Nanofabrication of Diamond-like Carbon Templates for Nanoimprint Lithography

L. Tao, S. Ramachandran, C. T. Nelson, T. H. Lee, L. J. Overzet, M. J. Goeckner, M. Kim, G. S. Lee, and W. Hu

Department of Electrical Engineering, University of Texas at Dallas, Richardson, TX, 75083

ABSTRACT

Diamond like carbon (DLC) films were deposited on Si and then patterned to form 40 nm features as nanoimprint templates. A plasma enhanced chemical vapor deposition (PECVD) system with CH₄ precursor was used to deposit DLC films on Si and quartz substrates. These films were then characterized using Raman spectroscopy, atomic force microscopy (AFM), nanoindentation, and contact angle measurement. By varying the RF power and pressure of the PECVD, DLC films with good uniformity, smooth surfaces (<0.2 nm RMS), low surface energy (~40 mJ/m²), and high hardness (~22 GPa) were achieved. Nanoimprint lithography and liftoff process were used to pattern Cr mask on DLC films. An inductively coupled plasma (ICP) etching process was performed with CF₄ to transfer the patterns into the DLC films to form nanostructured template for nanoimprint. Water contact angles on the patterned DLC templates were measured and were stable at about 70° under thermal annealing at 180 °C for more than 12 hours. With these DLC templates, UV and reversal UV nanoimprint lithography were carried out on SU-8 at typical imprint conditions. The fidelity of pattern-transfer was investigated. These experimental results indicate that DLC is an excellent material for nanoimprint templates because of its high wear resistance, robust low surface energy, UV transparency, and ease of patterning.

INTRODUCTION

Nanoimprint lithography (NIL) is basically a pressure induced transfer of topographic patterns from a rigid template into a thermoplastic polymer film heated above its glass transition temperature (T_g), or into UV curable polymers under UV exposure. Fine structures as small as a few nanometers have been fabricated in this way [1]. One of the key challenges of nanoimprint is how to make defect-free templates that offer robust low surface energy for template-substrate separation, long lifetime, and low fabrication cost [2]. However, due to the physical contact during imprinting, the conventional silicon and quartz templates suffer serious wearing damage after a certain number of imprint cycles, which shortens template life time and increases manufacturing cost [3,4]. To alleviate this problem, hard material such as diamond [5] and SiC [6] has been investigated to make high wear resistance templates. But both have major disadvantages: diamond is too expensive and too slow to grow while SiC is not transparent to UV light. In last decades, diamond-like carbon (DLC), a hard amorphous carbon (a-C), or hydrogenated amorphous carbon (a-C:H) [7] has been studied as a protective coating layer. Previously, we have systematically studied the property of DLC films and found it is an ideal material for NIL templates [8]. Here we demonstrate the fabrication of sub-100 nm DLC nanoimprint templates and successful UV and newly developed reversal-UV nanoimprint [9] with these DLC templates on SU-8 resists.

EXPERIMENTS

DLC films were deposited on Si substrates in a capacitively coupled reactor with our own modification of the configuration of electrodes in the previous study [8], which allows the flexible control of most parameters of the plasma enhanced chemical vapor deposition (PECVD) process. Under typical deposition conditions: rf power of 100–450 W resulting in a dc bias between –100 and –400 V, pressure of 30–100 mTorr, and deposition rate of ~10 nm/min, a DLC film layer of ~300 nm was deposited onto the Si substrates using a mixture of argon and methane as a precursor.

After the deposition of DLC films, a series of material characterizations were carried out. Raman spectra were collected at multiple points on a single sample using a Jobin Yvon Labram high resolution micro-Raman spectrometer with laser excitation at 633 nm. The spectra were fitted with disordered peak (D-peak) and graphitic peak (G-peak) to determine the structural property of the DLC films deposited. Surface roughness of the DLC film was measured using contact mode atomic force microscopy (AFM). The hardness and wear testing of the DLC film was measured using a Hysitron nanoindenter 11 (is nanoindenter 11 or nanoindenter 11) with 75 nm wide diamond tips and maximum loads of 100 μN and on the same nanoindenter using a 150 nm diameter diamond tip at normal loads of 40 μN to scan $5 \times 5 \mu\text{m}^2$ areas respectively. Contact angle for DI water and ethylene glycol were measured on a Ramè Hart manual contact angle goniometer to investigate the surface energy of the DLC film. In addition, the annealing effect at 180 °C in vacuum oven for 15 min to 12 hour of the DLC film surface energy on quartz substrate was also studied by measuring the contact angle for DI water.

Nanoimprint lithography and electron beam lithography were performed to generate nanoscale patterns in the PMMA resist that was spincoated on the DLC films. A metal lift-off process was performed to transfer these nanofeatures onto the Cr layer, which is used as a mask for the following ICP reactive ion etching using CF_4 at pressures between 5 and 15 mTorr, bias power of 100 W, and ICP power of 400 W for 1–2 minutes. After etching, the Cr residue was stripped away and DLC NIL templates were evaluated by AFM and SEM. At last, both the conventional UV nanoimprint and reversal UV nanoimprint was performed at 70 °C under 6 MPa for 10 min with 1s UV exposure on SU-8 coated glass substrates. UV light was induced through the glass substrates. Nanostructures on the templates and on the SU-8 layers were imaged using AFM and SEM.

