Fluorinated Diamond-Like Carbon Templates for High Resolution Nanoimprint Lithography

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Although the most popular materials for nanoimprint lithography (NIL) templates are currently oxidized silicon and quartz, diamond-like carbon (DLC) grown on silicon substrates has been introduced recently as an interesting and promising alternative[1]. Among the advantages of DLC are its mechanical strength, low surface energy and its ability to be etched in oxygen-based plasmas. However, the surface energy of DLC, while relatively low (~ 40 mJ/m^2), is not quite low enough for robust anti-adhesion and anti-wear, which are essential for successful template-substrate separation at the end of the NIL process. Thus, an additional treatment which lowers the DLC surface energy is required.

Surface energy reduction of DLC can be accomplished by several different methods, such as adding a fluorocarbon gas to the plasma mixture during the DLC growth[2] (which compromises the mechanical properties of the film), or by the formation of a fluorinated organic self-assembled monolayer on the DLC surface. In this work we present a method for reducing the surface energy of pre-patterned DLC templates by exposing them to a fluorocarbon based plasma. Detailed surface analysis shows that these films have a thin layer of high fluorine and carbon content which lowers the surface energy significantly.

DLC films grown by PECVD on Si substrates to a thickness of 100 – 200 nm were used. They were exposed to C_4F_8 or CHF_3 plasma, with the chamber pressure in the range of 33 - 88 mTorr and RF power in the range of 100 - 300 W. Null ellipsometry shows a minimal change in the thickness – from a reduction of few nm to the growth of an additional organic film with a thickness of few nm, depending on the process conditions. Water and glycerol contact angle measurements (Fig. 1) are indicative of the high hydrophobicity of the treated surfaces. Surface energies derived from these measurements were in the range of 19 - 25 mJ/m^2. AFM measurements show a small reduction in the RMS surface roughness from 0.72 nm to 0.45 nm. XPS analysis of the treated surfaces shows that the process results in the formation of a very thin (~ 0.5 -2.5 nm, depending on the process conditions) fluorocarbon layer, with a chemical content very close to that of PTFE, and consisted mostly of CF, CF_2 and CF_3 functional groups (Fig. 2).

The scheme of the DLC template fabrication and subsequent NIL process is shown in Fig. 3. NIL templates were fabricated using electron beam lithography with a negative-tone resist (HSQ), followed by reactive ion etching in an O_2 plasma, anti-adhesion plasma treatment (described above) and HSQ mask strip. The templates were used to imprint PMMA (M_w=25kg/mol), with high repeatability and durability. Sub-20 nm features were patterned using these templates (Fig. 4), and pattern transfer was demonstrated using Au/Pd e-beam evaporation through the imprinted mask and lift-off.

In addition to lowering the surface energy of the NIL template, we have found that the plasma fluorination process can be applied to the NIL resist film as well while the template surface (DLC or SiO_2) in this case can be untreated. Similarly, resist films that are used as molds for microcontact printing can be fluorinated for easy separation of the elastomers such as poly(dimethyl siloxane) (PDMS). In general, plasma fluorination provides a fast, simple, robust and reliable treatment for reducing the surface energy in NIL and molding lithography, compared to the traditional methods using fluorinated SAMs.

In this presentation we provide details of the plasma assisted anti-adhesion treatment of NIL templates, fabricated from DLC films on silicon. This work, which represents a new approach toward fabrications of NIL templates, also provides a fundamental study of the chemical and physical properties of the DLC surfaces, as modified by plasma processing.

