Preparation of Freestanding Diamond-Like Carbon Film using Plasma Ion Implantation Deposition for Microstructure Fabrications

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Abstract

We prepared freestanding diamond-like carbon (DLC) film and showed a possibility of fabricating microstructure body of the film by extracting from resin molds. A freestanding micro needle array, which was typically c.a. 50 μm in height and 2.1 of aspect ratio was prepared. It could be used for e.g. pinless needle for micro healthcare-devices. In order to prepare the microstructure, DLC film should possess small residual internal stress and be deposited in low substrate temperature (Tsub). For deposition of the DLC film, a hybrid process of a plasma-based ion implantation-ablation superposed accelerating high voltage (HV) pulse onto RF power (HF-PIRID) was used. By optimizing deposition parameters of the HF-PIRID method for the microstructure fabrication, the residual internal stress of the DLC film could be reduced to c.a. 0.1 GPa and the Tsub be to less than 100 °C, even for the 20-μm thick DLC film. These results show possibility of preparing freestanding microstructures of the DLC film. The DLC film developed in this study could be used in various micro electro-mechanical systems.

Keywords: diamond-like carbon, plasma-based ion implantation and deposition, PIRID, mold, Raman spectroscopy

1 INTRODUCTION

Diamond-like carbon (DLC) film would be one of the most interesting materials for micro electro-mechanical systems (MEMS) devices because DLC film possess some interesting properties such as high mechanical hardness, chemical inactivity, low friction coefficient, high wear resistant and low gas permeability, etc. [1-3]. However, few studies for the MEMS using the DLC film have been performed instead of DLC film, there have been reported some studies using a synthetic polycrystalline diamond film, where some microstructure such as arrays of capillary channels or pyramids for micro-fluidic application had been demonstrated. [4-5].

However, we consider that the synthetic diamond film would have some unsuitable points for industrial usages, e.g. it is necessary to deposit it at high substrate temperature (Tsub) of c.a. 1000 °C. [4]. Therefore, the synthetic diamond film cannot be deposited on materials having poor heat-resistance such as resins and glasses. Thus, the production cost would relatively increase.

On the other hand, mechanical and chemical properties of DLC film are similar to those of diamond film; furthermore it is possible to prepare it in relatively lower Tsub, additionally, to do it with low residual internal stress. [1,2]. Therefore, it would be suitable to employ DLC film for the MEMS devices.

In this study, a freestanding micro needle array of the DLC film was demonstrated, which would be used e.g. micro healthcare-devices. In order to prepare it, it is necessary that even thick DLC film possess low residual internal stress and are prepared in low Tsub. According to the requirements, a plasma based ion implantation-ablation (PIRID) method with accelerating negative high voltage (HV) pulse superposed onto RF power (HF-PIRID) was used for the preparation [6]. In this paper, we describe (1) effects of deposition conditions to the DLC film properties and (2) possibility of fabricating freestanding microstructures by extracting from resin molds, with a view of adding high performance and reducing the preparation cost.
2 EXPERIMENTS

2.1 DLC film deposition method

Figure 1 shows a schematic illustration of the HS-PBID apparatus. [6]. In the method, the RF and HV pulse are superposed and supplied to substrate from single feed-through; the substrate can be regarded as an anode of RF power and plasma is produced along the substrate. Thus the DLC film can be coated on three-dimensional substance without e.g. substrate mapping or plasma guiding. Due to reducing pulse width length of the HV, excessive substrate temperature can be prevented. It is well known that ion implantation method produces an inclined region onto the film and reduces internal stress of the film. Therefore, the PBID method, where the ion is being implanted during the deposition, will reduce the stress.

![Diagram of the HS-PBID apparatus](image)

Figure 1. Schematic illustration of deposition apparatus of the HS-PBID method.

Table 1 shows deposition conditions of the DLC film used in this study. Source gases used for the deposition were mixture of C₂H₄, CH₃OH, and N₂.

<table>
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<th>Table 1. Deposition conditions of the DLC Films</th>
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<tr>
<td>Deposition conditions</td>
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<tr>
<td>RF power (W)</td>
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<tr>
<td>HV pulse height (kV)</td>
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<tr>
<td>HV pulse width (μs)</td>
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<tr>
<td>Repetition frequency of HV pulse (Hz)</td>
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<td>Pressure (Pa)</td>
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The Tₘs was not controlled during the deposition. The Tₘs was measured by hemi-indicate paint, which indicates color change above 100 °C, thus the temperature was monitored to be below 100 °C.

2.2 Characterization of the DLC films

Chemical structures of the DLC films were characterized by Micro-Raman spectroscopy (System 2000, Renishaw Inc., UK) exited at 514 nm in wavelength of Ar⁺ laser. Residual internal stress of the DLC films was determined by radius-of-curvature measurement. In order to measure it, a 475 μm thick silicon wafer was used for a substrate and thickness of the film is about 1μm. Bending of the film on the substrate was measured by interferometer (GPX XP, Zygo Corp, USA).

