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Ion Beam Synthesis of the Anti-sticking Diamond-like Carbon Layers

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Ion beam deposited hydrogenated undoped as well as SiO_x doped diamond-like carbon (DLC) thin films were deposited and evaluated as anti-adhesive layers. Film surface contact angle with water was investigated as a measure of the surface free energy and anti-sticking properties. Contact angle dependence on the film thickness (7 – 200 nm) and air-annealing resistance in terms of the contact angle with water of the synthesized diamond-like carbon films were investigated. Contact angle of the 9 nm thickness DLC films deposited under appropriate process conditions was the same as one of the thicker (200 nm thickness) DLC films. It is shown, that it is more easy to grow ultra-thin anti-sticking DLC films at lower ion beam energies. It was explained by some ion induced intermixing at the DLC-Si interface. Contact angle with water of the 200 nm thickness DLC films was more sensitive to the air annealing than contact angle of the thinner (24 – 30 nm thickness) DLC films. Surface of the undoped DLC films was smoother than surface of the SiO_x doped DLC thin films. 250 min annealing at 200 °C temperature in air didn't cause any roughening of the undoped DLC film surface. While in the case of the SiO_x doped DLC thin film, decrease of the surface roughness was observed as a result of the air annealing.

Keywords: DLC films, ion beam deposition, contact angle with water, anti-sticking layers.

1. INTRODUCTION

Diamond-like carbon (DLC) films received considerable interest due to the outstanding mechanical and tribological properties as well as chemical inertness and hydrophobicity [1 – 5]. That combination is particularly interesting for possible application of the DLC as a anti-sticking layers in novel lithographic techniques such as nanoimprint lithography. Nanoimprint lithography received considerable interest as simple and cost effective alternative to the convenient lithographic techniques such as optical or electron beam lithography [6, 7]. However, one of the most important problems to be solved in the nanoimprint lithography is fabrication of the stamps with anti-sticking surface, because Si, quartz and Ni – the most often used materials for imprint stamp formation – have high surface energy and, as a result, bad anti-adhesive properties.

In present study ion beam deposited DLC films were investigated as possible candidates to increase anti-sticking properties of the imprint lithography stamps.

2. EXPERIMENTAL TECHNIQUES

In this research hydrogenated diamond-like carbon (DLC) films have been synthesized on crystalline silicon by direct ion beam deposition using acetylene gas as a hydrocarbon source. Hollow cathode electrostatic ion source has been used. Silicon oxide doped diamond-like carbon films have been synthesized by direct ion beam deposition from hexamethyldisiloxane vapor and hydrogen gas mixture ($(CH_3)_3SiOSi(CH_3)_3 + H_2$). In this case hydrogen has been used as a feed gas. Thin film synthesis conditions are presented in Table 1. Raman spectra of the deposited films were typical for diamond-like carbon [8, 9].

Table 1. Technological conditions of the carbon films deposition process

Reagents	C_2H_2, $(CH_3)_3SiOSi(CH_3)_3+H_2$
Substrates	Si(111)
Gas pressure	$(2\cdot10^{-2})$ Pa
Ion beam energy	(0.8±0.1) keV
Deposition temperature	293 K (room temperature)

Before the deposition Si(111) substrates have been washed by boiling dimethylformamide and acetone. In some cases substrates were additionally etched by $HF:HNO_3:H_2O$ solution to remove native oxide layer.

Wettability (anti-sticking properties) of the synthesized films was evaluated by measuring surface contact angle with water.

Surface morphology of the films was investigated by atomic force microscope NANOTOP-206. V-shaped "ULTRASHARP" Si cantilever (force constant 1.5 N/m) has been used. The measurements were performed using tapping mode.

Thickness and refractive index of the deposited films were measured by laser ellipsometer Gaertner L115 (λ = 633 nm). Possible presence of the native oxide layer at the DLC-Si interface wasn't taken into account during calculations. Therefore, in most cases values of the thin film thickness and refractive index presented in this article are values of the some effective layer consisting from the top layer of the DLC and lower layer (with thickness up to 10 nm) of the native silicon oxide.

3. EXPERIMENTAL RESULTS

3.1 The influence of the DLC film thickness on the contact angle with water

Data on SiO_x doped DLC films contact angle with water dependence on thickness are presented in Fig. 1, a. It

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can be seen, that for films of the measured lowest thickness of 12 nm surface contact angle with water still was in the range typical for thicker films – 68°.

