

Nucleation behaviour of diamond particles on silicon substrates in a hot-filament chemical vapour deposition

SOON-SUP PARK, JAI-YOUNG LEE

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Kusong Dong 373-1, Yuseong Gu, Taejeon, Korea

Diamond films and particles have been deposited on a silicon substrate using a hot-filament chemical vapour deposition (CVD) method in order to study the effect of hydrogen on the behaviour of diamond nucleation. The nucleation density of diamond was affected by both hydrogen treatment prior to deposition and filament temperature, T_f . The nucleation density was decreased markedly with increasing hydrogen-treatment time. The nucleation density also changed with increasing T_f , which increased initially and then reached a maximum at 2100 °C and decreased thereafter. Etching of the substrate surface was observed and enhanced with both increasing hydrogen-treatment time and increasing T_f . The changes in nucleation behaviour were related closely to the etching of substrate surface. These results are explained in terms of the etching of nucleation sites.

1. Introduction

Recently, studies on the synthesis of diamond films and particles under metastable conditions have been investigated by many researchers because of their great potential applications [1, 2]. Several synthesis techniques to prepare diamond films and particles have been proposed, including thermo-filament chemical vapour deposition (CVD) [3], plasma discharge [4, 5], and electron-assisted CVD [6], etc. Until now, a large number of reports has concentrated on the high growth rate of diamond films and their qualities. Specifically, atomic hydrogen, which exists in the superequilibrium state, has a strong promoting effect on diamond growth. A variety of CVD methods has been developed for producing a superequilibrium of atomic hydrogen. However, detrimental effects of hydrogen on the adhesion between diamond film and substrate and on the diamond nucleation have been also reported. Kweon and Lee [7] reported that in their hot-filament CVD system, the etching of silicon substrate by hydrogen atoms took place with diamond particle growth in the early stages of deposition. They suggested that the etching reaction inhibited the reaction between the depositing atoms and the substrate material, which resulted in poor adhesion between the diamond films and the substrate material. Saito *et al.* [8] observed that in their microwave plasma system, no deposits were obtained and the etching of silicon substrate by plasma took place when a substrate was placed at the centre of the plasma. They interpreted these results as the effects of the high concentration of electrons and hydrogens at the centre of plasma.

Although atomic hydrogen improves the growth rate and quality of diamond films, it seems that it has a detrimental influence on adhesion and nucleation. In order completely to utilize the excellent properties of diamond in applications, the hydrogen effect has to be fully understood. Unfortunately, it is unclear at this stage. Particularly, little is known about the hydrogen effect on the behaviour of diamond nucleation. In this paper, the effect of hydrogen on the behaviour of diamond nucleation is extensively investigated, in order to obtain a better understanding of the nucleation behaviour of diamond. The changes in the morphology of substrate surface due to hydrogen are also investigated.

2. Experimental Procedure

The diamond films and particles in this study were deposited in a hot-filament CVD system. The details of this system and the deposition procedure have been described in a previous paper [9]. (1 0 0)-oriented silicon single crystals were used as substrates. The substrate was scratched by diamond powder with a particle size of 1–2 μm before deposition to enhance diamond nucleation. After scratching of the substrate surface, all substrates were ultrasonically cleaned in acetone until no diamond particles were observed under the scanning electron microscope (SEM). Mirror-polished silicon wafers were also used as substrates. The size of the substrate used in this experiment was 5 × 5 × 0.5 mm³. The deposition conditions are given in Table I. To obtain a better understanding

of the effects of hydrogen on the diamond nucleation behaviour, two experimental variables were chosen: (1) the filament temperature, T_f , because hydrogen dissociation will be accelerated with increasing T_f , can contribute to the observation of changes in the nucleation behaviour with the degree of hydrogen dissociation, (2) hydrogen-treatment time prior to deposition. The hydrogen treatment consists in the substrate being exposed to a hydrogen atmosphere prior to deposition and the procedure is as follows. A silicon substrate is mounted on the holder. The reaction chamber is evacuated to a minimum pressure. Hydrogen is introduced into the reaction chamber and the filament is heated. When the substrate reaches the desired temperature, hydrogen treatment is begun. The hydrogen treatment conditions are gas pressure 20 torr, substrate temperature 750°C, filament temperature 2100°C, flow rate 100 standard cm³ min⁻¹. After hydrogen treatment for the desired time, methane is added to begin the diamond deposition.

