

Nanotechnological Manufacturing: Nanostructured Polymers Designed for Plasma/Energetic Beam Templating of Materials

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Controlled patterning of materials at the nanoscale will be one of the foundations of nanotechnological manufacturing. The extension of lithographic approaches to nanoscale technology not only involves photolithography, but increasingly organic mask patterns produced using soft lithography, block copolymer self-assembly, and extreme ultraviolet lithographic techniques. In each case an organic film-based image is produced which is subsequently transferred by plasma etching techniques into underlying films/substrates to produce nanoscale materials templates. One of the least understood elements of this approach is the interaction of the plasma species with the organic molecules representing the image, and the chemical, morphological and topographic changes induced by these interactions in the macromolecules themselves and macromolecule-defined nanoscale features. The demand for nanometer scale resolution of image transfer protocols requires understanding and control of plasma/organic mask interactions to a degree that is unprecedented and has not been achieved.

The overall scientific objective of this project is to obtain a fundamental understanding of the atomistic factors that govern chemical and morphological stability of polymer nanostructures in plasma environments used for pattern transfer, and how changes of specific molecular structures and the microscopic parameters of the plasma process (ion composition, ion/neutral ratio, ion energy, etc.) affects this. This understanding will be used to articulate organic imaging material design criteria required for superior chemical and morphological stability of nanoscale features in the plasma environment used for the pattern transfer. This work will establish molecular structure-property relationships of organic materials in the plasma processing environment so that the transfer of nanoscale images to underlayers/substrates is successful. We plan to leverage this scientific understanding for design of organic masking materials that will meet the requirements of nanoscale manufacturing.

This NIRT project brings together an interdisciplinary group of academic and industrial researchers with the expertise and research capabilities in complementary areas required for achieving the above objectives. The NIRT expertise includes design and synthesis of organic imaging materials and soft lithography (Willson, University of Texas, Austin), self-assembly of organic materials and industrial nanostructure fabrication (Alizadeh, GE Global Research), plasma-surface interactions and highly controlled plasma processing of nanoscale structures (Oehrlein, University of Maryland, College Park -UMD), beam-surface interactions and molecular dynamics simulations of plasma/materials interactions (Graves, University of California, Berkeley), and nanoscale materials and nanostructure characterization (Phaneuf, University of Maryland, College Park). Our approach is to use a broad set of model imaging materials and subject these to widely varying plasma and well-defined energetic beam exposure protocols. Comprehensive surface and materials characterization are used to establish the consequences of the exposures, and identify the role of composition and molecular structure in controlling plasma durability of nanostructured polymers. Molecular dynamics simulations are employed to interpret experimental data. Based on the framework of the macromolecular

features required for optimized plasma-durability of organic mask images, new materials will be synthesized that are consistent with the demands of nanotechnological manufacturing.

During the initial period we focused our research efforts to synthesis of various polymeric materials that should have similar plasma durability based upon a widely used model developed by Ohnishi in 1983 [1], and to testing of these in plasma and beam environments. The Ohnishi parameter is defined as the total number of atoms in the monomer over the number of carbon atoms minus the number of oxygen atoms. Ohnishi's model fails for many polymers, and it is one of our objectives to contribute to articulation of an improved model by establishing the behavior of well characterized polymer materials in plasma and beam environments. Figure 1 shows three polystyrene derivatives, which were obtained via anionic polymerizations. These structural isomers have identical Ohnishi parameters. Styrene and 4-methyl styrene (top and bottom at left in Fig. 1) undergo net cross linking when exposed to high energy radiation, whereas, alpha-methyl styrene (middle at left of Fig. 1) undergoes net chain-scissioning. In the right part of Fig. 1 polymers based on alicyclic monomers are shown that have Ohnishi parameter values equal to those of the polymers shown in the left of Fig. 1. Films of these materials were produced by spin-on on silicon wafers. These were plasma processed and also subjected to ion beam exposures.