[1] Ramachandran, S., Tao, L., Lee, T. H., Sant, S., Overzet, L. J., Goeckner, M. J., Kim, M. J., Lee, G. S., Hu, W., *J. Vac. Sci. Technol. B* **2006**. *24(6)*, 2993

[2] M. Hakovirta, D. H. Lee, X. M. He, M. Nastasi, J. *Vac. Sci. Technol.* (A) Vol. 19(3), 2001, pp.782-784

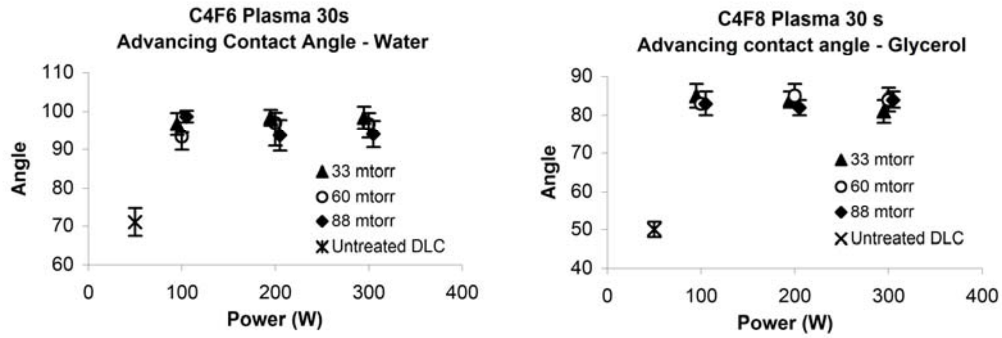

Figure 1. Contact angles of water and glycerol as the function of chamber plasma and applied RF power. The contact angle increases from ~70^o to ~90^o-100^o for water and from ~50^o to 80^o-90^o for glycerol.

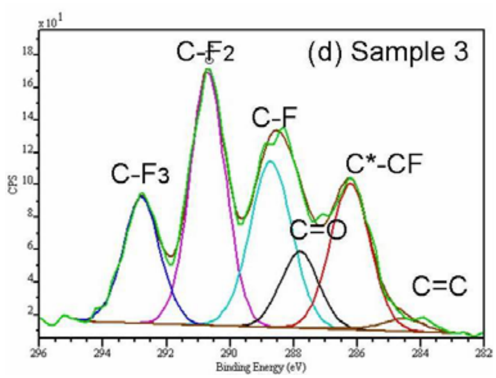

Figure 2. Deconvolution of XPS peaks for the DLC sample, treated with C4F8 plasma at 88mTorr and 100 W RF Power. CF, CF2 and CF3 functional group are dominant on the surface.

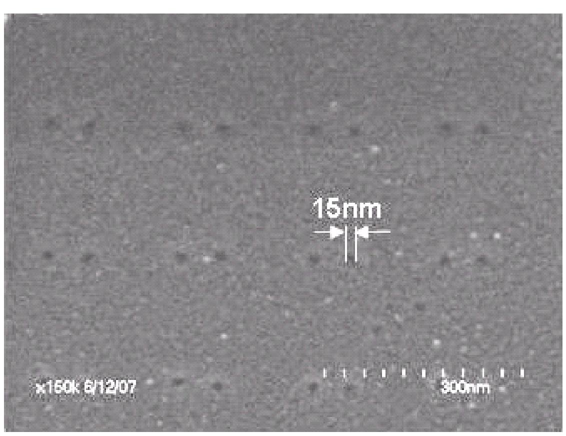

Figure 4. Sub 20nm dots in PMMA resist patterned by NIL with a fluorinated DLC template.

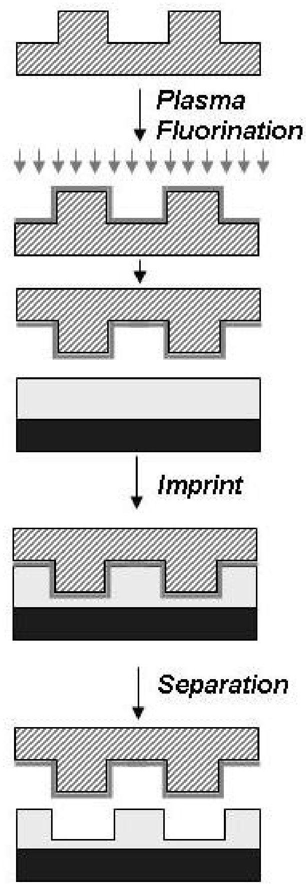

Figure 3. Schematic process flow of the DLC template plasma fluorination and NIL.