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Effect of Improved Surface Wetability and Adhesion of Undulated Diamond-like Carbon Structure with r.f. PE-CVD

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Abstract: This paper investigated the wetting and adhesion property of undulated DLC film with surface morphology controlled for a reduced real area of contact. The undulated DLC Films were prepared by 13.56 MHZ radio frequency plasma enhanced chemical vapor deposition (r.f. PECVD) by using nanoscale Cu dots surface on a Si (100) substrate. FE-SEM, AFM analysis showed that the after repeated deposition and plasma induced damage with Ar ions, the surface was nanoscale undulated. This phenomenon changed the surface morphology of DLC surface. Raman spectra of film with changed morphology revealed that the plasma induced damage with Ar ions significantly suppressed the graphitization of DLC structure. Also, it was observed that while the untreated flat DLC surfaces had wetting angle starting ranged from 72° and adhesion force of 333ni. Had wetting angle the undulated DLC surfaces, which resemble the surface morphology of a cylindrical shape, increased up to 104° and adhesion force decreased down to 11 nN. The measurements agree with Hertz and JKR models. The surface undulation was affected mainly by several factors: the surface morphology affinity to cylindrical shape, reduction of the real area of contact and air pockets trapped in cylindrical asperities of the surface.

Keywords: *undulated DLC, wetting angle, adhesion force, real area of contact*

1. Introduction

Advances in nanotechnology, including micro/nancelectro-mechanical systems (MEMS/ NEMS), have stimulated the development of new materials and design of surfaces which have hydrophobic surfaces and interfaces with low adhesion and friction. On the other side, by lowering wetting angle or increasing the surface force, the adhesion force can be increased to cause hydrophilic behavior in nano-scale. And increase nanoscale friction force [1-3]. To solve this problem, researchers focus on the roughening surface morphology. We report in this paper experimental results on the DLC films that by controlling surface contact conditions and surface modifications were made hydrophobic and had the adhesion force in nanostructures.

2. Experiments

To prepare undulated DLC surface, thin Cu film was deposited on Si (100) wafers by r.f. magnetron sputtering. Rapid thermal annealing (RTA) [4] of the sample at 800°C for 1min in pure Ar environment converted the Cu film into nanoscale dots. Size and width of the dots were dependent on the film thickness, RTA time and temperature. The DLC film was deposited on the Cu dot surfaces with 13.56 MHz r.f. plasma decomposition using mixed Ar and C_2H_2 precursor gases. For a fabrication of rough morphology, we used 3 layer deposited and plasma Ar etching. The total film thickness about 150 nm was deposited at working pressure 1.33 Pa. Surface morphology of samples was observed using atomic force microscopy CAF and field emission scanning electron microscope CFE-S. All measurements were carried out at 25±0.1°C. The wetting angle measurement was carried out by a goniometer that analyzes the image of a sessile droplet on the surface (Water rolume was 0.4 µl, each measured was repeated for 7 times and the average values were used). The surface wetting angle is related to the adhesion force, the force-displacement curve of the samples was measured with contact mode AFM with diamond coated tip (spring constant: 2.8 N/m, tip radius: 35 nm). Calculate real area of contact with Hertz and JKR models, the measured mechanical properties, such as hardness and elastic modulus of each layer by nano-indentation was used.

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3. Results and Discussion

3.1. Fabrication of undulated DLC surface

Undulated DLC film was deposited on the nanoscalec dots surface. After deposition, the plasma Ar etching of film was conducted at the pressure of 9 Pa for a 1 minute at 300 W r.f power. High working pressure was needed to the surface undulation. Fig. 1 shows, using FE-SEM microstructure images after each DLC layer deposited on a dots. The AFM

