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Effect of reaction pressure on the nucleation behaviour of diamond synthesized by hot-filament chemical vapour deposition

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Synthetic diamond particles were deposited on a Si (1 0 0) substrate using a hot-filament chemical-vapour-deposition method in order to study the effect of the reaction pressure on the nucleation behaviour. The reaction pressure was controlled, as an experimental variable, from 2 to 50 torr under the following conditions: a filament temperature of 2200 °C, a substrate temperature of 850 °C, a total flow rate of 200 s.c.c.m. and a methane concentration of 0.8 vol %. Diamond deposits on the Si wafer were characterized by micro-Raman spectroscopy, scanning electron microscopy (SEM) and optical microscopy.

The maximum nucleation density of diamond particles on the unscratched Si substrate is shown at the reaction pressure of 5 torr. These phenomena can be explained by the competition effect between β-SiC formation, which increases the diamond nucleation density, and atomic-hydrogen etching which decreases the nucleation sites.

A new fabrication method for a high-quality diamond film without any surface pretreatments is introduced using a combination process between diamond nucleation at low pressure (5 torr) and growth at high pressure (30 torr).

1. Introduction

In respect of materials science and engineering, diamond film is one of the most attractive materials in the world because of its superior and outstanding properties and its various fields of application [1]. From the beginning of the 1980s, many researchers have paid attention to synthetic-diamond formation by decomposition of various hydrocarbon gases mixed with hydrogen using the hot-filament chemical-vapour-deposition (HFCVD) technique [2]. There have been many efforts to control the nucleation and growth of diamond, but the basic mechanism of diamond nucleation and growth by chemical-vapour-deposition (CVD) methods has not yet been understood in terms of the deposition parameters. In order to control the nucleation process for various applications, it is essential to understand the dependence of the diamond-nucleation behaviour on the deposition parameters, that is, the reaction pressure, the flow rate of the reaction gas, the substrate temperature, the filament temperature and the methane concentration, etc.

However the many researches on the deposition parameters of the CVD method have, so far, been insufficient to understand and utilize the behaviour of diamond nucleation. Recently, Park [3] reported some details of the nucleation behaviour of diamond particles corresponding to the deposition parameters of HFCVD. A few reports on this topic have been published, but these are in an early stage. The effect of the reaction pressure, as a deposition parameter, on diamond nucleation has been virtually ignored in comparison with the other deposition parameters.

It is well known that the scratching of a Si-substrate surface by a diamond paste or a hard-material powder [4] can enhance the nucleation density of diamond films. Although these surface pretreatments may limit the application fields, such as optical and electronic coating materials, due to the substrate surface damage, it is impossible to fabricate thin, continuous diamond films without such surface pretreatments because of the reduction of the nucleation density. In addition, Joffreau *et al.* [5] have reported that refractory metal substrates which form stable carbides, (for example, Mo, W, Ti and Ta) are favourable for diamond nucleation. Several researchers [6, 7] have reported that a β-SiC layer plays an important role in diamond nucleation when using Si wafers.

In this study, diamond was synthesized using HFCVD, which has proven to be a very useful method, which is easily controllable by its deposition parameters. The nucleation behaviour of diamond particles was investigated with the reaction pressure in the range 2–50 torr using an unscratched Si (1 0 0) wafer. Subsequently, the formation of a diamond film was demonstrated on a Si substrate without any surface pretreatment by the HFCVD method, with the introduction of the combination process between diamond nucleation at low pressure (5 torr) and growth at high pressure (30 torr).

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2. Experimental details

Diamonds were synthesized from the decomposition of a mixture of hydrogen and methane, CH_4, using a HFCVD apparatus as described in [8]. The quartz tube used as the reactor was 260 mm in length and 34 mm in inner diameter. In order to decompose the mixture gas, a tungsten filament was made by winding 0.5 mm tungsten wire into coils with six turns, 5 mm in diameter, and suspended 5 mm above the substrate which rested on a titanium holder. The filament temperature was measured by an infrared (i.r.) thermometer (Minolta, IR-630); and the substrate temperature was measured with a K-type thermocouple, placed in contact with the titanium substrate holder. The gas-flow rate was controlled with flow meters and the pressure was measured by a U-manometer. The system was pumped by a mechanical pump.

