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Diamond Deposition Using a Grid Filament

D.M. Li, T. Mäntylä and J. Levoska*

Institute of Materials Science, Tampere University of Technology, P.O. Box 589, 33101 Tampere, Finland
* Microelectronics and Material Physics Laboratories, University of Oulu, P.O. Box 400, 90571 Oulu, Finland

Abstract. A grid tantalum filament of a dimension of $3 \times 4 \text{ cm}^2$ was used for diamond synthesis by hot-filament assisted chemical vapour deposition (HFCVD). After proper carburization, the filament could be used for multi-cycles of deposition. By heating the filament to 2400°C in 8% CH_4 mixed with H_2 , diamond has been deposited at rate of about $5 \mu\text{m}/\text{hour}$ on (100) oriented silicon substrate placed 5 mm away from the filament. By X-ray diffraction (XRD), the structure of the films deposited in the mixture of CH_4 and H_2 was characterized as diamond, while tantalum oxide was found in the presence of oxygen during deposition. The deposited diamond appeared uniform over an area of $2 \times 3 \text{ cm}^2$ observed by scanning electron microscopy (SEM) perhaps due to the stable filament geometry. Raman spectra of these films showed a sharp peak near 1332 cm^{-1} , which indicated the presence of a large amount of sp^3 bonds in the film. The present grid filament can be scaled-up for large area diamond deposition.

1. INTRODUCTION

Hot filament assisted chemical vapour deposition (HFCVD) is one of the effective techniques to deposit diamond in metastable conditions. Generally, the deposition rates of diamond by this technique are lower than $2 \mu\text{m}/\text{h}$ at filament temperatures below 2300°C . Recently, the deposition rate has been improved by using higher filament temperatures and higher methane concentrations [1-3]. For large area diamond deposition, a bigger filament is needed. In HFCVD it is common to shape the filament into the geometry of a coil. Farabaugh *et al.* [4] used dual coiled filaments which were made of tungsten wire to enlarge the deposition area. Diamond was deposited at the rates of lower than $0.4 \mu\text{m}/\text{h}$ and the uniformity of the deposition was not reported. A few tests have also been carried out using grid filaments to deposit diamond films on large areas. Rhenium filament can be used for long period time, at temperatures around 2000°C , but the diamond deposition rates are very low [5]. Joeris *et al.* [6] claimed that their tungsten grid filament could be used in many cycles of operation. However, diamond deposition rate was not reported. Schäfer *et al.* [7] used vertically arranged tantalum wires as their filament. They found that diamond deposition rates were lower than $0.5 \mu\text{m}/\text{h}$ and the rate varied considerably at different substrate positions.

The present study intends to use a carburized tantalum grid filament to deposit diamond on a large area with an improved deposition rate by using filament temperatures higher than the grid filaments mentioned above.

2. EXPERIMENT

The HFCVD apparatus used in this study consists of a cylindrical stainless steel chamber, a power supply and a gas feeding system. The essential component of the apparatus is the filament arrangement which is schematically shown in Fig. 1. The grid filament having dimensions of $3 \times 4 \text{ cm}^2$ consists of several tantalum wires in parallel. On a water cooled substrate holder, a silicon substrate with dimensions of $2 \times 3 \text{ cm}^2$ is placed 5 mm below the filament. The substrates were polished with $1 \mu\text{m}$ diamond spray prior to deposition. In this process, the filament temperature was measured by a two wave-length optical pyrometer which had been calibrated with a black-body radiator. The substrate was heated by the filament radiation and the substrate temperature was measured by a thermo couple mounted beside the substrate. The water cooled substrate holder can be adjusted to regulate the distance from the substrate to the filament.

Typical deposition time was 1 hour. To avoid the substrate overheating, it was lowered to about 10 mm away from the filament after 1 hour deposition in order to let the substrate cool down. After a 10 min cooling period the substrate was erected to the position where the deposition continued. The filament was carburized in 6% $\text{CH}_4 + 94\% \text{H}_2$ at temperatures of 2000~2400°C. Deposition parameters are listed in Table 1. The deposited films were characterized by X-ray diffraction (XRD, D500, Siemens), scanning electron microscopy (SEM 515, Philips) and Raman spectroscopy (Jobin-Yvon T64000).

