PLASMA OXYDATION PRINTING ONTO CARBON-BASED COATINGS FOR MICRO-TEXTURING

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ABSTRACT

The carbon based coatings such as the diamond-like carbon and CVD-diamond coatings had been widely used as a protective layer of tools and dies. They had high hardness and chemical inertness so that many other applications than protective coatings were present in practice; e.g., sensor and actuator working in the severe circumstances or at the elevated temperature. Since almost all the metallic, ceramic and polymer products could be coated by DLC, various micro-textures to be used for detection and sensing might well be accommodated onto the DLC coatings. Diamond films were also expected to be a MEMS to be working with low friction and wear. Toward those purpose, these carbon based films must be micro-and nano-textures as being designed in CAD system. In the present paper, both the DLC and CVD diamond coated substrates were prepared as a test-specimen to make micro-texturing experiment. At the first step, the mask less patterning by lithography was employed to make micro-patterning onto DLC and diamond films. At the second step, the oxygen plasma etching was utilized to employ these micro-patterns as a mask and to chemically remove the unmasked surface areas. The optical microscope and SEM were utilized to measure the surface profile after plasma etching process.

1. INTRODUCTION

Diamond-like carbon (DLC) is a metastable form of amorphous carbon containing a significant fraction of sp^3 bonds. It has high hardness with variety in mechanics, chemical inertness, and, optical transparency. It works as a wide band gap semiconductor (Robertson, 2002). DLC-films have a widespread application as protective coating for various kinds of products, such as magnetic storage disk, optical windows, and biomedical coatings and the micro-electro mechanical device (MEMS) (Hanada, 2003). Most of MEMS devices under developments are mainly based on the silicon because of the available surface machining technology in the so-called silicon technology for fabrication. However, silicon has relatively poor mechanical properties (Berts, 2002). DLC filmhas become a candidate to replace silicon as base material and solve this problem.

How to mae micro-texturing into DLC coating on the substrates coating has been also investigated in various ways. After imprinting theinitial micro- or nano-patterns on the DLC film, its un-imprinted surface areas are etched away. One of the most common methods is a wet chemical etching. The chemical solutions remove the DLC during the etching process, but the residual solution is harmful to the environment (Yao, 2014). Recently, the dry etching is chosen to make etching in coating material. Dry etching can be done by using plasma technology. There are many types of plasma system for etching process. Among them, the plasma jet was used to make dry etching; after (Urruchi, 2006), its etching rate is still low by 24.9 nm /min. High etching rate and homogeneous plasma etching are expected for plasma etching technology.

In the present study, the high density RF-DC plasma oxygen is utilized to make homogenous plasma etching of the DLC films with the platinum mask. This platinum mask is imprinted on the substrate by using the mask less lithography; various kinds of micro-patterns can be printed on any substrates without use of masks. In the following experiments, the circular dot-patterns with the variable diameter from 50μm down 3μm are employed to investigate the effect of geometric mask size on the spatial resolution in etching into DLC film. The oxygen gas is only employed to make plasma oxidation for dry etching process. The SEM observation demonstrates the homogeneous micro texturing of DLC-films by the present plasma oxidation.

2. EXPERIMENT

The SUJ-2 substrate with the size of 12 x 12 x 5 mm^3 was utilized as specimen in the present study. The DLC films with the thickness of 12μm were deposited by CVD. The circular platinum dot-patterns was imprinted by mask less lithography to make micro-texturing onto DLC films. The diameter of circle dots were varied by 50μm, 30μm, 20μm, 15μm, 10μm, 5μm, and 3μm as depicted in the Fig.1. The pitches of circular dots were also varied in this imprinting; e.g., the left area in Fig. 2 has a narrow pitched micro-dot pattern, and, the right area, a wider pitched micro-pattern.

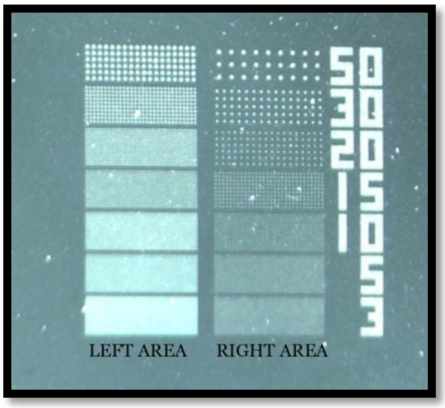

Fig. 1 DLC film with different mask size by lithography

The etching processes were performed by using RF-DC plasma etching system. The system consists of the vacuum chamber, the plasma generator, the control unit, and the carrier gas supply. The chamber is neutral in electricity, RF dipole electrodes and DC-bias work independently to generate RF and DC plasmas. Hence, the ionized species and activated radicals in the RF plasma are attracted to the DC bias plate with kinetic energy. Either RF-plasma or DC plasma or, both are ignited by switching on either or both on the control panel. In addition there is no mechanical matching box for RF plasma generation in this system. Input and output powers are automatically matched by frequency adjustment around 2MHz. The schematic of RF-DC plasma in the present study is depicted in the Fig.2.