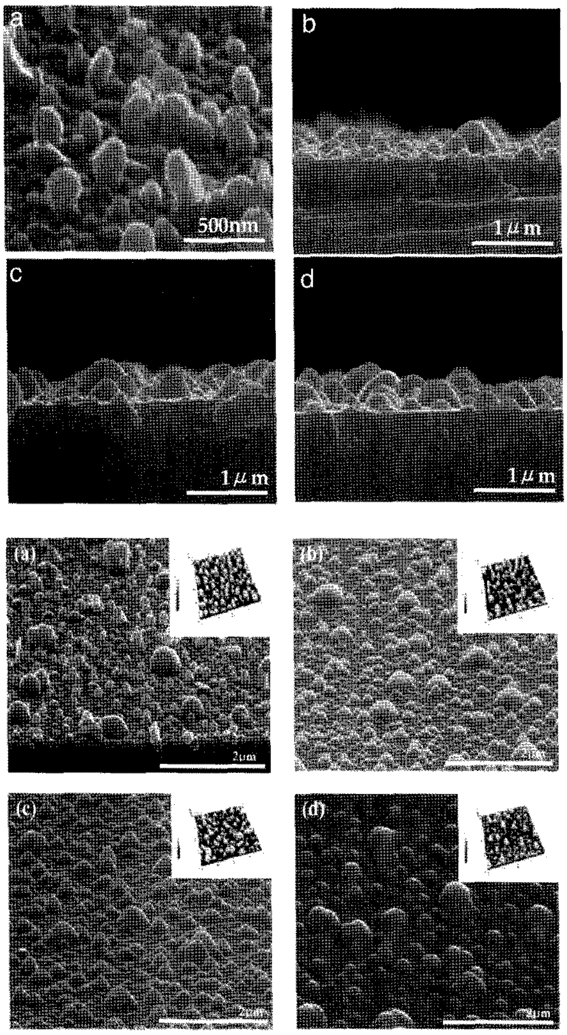

Fig. 1. FE-SEM microstructure and AFM images of the undulated multi-DLC surfaces deposited on Cu nanodots. (a) Cu nanodots surface, (b) 1st layer-(Ar + C_2H_2 mixed), (c) 2nd layer- (C_2H_2 mixed), (d) 3rd layer-(Ar + C_2H_2 mixed).

images of the surface are presented. Fig. 1(a) shows the morphology of Cu dots prepared by RTA treated in pure Ar environment. Tere's height and width were 650 and 158 nm, respectively. RMS roughness was 49.2 nm. Fig. 1(b), (c) and (d) show the morphologies of the undulated DLC surface after plasma Ar etching. When etching with glow discharge of C_2H_2 and Ar gas mixture, heavily undulated surface shapes are found to cylindrical asperity (see Fig. 1 (d)). RMS roughness and the width and height of asperity were 75, 631, 206 nm. This could be explained by the Ar ions induced damage after through deposition. Through the observation, we could see re-cohesive among atoms by recombination of clusters. Using these processes, we see that deposition with high r.f. power and re-cohesive with plasma Ar etching could be induce surface undulation.

3.2. Structure analysis of the undulated DLC surface for etch layer

The re-cohesive and undueated shapes of deposited film were confirmed by Raman analysis. Fig. 2 displays the spectra for the films with different stages. The flat DLC film (fig. 2(a),(b), has typical shape of the hydrogenated amorphous carbon film deposited by r.f. PECVD. In undulated DLC surface Fig.2(c), (d) and (e), disorder peak near at 1350 cm^{-1} appears. The film has also a more graphite-like ring structure and the numbers of would increase in sp^2 bondings by graphitization due to plasma Ar etching and deposition. In addition, the G band gradually shifts toward a higher wave number up to 1549.9 cm^{-1}, 1570 cm^{-1} and 1593 cm^{-1}, which is due to C=C stretching vibrations.

Therefore, in the case, graphite-like ring structures would increase with the deposition with plasma etching. From this analysis, high power etching and deposition significantly affects the formation of the sp^2 clustering structures.

