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Influence of Filament Geometry on Hot Filament Growth of Diamond Films

by

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INFLUENCE OF FILAMENT GEOMETRY ON HOT FILAMENT CVD GROWTH OF DIAMOND FILMS

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ABSTRACT

The influence of filament geometry on growth rate and morphology has been observed on diamond films deposited on single crystal silicon substrates in a hot filament CVD reactor. Single and dual helical W filaments having 5, 10, or 15 turns and $CH_4:H_2$ ratios of 0.25%-1.00% were used. With single filaments the deposition rate was approximately proportional to the number of turns in the filament for a given feed gas composition. Dual 5 turn filaments produced higher, dual 10 turn filaments produced equal and dual 15 turn filaments produced lower deposition rates, compared to single filaments for depositions carried out at the same $CH_4:H_2$ of 0.5%. Employing dual filaments doubled the area of uniform growth. Faceting of our films changed from {111} to {100}, as the $CH_4:H_2$ ratio was increased. Gas flow relative to substrate and filament positions influences the deposition rate and uniformity of growth. The best arrangement appears to be flow directed over the filaments normal to the substrate surface.

INTRODUCTION

A better understanding of the effect of chemical vapor deposition (CVD) growth conditions on film growth rates, morphology and perfection is essential to further development of diamond technology. Recent transmission election microscopy (TEM) work by Hetherington et al.[1] on microwave plasma assisted CVD deposited films and the study of Kaae et al.[2] of hot cathode DC plasma assisted CVD grown diamond films have shown that the perfection of polycrystalline diamond films is improved when the predominate morphology consists of {100} crystallite faceting parallel to the substrate. In this paper we report on the effects of filament geometry on the morphology of diamond films prepared by hot filament CVD and observe a transition from {111} faceting to {100} faceting. Variations in filament geometry consisted of single and dual helical filaments with 5, 10, or 15 turns. With the use of 5 turn filaments, the deposition rates with dual filaments were higher at all CH_4 concentrations. For depositions done at $CH_4:H_2$ of 0.5%, deposition rates for single and dual 10 turn filaments were equal, when 15 turn were used the dual filament deposition rate was lower than that of a single filament; however, the area of uniform growth was about doubled when dual filaments were used.

We also examined the effects of feed gas flow direction and methane concentration on film morphology and growth rate. The highest growth rate occurred with the flow across the filament and normal to the specimen surface.

These results demonstrate that proper design of the deposition chamber must take into account filament design and gas flow geometries.

EXPERIMENTAL

A hot filament CVD reactor, described previously [3] was used to produce the diamond films. The filament holder was capable of supporting single and dual filaments (2 parallel filaments equidistant from the specimen surface). The filaments were of a helical shape prepared from 0.12mm W wire with a

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~1mm turn diameter and were 3cm long. The number of turns in each filament was 5, 10, or 15. One purpose of the dual filaments was the deposition of diamond films over larger surface areas. The filament lifetime was typically 400 hours or longer.

The standard feed gas flow pattern consists of flowing the gas down over the filament. The gas enters the chamber through a circular tube approximately 10mm in diameter. The open end of the tube, approximately 25mm above the filament, directs the feed gas downward over the filament (or filaments in the dual filament system) and normal to the substrate surface.

To check the uniformity of deposition, four 1cm x 1cm Si specimens were placed on the substrate holder which was positioned 4mm below the filaments. Scanning election microscopy (SEM) characterization of each specimen provided morphology and thickness information from 4 different regions of the deposition. Thicknesses were measured both from SEM cross sectional micrographs and from the weight of the specimens before and after deposition. All substrates were single crystal Si wafers that had been rubbed with 1μm diamond paste and cleaned before insertion in the reactor. Deposition parameters used were: nominal substrate temperature, 750°C; pressure, 5×10^3 Pa; flow, 52sccm; nominal filament temperature 1800°C; deposition time 48 hrs. The $CH_4:H_2$ ratios were 0.25%, 0.50%, 0.75% and 1.00%.

Several depositions were carried out with 0.24mm diameter W wire filaments. Although these filaments appeared to hold their original shape better than the 0.12 mm diameter filaments, they were more fragile and prone to breakage during specimen removal and replacement. No appreciable increase in deposition rates were observed with the larger diameter filament wire. For these reasons, the depositions discussed were all made with 0.12mm W wire.

