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Oxygen Ion Beam Etching of Diamond Like Carbon Films

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Effects of the oxygen ion beam etching of ion beam synthesized diamond like carbon (DLC) films were investigated in present study. The etching rates as well as contact angle with water and surface morphology before and after the oxygen ion beam treatment were studied. "Conventional" hydrogenated diamond like carbon (DLC) films were synthesized from acetylene gas, while silicon and SiO_x doped DLC films were deposited from hexamethyldisiloxane vapor and acetylene gas mixture, and hexamethyldisiloxane vapor and hydrogen gas mixture respectively. In all cases ion beam etching resulted in flat smooth surfaces. Etching rate of the "conventional" DLC films synthesized from acetylene and DLC films deposited from hexamethyldisiloxane vapor and acetylene gas mixture was 44 nm/min and 29 nm/min respectively. Thickness of the SiO_x doped DLC film synthesized from hexamethyldisiloxane vapor and acetylene gas mixture slightly increased as a result of the oxygen ion beam treatment. Contact angle with water of the DLC films synthesized from acetylene after the ion beam etching remained the same. While contact angle of the diamond-like carbon films deposited from hexamethyldisiloxane vapor and acetylene gas mixture decreased from 68° to 55°. Contact angle with water of SiO_x doped DLC films after the oxygen ion beam treatment was similar to the contact angle with water of the silicon dioxide. Observed results were explained by different etching rates of the different carbon and hydrocarbon fractures as well as by competition between two processes: ion beam etching and oxidation of the Si and SiO_x.

Keywords: diamond like carbon, oxygen ion, ion beam etching.

INTRODUCTION

Diamond like carbon (DLC) films remain at the top of the considerable interest due to their very interesting properties [1]. High hardness and wear resistance, low friction, corrosion resistance, hydrophobicity, high thermal conductivity, high optical transmittance in near ultraviolet, visible light and near infrared ranges can be mentioned. Therefore, various applications of the diamond like carbon films are considered [1]. Particularly, use of the diamond like carbon films for novel lithographic technologies applications as well as a material for fabrication of the different microstructures and micromechanical devices have been already considered [2 – 7]. In the first case mechanical and hydrophobic (antisticking) properties of DLC can be used to solve one of the important problems of the nanoimprint lithography – fabrication of the stamps with anti-sticking surface. Thick DLC layers were reported as an efficient mould material, when being used in the imprint technology [2, 3]. The imprint stamp pattern can be formed directly in the CVD deposited polycrystalline diamond [8 – 10]. The fabrication of diamond like carbon based imprint stamps using focused ion beam CVD was reported as well [2, 3]. In the second case application of the DLC for fabrication of the microfluidic devices [4], micromachine components [5], different MEMS [6], piezoresistive sensors [7] were already studied. As it was mentioned above, diamond like carbon films are resistant to the "wet" chemical etching. Therefore, different plasma and ion etching techniques should be used for fabrication of DLC microstructure of the necessary pattern. However, there are few studies on RIE or ion beam etching of the diamond like carbon films.

In present study etching of both hydrogenated DLC films and doped hydrogenated DLC films by oxygen ion beam were investigated. Effects of the doping on etching rate were studied. Hydrophobic properties and surface morphology of the films were studied before and after the etching.

EXPERIMENTAL

Commercially available crystalline n-Si <111> wafers have been used as substrates for deposition of the DLC films. Diamond like carbon films were deposited by direct ion beam synthesis using a closed drift ion source. "Conventional" hydrogenated diamond like carbon films were synthesized using acetylene gas as a hydrocarbon source. Silicon oxide and silicon doped DLC have been synthesized using mixtures of the hexamethyldisiloxane vapor with hydrogen ($HMDSO + H_2$) or acetylene ($HMDSO + C_2H_2$) as hydrocarbon, silicon and oxygen gas sources. Hydrogen or acetylene has been used as a feed gas. Technological parameters of the deposition process are presented in Table 1.

DLC microstructures (surface relief gratings) were fabricated by combination of the microlithographic techniques and oxygen ion beam etching by closed drift ion source.

Ion beam etching rate of the diamond like carbon films was established by measuring of the DLC grating step height using an atomic force microscope NANOTOP-206. V-shaped "ULTRASHARP" Si cantilevers (force constant 1.5 N/m) have been used. Surface morphology of the DLC

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Table 1. Conditions of the diamond like carbon films deposition process

Reagents	C_2H_2 $(CH_3)_3SiOSi(CH_3)_3 + H_2$ $(CH_3)_3SiOSi(CH_3)_3 + C_2H_2$
Base pressure	$(2 \cdot 10^{-4})$ Pa
Work pressure	$(2 \cdot 10^{-2})$ Pa
Ion beam energy	800 eV
Deposition temperature	293 K (room temperature)
Substrate	Monocrystalline Si(111)