In the present work, a silicon wafer with a (1 0 0) orientation was used as a substrate. The Si substrate was not scratched with diamond powder (to calculate the nucleation density of diamond particles), because substrate scratching results in a continuous diamond film due to high nucleation density [9]. The substrates, $5 \times 5\ mm^2$ in area and 0.5 mm thick, were ultrasonically cleaned for 20 min in acetone and finally dried in air. Typical experimental conditions are listed in Table I. The only deposition parameter varied was the reaction pressure of the mixture gas.

After the diamond-deposition procedure, the samples were characterized by scanning electron microscopy (SEM), optical microscopy (OM), and micro-Raman or Raman spectroscopy. SEM and OM photographs were used to observe the morphology of the diamond particles and to calculate the diamond nucleation density. Raman spectroscopy was excited using an Ar-ion laser, which is a useful and powerful instrument for characterizing the quality of diamond.

3. Results and discussion

3.1. Effects of the reaction pressure on the diamond-nucleation behaviour

Fig. 1 shows SEM micrographs of diamond deposited at reaction pressures of 2, 5, 15, 30 and 50 torr, with all the other deposition parameters fixed. The number of diamond particles increases as the reaction pressure decreased, and the nucleation density (the number of diamond particles per square centimetre) had a maximum value at 5 torr of over $10^6\ cm^{-2}$. It is generally known that it is almost impossible to get such a nucleation density using an unscratched Si wafer. Also it was clearly shown that continuous nucleation occurs during deposition at low pressures (2, 5 and 15 torr) from the fact that the samples had various sizes of diamond particles. In diamond deposition at high pressures (30 and 50 torr), the majority of the diamond particles were of a similar size, indicating that diamond crystals grow rapidly after a short nucleation period. Diamond particles at these pressures have a large particle size due to the high growth rate, with a relatively high density of carbon species. The variation of diamond particle size with reaction pressure can be explained by the initiation period required in diamond nucleation; this is the finite time necessary to nucleate diamond particles before growth occurs [10]. Therefore it was found that the initiation period increased with a decrease in the reaction pressure.

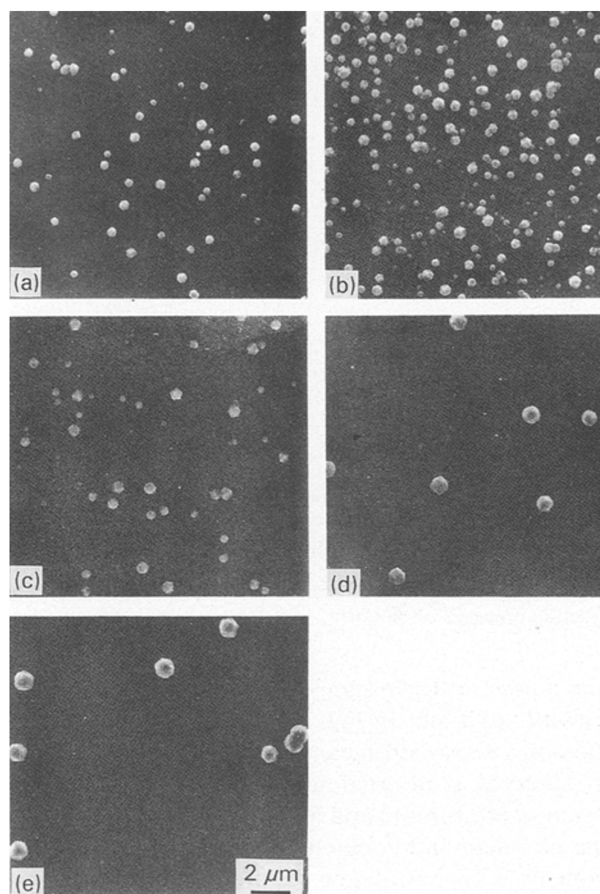


Figure 1 Scanning electron micrographs of diamond particles deposited at the following reaction pressures: (a) 2 torr, (b) 5 torr, (c) 15 torr, (d) 30 torr, and (e) 50 torr.

