SUMMARY

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Ion Beam Surface Modification

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The following summary represents the essential details of a two-year study on the practical applications and mechanisms of polymer sputtering via Argon ion impact. Two publications are in preparation and will constitute the final report.

There are several motivations for scientific study into the mechanisms of ion beam sputtering. In this work, a primary motivation was the potential to modify the properties of polymer surfaces to improve their adherence, durability, biocompatibility, or other desirable properties. The results benefit those who wish to use ion beam milling as an analytical tool (to obtain composition versus depth information): changes in chemistry and topography induced by the ion beam must be separated from the sample characteristics. Also, it turns out that ion impact from a directed ion gun source specifically etches polymer structures according to their morphologies, therefore this technique may be useful to study unknown or new morphological features. The questions that we sought to answer were related to: (1) the texture that arises on a polymer target after ion impact, (2) the chemistry of the top surface after ion impact, (3) the chemistry of sputtered films of polymeric material deposited on substrates placed adjacent to targets during ion impact, and (4) practical properties of textured polymer targets, specifically the wettability and adhesive bonding properties. In general, the results obtained by x-ray photoelectron spectroscopy and scanning electron microscopy enabled us to explain the wettability and adhesion properties.

The materials originally studied were chosen for their potential in biomaterials applications. During the second year of work additional polymers were chosen for specific morphologies in order to test the hypothetical sputtering mechanisms derived from the first year's work. During the first year, three crystalline polymers - polyethylene, polytetrafluoroethylene, and polyoxymethylene - were textured, as well as two amorphous polymers, polyurethane and polydimethyl silcxane. Sputter deposits of several halocarbons also were studied. During the second year, crystalline polymers Nylon 66 and Mylar (annealed and oriented) were textured. Amorphous polyamide and polyester, along with amorphous polycarbonate, an epoxy network polymer (Epon 828) and a liquid crystalline copolyester completed a wide enough range of composition and structure to allow important generalizations to be made.

Most specimens of ion beam-textured targets were prepared at NASA Lewis Research Center using ion beam thrusters. Relatively low ion energies (<1000 eV), current in the range of 0.1 ma/cm^2, and time periods ranging from minutes to hours, were employed. Most of the XPS spectra were obtained on a Dupont 650B photoelectron spectrometer. Photomicrographs were obtained in an AMR-900 scanning electron microscope. Some studies were carried out in a Perkin Elmer Model 550 ESCA/SAM spectrometer. This instrument allows ion beam sputtering to be performed with the sample in place in the high vacuum for ESCA analysis.

The results can be generalized in several ways. First, the specific functional group chemistry of the polymers appears to have little to do with the topography or texture that develops on the target after sputtering. Morphology (crystalline, amorphous or network) is the controlling factor.

All crystalline polymers developed high aspect ratio cone structures on the surface after sputtering, but none of the amorphous structures produced any cones at all. In all the amorphous polymers, surface defects were sites of rapid etching, independent of chemical composition. The texture that arose was an exaggerated version of the original surface texture. The network polymer did show periodic regions of sputter resistance that may correspond to variations in crosslink density.

The second generalization that can be made is that new chemistry forms in the first atom layer or two (the selvedge layer) of the target after ion impact. This new surface chemistry bears a close resemblance to the chemistry found in the respective sputter deposits. In every case, reduction takes place under the ion beam, leaving the composition depleted in the more electronegative atoms, such as fluorine or oxygen. Undoubtedly, this new chemistry also leads to crosslinking in the target surface and deposits, independent of specific chemical composition.

Particularly good cases in point were identical in chemistry, i.e., Mylar polyester and Nylon polyamide. In those cases specimens were prepared with varying degrees of crystallinity. After sputtering, the size and number of cone structures varied directly with the degree of crystallinity. With the amorphous polymers, original defects in the sample surface were preferentially etched.

Based on these results we have developed the following general model of the process that occurs during polymer sputtering with Argon ions. In the selvedge layer a plasma is created by the ion impact. In this region, a large percentage of the chemical bonds are broken and reformed. During this reorganization new oxidation states may arise by new combinations of the same atoms originally present. However, for the electronegative elements (e.g., oxygen and fluorine) combinations that lead to pairing with a like atom are volatile and escape into the vacuum, leaving the surfaces depleted of electronegative elements. Since the selvedge region gives rise to sputtered particles, it is sensible that the chemical composition of sputter deposits resembles that of the new chemistry that arises in the selvedge layer of the target.

To summarize the basic mechanisms, the microscopic topography that develops is determined by two factors: (1) sputter resistant zones that consist either of crystallites or regions of high crosslink density and (2) the impact angle between the ion beam and the sample surface. In the case of amorphous polymers, the original surface roughness presents varying impact angles to the incoming ions, and this results in the original surface defects being the site of preferential etching on linear amorphous materials. The crosslinked amorphous polymer shows alternating regions with high and low etch rates, producing a patchwork of solid and holes. The crystalline polymers have small centers of sputter resistance that become the points of the cones that arise as regions around the centers of spherulites are preferentially sputtered away. The subsequent effect of decreasing impact angle produces even more rapid sputtering from the region around the center of the crystallite, giving rise to a sharp cone on the surface.

In most cases the wettability of sputtered polymer targets does not change much from its value before sputtering. This appears due to competing effects of increasing surface roughness and chemical reduction. In three cases, dramatic changes in wettability were obtained that can be explained by chemistry and topography determined by XPS and SEM. The wettability of Teflon decreases while that of Delrin and Silastic increases dramatically. In the case of Teflon and Delrin, the effects are caused by the high-surface-area roughness created by sputtering. The changes are dominated by the fact that non-wettable surfaces become even less wettable when roughened (Teflon), while a wettable surface becomes even more wettable when roughened (Delrin). In the case of Silastic, the original surface was rich in methyl groups conferring low wettability. After sputtering silicon-oxygen linkages dominate the top surface, increasing wettability.

It appears that the improvements obtained in adhesive bonding to ion sputtered polymers may result from crosslinking that occurs during the chemical reorganization of the selvedge layer. Evidence for this is the fact that textured Teflon is less wettable, but shows improved bond strength compared to an untreated control. Furthermore, XPS examination of the fracture surfaces showed that much more Teflon transfers to the adhesive surface after fracture than in the textured Teflon case, in spite of the much greater surface area of the latter. This indicates a mechanically stronger surface region in the ion beam sputtered Teflon target.