Evaluation of Fluorinated Diamond Like Carbon as Antisticking Layer by Scanning Probe Microscopy

Makoto Okada¹, Masayuki Iwasa², Ken-ichiro Nakamatsu¹,³, Noriko Yamada¹, Kazuhiro Kanda¹, Yuichi Haruyama¹, and Shinji Matsui¹

¹Graduate School of Science, LASTI, University of Hyogo, 3-1-2 Koto, Kamigori, Ako, Hyogo 678-1205, Japan
²SII Nanotechnology Inc., RBM Tsukiji Bldg. 2-15-5 Shintomi, Chuo-ku, Tokyo 104-0041, Japan
³JSPS, 6 Ichibancho, Chiyoda-ku, Tokyo 102-8471, Japan

E-mail: m.okada@lasti.u-hyogo.ac.jp

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1. Introduction

Nanoimprint lithography (NIL)¹-³ is a useful technique for fabricating mass nanostructure devices with a high-throughput and a low cost. Nanoimprint lithography molds are in direct contact with replication materials. The NIL molds are therefore coated with an antisticking layer to avoid the adhesion of replication materials. Diamond-like carbon (DLC) has several properties such as high hardness, low friction coefficient, and abrasion resistance. The DLC thin film is mainly used for coating machine parts and several industrial tools by taking advantage of these properties. However, DLC cannot be used as an antisticking layer because it has high surface energy. On the other hand, Fluorinated diamond-like carbon (F-DLC) has attractive properties, such as high hardness and high detachability.

Nakamatsu and Yamada et al. reported that F-DLC can be applied as an antisticking layer in NIL⁴,⁵. A schematic of the demolding process in NIL is shown in Fig. 1. Adsorption occurs between the upper and bottom surfaces of a nanostructure mold and NIL resin. In addition, the sidewalls of the nanostructure mold cause friction with NIL resin during demolding. If the adsorptivity and frictional force between the antisticking layer and resin are low, adhesion between the mold and resin can be avoided. The measurement of adsorptivity and frictional force is therefore important.

![Fig. 1. Schematic demolding process in NIL](communication/journal_of_photopolymer_science_and_technology/21/4/597-599/597.png)

2. Experimental

To compare the nanoscale release effect of
F-DLC with that of DLC, we measured adsorptivity and frictional force of F-DLC and DLC by scanning probe microscopy (SPM).

The F-DLC and DLC thin film were coated on Si wafer by radio-frequency (RF) plasma chemical vapor deposition. To confirm the chemical composition of DLC and F-DLC, X-ray photoelectron spectrum (XPS) measurement was carried out using the conventional photoelectron spectroscopy apparatus, which was mounted with a hemispherical electron energy analyzer (VSWCL150). The Mg Kα line (hν = 1253.6eV), used as X-ray source, was incident at 45° with respect to the surface normal. The total energy resolution was approximately 1.0eV. The base pressure in the photoelectron analysis chamber was 2 × 10⁻⁸Pa.

![Fig. 2. XPS spectra of (a) the wide scan and (b) the C 1s region of the F-DLC and DLC.](image)

3. Results and discussion

Fig. 2(a) and (b) show the XPS spectra of wide scan and C1s region. The intense C 1s peak appeared in the wide scan spectrum of the DLC. On the other hand, the intense F 1s peak was observed in the wide spectrum of the F-DLC, as shown in Fig. 2(a). In the C1 s region spectrum of the DLC, the intense C-C peak appeared. On the other hand, the intense CF3, CF2 and CF peaks are observed in the spectrum of F-DLC, as shown in Fig. 2(b). These results prove that the F-DLC surface is consisted of fluorocarbon.

To evaluate the macroscale release effect of DLC and F-DLC, we measured water contact angle of those using a commercially available contact angle meter (Drop Master 500: Kyowa Interface Co.). Fig. 3(a) and (b) show the water contact angles of DLC and F-DLC. The contact angle of F-DLC is higher than that of DLC. The surface energies of DLC and F-DLC were 45 and 23 mJ/m², respectively, which were calculated from the contact angles of water, formamide, and methylene iodide. The surface energy of the F-DLC was the same as that of Teflon (23 mJ/m²). This result indicates that F-DLC has beneficial macroscale release effect compared to DLC.

![Fig. 3. Water contact angles on (a) DLC and (b) F-DLC.](image)

To examine the nanoscale release effect of F-DLC and DLC, we measured adsorptivity and frictional force by SPM (E-sweep/NanoNavi Station: SII NanoTechnology Inc.) using a Si cantilever. The adsorptivity between substrate and cantilever is obtained from the force curve. The frictional curve from torsional displacement of a cantilever is used to obtain the surface frictional force. We evaluated the frictional force from the difference between the upper and lower sides of the frictional curve. In this measurement, the spring constant of the cantilever was 0.15 N/m. The displacement of the cantilever was about 78 nm when the cantilever was in contact with the substrate. The contact force therefore was about 10 nN. In addition, measuring the adsorptivity and frictional force was performed with air humidity at around 80%.

The adsorptivity of DLC and F-DLC are 6.7 and 3.6 nN, respectively. Figure 4(a) and (b) show the
frictional force of DLC and F-DLC. The adsorptivity of F-DLC was about 0.5 times lower than that of DLC. We assume from XPS measurement result that the low adsorptivity of F-DLC is due to fluorocarbon included in that. However, the frictional force of F-DLC was nearly the same as that of DLC. The frictional force may be affected by both surface energy and surface roughness.

4. Conclusion

In summary, to examine the nanoscale release effect of DLC and F-DLC, we measured the adsorptivity and frictional force of those by SPM and observed the surface of those by AFM. The adsorptivity of F-DLC was lower than that of DLC. On the other hand, the frictional force of F-DLC was nearly the same as that of DLC because the average surface roughness of F-DLC is 2 times higher than that of DLC. These results indicate that the adsorptivity was due to the fluorinated carbon included in F-DLC and the frictional force may be affected by both surface energy and surface roughness.

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References