TABLE I Experimental conditions of diamond deposition

Deposition parameters	Range
Filament temperature (°C)	2200
Substrate temperature (°C)	850
CH_4 concentration in H_2 (vol %)	0.8
Total flow rate (s.c.c.m.)	200
Filament–substrate distance (mm)	5
Deposition time (h)	4
Reaction pressure (torr)	2–50

Fig. 2 shows the variation of the nucleation density with the reaction pressure. The nucleation density was calculated and averaged using the nucleation densities at several different sites of the sample. The nucleation density of diamond particles was a maximum at 5 torr, and then it monotonically decreased with increasing reaction pressure.

The micro-Raman spectra of diamond particles deposited at each reaction pressure are shown in Fig. 3. It is well known that a sharp peak at $1332\ cm^{-1}$ arises from the diamond, and broad peak occurring at the $1550\ cm^{-1}$ wavenumber arises from graphite and other forms of carbon (including amorphous carbon),

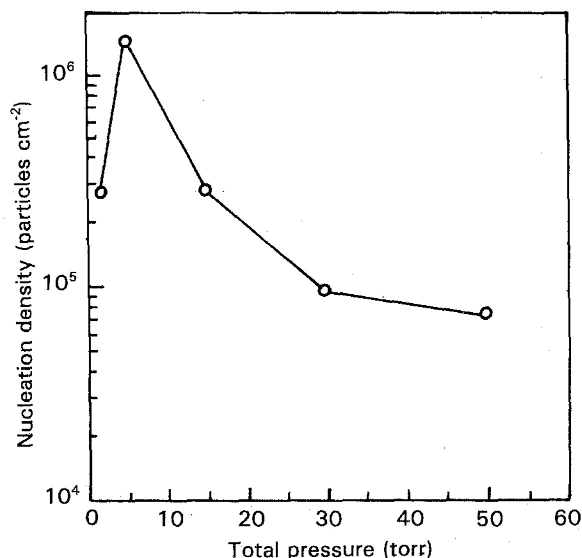


Figure 2 Variations of the diamond nucleation density with total reaction pressures on Si (1 0 0).

and a peak at the 960 cm^{-1} wavenumber is due to the presence of β-SiC. In Fig. 3, the characteristic peak of diamond is very strong and the presence of β-SiC can be observed at all reaction pressures, especially at low reaction pressures (2 and 5 torr). The intensity ratio of the non-diamond components to the diamond components is higher at low reaction pressures than at high pressures. As the reaction pressure decreased further, diamond particles, with small amounts of non-diamond components, appeared. High-magnification SEM was used to compare the surface morphology of diamond particles with the Raman-spectra analysis. A typical cubo–octahedral shape is shown at all reaction pressures and the diamond particle shape is rougher at low pressures than at high pressures. These results indicate that the surface morphology is closely related to the relative amounts of the diamond and non-diamond carbons in the films [11]. The high-quality diamond can be deposited at higher reaction pressures (30 and 50 torr), as confirmed by the Raman-spectra study.