3. Results and discussion

Fig. 1 shows a scanning electron micrograph of diamond particles deposited on a silicon substrate which was scratched by diamond powder with a particle size of 1–2 µm after 2 h deposition at $T_f = 2100^\circ\text{C}$. The nucleation density of diamond deposited on the left-hand side is higher than that on the right-hand side. The right-hand side of the substrate surface was exposed to hydrogen for 30 min before deposition, while the left-hand side was protected from this treatment by covering with a second piece of silicon. It is obvious that the hydrogen treatment prior to deposition inhibits diamond nucleation.

Fig. 2 shows the changes in the nucleation density of diamond deposited on a silicon substrate as a function of hydrogen-treatment time. The deposition was performed for 2 h at $T_f = 2100^\circ\text{C}$. The nucleation density decreases rapidly as the hydrogen-treatment time increases. No deposits were observed after 60 min hydrogen treatment. These results imply that a reaction

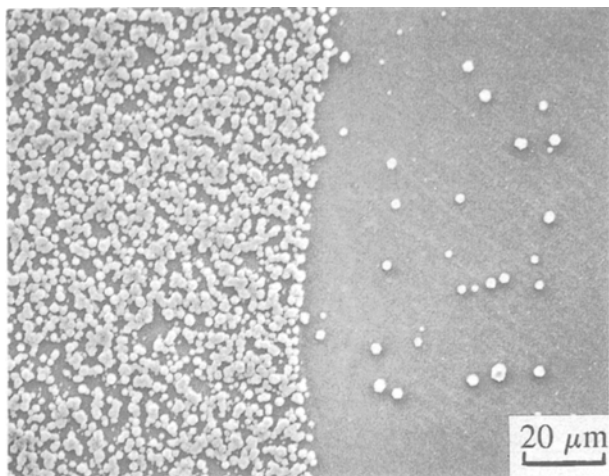


Figure 1 Scanning electron micrograph of the diamond deposited on a silicon substrate after hydrogen treatment (right-hand side) and without hydrogen treatment (left-hand side).

between nucleation sites and hydrogen can occur and the degree of this reaction depends on the hydrogen-treatment time.

The changes in the morphology of the substrate surface after 30 and 60 min hydrogen treatment, respectively, which had been prepared separately, are shown in Fig. 3. The surface was roughened by hydrogen treatment. It is considered that the surface was etched by active atomic hydrogen [7, 8], the degree of etching increasing with increasing hydrogen-treatment time. No deposits were observed on the surface condition of Fig. 3b. This implies that the nucleation sites created on the substrate surface during scratching with diamond powder, were etched by active hydrogen atoms, resulting in a decrease of the nucleation density. As shown in Fig. 2, this takes place very rapidly during the early stage of hydrogen treatment.

Recently, Celii and Butler [10] reported that the quantity of atomic hydrogen varied significantly with the reactant CH₄/H₂ fraction as well as the filament temperature in the filament-assisted diamond-growth environment. Although the filament temperature at which hydrogen dissociation commences varied somewhat with the reactant CH₄/H₂ fraction, the hydrogen dissociation was increased significantly with increasing filament temperature. In this work, the effect of T_f on diamond nucleation was investigated to observe the changes in the nucleation behaviour with the degree of hydrogen dissociation.

Fig. 4 shows the changes in the nucleation density of diamond particles as a function of T_f . The other deposition parameters are fixed, as described in Table I. The substrate used was a mirror-polished silicon wafer. No hydrogen treatment prior to deposition was performed. At $T_f < 1800^\circ\text{C}$, no deposits were observed, due to the low chemical reactivity [11]. A measurable nucleation density was obtained only at $T_f > 1900^\circ\text{C}$. However, the deposits formed at 1900°C showed a ball-like morphology which included many non-diamond components. Above 2000°C, well-faceted diamond particles were observed. As shown in Fig. 4, the nucleation density increases initially, reaches a maximum at 2100°C, and then decreases.