3.3. Wetting and adhesion force behaviors of undulated DLC film

Surface undulation affects the conventionally measured

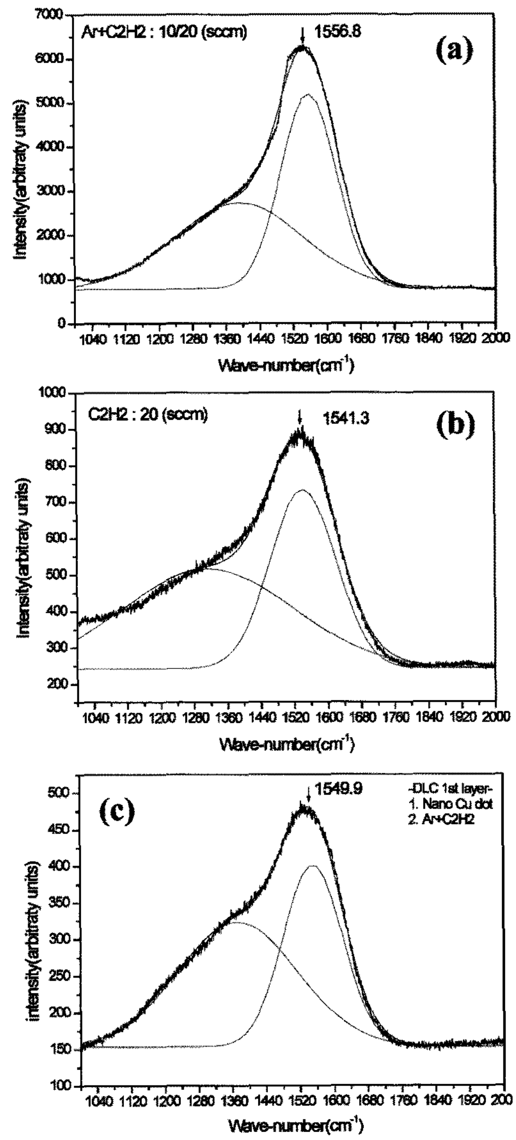

Fig. 2. continued

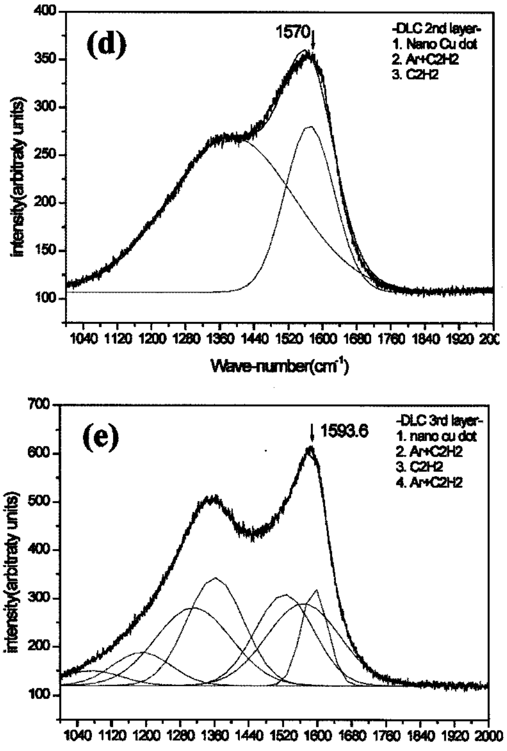

Fig. 2. Raman spectra of the nano undulated DLC surface for each layers. (a) flat a-C:H surface-(Ar + C_2H_2 mixed), (b) flat a-C:H surface-(C_2H_2 mixed) (c) 1st layer-(Ar + C_2H_2 mixed), (d) 2nd layer- (C_2H_2 mixed), (e) 3rd layer-(Ar + C_2H_2 mixed).

wetting angle of the each DLC layer. In the case of a flat surface, when the water droplet attached to a dry surface, the wetting angle has a value of around, 72°, 76°. Howerer, modifying the surface increase to, 83°, 95° and finally 103.3°. It can be seen that wetting angle change was air-pockets trapped among cylindrical dots and re-cohesive due to the induced Ar plasma damage caused by this happens even though is that the hydrogen content increase with each layer. Fig. 3(a) shows that the increases almost linearly with the hydrogen content and surface contact area. The contact area is shown in Fig. 3(b).

When the AFM diamond coated tip is contacting the flat surface, the adhesion force is high because of large contact area, 277 and 333 nN. In table 1, the difference in real area of contact size among the DLC samples are shown. For these experiments, only the 35 nm radius tip was used to study the effect. At the contact area, wetting results in the formation of surface force at the area between hydrophilic flat surface and diamond coated tip, which causes higher adhesion. However, as shown in fig. 3(a), the adhesion force rapidly decreases when the undulated surface is used. The adhesion force drops to 8, 16 and 11 nN. This decrease is due to smaller real area of contact between tip and asperities. However, as shown in fig. 3(a), the adhesion force rapidly decreases when the undulated surface is used. The adhesion force decrease as the water wetting angle increases, i.e. as the surface becomes hydrophobic. This result implied that there could be two important factors that were affected the adhesion. The first,

Table 1. Real area of contact calculated Hertz & JKR model.