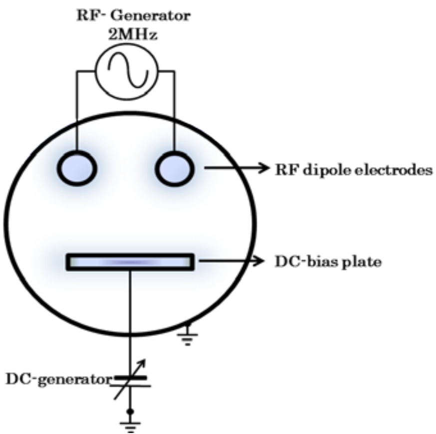

Fig. 2 Schematic view of RF-DC oxygen plasma etching.

The standard experiment set up is explained as fellows. The base pressure is less than 5 x 10^{-3}Pa, and the pure oxygen gas (purity; 99.99%) is only used as a carrier gas. RF-voltage, DC bias, and pressure are varied in a range 100V to 250 V, from -300 V to -500 V, and from 25 Pa to 100 Pa, respectively. The specimen is placed in the center of DC-bias plate to be processed for 3600 second. Table 1 summarizes the present oxygen plasma etching condition to be utilized. The optical microscope and SEM are utilized to measure the substrate condition before and after etching process.

Table 1. The oxygen plasma etching conditions

RF-voltage (V)	DC-bias voltage (V)	Pressure (Pa)	Processing time (second)
250	350	65	3600

3. EXPERIMENT RESULTS

The plasma condition in the Table 1 was employed for plasma oxidation of the DLC film with platinum mask. Figure 3 a) depicts the etching DLC surface with the circular platinum dots with the diameter of 50μm. The unmasked DLC surface by these dot-patterns is etched away while the masked DLC film remains as it was before etching. This implies that the platinum micro-patterns protect the DLC film from oxygen ion plasma bombardment. In addition, the circular shape of dots is accurately preserved even after etching. Furthermore, the whole DLC surface is homogeneously plasma-etched to form the circular DLC convex discs after etching. Figure 3 b) shows the SEM image on the etched DLC surface in Fig. 3 a). No over-etched or damaged micro-patterns are seen in the mask area after etching process. In addition, no residuals of DLC were left on the etched surface of substrates.

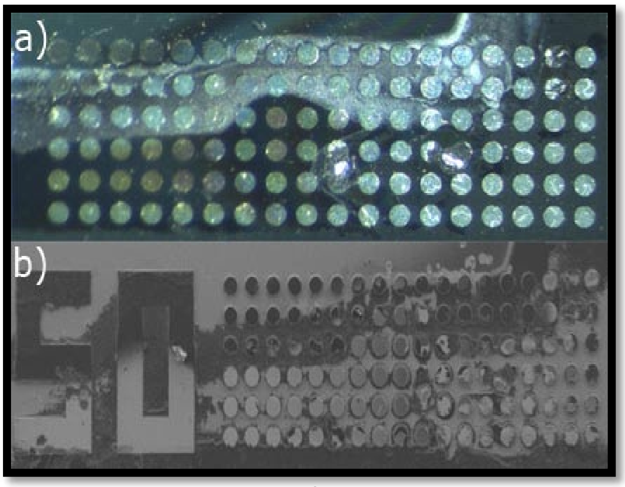

Fig. 3 The etched DLC surface. a) Optical microscopic image, and, b) SEM image.

Let us investigate how the etching process takes place with reduction of the circular dot diameter (D). Figure 4 shows the SEM image of etched DLC surface when D = 30 μm. Just as seen in Fig, 3, the initial two dimensional circular dot-patterns transformed to the regular alignment of circular DLC-pillars through the plasma oxidation. This regularity in alignment proves that the etching process takes place homogeneously on the whole DLC film surface.