RESULTS AND DISCUSSION

Growth rate and morphology

The growth rates of single filament depositions as a function of number of filament turns are shown in Fig. 1, for a fixed ratio $CH_4:H_2$ of 0.5%. The maximum growth rate, 0.30μm/hr, was achieved with a single 15 turn filament. The growth rate increases nearly linearly with increasing number of filament turns. Fig. 2 shows SEM micrographs of the surface morphology of this set of films. The surface of the film made with a 5 turn filament, Fig. 2a, has predominately {111} faceting. The surface of film deposited with a 10 turn filament, Fig. 2b, shows a different kind of faceting. In addition to {111} faceting, a morphology is present which appears similar to that observed by Harker[4] and which Harker identified as a (220) orientated diamond film. The film shown in Fig. 2c, grown with a 15 turn filament, shows faceting similar to that seen in 2(b) together with a lot of secondary nucleation.

The growth rates of dual filament depositions vs. the number of filament turns are also shown in Fig. 1, for a 0.5% $CH_4:H_2$ ratio. The growth rate was nearly independent of the number of turns. Furthermore, only in the case of the 5 turn filaments did the dual filament growth rate exceed the single filament growth rate. This suggests that for the 0.5% $CH_4:H_2$ ratio and 52sccm flow rate used, the greater amount of filament material in the dual filament system is not effective in increasing the deposition rate due to a depletion of the methane in the gas phase reactions occurring at the filaments.

Effect of methane concentration

The effect on the growth rate of employing single 5 turn and dual 5 turn filaments with different feed gas compositions is shown in Fig. 3. The +

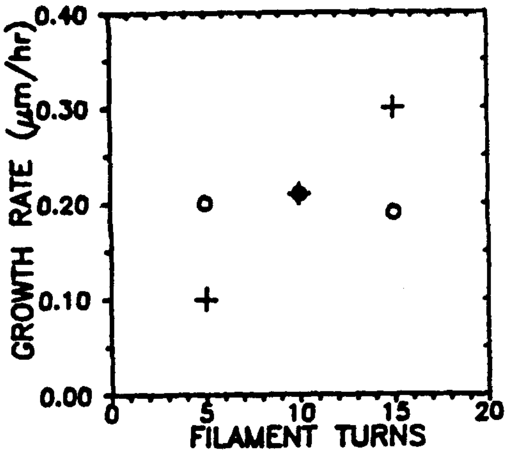

FIG. 1 Growth rate vs. number of turns for dual (o) and single (+) filaments for a fixed ratio $CH_4:H_2$ of 0.5%.

FIG. 2 SEM micrographs of films deposited using (a) 5 turn, (b) 10 turn and (c) 15 turn filaments. All micrographs are to the same scale.

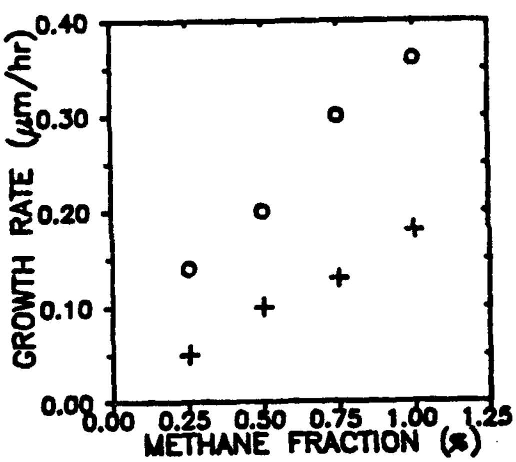

FIG. 3 Growth rate vs. % CH_4 for dual 5 turn filaments (o) and single 5 turn filaments (+).