Real area of contact	Pure Si	Flat a-C:H	Undulated a-C:H
Hertz model	1.96	Ar+C_2H_2 mixed : 1.86 C_2H_2 : 1.89	1st layer (Ar + C_2H_2 mixed) 2.214 2nd layer (C_2H_2) 2.21 3rd layer (Ar+C_2H_2 mixed) 2.09
JKR model	3.35	Ar+C_2H_2 : 6.68 C_2H_2 : 7.15	1st layer (Ar + C_2H_2 mixed) 4.10 2nd layer (C_2H_2) 4.45 3rd layer (Ar+C_2H_2 mixed) 4.08

real area of contact of the undulated DLC surface was lower than that of flat surface. Therefore, adhesion force could be decreased. In case of flat DLC surface, the real area of contact are calculated form JKR model [6-7] was 5 times higher than from Hertz model at the same 40nN load. In the case of an undulated DLC, It was only 2 times higher. The second factor is the different precursor gases cause different component and

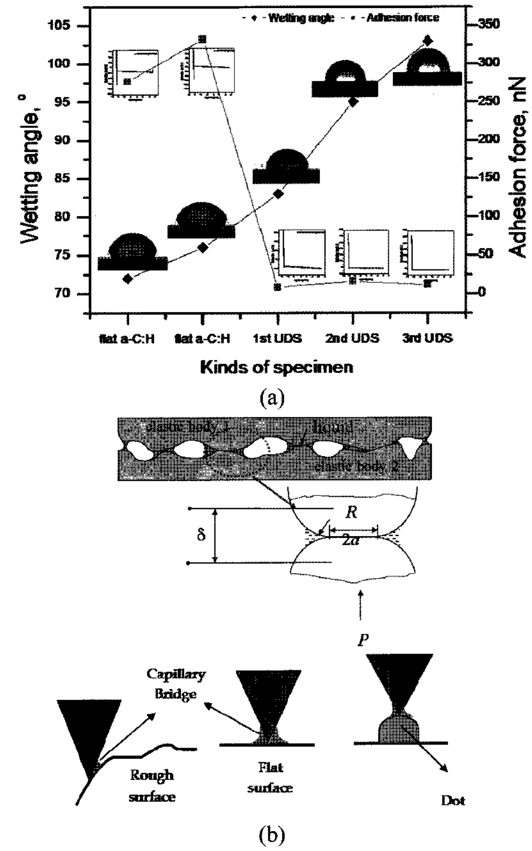

Fig. 3. (a) Adhesion force and the wetting angle for the different layers (b) different contact area of each surface.

surface morphology after deposition. Ar ions bombardment can change the dot shape. This phenomenon can be explained by the fact that the adhesion force of 2nd layer was bigger than that of 1st layer. Ar ions bombardment can change the dot shape. This phenomenon can be explained by the fact that the adhesion force of 2nd layer was bigger than that of 1st layer. This can be further confirmed by that the adhesion force of 3rd layer is even more decreased. This difference of adhesion force is not connected to coefficient of friction directly, but it shows the tendency.

4. Conclusions

In this research, we intended to change the DLC film which is normally hydrophilic to, hydrophobic by topographical modification of rough structure to reduce surface force. We expect to reduce real area of contact by air-pockets trapped among asperities. The experimental results of this work can be summarized as follows.

1. We fabricated with undulated DLC structure by using rapid thermal annealing (RTA) and plasma induced damage of Ar ionswhen film was deposited.
2. The undulated DLC structure shows wetting angle (103°) and low adhesion force (11 nN) due to reduction of real area of contact and helping the air pockets effect.
3. In case of DLC film deposited by CVD method, it is impossible to remove hydrogen completely. But by a making modification of surgace morphology of DLC, we are able to reduce hydrophilic components from rough structure.

Acknowledgment

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