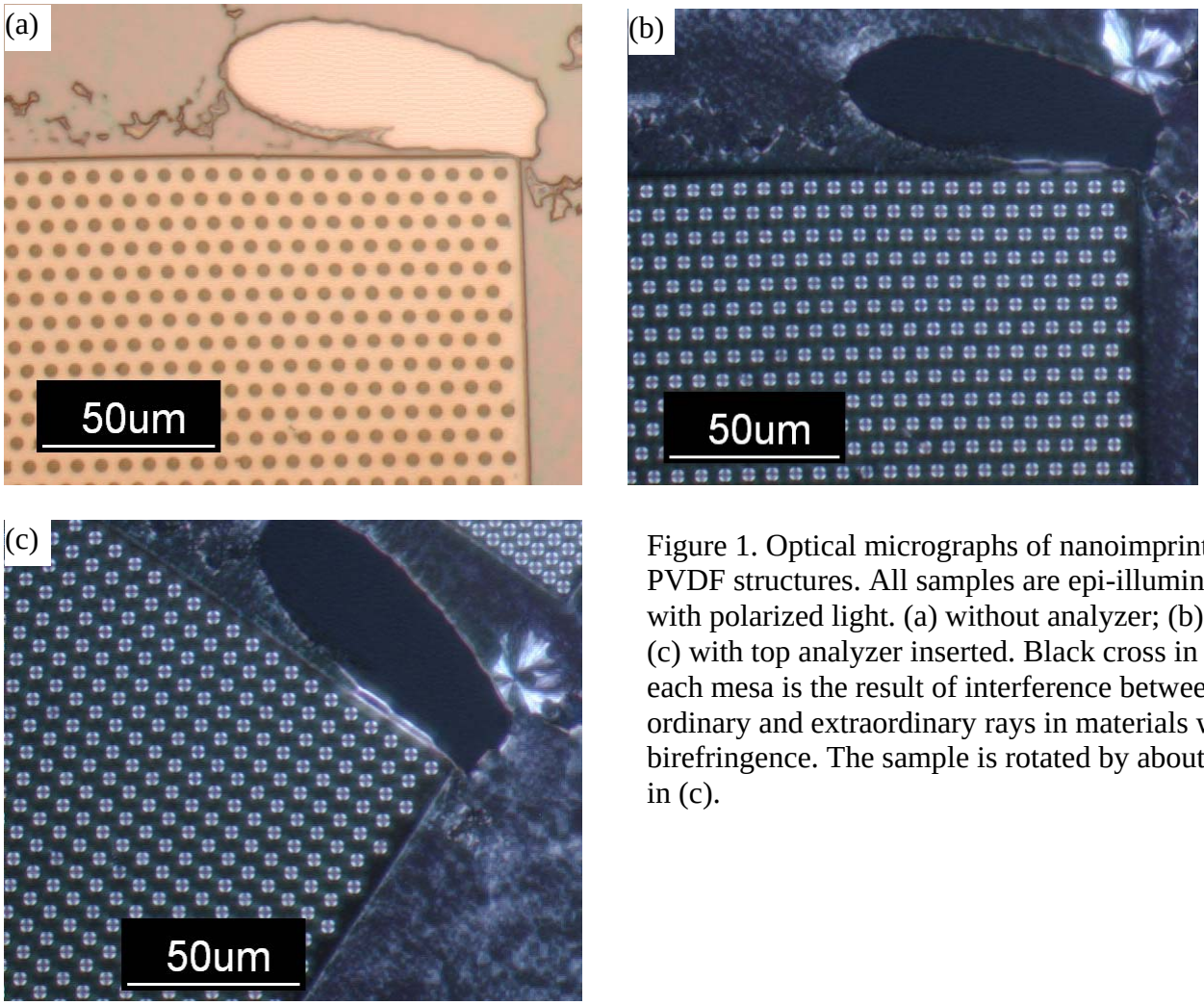

Figure 1. Optical micrographs of nanoimprinted PVDF structures. All samples are epi-illuminated with polarized light. (a) without analyzer; (b) and (c) with top analyzer inserted. Black cross in each mesa is the result of interference between ordinary and extraordinary rays in materials with birefringence. The sample is rotated by about 45^{o} in (c).

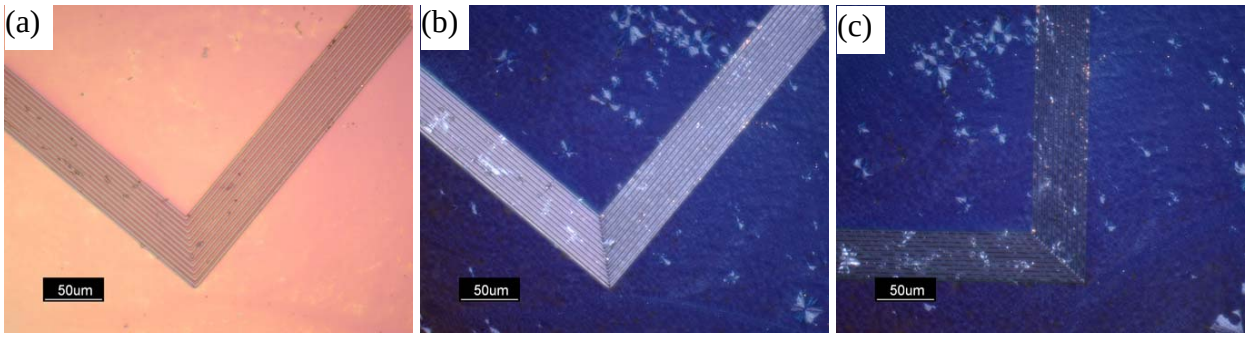

Figure 2. Optical micrographs of nanoimprinted PVDF structures. (a) without analyzer; (b) with analyzer inserted; (c) with analyzer inserted. Sample is rotated by about 45^{o} with respect to (b).