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# The Effect of Crystallinity on Materials Removal Rate of Polyolefins During $Ga^+$ Focused Ion Beam Nanomachining

K.C. Wong,[1,2] A.D. Batchelor,[1,2] C.M. Balik[2] and D.P. Griffis[1,2]

[1]Analytical Instrumentation Facility, North Carolina State University, Campus Box 7531 Room 318 EGRC, 2410 Campus Shore Dr., Raleigh, NC 27695
[2]Department of Materials Science and Engineering, North Carolina State University, Campus Box 7907, Raleigh, NC 27695-7907

The development of optimized focused ion beam (FIB) nanomachining methodologies is essential to the advancement of FIB for characterization polymeric materials. The ability to examine the topographical and morphological properties of polymeric materials can provide significant insight into their functional properties. Recently, a FIB in situ technique was developed for revealing and imaging the cross sectional morphology of the polymeric components in a bicomponent polymeric fiber with the island-in-the-sea (I/S) structure [1]. This technique exploits the topographical contrast generated as a result of differential sputtering. When combined with the high surface specificity and high signal-to-noise ratio obtained using $Ga^+$ FIB induced secondary electron (ISE) imaging, the capability of FIB technology to provide a useful approach for efficient characterization of the cross-sectional morphology of bicomponent polymeric fibers was demonstrated without any sample pretreatment. While the utility of FIB nanomachining and ISE imaging was demonstrated for two specific bicomponent polymer systems, harnessing the full potential of nanomachining and differential sputtering to reveal morphology hinges on the ability to optimize FIB sputtering conditions for different polymeric systems. Sputtering of polymers is likely a complex process dependent on both the polymer's properties and FIB beam parameters [2,3]. Of all the polymer properties, crystallinity influences many of the polymer mechanical properties such as hardness. To gain a better understanding of the process of the nanomachining of polymers, the fundamental relationships between material removal rate and dose for polymers having different cystallinities were investigated.

Two technologically important polyolefins, linear low density polyethylene (LLDPE; Dow Chemical Company, USA) and isotactic polypropylene (PP; Product CP360H, Sunoco Chemicals Polymers Division, USA), were investigated in this study. Polymer beads of LLDPE and PP were melted at 140°C and 180°C, respectively, in an oven (Model 280A, Fisher Scientific, USA) under argon gas flow. Polymers beads were melted between two pieces of Si to form the polymer into a film having a smooth surface. The polymer melt films were then quenched in a commercial freezer to -15°C. Subsequent thermal annealing of each polymer was carried out at 115°C and 125°C for LLDPE and PP, respectively, for different time intervals to produce different levels of crystallinity. The crystallinity of the annealed polymer samples was measured using a SmartLab x-ray diffractometer (XRD) and quantified with the SmartLab Guidance software (Rigaku Americas, USA). A Quanta 200 3D DualBeam FIB/SEM system (FEI Company, USA) with a 30kV $Ga^+$ beam was used for all sputtering experiments. To determine the material removal rate for each polymer sample, 5µm x 5µm and 10µm x 10µm craters were sputtered into the respective polymer films under various experimental conditions. Craters were sputtered by scanning the $Ga^+$ beam in a serpentine pattern at normal incidence using nominal beam currents ranging from 0.1 to 5 nA $Ga^+$ with the sputter time varied to maintain a constant total dose (up to $2nC/\mu m^2$ or $1.2x10^{18} ions/cm^2$).

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The sputtered craters (see example in Figure 1) were scanned with a Digital Instruments D3000 atomic force microscope and the crater depths were measured using the NanoScope software ( Bruker AXS Inc., USA). Material removal rates were then calculated based on the calculated crater volume divided by the $Ga^+$ dose required to remove that volume. The material removal rates and other nanomachining effects such as topography generation for LLDPE and PP having different cystallinities were studied both with and without the use of $H_2O$ for material removal rate enhancement. Preliminary results based on sputtering experiments on LLDPE and PP at their minimum and maximum crystallinities, appear to show that the sputter rate decreases with increasing crystallinity for both polymers (Figure 2) when sputtered with a Ga+ FIB beam at 30kV with beam current between 270pA to 1140pA.

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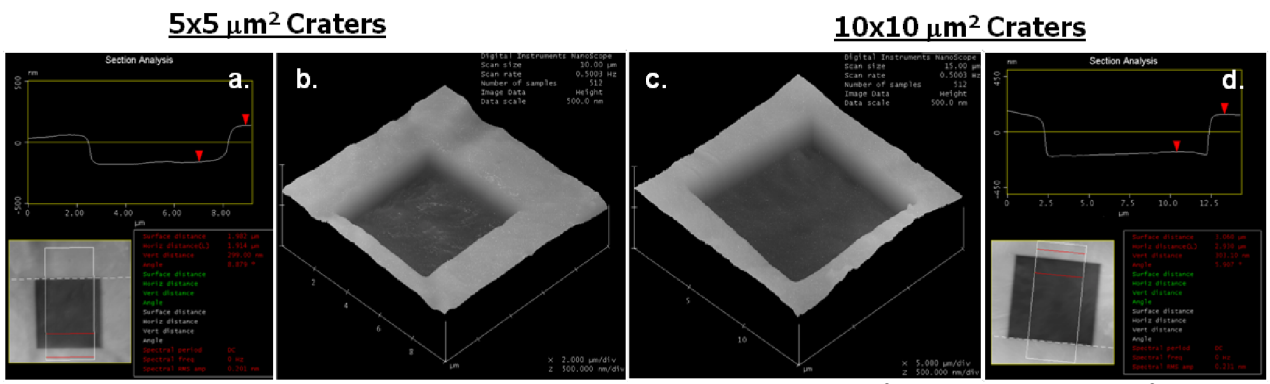


**Figure 1.** AFM micrographs revealing the topography of (b) 5x5$\mu m^2$ and a (c) 10x10$\mu m^2$ craters in LLDPE. These example craters were sputtered by a 30kV $Ga^+$ FIB beam at a beam current of 270pA. The total dose used was kept constant at 1nC/$\mu m^2$ ($6.2x10^{17}$ions/$cm^2$) for both craters. After acquiring the AFM images, depth measurements were made using the NanoScope III software (a,d).

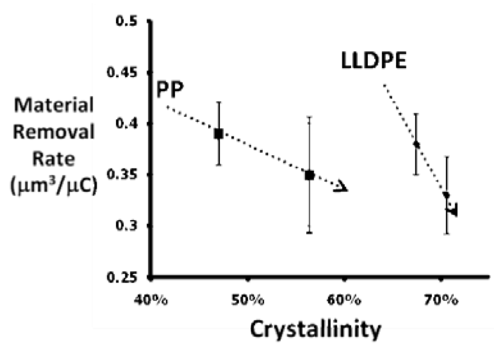


**Figure 2.** An apparent inverse correlation between the material removal rate and crystallinity for linear low density polyethylene (LLDPE) and polypropylene (PP) was observed (additional data will be presented to confirm). Craters were sputtered with a 30kV $Ga^+$ FIB beam with beam currents of 270pA, 630pA, and 1140pA while maintaining a constant dose of 1nC/$\mu m^2$ ($6.2x10^{17}$ions/$cm^2$) for all craters.

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