The maximum nucleation density can be achieved at 5 torr, which can be explained as follows. It is reported that the role of the carbide layer between the diamond film and the substrate is very important, and the intermediate layer is first formed prior to and during diamond nucleation in the initial stage of diamond deposition [5–7, 12, 13]. The formation of a carbide layer has been shown to be a necessary step prior to diamond nucleation on carbide-forming substrates. Badzian [14] have proposed that β-SiC can act as a nucleation site for diamond synthesis on silicon substrates due to the partial lattice matching of the {1 1 0} planes of diamond and β-SiC. Recently, several researchers [6, 12] have estimated that the thickness of the β-SiC layer is about 10.0 nm. Because the presence of a β-SiC intermediate layer is identified from Raman analysis in Fig. 3, the formation of a β-SiC layer may play an important role in the increase in the nucleation density at low pressures.

The etching effect of atomic hydrogen is another important factor in the diamond-deposition process.

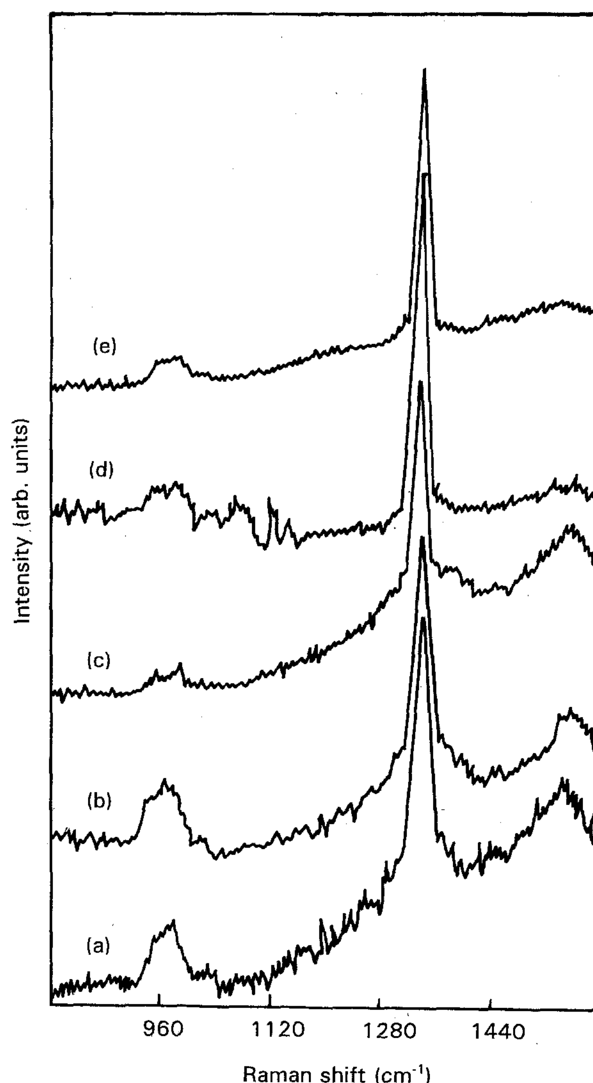


Figure 3 Micro-Raman spectra of diamond particles as a function of the following reaction pressures: (a) 2 torr, (b) 5 torr, (c) 15 torr, (d) 30 torr, and (e) 50 torr.

During diamond deposition, there is growth competition between diamond and graphite; diamond growth predominates due to the higher etching rate of graphite by atomic hydrogen. According to the kinetic theory of molecular gases, the mean free path of a gas atom at constant temperature has a value which is in an approximately inverse proportion to the pressure. The etching by atomic hydrogen is enhanced at lower pressures because the flux of atomic hydrogen reaching the substrate increases as the pressure decreases due to the longer mean free path. Buckley *et al.* [15] have reported the characteristics of diamond film using HFCVD by Raman spectroscopy. The diamond films have a higher defect density as the reaction pressure decreases, which can be understood in terms of the relatively higher electron and ion fluxes at the substrate for diamond films at low pressure. From the Raman spectra in Fig. 3, the amount of the non-diamond component increases as the reaction pressure decreases (2, 5 and 15 torr).