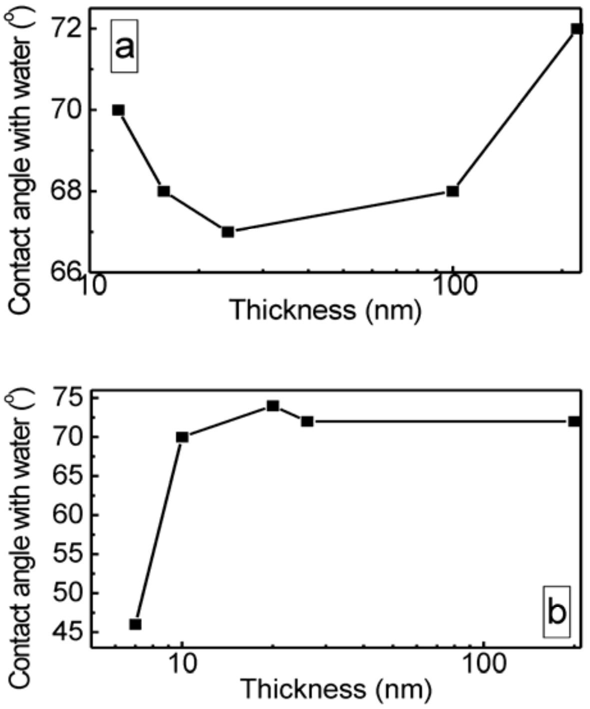

Fig. 1. The dependence of the contact angle with water of SiO_x doped (a) and undoped (b) DLC film on layer thickness(ion beam energy during deposition 800 eV)

Table 2. Contact angle with water and refractive index of the undoped DLC films

Ion energy (eV)	Ion current density ($\mu A/cm^2$)	Thickness measu-red by laser ellipsometer (nm) *	Refractive index*	Contact angle with water (°)
1000	100	72	2.1	76
1000	100	26	2	70
1000	100	10	1.6	30
1000	50	29	1.7	49
1000	25	21	1.6	48
800	100	20	2	74
800	100	9	1.8	70
800	50	7	1.7	46
300	40	16	1.6	74

* In the calculations on layer model was used (DLC on Si).

The dependence of the contact angle on thickness of the undoped DLC films is presented in Fig. 1, b. Table 2 summarizes dependence of the refractive index and contact angle of undoped DLC on thickness of film and technological parameters (i.e. ion energy and ion current density). It can be seen, that 72 nm thickness undoped DLC films with contact angle 76° were deposited by 1000 eV ion beam at current density 100 $\mu A/cm^2$ and deposition time 10 min. Decrease of the deposition time to 5 min resulted in films with 26 nm thickness and contact angle 70°. After the 3 min deposition DLC film thickness was 10 nm and contact angle with water decreased to 30°. Decrease of the ion current density to 50 $\mu A/cm^2$ resulted in film with total thickness 29 nm and 49° contact angle. Further decrease of the ion current density to the 25 $\mu A/cm^2$ resulted in slightly thinner film (21 nm) and similar surface contact angle (48°). Decrease of the ion beam energy to the 800 eV (ion current density 100 $\mu A/cm^2$) resulted in better results. It can be seen from Table 2, that contact angle of the grown 9 nm total thickness film was 74°. Refractive index value of this film (1.8) was somewhere between the typical to the SiO_2 (1.45 – 1.5) [10, 11] and typical to the thicker DLC films (in our case 2.2). Two-times decrease of the ion current density (twice decreased deposition rate) results in deposition of 7 nm thickness of thin film with refractive index 1.7 and contact angle 46°. Refractive index of 16 nm thickness DLC film deposited by 300 eV ion beam was 1.6. This value is close to the refractive index of the SiO_2 and substantially lower than refractive index of the 200 nm thickness DLC film deposited under the same conditions (2.2 – 2.3). It seems, that at higher ion energies some intermixing at the DLC-Si interface takes place.

