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Diamond films grown on seeded substrates by hot-filament chemical vapour deposition with H_2 as the only feeding gas

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Abstract
Diamond films have been grown on polished Si substrates seeded with nanocrystalline diamond powder colloid using hot-filament chemical vapour deposition. Instead of using the conventional gaseous carbon source, a carbonized W filament was used as the carbon source. The only feeding gas was hydrogen. Compared with those produced by traditional methods, the polycrystalline diamond grown by this new method has smaller grain size. The growth mechanism is also discussed.

1. Introduction

Several surface treatments have been applied to enhance and control nucleation and growth of diamond on a large variety of substrates [1–3]. It seems that most methods for nucleation enhancement are efficient in creating diamond seeds larger than a minimum critical size on the substrate surface.

Makita *et al* [4] attempted to seed the Si substrate with well-defined nanocrystal diamond powder of 5 nm average particle size synthesized by an implosion process [5]. The particle diameter is in agreement with the critical nucleus of CVD diamond reported by Yugo *et al* [6]. A nucleation density of the order of 10^{10}–10^{11} nuclei cm^{-2} was achieved. The process proved to be simple, efficient and far less damaging to the substrate. In addition, diamond film can be uniformly fabricated on a substrate of a larger size and a different material. This is just the method that we adopted in our experiment.

In particular, we found that the diamond film can be deposited on seeded substrates with H_2 as the only feeding gas. Also, a carbonized W filament was used as the carbon source. Compared with those produced by traditional methods, the polycrystalline diamond grown under these conditions has smaller grain size. The growth mechanism is discussed in this paper.

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2. Experimental details

Hot-filament chemical vapour deposition (HFCVD) was used to grow the diamond films. Before deposition, the filament needs to be carbonized so as to keep it stable during the diamond growth process. A 16 cm long and 0.5 mm diameter tungsten filament was coiled into six turns. The resistance of the filament before carbonization was 1 Ω. The parameters of the carbonizing of the filament are as follows.

Base pressure:	10^{-3} Torr
Chamber pressure:	100 Torr
Filament temperature:	2300 °C
Heating current:	25 A
Final voltage:	175 V
Hydrogen flow rate:	100 sccm
Methane flow rate:	1.0 sccm
CH_4/H_2 ratio:	1.0%
Carbonization time:	1 h

During the carbonization, the heating current is kept constant by adjusting the heating voltage. After 1 h of carbonization, the heating current is stable at 25 A and the carbonization is complete. The resistance of the carbonized W filament is 1.7 Ω. The filament was heated up to 2500 °C at the heating current of 25 A, as measured with a two-colour optical pyrometer.

The starting substrate was a mirror-polished n-type, (100)-oriented Si wafer with a resistivity of 3–5 Ω cm. The cleaned wafer was seeded with the prepared nanodiamond lyophobic colloid [7]. No further treatment of the wafer was needed before growth besides cleaning and evaporation.

Diamond film was usually obtained after 1 h of deposition under the following growth conditions.

Base pressure:	10^{-3} Torr
Chamber pressure:	40 Torr
Filament temperature:	1900 °C
Substrate temperature:	870 °C
Hydrogen flow rate:	100 sccm
Methane flow rate:	0 sccm
Distance between filament and substrate:	1 cm

3. Results and discussion

The SEM image and Raman spectrum of the diamond films deposited on the seeded Si substrate are shown in figures 1 and 2, respectively.

The results (the SEM images and Raman spectrum) show that the quality of diamond film grown on the seeded Si substrate with H_2 as the only feeding gas is good. Further, the diamond grain size is about 250 nm, which is smaller than that for diamond deposition with CH_4 and H_2 as feeding gases [8].

With H_2 as the only feeding gas, polycrystalline diamond films have been grown not only on a seeded Si substrate but also on a seeded Si_3N_4 substrate [8]. Obviously, the original carbon source is a solid carbon source. Where does the solid carbon source come from?