Fig. 1. The arrangement of grid filament

Table 1. Deposition parameters

Filament temperature (T_f)	2400°C
Substrate Temperature (T_s)	950~1050°C
Total gas pressure (P)	4 kPa
Total gas flow rate	100 sccm
CH_4 concentration	6-8%
O_2 concentration	0, 2%
Filament to substrate distance (d)	5 mm
deposition time	1 h, 2 h

3. RESULTS

After 2.5 hours of heating, a newly installed filament was fully carburized into TaC as characterized by XRD (Fig. 2). Such carburized filament can be repeatedly used for diamond deposition. Films deposited in 1 hour showed well defined crystalline features (Fig. 3). The crystal structure of the films were identified by XRD to be pure polycrystalline diamond (Fig. 4). The sharp peak in 1332 cm^{-1} of the Raman spectra of these films (Fig. 5a~c) indicated that the films were essentially sp^3 bonded. The broad band in the spectra near 1550 cm^{-1} represented the presence of amorphous carbon in the films, but the bonding in the film is sp^3 dominated.

Fig. 2. X-ray diffraction pattern of carburized filament, Cu K α radiation

It was found difficult to control the substrate temperature during the deposition. The substrate temperature increased gradually as deposition proceeded although the flow of cooling water was continuously increased. As the deposition exceeded 1 hour the film began to become dark in the middle and this dark area expanded due to the substrate overheating. The grains of this dark area became hemispheres as observed by SEM (Fig. 6). No diamond was found in this area by Raman spectrum, and the centre of the broad band was shifted to the range of 1580 and 1600 cm^{-1} (Fig. 5d) which indicates the formation of graphite [8]. The

Fig. 3. Morphology of diamond films obtained with different methane concentrations

a. 6% CH₄   b. 7% CH₄
c. 8% CH₄   1 hour

Fig. 4. X-ray diffraction pattern of diamond films, Cu K α radiation. a, b, c refer to the corresponding morphologies in Fig. 3.

Fig. 5. Raman spectra of diamond films. a, b, c refer to the corresponding morphologies in Fig. 3. d to the film shown in Fig. 6.

filament showed brown color when 2% O_2 was used. It was found by XRD that the filament was oxidiz

In two hours deposition with 10 min cooling interval, the substrate was not observed to be overheated. The film morphology was uniform throughout the substrate area as shown in Fig. 7. The Raman spectra of such deposited film also showed a good uniformity of the diamond film (Fig. 8). The deposition rate of diamond film was about 5 $\mu\text{m}/\text{h}$ with 8% CH_4 concentration. The film thickness of the centre region of the film is slightly thinner than that of the edge region with the maximum difference of about 10 %.

Fig. 6. Schematic illustration (a) of overheated substrate area and the morphology of the film in this area

Fig. 7. Surface morphology of diamond film over $2 \times 3 \text{ cm}^2$ deposition area. The film was deposited in 2 hours with 10 min interception after 1 hour. 8% CH_4 , 4 kPa and 5 mm of filament-substrate distance

Fig. 8. Raman spectra of diamond film shown in Fig. 7. a, b and c show the locations of Raman measurements

4. DISCUSSION

A certain concentration of atomic hydrogen is necessary for diamond deposition at a fixed CH_4 concentration. Diamond deposition rate is, in general, proportional to the CH_4 concentration. In HFCVD

the concentration of atomic hydrogen is increased when the filament temperature increased [9]. In the case of coil filament, it has been proved that CH_4 concentration can be increased when the filament temperature is increased [1~3]. Our present study proved that, with the grid filament, high CH_4 concentrations up to 8% can be applied to deposit pure diamond film at T_f of 2400°C.

The overheating of the substrate is the main problem with grid filament. This limits both T_f and deposition time and consequently the deposition rate. In our early studies [2~3] much higher filament temperatures, 2600°C to 2890°C, could be used for high quality diamond deposition. In the present study even at T_f of 2400°C the radiation from the filament resulted after 1 hour in overheating of the center part of the substrate. This could not be avoided by enhanced substrate cooling. The intercepted deposition, allowing the cooling after 1 hour deposition, was an effective way to avoid the local substrate overheating and made it possible to grow thicker diamond films.

In the present study, T_f was measured as an average value of the filament temperature. The actual temperature in the middle of the filament may be higher than that of filament edge due to temperature gradient from the filament to the chamber wall which means it is difficult to determine the temperature distribution of the filament. Further studies are needed to measure the real temperature distribution of the filament and the substrate. This information is needed to improve the temperature uniformity and to optimize the geometry design of the filament. This can result in grid filaments which make possible the deposition of uniform diamond structure over extended substrate areas with reasonable deposition rate.

5. CONCLUSIONS

Using a grid TaC filament diamond films could be deposited on silicon substrate over an area of $2 \times 3 \text{ cm}^2$. At T_f of 2400°C and 8% CH_4 diamond films have been deposited with a rate of about 5 $\mu\text{m/h}$. The substrate was overheated by the filament when deposition exceeded 1 hour. Such overheating can be avoided by an interrupted deposition. By careful optimization of the geometry of the grid filament and the heat balance of the system, it is possible to deposit diamond films even on larger substrate areas with reasonable rate.

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