RESULTS AND DISCUSSION

Structural and mechanical properties of the DLC film

The raw Raman spectrum, as shown in Fig.1, confirms that the film structure is similar to that of DLC and the absence of a sloping photoluminescence background confirms that it is closer to diamondlike a-C:H, as opposed to a polymerlike a-C:H [10].

The variations in the fitting parameters (G- and D-peak center positions, their widths and area ratios) that enable one to qualitatively estimate changes in the ratio of sp^3 bonded carbon to sp^2 bonded carbon. These parameters have been studied as functions of PECVD power and

pressure [8]. From the Raman data, these films were rather more diamondlike than graphitic atomic structure in nature.

Figure 1. A typical Raman spectra of the DLC film deposited at 300 W rf power and 50 mTorr chamber fitted with disordered carbon peak (D peak) and graphite peak (G peak).

Mechanical testing measurements indicated that these DLC films ranged from 18 to 23 GPa and that larger deposition powers resulted in harder films. The DLC templates were found to be about 2 times harder than Si (10.6 GPa) and quartz (9.3 GPa). The abrasive wear of DLC films on Si and quartz were investigated. As shown in Fig. 2, DLC films showed wear depths of about 2.00 nm, while the wear depth of quartz was 6.39 nm under the same force load of 40 μ N on a 150 nm diamond tip. The wear resistance of a DLC template is 3 times better than quartz and almost 2 times better than Si.

Figure 2. Topographical *in-situ* AFM image of DLC films on Si (left) and a bare quartz substrate (right) after pin-on-plate wear testing with 40 μ N load on a 150 nm diamond tip.

Surface energy property(maybe properties)

The surface energies of the material used as a template in NIL applications play a crucial role in defining the fidelity of the pattern transfer. Contact angle measurements were performed with water and ethylene glycol on the DLC films, and the polar and dispersive components of the surface energy were calculated using the two-liquid method [11]. The calculated surface energies are shown in Table I, which shows the DLC films have a surface energy of 35–50 mJ/m². CF₄ etching reduced the DLC surface energy from 49 mJ/m² to lower than 40 mJ/m² due to the formation of a thin CF_x(should there be a 4 here) film over the a-C:H film. The thermal annealing of the DLC films deposited with varying PECVD power is studied for its effect on water contact angle, as shown in Fig 3. The water contact angles on the DLC films were not reduced by this thermal annealing process even at 180°C for more than 12 hours. This satisfies the requirements of thermal nanoimprint process.

Table I. Surface energies of DLC films before and after ICP etch.

ICP etch conditions	contact angle (°)		surface energy* ($\gamma = \gamma^d + \gamma^p$) (mJ/m ²)		
	H ₂ O	Ethylene glycol	γ^p	γ^d	γ
Before etch	57.0	52.5	45.8	2.9	48.6
CF ₄ , 20 mTorr	89.5	55.0	1.4	36.6	38.0
CF ₄ , 60 mTorr	90.0	61.0	2.7	28.0	30.7

*Surface energy γ is the sum of γ^d (dispersion component) and γ^p (polar component)

Figure 3. Effect of thermal annealing (180°C) on the water contact angle of the DLC films deposited with varying plasma power (50-150 W).

Fabrication of DLC templates and imprint testing

Nanoimprint lithography and electron beam lithography were used to pattern PMMA. A liftoff process generated Cr nanostructures on the DLC films, which were used as etching masks for an ICP etching process with CF_4 to form nanostructures in the DLC films. The etch rate of DLC was about 100 nm/min. Fig. 4 shows the cross-sectional view of a DLC template with 200 nm lines etched for 2 mins. The RMS roughness of the DLC film before and after the ICP etch was nearly the same ~ 0.1 nm.

Figure 4. The SEM cross sectional view of the DLC mold etched by ICP etch using 30 SCCM CF_4 at 5-15 mTorr for 2 min. This kind of cross section is a benefit to the demolding after the nanoimprint.

UV and reversal UV imprint process were carried out with the patterned DLC template at 70 °C and 6 MPa for 10 min in 300-nm-thick SU-8 on glass substrates with 1s UV exposure (UV was induced through the glass substrates). Fig. 5 shows the AFM images of 40 nm line and space structures on the DLC templates and also UV imprints in SU-8, indicating good fidelity during imprint process.

Figure 5. AFM images of a) the DLC template with ~ 40 nm lines and space and b) SU8 imprinted gratings.

CONCLUSIONS

PECVD Deposition and nanopatterning of DLC films were demonstrated as scratchproof nanoimprint templates that offer robust low surface energy for both thermal and UV nanoimprint processes. In particular, the natural low surface energy of the DLC films allows spincoating of SU-8 on the template for reversal UV imprints [9]. With the DLC templates, reversal UV nanoimprint was used pattern SU-8 gratings with 40 nm linewidth (80 nm pitches) and 100 nm depth.

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