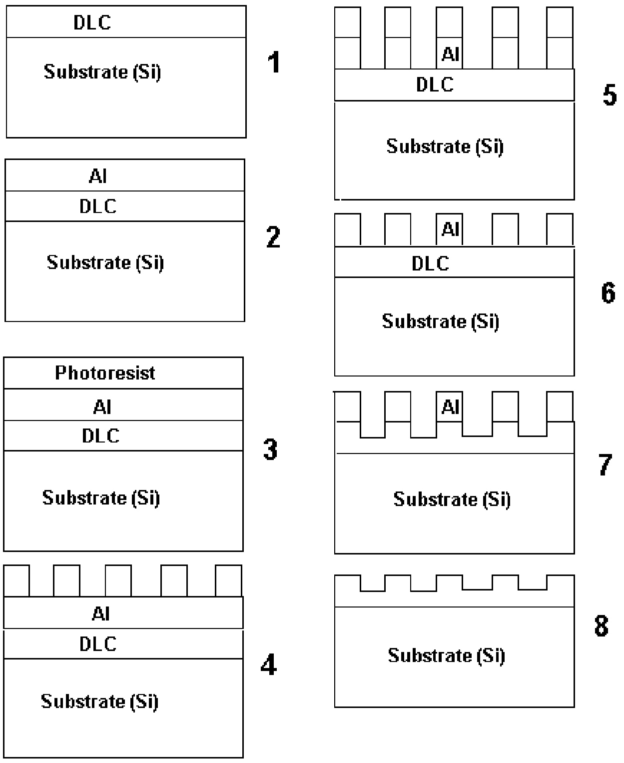

Fig. 1. Fabrication of the diamond like carbon film microstructure: 1 – DLC synthesis, 2 – e-beam evaporation of Al onto DLC, 3 – spin-coating of the photoresist, 4 – fabrication of the pattern in photoresist by conventional optical lithography techniques, 5 – transfer of the pattern through the photoresist mask to the Al (Al grating fabrication), 6 – removal of the photoresist, 7 – Oxygen ion beam etching of DLC through the Al mask, 8 – removal of Al by wet chemical etching

films before and after the ion beam treatment was investigated by AFM as well. Wettability of the synthesized films before and after the ion beam treatment was evaluated by measuring surface contact angle with water. Contact angle goniometer has been used for those measurements.

EXPERIMENTAL RESULTS AND DISCUSSIONS

Fig. 1 illustrates main steps of fabrication of microstructures in diamond like carbon films. The steps 1 – 6 show typical procedures that are usually used during formation of pattern. The step 7 was analyzed systematically in terms of rate of etching, wettability, roughness etc. versus type of the used DLC.

It was found, that 44 nm/min and 29 nm/min etching rate can be achieved for the undoped DLC and DLC deposited from HMDSO + C_2H_2 gas mixture, while no etching was observed for the SiO_x doped DLC film deposited from HMDSO + H_2 gas mixture (Table 2). Oxygen ion beam etching/treatment did not change contact angle with water of the undoped DLC films. The contact angle of the DLC film deposited from the HMDSO + C_2H_2 gas mixture decreased from 68° to 55° (Table 2). The contact angle of the DLC film deposited from the HMDSO + H_2 gas mixture decreased from 72° to 25°.

Table 2. Effects of the oxygen ion beam etching: etching rate, contact angle before and after the ion beam etching

Coating (gas used for deposition)	Thickness of the etched layer (nm) (1.5 min etching)	Contact angle (before etching)	Contact angle (after etching)
C_2H_2	66	73	73
HMDSO + H_2	– 6*	72	24 – 25
HMDSO + C_2H_2	44	68	55

*thickness of the DLC film increased as a result of the ion etching from 256 nm to 262 nm.

Oxygen ion beam etching of the DLC films resulted in an increased roughness (RMS = 1.4 nm after the etching vs 0.4 nm before etching) of the undoped DLC films (see Fig. 2), while DLC deposited from hexamethyldisiloxane and acetylene gas mixture and SiO_x doped DLC deposited from hexamethyldisiloxane and hydrogen gas mixture remained very flat (RMS was 0.4 nm and 0.3 nm respectively).

There were already reported, that oxygen ion etching rate is higher for sp^2 bonding fractions in comparison with sp^3 ones [11]. While hydrogenated carbons in DLC are etched by oxygen ions slower than non-hydrogenated ones [12]. Therefore, in the case of the "conventional" DLC slight increase of the film roughness can be explained by different etching rates of the different components of the DLC film.

Resistance to the etching by oxygen ion beam of SiO_x doped DLC deposited from hexamethyldisiloxane and hydrogen gas mixture may be explained by further oxidation of the SiO_x. Decrease of the contact angle with water of the films to the value close to the contact angle with water of the silicon dioxide is in good agreement with such an assumption. Slightly increased thin film thickness as a result of the ion beam treatment as well as decreased SiO_x doped DLC film roughness shows, that oxidation processes possibly blockaded oxygen ion beam etching.