Fig. 5 shows the surface morphology of the substrate before and after 4 h deposition at $T_f = 2000$ and 2300°C, respectively. The surface is roughened during deposition. The surface morphology of the substrate is somewhat different with T_f . At 2000°C, pits were formed partly on the substrate surface (Fig. 5a). However, at 2300°C, the whole substrate surface consisted of hillocks and furrows (Fig. 5b). This is similar to the interface morphology between diamond films and silicon substrate reported by Kweon and Lee [7], who interpreted the morphology change as the etching of the silicon substrate by atomic hydrogen.

It was reported that the diamond growth rate increased at T_f in the range 2000–2300°C [11, 12]. However, in this work, the nucleation density increased up to 2100°C and then decreased. The gas species decomposed by thermal energy of hot filament may have an influence mainly on the behaviour of diamond nucleation, because the other deposition

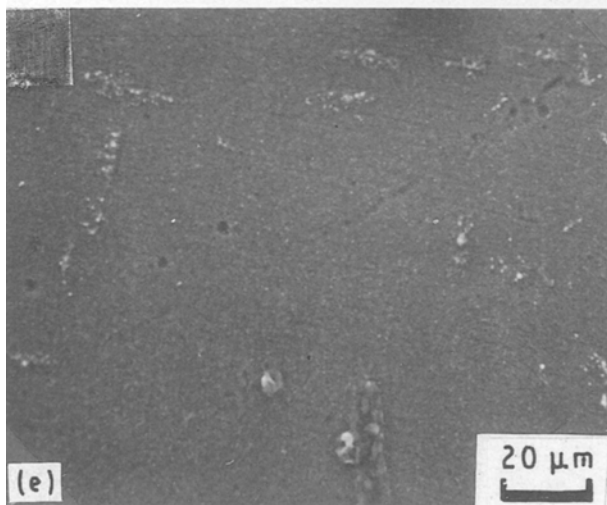
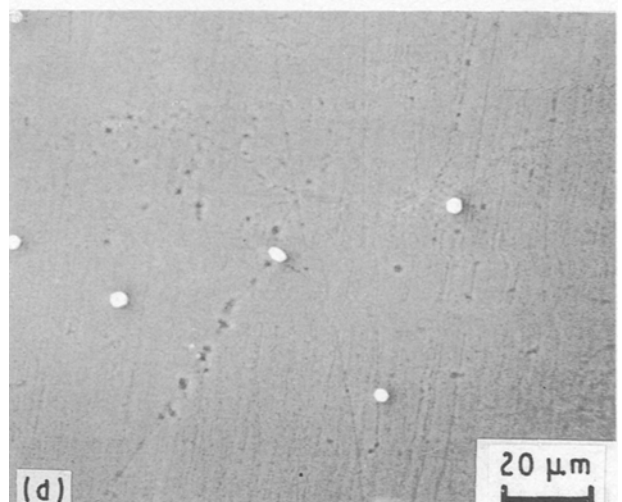
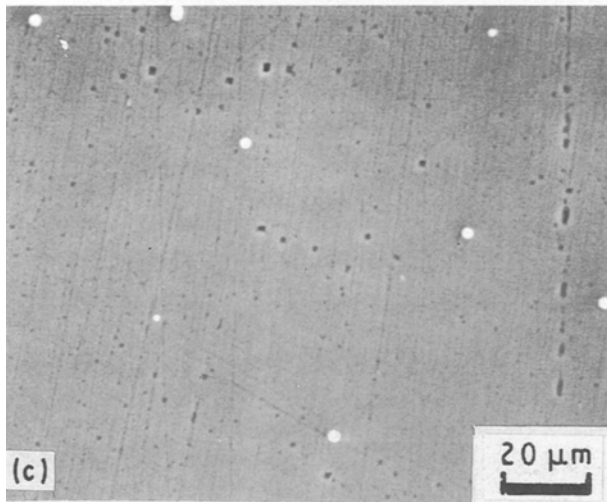
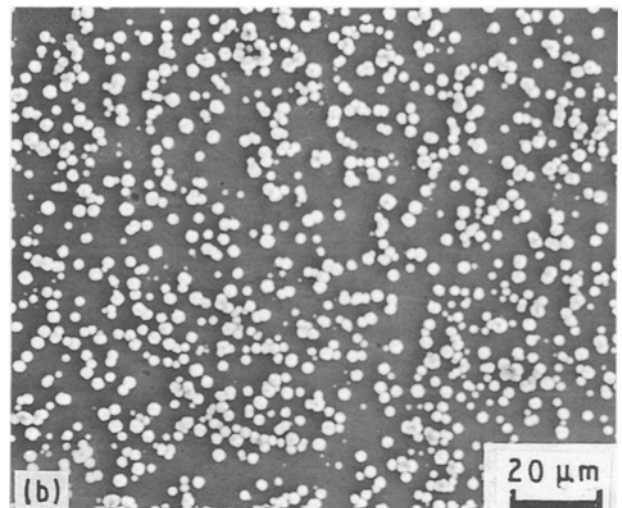
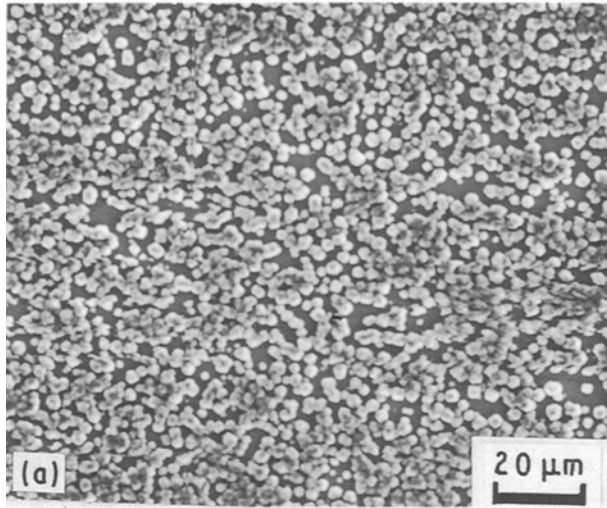