In the present work, the maximum nucleation density of diamond was achieved at 5 torr, as shown in Figs 1 and 2. This phenomena was not reported by earlier researchers, which can be explained, in part, by

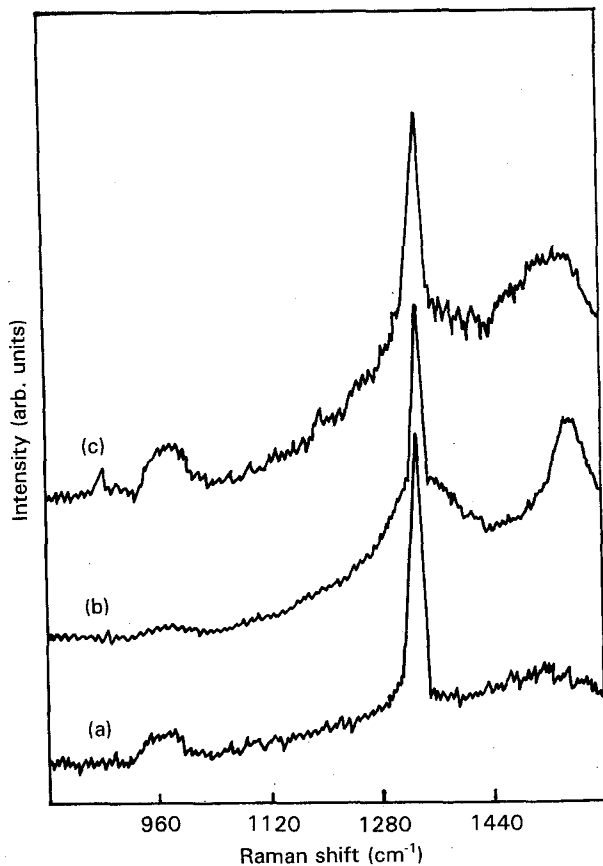
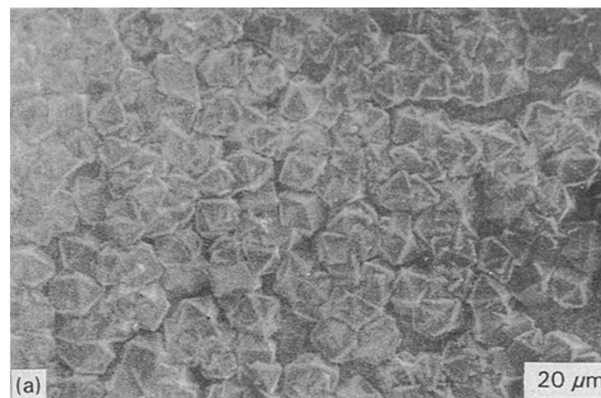


Figure 4 Micro-Raman spectra of the samples of diamond deposition using the high-growth-rate process, after different nucleation times at 5 torr: (a) 0.25 h, (b) 0.5 h, and (c) 1 h.

considering the mechanism of β-SiC formation and the etching effect of hydrogen atoms. It was proposed that, in the pressure range below 30 torr, nucleation of β-SiC is much more pronounced than at higher pressures [16]. Since β-SiC plays a strong role as a source of nucleation sites, β-SiC formation results in an increase in diamond nucleation. As the kinetic energy of atomic hydrogen is dependent on the total reaction pressure, the etching of nucleation sites by atomic hydrogen is more enhanced at low pressure. Consequently, the phenomena of maximum nucleation density is the result of a compromise between β-SiC formation and atomic-hydrogen etching. The former enhances diamond nucleation because of an increase in nucleation sites, and the latter suppresses diamond nucleation. As the reaction pressure decreases, both β-SiC formation and atomic-hydrogen etching may increase simultaneously, but the nucleation-site enhancement by β-SiC formation has priority over the nucleation density increase. But as reaction pressure decreases, the etching of nucleation sites by atomic hydrogen predominates at very low pressures (2 torr), resulting in a decrease in the nucleation density. As a result, the maximum nucleation density of diamond appeared at 5 torr in the present study.