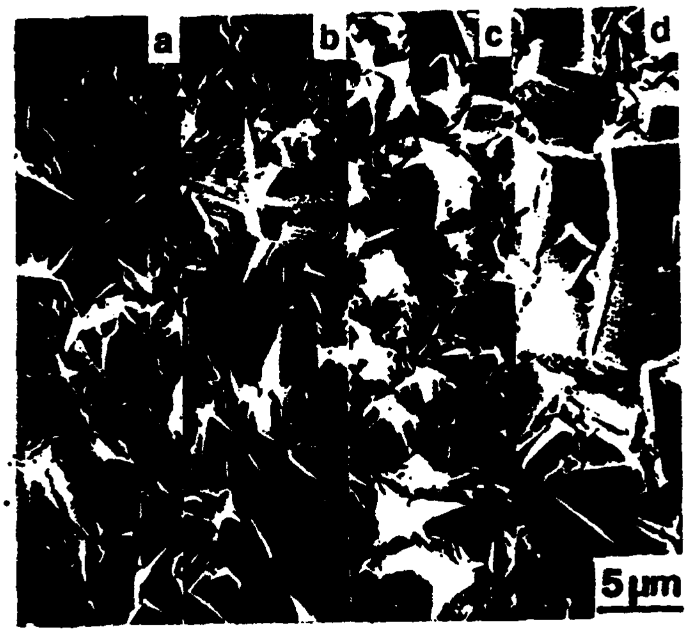

FIG. 4 SEM micrographs of films deposited using dual 5 turn filaments with (a) 0.25%, (b) 0.50%, (c) 0.75% and (d) 1.00% CH_4 in the feed gas. All micrographs are to the same scale.

are for a 5 turn single filament reported earlier [3] and the o are data for dual 5 turn filaments. These dual and all other dual filament deposition rates increased with increasing CH_4 content. The highest growth rate is 0.36µm/hr for a dual filament operating in a feed gas $CH_4:H_2$ ratio of 1.00%. In all of these cases the dual filament system showed a greater growth rate. Fig. 4 displays SEM micrographs of the surfaces of the dual filament films.

Each of the micrographs shows a different morphology. (111) faceting is the dominant morphology seen in Fig. 4a (0.25% $CH_4:H_2$ ratio). Some (111) faceting and some morphology suggesting (220) diamond are seen in Fig. 4b (0.5% $CH_4:H_2$ ratio). In Fig. 4c, (0.75% $CH_4:H_2$ ratio) some (100) faceting is evident even though the predominate morphology is that of (220) diamond. However, in Fig. 4d (1.00% $CH_4:H_2$ ratio), (100) faceting is the predominant surface morphology. Please note that no (100) faceting had been seen in the films we had described earlier[3]. However, similar morphology changes have been seen before by Williams and Glass[5] and Williams et al.[6] who have reported changes in morphology of films produced with different $CH_4:H_2$ ratios in a microwave CVD reactor. They had reported that with a 0.3% $CH_4:H_2$ ratio, (111) faceting predominated, while with 1.0% and 2.0% $CH_4:H_2$ ratios, (100) faceting predominated. Setaka[7] found that with 0.5% $CH_4:H_2$ ratios, the morphology of microwave assisted CVD films was composed of both (111) and (100) faceting.

In the case of the dual filament depositions, no changes in morphology were seen in the SEM micrographs of the four substrates coated simultaneously. Furthermore, the growth rates on each of the substrates were essentially the same.

Fig. 5 shows the growth rates obtained with dual 10 turn filaments and with a single 10 turn filament. Note that the growth rates are the same at $CH_4:H_2$ of 0.50%. The use of dual filaments did not improve the growth rate even though an improvement was observed with the 5 turn filaments. (See Fig.3 for comparison.) The highest growth rate shown in the figure is 0.27μm/hr with the 1.00% $CH_4:H_2$ gas ratio. Fig. 6 shows SEM surface micrographs of the films deposited in this series. Again differences in morphology are seen. In Fig. 6a, (0.25% $CH_4:H_2$ ratio) the film displays a dominant (111) habit. With increased CH_4 content, (100) facets appear in Fig. 6b. Well defined (100) growth is evident in Fig. 6c, (0.75% $CH_4:H_2$ ratio). In Fig. 6d, (1.00% $CH_4:H_2$ ratio) secondary nucleation obscures much of the faceting, but it is seen that the (100) morphology predominates. Not identified in this series were any morphologies of the (220) type diamond.