Figure 2 Scanning electron micrographs of the diamond deposited on silicon substrates after hydrogen treatment for (a) 5 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 60 min.

parameters were fixed. The active carbon-containing species and atomic hydrogen, which can contribute to the diamond deposition, increased with increasing T_f , resulting in an increase in the diamond growth rate. However, very little is known about the behaviour of diamond nucleation under these conditions. Therefore, in this work, two possibilities were considered to interpret the changes in the nucleation behaviour with T_f .

The first possibility is the stability of deposits. Growth takes place on the film material already

deposited or on a substrate made of the same material. However, at the nucleation stage, the substrate will have a chemical nature different from that of the film material. Under these conditions, a third phase must be considered (the adsorbed phase), in which vapour atoms are adsorbed on the substrate but have not yet combined with other adsorbed atoms. Nucleation is initiated by the formation of critical-size nuclei through the combination of several adsorbed atoms. Immediately after formation, a critical nucleus will grow by acquiring more atoms, and it becomes stable. However, if an atom has the chance if taken away from the subcritical size aggregate, it dissociates again. The probability of the formation of stable nuclei depends on the deposition conditions. In this work, as mentioned above, the gas species decomposed by the hot filament may influence mainly the behaviour of diamond nucleation. The active carbon-containing species which can contribute to the deposition will be increased with increasing T_f , which will contribute to the increase in the number of stable nuclei. However, the quantity of atomic hydrogen will also be increased simultaneously with increasing T_f . It is thought that