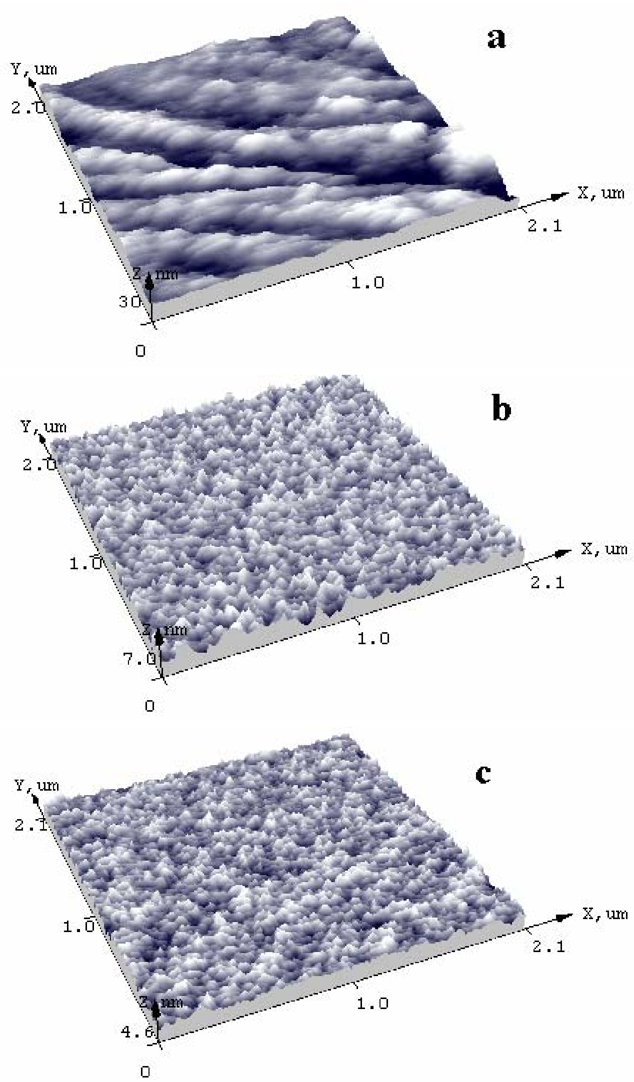

Fig. 2. Surface morphology of the DLC + SiO_x thin films. Thin film thickness was 24 nm (a), 52 nm (b), 200 nm (c)

Extra chemical polishing of the native oxide of the Si(111) (down to 3 nm) didn't change essentially contact angle with water of the DLC films as compared to ones deposited on unpolished substrates under the same conditions.

Surface smoothness of the 30 nm thickness undoped DLC films deposited by 1000 eV energy ion beam was nearly the same as smoothness of the 200 nm thickness film (RMS was 0.5 nm and 0.2 nm respectively). While surface morphology of the SiO_x doped diamond-like carbon films depended on the thickness (Fig. 2, Table 3).

Table 3. RMS and refractive index of the SiO_x doped DLC films

Thickness (nm)	RMS (nm)	Refractive index
24	3.3	1.6
52	0.9	1.7
200	0.6	1.8

3.2 Thermal stability of DLC films during air annealing

To test thermal stability of the films the dependence of the contact angle with water on thermal annealing was investigated. Air annealing was performed partially to simulate hot stamping conditions. Undoped and SiO_x doped DLC films were investigated. Results of the experiment are presented in Fig. 3. The dependence of the contact angle with water on annealing time of the thicker (200 nm thickness) DLC films is added for the comparison purposes. It can be seen, that contact angle of the ticker films decreased for both types of the investigated films. While in the case of the thinner films contact angle still remained enough high (68° for 250 min annealed undoped DLC film) or even slightly increased (for DLC + SiO_x films) illustrating long term stability.

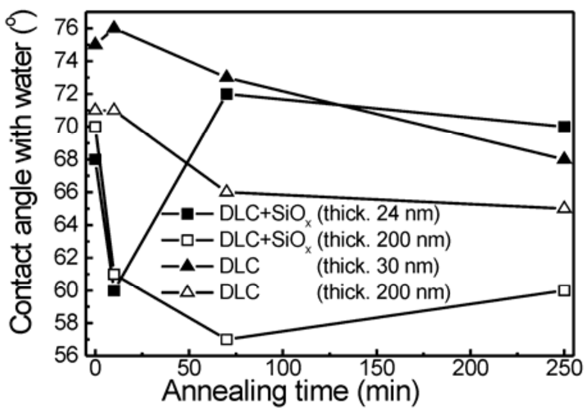

Fig. 3. Effects of the annealing time on the contact angle with water of the DLC and DLC + SiO_x films. Annealing temperature – 200° C, abbreviation thick. refers to the thin film thickness

Surface roughness (RMS) of the 24 nm thickness SiO_x doped diamond-like carbon film decreased from 3.3 nm to the 1 nm as a result of the 250 min air annealing. Whileroughness of the undoped DLC film remained 0.5 nm after the 250 min annealing in air ambient.

CONCLUSIONS

In conclusion ion beam deposited hydrogenated DLC thin films were evaluated as a possible anti-sticking layers on crystalline silicon for nanoimprint lithography. Film surface contact angle with water was investigated as a measure of the surface free energy and anti-adhesive properties. There were shown, that DLC films as thin as 9 nm can be used as an anti-sticking layers. However at higher ion beam energies decreased contact angle with water was observed for 10 nm thickness DLC film. It was explained by ion induced mixing at the DLC-Si interface. Surface smoothness of the 30 nm thickness undoped DLC films deposited by 1000 eV energy ion beam was nearly the same as smoothness of the 200 nm thickness film. While SiO_x doped diamond-like carbon films were rougher than undoped DLC films. Surface morphology of these films depended on the thickness.

Air annealing was performed as a partial simulation of the hot stamping conditions during nanoprint. There were revealed, that contact angle with water of the 24 – 30 nm thickness DLC films was more resistant to the air annealing than contact angle of the thicker (200 nm thickness) films. There were observed no roughening of the 24 – 30 nm thickness DLC films as a result of the air annealing.

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