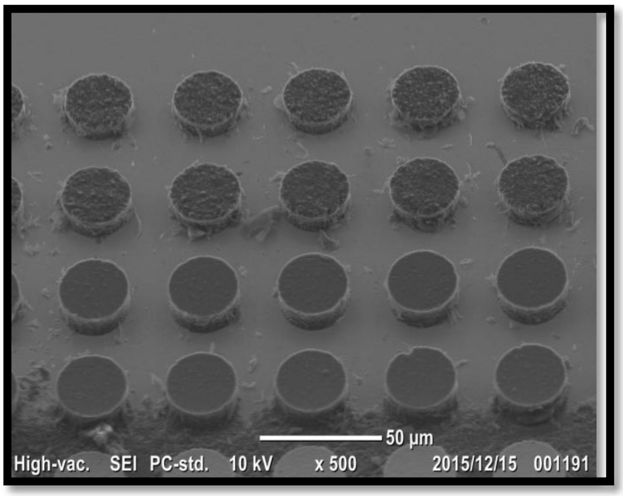

Fig. 4 SEM image of the etched DLC film when D = 30µm.

In final, let us investigate the etching process when D is down-sized to 3µm. As shown in Fig. 5, homogenous etching takes place on the DLC films. The circular discs with bright color correspond to the masked area; their spatial alignment is just equal to that in Fig. 1.

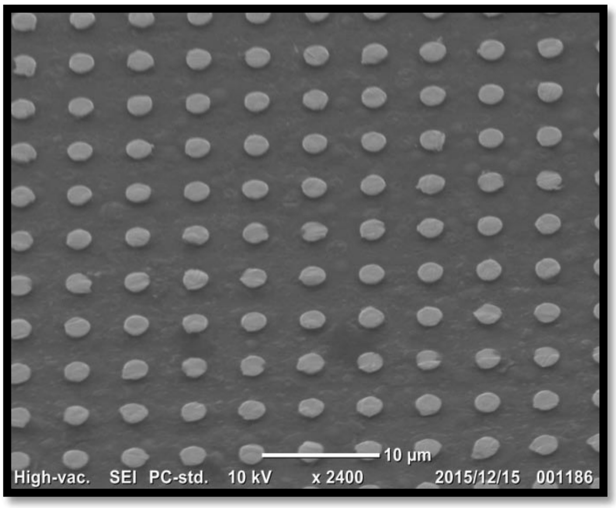

Fig. 5 SEM image of the etched DLC film with D = 3µm.

4. DISCUSSION

The plasma oxidation by the present RF-DC plasma system enables to make homogenous transformation from two dimensional micro-patterns to three dimensional DLC micro-textures on the substrate. Among the processing parameters in Table 1, the RF-voltage has much influence on the ionization process. The DC-bias drives the bombardment of oxygen species in the plasmas. Hence, its temporal sequence control is needed to be free from over-etching of platinum masks. The pressure affects on the population of oxygen ions and electrons generated in the inside of the chamber. The middle range of pressure supplies the ion and electron density in the order of 10^{17} to 10^{18} m^{-3} (E.E. Yunata, 2014). Under the appropriate conditions, both the oxygen and electron densities have less possibility to make damage to the masking area. This selection to use the meso-plasma working area provides a new technique in the plasma etching processing with difference from the normal plasma etching in the low pressure range.

The etching rate in the present plasma oxidation is discussed by comparison between the etching processes when D = 50 µm and 30 µm.

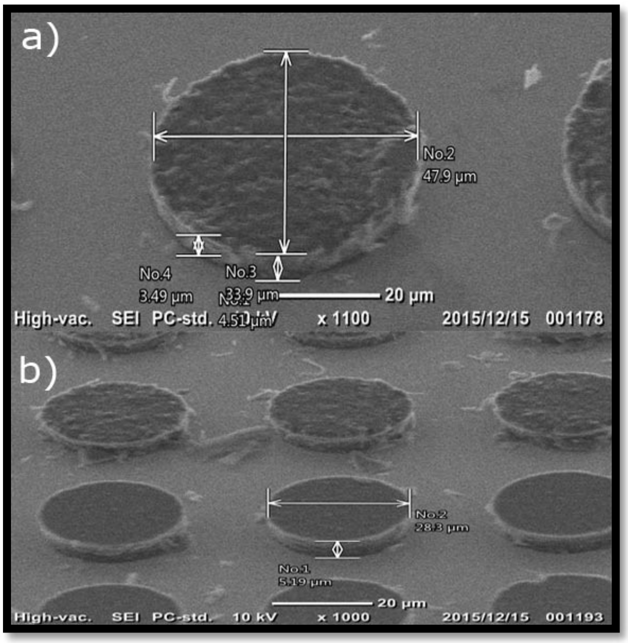

Fig. 6 The thickness of micro-patterning after etching process in a) 50µm and b) 30µm of mask diameter.

