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イオン化蒸着法によるダイヤモンド 薄膜の硬度と結晶構造

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Hardness and Structural Studies of Diamond Thin Films Prepared by Ionized Deposition

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Hardness and structure of diamond thin films prepared by deflected beam of methane ions in comparison with the direct flow have been studied. The physical and structural properties of the films were examined through scanning electron microscopy (SEM), transmission electron diffraction (TED), transmission electron microscopy (TEM), and micro-Vickers hardness measurements. The results show (i) the surface morphology of the films prepared by deflected methane ions suggested a relatively better surface when it is compared with those of direct flow, (ii) TED observation of deflected ions indicated a fine spotty patterns with a large grain size polycrystalline, and (iii) a relatively higher hardness was attained for the films grown by bended ion beam.

1. INTRODUCTION

The unique combination of excellent characteristics such as mechanical, physical, chemical, and optical properties of diamond makes it an attractive candidate for various industrial applications. Interest in depositing single crystal of diamond is growing rapidly because of its extensive demand specially in semiconductor technology. Different methods including ion beam deposition¹⁻³⁾, sputtering⁴⁻⁶⁾, dc., rf-plasma deposition⁷⁻¹⁰⁾, using hydrocarbon gases have been attempted, however, all the films prepared were polycrystalline with small grain size. We also paid attention to this point by using an ionized deposition technique^{11,12)}. To minimize the effect of neutral particles such as soot and carbon clusters emitted from the ion source, the flow of methane ion

was bended by a magnetic field applied on top of the ion source and deposited in a separate substrate. In the present paper the surface morphology, crystal structure, and hardness of the films prepared by both direct and deflected flow of methane ions were studied.

2. Experimental procedure

The schematic diagram of ionized deposition system is shown in Fig. 1. The flow of ions is deflected by a magnet which is shown in the figure. The magnet can also be removed if zero deflection is desired. For the measurement of ion current density, a Faraday cage was placed in the same location as the substrate. The operation conditions of the ion source were as follows: An oil diffusion pump was used for the vacuum system. After suffi-

Fig. 1 Schematic diagram of ionized deposition system.

cient pumping the methane gas was introduced to the ion source. For a gas pressure of 10 Pa, and a magnetic flux density of 550 G, the substrate potential varied from 100~600 V, together with the substrate temperature ranging from 200 to 400°C. For the substrate material MgO or silicon wafer was used depending on the experimental conditions. The deposition rate was determined from the deposition time and the film thickness which was measured by an optical interferential microscope.

3. Results and discussion

Fig. 2 indicates the deposition rate as a function of ion current density. The upper curve (a) in the figure is the rate for typical ionized deposition, while the lower curve (b) indicates the growth rate when the flow of ion is deflected at the top of the ion source. It was found that, the deposition rate indicated by curve (a) is always greater than that of curve (b) independent of deposition conditions such as gas pressure, substrate potential and temperature.

Replica of the films with a thickness of 1 μm were prepared for the analysis of the surface structure through TEM observation. Fig. 3(a) shows a TEM pattern of the film deposited by the direct ion

Fig. 2 Deposition rate depending on ion current density. The film (a) and (b) are prepared at the deflection angle of $\theta=0^\circ$, and $\theta=45^\circ$, while the parameters P, Va and Id are the pressure, acceleration voltage and discharge current, respectively.

beam deposition. The hillocks on the surface of the film were observed occasionally, and are believed to be formed from the artifacts such as soot particles emitted from the ion source. Fig. 3(b) is the TEM pattern of a film formed by the deflected methane ion deposition. When the two surfaces are compared, it can be understood that, the film prepared with only CH_4^+ ion has a relatively smooth surface.

The crystal structure of the films produced by both conditions were observed through TED, and TEM. Films with the thickness of a few hundred angstroms were peeled from the surface of MgO substrate. The identical experimental conditions for the films formation were as follows: Discharge current was set to 0.3 A with an acceleration voltage of 300 V, and substrate temperature of 280°C. Ring patterns with occasional spots were obtained for the films prepared by direct ion beam deposition, while clear spot patterns were obtained for deflected methane ions deposition. A slight adjustment of acceleration voltage to 400 V, and substrate temperature to 320°C in case of deflected flow, resulted in a very fine

(a) Replica of the film for $\theta=0^\circ$ (b) Replica of the film for $\theta=45^\circ$ **Fig. 3** Surface roughness of the films observed by TEM.

spotty pattern as shown in **Fig. 4**. In the same figure TED patterns of the films indicating a large grain size polycrystalline diamond are compared with those of diamond powder with an average grain size of $0.5 \mu\text{m}$. Furthermore, the relation between the crystal structure and the hardness is also examined.

Fig. 4 Comparison of diffraction patterns.

(a) Diamond powder with an average grain size of $0.5 \mu\text{m}$.

(b) Film deposited at $\theta=45^\circ$

Fig. 5 Vickers hardness as a function of substrate voltage. The hardness of sapphire (Al_2O_3) and silicon (Si) is used for comparison. The parameters T_s , P , B and I_d are the substrate temperature, pressure, magnetic flux density and discharge current, respectively.

Indentation test measurement was used to determine the Vickers hardness of the films. To avoid indentation size effect a minimum load of 30 g was applied to the surface of each film having an average thickness of $3 \mu\text{m}$. The influences of substrate potential and temperature on the film hardness have been examined. **Fig. 5** indicates the Vickers hardness as a function of substrate potential. The experimental parameters for both conditions were as follows: Methane gas pressure was kept at 0.1 Torr, for a magnetic flux density of 550 G, together with the discharge current of 0.3 A. Films deposited with a substrate temperature of 300°C and potential of 250 V showed a maximum hardness of 6500 kg/mm^2 for the direct ion beam deposition and 7200 kg/mm^2 for the deflected methane ions.

4. CONCLUSION

Comparison of the two deposition rates with and without ion beam deflection indicated that, in case of typical ionized deposition, a considerable amount of other particles such as soot and neutral particles are deposited together with the desired methane

ions.

Results of TEM and TED observation for the deflected ion beam deposition suggested a relatively smooth surface, and a fine spot pattern of diamond which is fully coincident with those of diamond powder. A high hardness of 6500 kg/mm² for the direct beam, and 7200 kg/mm² for the deflected flow is also in good agreement with the reported values of bulk diamond ranging from 5700 to 10400 kg/mm².¹³⁾ Judging from the experimental results of TED, TEM, and the hardness for both conditions, it becomes evident that, the films prepared by deflected ion beam are composed of a large grain size polycrystalline diamond.

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