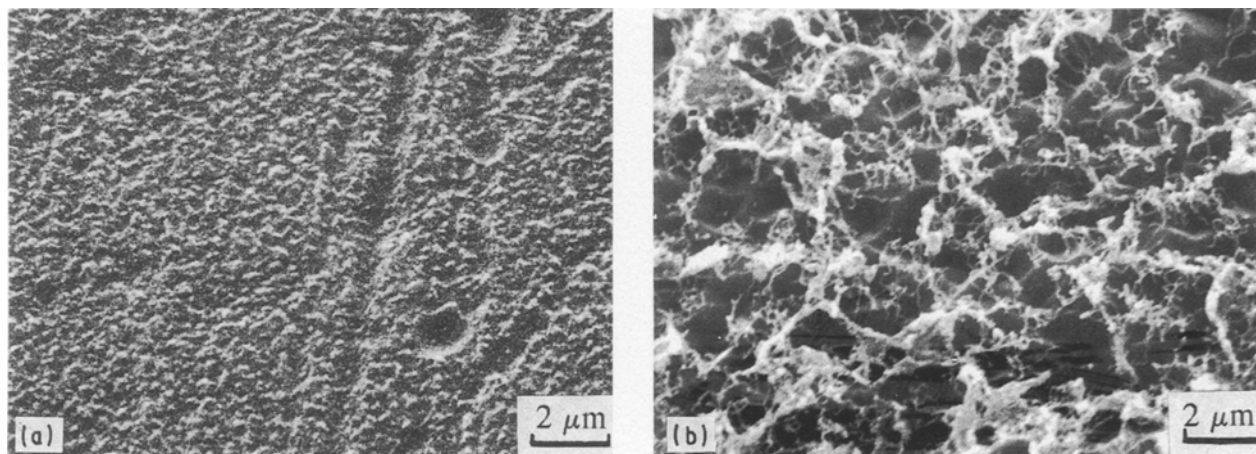


Figure 3 Scanning electron micrographs showing the changes in surface morphology (a) after 30 min hydrogen treatment, (b) after 60 min hydrogen treatment.

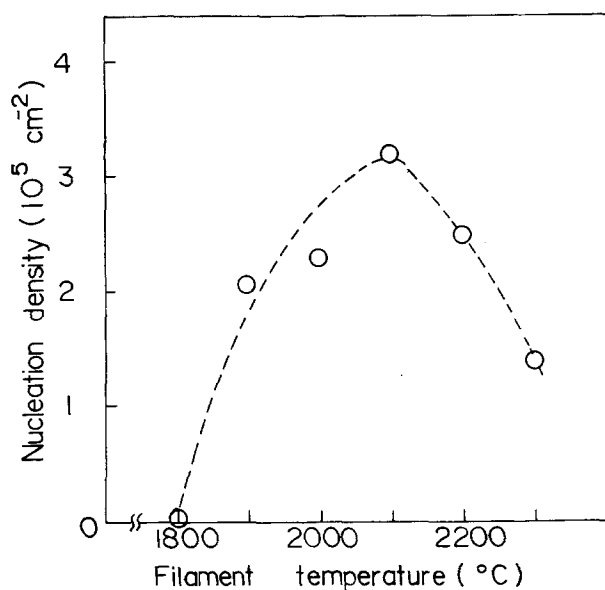


Figure 4 Nucleation density of diamond plotted versus filament temperature.

the reaction between atomic hydrogen and subcritical-size nuclei occurs actively, compared with stable nuclei, which contribute to the re-evaporation of subcritical-size nuclei. The degree of reaction will be increased with increasing T_f . This reverse tendency with increasing T_f may be a reason for the changes in the nucleation behaviour.

The second possibility is the etching of nucleation sites. As shown in Fig. 5, the substrate surface is severely etched with increasing T_f . The weight of the silicon substrate was measured using a microbalance before and after 4 h deposition at T_f of 2000 and 2300 °C, respectively. No detectable weight change was observed at 2000 °C. However, a weight loss of 1×10^{-4} g is observed at 2300 °C. The precision of weighing was $\pm 2 \times 10^{-5}$ g. The diamond particles deposited on the substrate may also contribute to the weight change: the weight increase due to the diamond particles deposited on the substrate was calculated, assuming that the diamond particles are spherical and

TABLE I Deposition conditions

Filament temperature	1800–2300 °C
Substrate temperature	750 °C
Total pressure	20 torr
CH ₄ concentration in H ₂	1 vol%
Total flow rate	200 standard cm ³ min ⁻¹

found to be about 2.2×10^{-5} g. Therefore, the real weight loss of the substrate during deposition is about 1.22×10^{-4} g. This value indicates that the silicon substrate used in this experiment can be etched to 1.4 μm depth from the top of the original substrate surface. The etching of the substrate surface can be closely related to the etching of the nucleation sites.