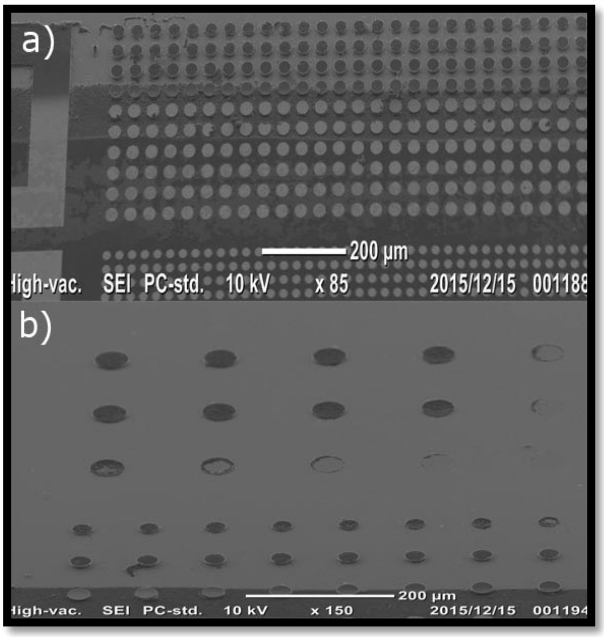

Fig. 7 Spatial resolution in the present etching. a) Narrow pitched pattern, and, b) Wide pitched pattern.

The etching rate (v) to remove the DLC film when D = 50μm reaches to v = 4.51μm/h; v = 5.19 μm/h when D = 30μm. After (Aizawa, 2013), the average etching rate of DLC films was reported to be v = 6.0 μm/h when using the metallic masc. On the other hand, v = 14 μm/h was reported for micro-texturing with use of the ink-jet printed dot-patterns but v = 3 μm/h for line-etching with use of the platinum patterned masks in (Aizawa, 2015). This implies that the etching rate of DLC strongly depends on the effective flux of oxygen species in the plasma sheath on the DLC film. With increase of the masked surface area, the effective flux of oxygen species reduces so that the etching process is retarded significantly.

Let us discuss over the spatial resolution of oxygen etching by varying the pitch between the adjacent neighboring dots. Figure 7 compares the etched DLC surface between the narrow and wide pitches. Homogenous etching process is common to two cases. In case of the narrow pitched patterns, anisotropic etching process is controlled by the presence of platinum masks; fine micro-texturing takes place with low damage to masks. On the other hand, over-etching or damage to masks occurs with increasing the pitch in the original micro-pattern. This suggests that the flux of oxygen species should be finely controlled to make anisotropic etching with less damage.

5. CONCLUSION

The RF-DC plasma etching is employed to make micro-texturing into the diamond-like carbon (DLC) coating with use of the platinum masks. Through this plasma oxidation process, the initial two dimensional imprinted patterns on the DLC film is successfully transformed to the three dimensional micro-textures of DLC pillars on the substrate. Owing to homogeneous plasma oxidation of DLC films, local anisotropic etching of DLC advances with nearly constant rate on the whole surface. No damage or no over-etching is observed in this etching process. Irrespective of the size of micro-pattern, fine spatial resolution is preserved in each micro-texture through this plasma oxidation process. The effect of pitch between neighboring units in micro-patterning on the damage must be lowered by controlling the oxygen species flux onto the DLC films.

Among the plasma oxidation processing parameters, selection of meso-pressure regime provides a new solution for micro-texturing into the carbon based coatings including DLC instead of normal methods working in the low pressure range.

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REFERENCES

Aizawa, T., Mizushima, K., Redationo, T.N., Yang, M., 2013, Micro-imprinting onto DLC and CNT coatings via high density oxygen plasma etching, Proc. 8th ICOMM, pp. 459-466.

Aizawa, T., Amano, S., Tamagaki, H., 2015, Micro-texturing into thick DLC films for fabrication of micro-staping dies, Proc. 8th AWMFT (CD-ROM).

Bertz, A, et al., A novel high aspect ratio technology for MEMS fabrication using standard silicon wafers, Sensors and actuators A:physical, 97-98, pp. 691-701, 2002.

Hanada, K., et al., Fabrication of diamond dies for micro forming, Diamond related material, 12, pp. 757-761, 2003.

Robertson, J., Diamond-like amorphous carbon, *Material Science and Engineering*, R 37, pp. 129-281, 2002.

Uruchi, W., et al.,Etching of DLC films using a low intensity oxygen plasma jet, *Diamond and related material*, 9, pp. 685-688, 2000.

Yao, Z, et al.,Defined micro-patterns of platinum thin films by using inductively coupled plasma etching using $SF_6/Ar/O_2$ mixture gas, *Materials science in semiconductor processing*, 27, pp. 228-232, 2014.

Yunata, E, E., T. Aizawa.,Characterization of hollow cathode plasma for etching and ashing processes, 8th SEATUC symposium, 1410, pp 86, 2014.

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