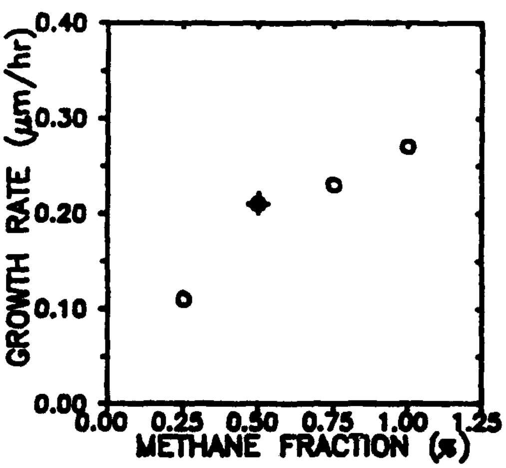

FIG. 5 Growth rate vs. % CH_4 for dual 10 turn filaments (o) and a single 10 turn filament (+).

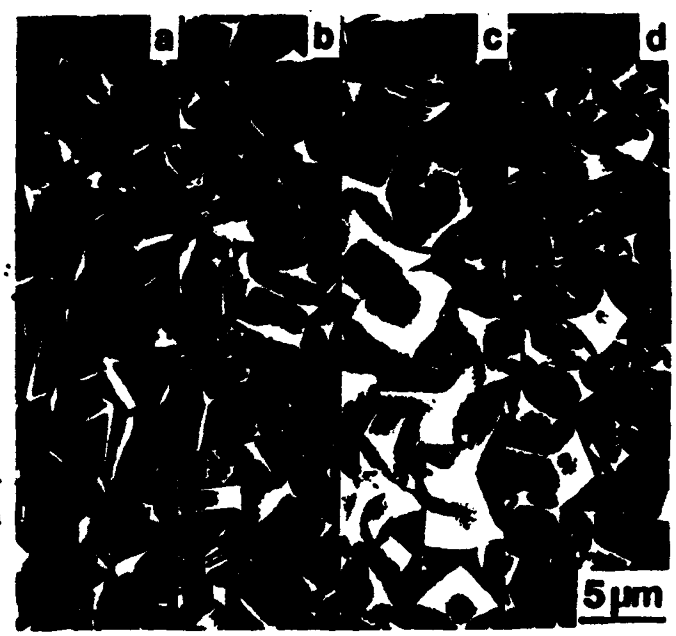

FIG. 6 SEM micrographs of films deposited using dual 10 turn filaments with (a) 0.25%, (b) 0.50%, (c) 0.75% and (d) 1.00% CH_4 in the feed gas. All micrographs are to the same scale.

a single 15 turn filament. This figure reveals that there are three instances where the growth rate for dual filaments was less than that using a single 15 turn filament. The rate measured for the film deposited with 1.00% $CH_4:H_2$ gas mixture was 0.30μm/hr, equal to that resulting from the use of a single 15 turn filament and 0.5% $CH_4:H_2$ gas mixture. There is no predominate (100) habit seen in the micrographs, even at the highest, 1.00%, CH_4, concentration. At the lower end of the CH_4 concentration, Fig. 8(a) shows that the film morphology for a 0.25% CH_4 deposition is composed of (111) faceting. In the other surface micrographs of 0.5%, 0.75% and 1.00% $CH_4:H_2$ depositions, the morphology is most easily identified as being similar to the (220) diamond. Secondary nucleation is also present, especially in the 0.75% $CH_4:H_2$ gas mixture deposition.

Changes in film morphology from predominately (111) to (100) faceting are essentially explained by the increasing presence of CH_4 in the feed gas mixture. In the case of the dual 15 turn filaments, the effect of the filaments is to reduce the amount of carbon available for sp^3 bonding, resulting in deposition of films whose morphology is characteristic of lower CH_4 depositions. It is possible that this also explains the lower than expected growth rates for the 15 turn filaments.

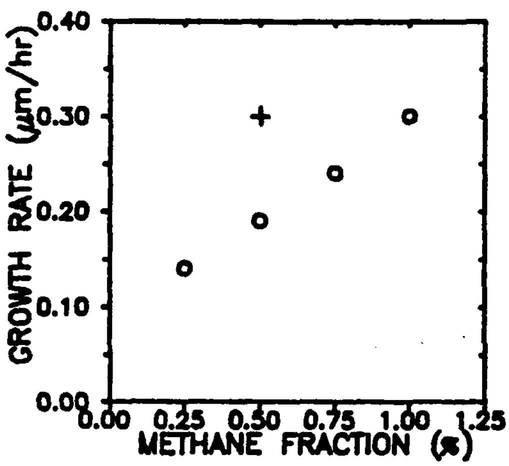

FIG. 7 Growth rate vs. % CH_4 for dual 15 turn filaments (o) and a single 15 turn filament (+).