It was reported that the nucleation density of diamond deposited on the various substrates increased initially and saturated with increasing deposition time [13, 14]. In particular, Kamo *et al.* [13] reported that the nucleation rate of diamond deposited on silicon increased for the first 6 h and then decreased. A similar trend in nucleation density with deposition time was observed in this work. This implies that the nucleation does not occur simultaneously on all nucleation sites, but takes place gradually with the order of site energy. Thus, it may be expected that the nucleation rate decreases as the nucleation sites become less favourable for nucleation. If the etching rate of the nucleation sites due to atomic hydrogen is faster than the nucleation rate on nucleation sites, nucleation can no longer take place. Assuming that the etching of the substrate surface is directly related to the etching of nucleation sites, the number of nucleation sites etched by atomic hydrogen is increased as T_f increases. Therefore, it may be thought that the changes in the nucleation behaviour shown in Fig. 4 are the result of the competition between nucleation rate and etching rate of nucleation sites. As mentioned above, two possibilities, the re-evaporation of subcritical size nuclei as well as the etching of the nucleation sites, are important for diamond nucleation. However, it cannot be confirmed which is the more important effect at this stage.

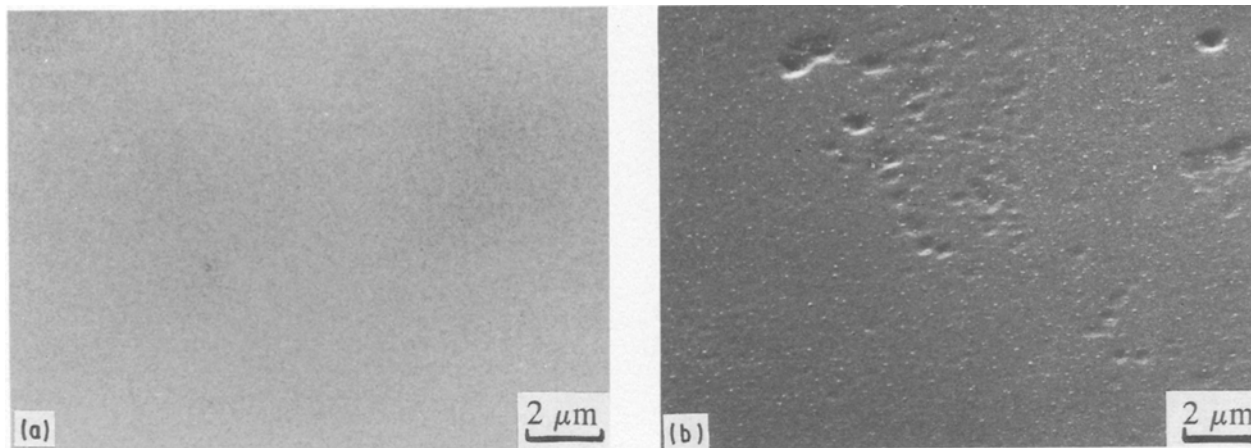


Figure 5 Scanning electron micrographs showing the surface morphology of silicon substrate: (a) before, (b) after 4 h deposition at $T_f = 2000^\circ\text{C}$, (c) after 4 h deposition at $T_f = 2300^\circ\text{C}$.

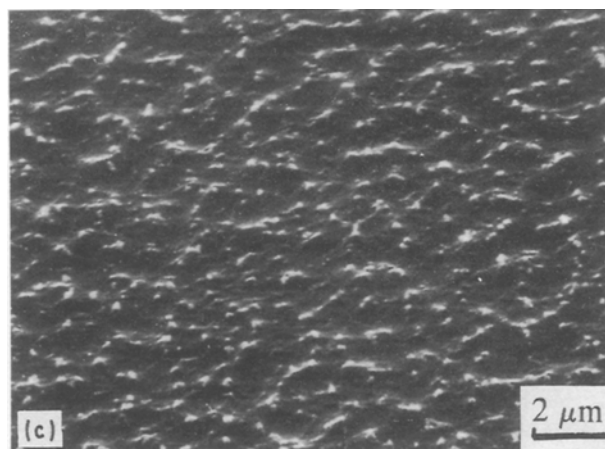


Fig. 6 shows the diamond particles deposited on a silicon substrate. Hydrogen treatment prior to deposition was performed for 20 min. The deposition conditions and the substrate used were identical to those of Fig. 2. However, two substrates underwent a different thermal path before deposition. In the case of Fig. 6a (case A), the CH_4 source gas was introduced instantly to begin deposition after hydrogen treatment. In the case of Fig. 6b (case B), however, cooling of the substrate to room temperature in hydrogen atmosphere was introduced after hydrogen treatment and then deposition of diamond was performed. As shown in