Plasma processing of these materials showed distinct behavior. Selected results for the styrene-based polymers and adamantane-based polymers (poly(hydroxyadamantyl methacrylate) (HAMA) and

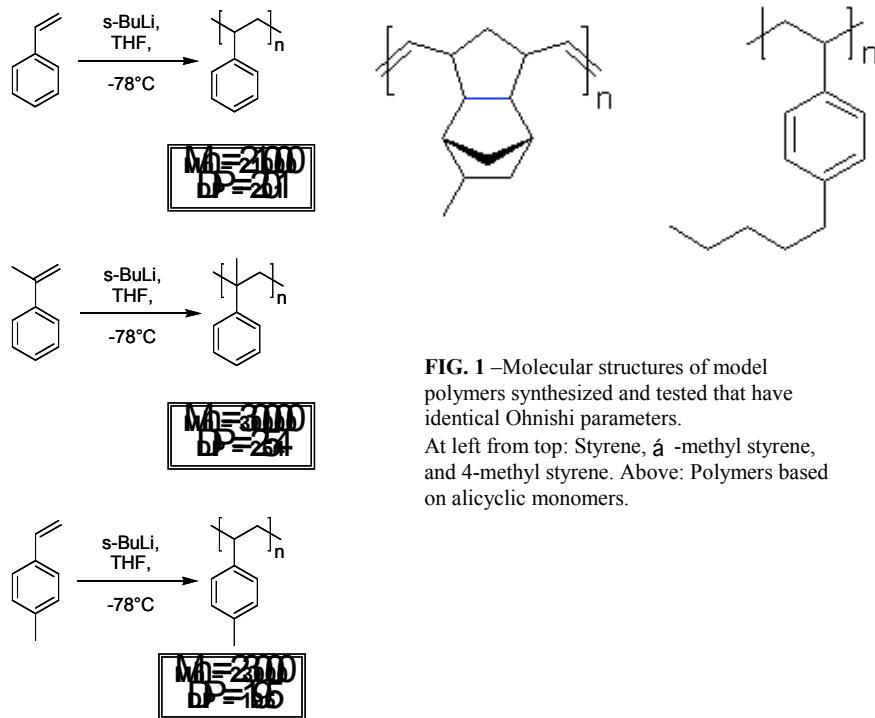


FIG. 1 –Molecular structures of model polymers synthesized and tested that have identical Ohnishi parameters.
 At left from top: Styrene, α -methyl styrene, and 4-methyl styrene. Above: Polymers based on alicyclic monomers.

poly(hydroxyadamantyl acrylate) (HAdA)) are shown in Fig. 2. Fig. 2 (a) displays AFM images after 2 different plasma processing times for 5 polymers, whereas Fig. 2(b) shows the RMS roughness versus time. Our results indicate that the placement of the methyl group on the polymer backbone increases polymer surface

roughening under plasma exposure, e.g. PaMS and HAMA in Fig. 2. On the other hand, PS, P4MS, and HadA show lower etching rates (not shown) and a slower rate of surface roughening. It is known that polymers with a methyl group on their backbone undergo an increased rate of chain scission under radiation compared to polymers without this group, whereas pendant aromatic rings in polymers are prone to crosslinking the polymer under radiation. Current efforts are aimed at establishing the degree of crosslinking induced by plasma or energetic beam exposure for these materials, and linking this to the strong compositional changes seen for the surface regions (hydrogen loss and fluorination for C_4F_8/Ar discharges).

The computational studies have examined the effects of Ar⁺ impacts on polystyrene thin films, and focused on the rapid temporal decrease in sputtering yield, which is observed experimentally. The cause of this drop in yield has been clearly identified as due to dehydrogenation and carbon cross-linking in this region. We also have examined the effects of F addition to this system, which causes an increase in the etch yield.

We conclude that existing models of plasma etching resistance of polymers in plasma environments, e.g. the Ohnishi model, cannot be applied to polymer surface morphology evolution, which is an important figure of merit for nanoscale manufacturing processes. More realistic models need to take into account arrangement of specific groups relative to the main chain, hydrogen content, and neighbor-neighbor interactions, rather than simply polymer stoichiometry.

Our current work is aimed at building actual nanostructures employing the model polymers studied so far using imprint techniques. The goal is to examine the relationship between the observed surface roughness differences and line edge

roughness introduction for nanostructures, and demonstrating the implications of our findings for improved control of 3-D nanostructure fabrication. More complex polymer materials required for a number of advanced lithographic approaches, e.g. containing silicon and oxygen, are also being studied.

1 H. Gokan, S. Esho, and Y. Ohnishi, „Dry Etch Resistance of Organic Materials”, J. Electrochem. Soc. **130**, 143 (1983).

2 For further information on this project contact G. S. Oehrlein at oehrlein@glue.umd.edu