3.2. Diamond-film fabrication on unscratched Si wafers

As mentioned above, the surface pretreatment may limit the application fields of diamond films. This



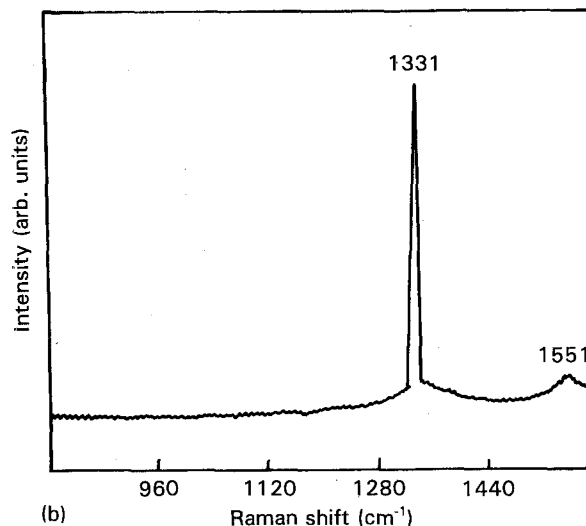


Figure 5 (a) SEM micrograph of a diamond film deposited at 5 torr for 1 h and at 30 torr for 9 h, and (b) a Raman spectrum of the diamond film.

paper presents a simple method of preparing diamond films without surface pretreatment using previous results.

To obtain high-quality diamond films on unscratched silicon wafers, a combination of the low-pressure (5 torr) process, (to get a high initial nucleation density) and the high-pressure (30 torr) process (for a high growth rate at a later stage) should be applied.

Fig. 4 shows micro-Raman spectra of the samples of diamond deposition using the high-growth-rate process at 30 torr after different nucleation times (0.25, 0.5, and 1 h) at 5 torr, respectively. The diamond nucleation density is enhanced with an increase in the nucleation time. From the Raman-spectra analysis, it is observed that the non-diamond-component peak about 1550 cm^{-1} is reduced as the nucleation time at 5 torr decreases, and high-quality diamond particles can be obtained as the holding time at 30 torr increases.

Fig. 5a and b shows a SEM micrograph and a Raman-spectrum analysis of a diamond film deposited by a combination of processes: a nucleation process at 5 torr for 1 h and a growth process at 30 torr for 9 h. The diamond film could be fabricated as shown in Fig. 5a; it was composed of diamond particles about 15 μm in diameter. In Fig. 5b, the Raman-spectrum analysis

is conclusive evidence of a high-quality diamond film, as it shows an increase in the intensity of the characteristic diamond peak and a decrease in the non-diamond peak. It is demonstrated that high-quality diamond film can only be obtained by a change in the reaction pressure, without surface pretreatment of Si (1 0 0) wafers.

4. Conclusions

In this paper, the nucleation behaviour of an unscratched Si (1 0 0) wafer was studied by investigating the effect of the reaction pressure as a deposition parameter in the HFCVD method. These results lead to the following conclusions.

1. Under the present experimental conditions on an unscratched Si (1 0 0) wafer, maximum nucleation density is obtained at 5 torr, and a higher growth rate is obtained at higher reaction pressures.
2. From the Raman-spectra analysis, the diamond particles grown at high reaction pressures (30 and 50 torr) are of higher quality than those deposited at low reaction pressures (2, 5 and 15 torr).
3. It is suggested that the maximum in the diamond nucleation density (as the reaction pressure varies) is attributed to competition effects between β-SiC formation and atomic-hydrogen etching.
4. By the introduction of both a low-pressure (5 torr) nucleation and a high-pressure (30 torr) growth process, high-quality diamond films can be fabricated on Si (1 0 0) wafers without any surface pretreatments.

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