It seems, that the case of the DLC films synthesized from the hexamethyldisiloxane vapor and acetylene gas mixture is somewhere between the "conventional" and SiO_x doped DLC. In the case of DLC films synthesized from the hexamethyldisiloxane vapor and acetylene gas mixture, both decrease of the oxygen ion etch rate in

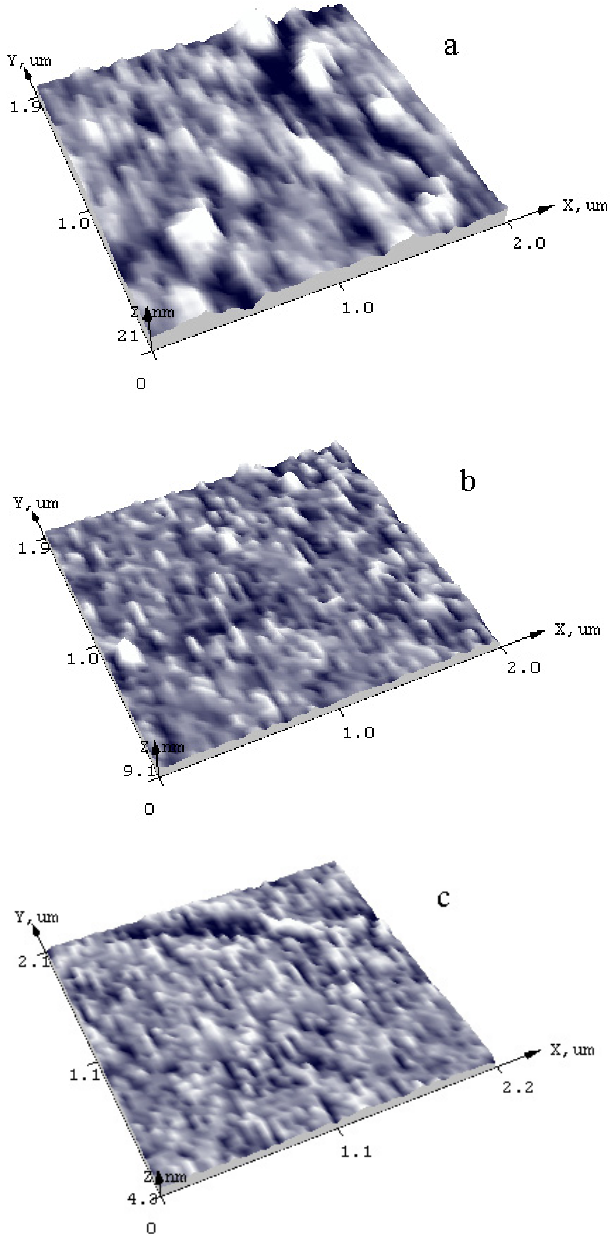

Fig. 2. Surface morphology after oxygen ion beam etching: undoped DLC (a), DLC deposited from hexamethyldisiloxane and acetylene gas mixture (b), SiO_x doped DLC deposited from hexamethyldisiloxane and hydrogen gas mixture (c)

comparison with "conventional" DLC and decrease of the contact angle with water take place. On the other hand surface roughness remains nearly the same. In our previous study we have shown, that those films contain 2 atomic percents of Si (mostly in SiC form) and 9 atomic percents of the hydrogen [13] – amounts substantially lower than in SiO_x doped DLC films. I_D/I_G peak ratio (proportional to the sp^2/sp^3 bond ratio) of the Raman scattering spectra of DLC films synthesized from the hexamethyldisiloxane vapor and acetylene gas mixture was higher than in "conventional" DLC films deposited from acetylene [14]. Therefore lower oxygen ion beam etching rate in the case of the diamond like carbon films synthesized from the hexamethyldisiloxane and acetylene gas mixture in comparison with "conventional" DLC despite higher amount of sp^2 bonding fraction can be explained by competition between the increased ion etching rate due to the increased sp^2 bonding and decreased ion etching rate due to the silicon oxidation processes.

CONCLUSIONS

In conclusion oxygen ion beam etching rates for different DLC films were measured. Effects of the ion beam treatment on hydrophobic properties and surface morphology were investigated. 44 nm/min and 29 nm/min etching rate was achieved for "conventional" DLC synthesized from acetylene and DLC deposited from hexamethyldisiloxane vapor and acetylene gas mixture respectively. Slight increase of the thickness of SiO_x doped DLC film synthesized from hexamethyldisiloxane vapor and acetylene gas mixture was observed as a result of the oxygen ion beam treatment. In all cases ion beam etching resulted in flat smooth surfaces. However, roughness of the oxygen ion beam etched "conventional" DLC surface was slightly higher than roughness of the other oxygen ion beam treated diamond like carbon films. DLC films deposited from acetylene appeared to have the best combination of the ion beam etching rate and hydrophobicity. DLC synthesized from hexamethyldisiloxane vapor and acetylene gas mixture are suitable for micromachine fabrication applications as well due to their ultrasmoothness after the ion beam etching. While SiO_x doped DLC films can be used as a mask for diamond like carbon film microstructure fabrication by oxygen ion beam etching process.

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