![Diagram showing characterization process](image)

Figure 2. Process flow of the type-2 film

1. Preparing micro needle array mold
2. Depositing DLC film
3. Removing the Al mold
4. Obtaining freestanding DLC
2.3 Fabrication of DLC film microstructures

3 types of DLC films were prepared in this study: (1) freestanding thick DLC film with c.a. 20 μm in thickness, (2) a freestanding micro needle array of DLC film and (3) DLC film coated micro-structured resin.

In both the type-1 and the type-2, the DLC films were prepared on an Al substrate. The Al substrate was finally removed from the DLC film as a sacrificial material. Figure 2 shows typical process flow for the type-2 film.

In the type-3, the DLC film was prepared on a microstructure using polypropylene (PP) resin, which was prepared by a lithographic, galvanoforming and afterforming (LIGA) process developed by the research group of Ritsumeikan University and Nissan Dioxide and System Research Inc [7].

3 RESULTS AND DISCUSSION

3.1 Properties of the DLC films

Figure 3 shows the residual internal stress of the DLC films as a function of voltage of HV pulse, in which all films exhibited compressive internal stress. Above 5 MPa of internal stress was obtained at HV = 24kV. It should be noted that the residual stress is smaller in over one order in comparison to that of other deposition methods, e.g. plasma enhanced CVD [3].

![Graph showing residual internal stress vs HV pulse height](image)

Figure 3: Residual internal stress of the DLC film depending on voltage of the HV pulse.

Indicates that there is a potential for depositing the DLC onto several kind of resins by the HIS-PBHD method.

![Photo of freestanding DLC film](image)

Figure 4: Photo of a freestanding DLC film (type-1) with c.a. 20 μm in thickness.

Figure 5 shows a typical Raman shift spectrum of the DLC film deposited by HV = -24kV. It shows a significant peak around 1500 cm⁻¹, which is a typical spectrum of the DLC film reflecting of sp² (centered at 1540 cm⁻¹) and sp³ (centered at 1340 cm⁻¹) electron-structures of carbon. It should be noted that the film prepared even in such low T_Ah has DLC structure.

![Raman spectrum graph](image)

Figure 5: Raman spectrum of the DLC film deposited by HV=-24kV.
However, there would be two issues to be solved: (1) distribution of the residual internal stress along the normal direction of the film and (2) slow deposition rate.

As shown in Figure 4, the freestanding DLC film was curved. It suggests there is distribution of the internal stress along the normal direction of the film and the stress at surface is greater than one near the substrate. It would be a reason that the surface temperature of the film would increase according to increase of the film thickness, even in case the $T_{max}$ is below 100°C.

The deposition rate of the DLC film was typically c.a. 10 nm/min and is similar to that of films in some conventional optical coatings. But it would be too slow for preparing freestanding structures with over 100 μm thick films. For improving the deposition rate, it is expected e.g. to increase plasma density by applying magnetic field.

3.2 DLC microstructure

Figure 6 shows the type-2 sample, which is a typical freestanding DLC microstructure. Each needle has a shape with height of about 100 μm and with aspect ratio of 2:1. It is suggested this the residual internal stress of the film would be sufficiently small to prevent the film from collapsing itself and obtain a freestanding structure.

![Figure 6](image)

Figure 6. Typical photo of the type-2 sample, which is the freestanding microstructure of the DLC removed from the sacrificial Al substrate.

Fig. 7 shows the type-3 sample, which is needle array coated by the 20 μm thick DLC film on the PP microstructure. The photo shows scarce damage in the shape. It suggests that the DLC film can be deposited at sufficiently low temperature to resin substrates by the HS-PBIID method.

![Figure 7](image)

Figure 7. Typical photo of the type-3 sample, which is deposited the DLC film on the PP microstructure.

Finally, we achieve the DLC film by the HS-PBIID method would be widely used in the MEMS devices. Especially, for micro fluidic devices, where polymers or glasses are frequently used, a passivation coating by the DLC would be effective. The HS-PBIID method can prepare the DLC film for such devices, because of the small residual internal stress and low deposition temperature.

4 SUMMAY

We developed freestanding microstructures of DLC and showed possibility of preparing it from resin molds. The DLC film was deposited by the HS-PBIID method. To optimizing the deposition parameters of the HS-PBIID method, the residual intrinsic stress of the DLC film can be reduced to about 0.1 GPA and temperature of the substrate can be preserved in low than 100°C even though 20-μm thick film was deposited. As an example of freestanding microstructures...
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References


Biography

Ryоshі YAMAMOTO received the M.S. from Kyoto University and the B.S. degree from Kwansei University.

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Kangshin INOUE graduated Kyoto College of Engineering and is developing a deposition system of DLC.