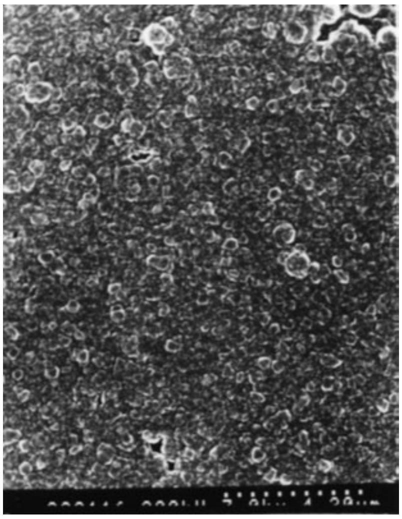

Figure 1. The SEM image of the diamond film deposited on the seeded Si substrate with H_2 as the only feeding gas.

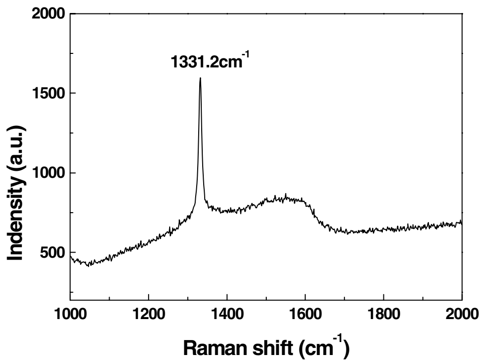

Figure 2. The Raman spectrum of the diamond film deposited on the seeded Si substrate with H_2 as the only feeding gas.

Three sources are possible: the residue solid carbide in the CVD reactor, the diamond seeds on the substrate and the carbonized W filament.

In order to determine which source is dominant, a simple experiment was done. A W filament that had not undergone carbonization treatment was used instead of the carbonized W filament. The resistance of the pure W filament was less than that of the carbonized W filament, so the deposition conditions had to be modified in order to keep the temperature of the pure W filament unchanged. The seeded Si substrate was used to grow diamond film. The deposition parameters are as follows.

Base pressure:	10^{-3} Torr
Chamber pressure:	100 Torr
Filament temperature:	2300 °C
Substrate temperature:	800 °C
Heating current:	22 A
Final voltage:	150 V
Hydrogen flow rate:	100 sccm
Methane flow rate:	0 sccm
Deposition time:	1 h

The experimental results show that diamond films cannot be grown under the above conditions. This means that the solid carbon source is the carbonized W filament, rather than the residue solid carbide in the CVD reactor or the diamond seeds on the substrate.

In the experiment with H_2 as the only feeding gas, the diamond deposition may involve the following processes:

(a) Activation of hydrogen by the filament to form atomic hydrogen.
(b) Reaction of atomic hydrogen with the carbonized W filament to form hydrocarbon species.
(c) Transport of the hydrocarbon species to the substrate surface to form diamond.

The hydrocarbon species formed are still unknown; they are also different from the species in the experiment of Woo *et al* [9]. In their study, the diamond films are also deposited by HFCVD from a solid carbon source. The hydrocarbon species are formed by the reaction of atomic hydrogen with the graphite placed on the filament. These species are more effective precursors for diamond nucleation. The continuous diamond films can be grown on various substrates including mirror-polished silicon substrates without any substrate pretreatment such as diamond powder scratching or negative substrate biasing. The efficiency and the nucleation density of the method are found to be five times and five orders of magnitude higher than those of the conventional HFCVD method, respectively. However, the production of the hydrocarbon species formed in this study is only effective with seeded substrates. The diamond films cannot be grown on Si substrate abraded with diamond powder under the same deposition conditions. The analysis of these hydrocarbon species is being studied further.

4. Conclusions

With hydrogen as the feeding gas and with a carbonized W filament as the carbon source, polycrystalline diamond film has been deposited on a polished Si substrate seeded with nanocrystalline diamond powder using HFCVD. In comparison with diamond grown under conventional deposition conditions with CH_4 and H_2 as feeding gases, the polycrystalline diamond grown by this new method has smaller grain size. The production of hydrocarbon species by reaction of atomic hydrogen with the carbonized W filament is only effective with seeded substrates, not for Si substrates abraded with diamond powder.

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