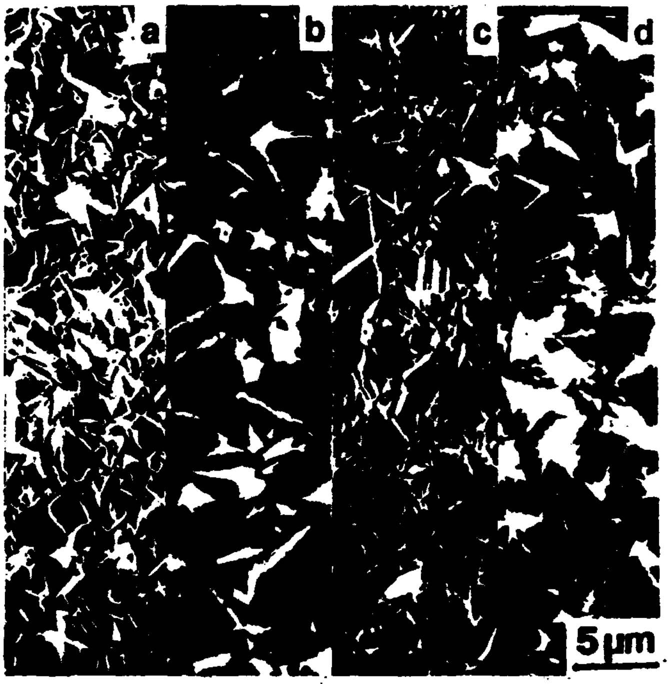

FIG. 8 SEM micrographs of films deposited using dual 15 turn filaments with (a) 0.25%, (b) 0.50%, (c) 0.75% and (d) 1.00% CH_4 in the feed gas. All micrographs are to the same scale.

Direction of feed gas flow

The direction of the feed gas flow was modified in several depositions. In one case, the gas flow was directed horizontally across the surface of the substrate and across the dual filament array. The purpose was to keep the growing surface of the diamond film free of debris that might fall from the filaments during the deposition. We immediately observed that the two filaments cured at different rates. In order to cure both filaments equally, the standard flow configuration was used. The flow was then directed horizontally for deposition. Growth rates obtained using this type of flow were found to be lower than the rates obtained when flow was directed down onto the filaments and normal to substrates.

In another configuration, a feed gas nozzle approximately 25mm square, the same size as the square substrate holder, replaced the standard circular feed gas opening. The growth rate was unchanged.

Finally, the feed gas was admitted at the base of the reactor, away from the substrate holder and the filament. The growth rates with this configuration were lower than the growth rates with the standard configuration. With a dual 10 turn filament in this alternate configuration, the growth rate was 0.14μm/hr (0.5% $CH_4:H_2$ ratio). In the standard configuration, the growth rate was 0.21μm/hr.

CONCLUSIONS

Deposition of diamond films under different conditions of filament geometry and feed gas flow have been carried out. The morphology variations we observed in our hot filament reactor depositions have previously been reported for microwave assisted CVD depositions.

With single filaments, the deposition rate was proportional to the number of turns, increasing with increasing turns. Growth rates using dual filaments increased with increasing CH_4 content. Dual 5 turn filaments showed increased growth rates compared to single 5 turn filaments. Using $CH_4:H_2$ of 0.5% with 10 turns, deposition rates with dual and single filaments were equal; with 15 turns deposition rates with dual filaments were lower than a single filament deposition rate. The area of uniform growth with dual filaments was about doubled. Predominant faceting changes from {111} to {100} with increasing $CH_4:H_2$ ratios in the feed gas. The morphologies and growth rates of films grown with dual 15 turn filaments appear to be characteristic of morphologies and growth rates of films grown with single filaments at lower $CH_4:H_2$ ratios. Growth rates were unchanged by changing the shape of the gas feed tube and decreased when the feed gas was admitted to the reactor away from the filament and specimen holder. We are planning a more complete set of data to verify our conclusions.

While the specific numerical results may be unique to our system, the trends we have observed should be helpful in the design of other hot filament reactors.

ACKNOWLEDGEMENT

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