Fig. 6, the nucleation density of diamond particles deposited in case B is higher than that in case A. Thus the surface condition of case B is more favourable for nucleation than that of case A. It may be considered that the etching rate of the silicon substrate due to atomic hydrogen increases initially and reaches a steady state with increasing deposition time. Comparing Figs 3 with 5, the etching rate by atomic hydrogen alone is faster than that by the CH_4/H_2 mixture. Therefore, when CH_4 is introduced into the chamber to begin the deposition, the etching rate in case A will be decreased to the value which corresponds to the etching rate by the CH_4/H_2 mixture (rate S, S denotes the steady state). However, in case B, the etching rate increases from nearly zero to rate S with increasing deposition time. This implies that the etching rate of case A may be faster than that of case B in the initial stage of deposition, which in case A can lead to a decreasing probability of diamond nucleation.

When considering the effect of hydrogen on the nucleation behaviour of diamond, the competition between diamond nucleation and etching of nucleation sites must be considered. Although the atomic

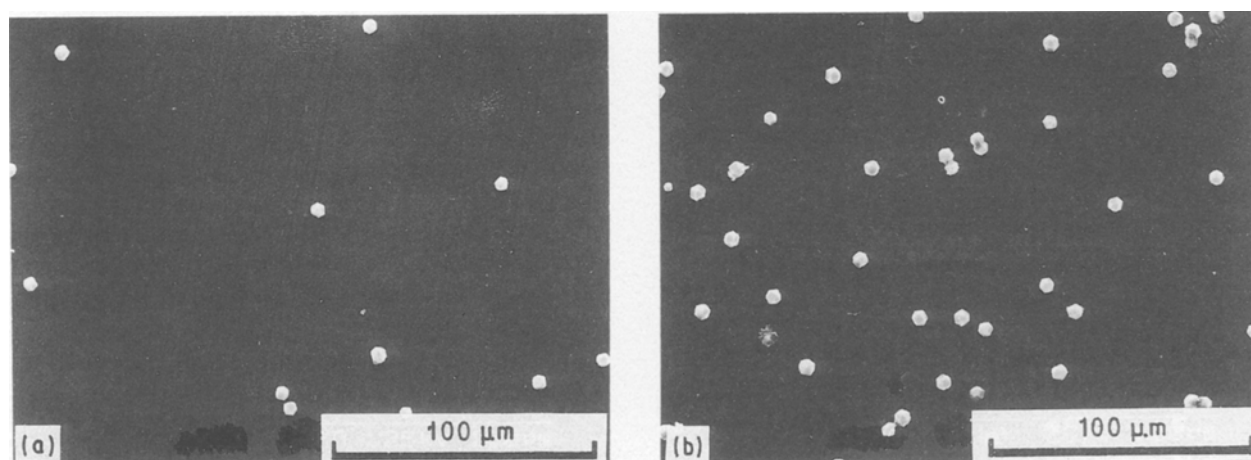


Figure 6 Scanning electron micrographs of diamond particles deposited on a silicon substrate after 20 min hydrogen treatment: (a) no cooling of the substrate was performed prior to deposition, (b) cooling of the substrate was performed prior to deposition.

hydrogen plays an important role in diamond growth, atomic hydrogen can also suppress diamond nucleation because the nucleation sites can be etched by the atomic hydrogen.

4. Conclusions

The effects of hydrogen on the behaviour of diamond nucleation were studied using a hot-filament chemical vapour deposition. The nucleation density of diamond decreased dramatically with increasing hydrogen treatment time prior to deposition. The filament temperature also affected the nucleation behaviour of diamond. The nucleation density of diamond increased initially and then reached a maximum at 2100 °C and then decreased. The changes in the morphology of substrate surface with both hydrogen-treatment time and filament temperature, were also observed. The etching of the substrate surface was enhanced by both increasing hydrogen-treatment time and increasing filament temperature.

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