A Raman spectroscopic study of polymer chain conformation after nanoimprint

Dehu Cui and Xing Cheng
Department of Electrical and Computer Engineering
Texas A&M University, College station, TX 77843-3128

Nanoimprint is a high-resolution, high-throughput and low-cost patterning technique for soft materials. Recently, we observed ubiquitous chain ordering in nanoimprinted polymer micro- and nanostructures by polarizing microscopy. Since the physical properties of polymers are usually affected by their chain configuration, this opens a route for fine-tuning polymer properties by nanoimprint. The polymer chain orientation during nanoimprint may originate from multiple factors including flow-induced chain alignment, polymer chain conforming to mold surface and polymer crystallization in micro- and nanostructures.

In this paper, we use polarized Raman spectroscopy to investigate polymer chain conformation in nanoimprinted polymer microstructures. Poly(methyl methacrylate) (PMMA) solution in toluene (5 wt %) was spin-coated on 100 nm thick silver on Si wafer to achieve a film thickness of 200 nm. Si grating mold with 700 nm period and 50% duty cycle was coated with 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FDTS) for easy mold releasing after nanoimprint. The nanoimprint was carried out at 120^{o}C, 150^{o}C and 180^{o}C, with a pressure of 50 kN/cm^{2}. Polarized Raman spectra were recorded with 633 nm HeNe laser. The Raman spectra of PMMA gratings of 15k and 75k molecular weight after nanoimprinting at various temperature and processing time are shown in Fig. 1 and 2. The Raman peaks at about 813 and 990 cm^{-1} are assigned to the μ_s(C--O---C) and (α-CH_3)[1] modes. It is found that shorter processing time and lower nanoimprint temperature increase the ratio of the two peaks. The Raman spectra of 75k PMMA nanoimprinted at 150^{o}C with different processing times are shown in Fig.2. Compared to the 15k PMMA, it is found that higher molecular weight sample exhibits greater polarization ratio. A systematic investigation on how nanoimprint processing parameters such as nanoimprint temperature and processing time impact polymer chain conformation will be presented. Because polymer properties depend on chain conformation, nanoimprint opens up an easy route toward manipulating polymer properties in addition to polymer patterning.

Reference

[1] H. A. Willis, M. V. J. I. Zichy and P. J. Hendra, *Polymer*, 7, 737-746, 1969.

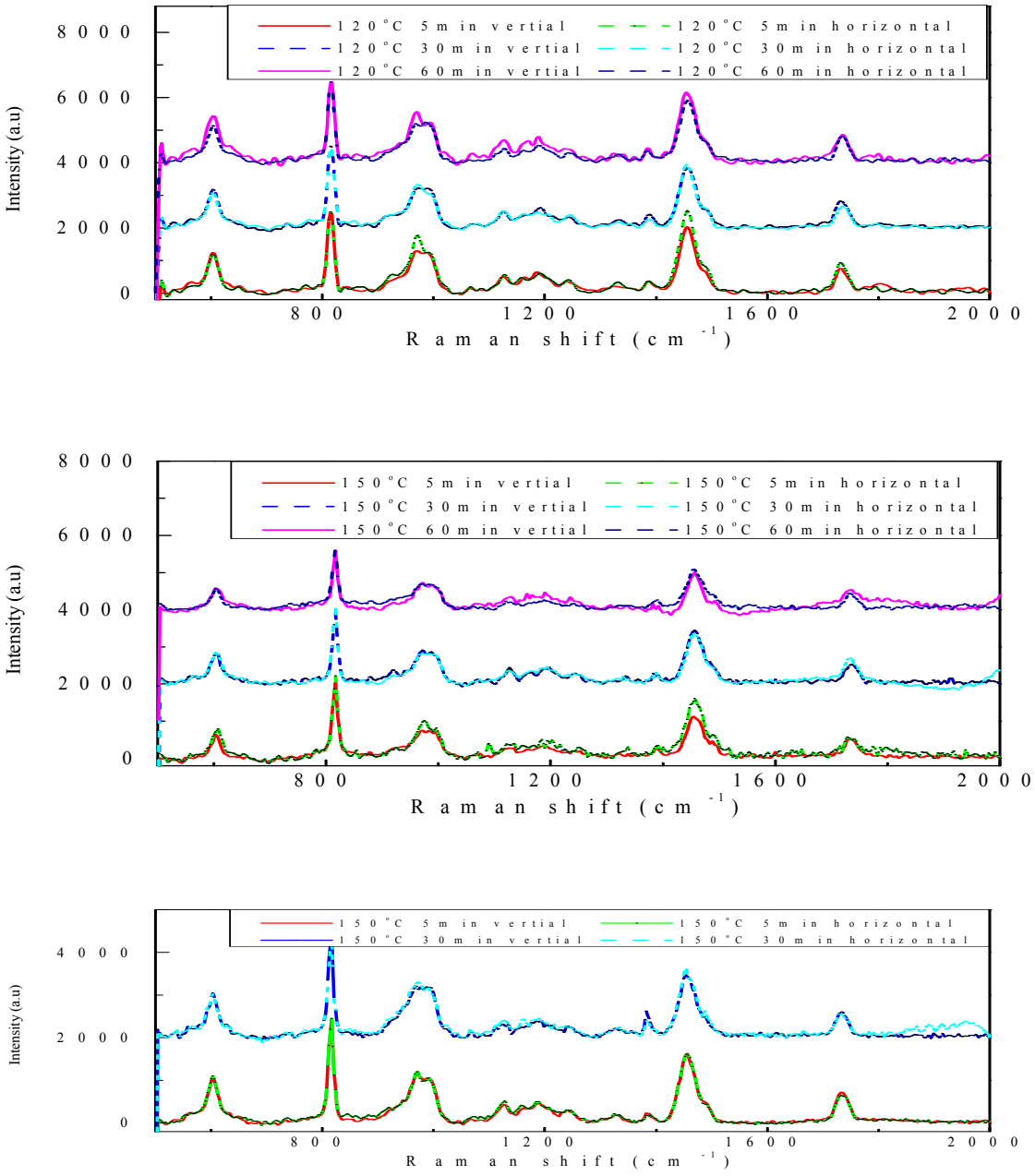

Figure 1 Polarized Raman spectra of 15k PMMA nanoimprinted at 120°C, 150°C, 180°C

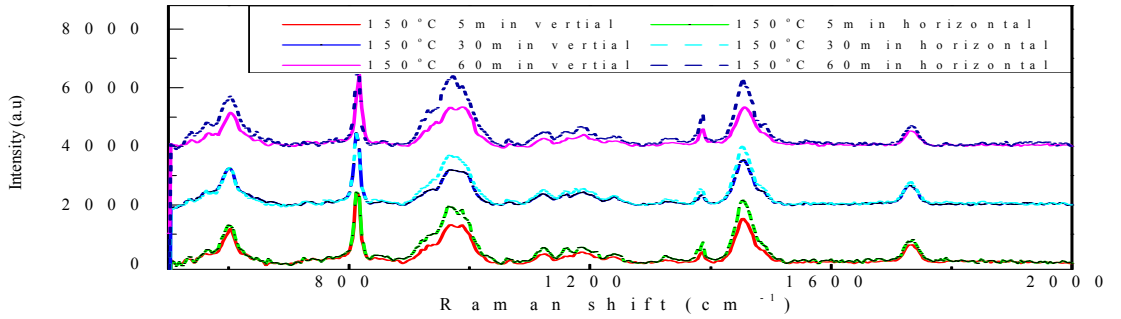

Figure 2 Polarized Raman spectra of 75k PMMA nanoimprinted at 150°C.