

## Pressure effect on diamond nucleation in a hot-filament CVD system

S. T. Lee and Y. W. Lam

*Department of Physics & Materials Science, City University of Hong Kong, Kowloon, Hong Kong*

Zhangda Lin, Yan Chen, and Qijin Chen

*State Key Laboratory of Surface Physics, Institute of Physics, Chinese Academy of China, Beijing 100080, China*

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Using extraordinarily low pressure (0.1–1 Torr) we obtained high-density nucleation of diamond on mirror-polished silicon in a hot-filament chemical vapor deposition (HF-CVD) system. A diamond nuclei density as high as  $10^{10}$ – $10^{11}$   $\text{cm}^{-2}$  was achieved, which was comparable to the largest nuclei density obtained in a microwave-plasma chemical vapor deposition system. The low-pressure nucleation technique and the pressure effect on diamond nucleation were discussed in detail based on molecular dynamics. The enhanced nucleation at low pressure was attributed to an increased mean free path, which gave rise to an increased concentration of nucleating species at the substrate and other beneficial nucleating factors. The present work suggests that very low pressure may be an effective approach to nucleate and grow diamond films on untreated substrates via HF-CVD. [S0163-1829(97)04524-4]

### I. INTRODUCTION

Nucleation is the first step of diamond growth. During the early development of diamond growth by the chemical vapor deposition (CVD) method, diamond seeds were used as nuclei.<sup>1</sup> Subsequently, the work of Matsumoto *et al.*<sup>2</sup> in 1982 showed that diamond could be grown without the need of diamond seed, although a very low nuclei density was obtained. Later on, it was found that substrate scratching with diamond powder could greatly enhance nucleation.<sup>3</sup> Since then diamond scratching of substrate has become a common method for obtaining high density of nucleation. For Si, the most frequently used substrate, a density of  $10^7$ – $10^8$  nuclei  $\text{cm}^{-2}$  can be achieved after optimum scratching with diamond powder, whereas only  $10^4$  nuclei  $\text{cm}^{-2}$  can be obtained for an unscratched, mirror-polished Si. To date, numerous methods of pretreating the substrate to enhance nucleation have been tried. They include the predeposition of graphite,<sup>4</sup> amorphous carbon,<sup>5</sup> diamondlike carbon,<sup>6</sup> or even the smearing of mechanical oil<sup>7</sup> on substrate. All these methods have shown varying degrees of promoting effect on nucleation. Nevertheless, the nucleating methods mentioned above led only to the unoriented growth of diamond, and failed in achieving diamond heteroepitaxy on nondiamond substrate.

In order to grow diamond epitaxially, proper control of diamond nucleation on mirror-polished Si is essential. Towards this goal, by applying a bias voltage to substrate in a microwave-plasma (MP) CVD system, Jeng *et al.*<sup>8</sup> obtained oriented nucleation with a density of about  $10^7$  nuclei  $\text{cm}^{-2}$  at a local area on a mirror-polished Si substrate. Later, Yugo *et al.*<sup>9</sup> obtained a nucleation density as high as  $10^9$ – $10^{10}$   $\text{cm}^{-2}$  by using a similar approach. Currently, the highest nucleation density on Si was  $10^{10}$ – $11^{11}$   $\text{cm}^{-2}$  reported by Stoner *et al.*<sup>10</sup> Based on this biasing method, it has now been possible to grow highly oriented diamond on Si single crystal. In a hot-filament (HF) CVD system, another important method for diamond growth, high nucleation den-

sity, also has not been obtained on mirror-polished Si. In 1995, Zhu *et al.*<sup>11</sup> studied the effect of negative bias on nucleation in a HF-CVD system and found that the enhancement of diamond nucleation occurred at the edge of sample.

In the normal practice of CVD diamond growth, the pressure used for both nucleation and growth is about the same, ranging from several tens to several hundreds of Torr. In this nominally high-pressure range high nucleation density ( $>10^7$   $\text{cm}^{-2}$ ) has not been obtained on mirror-polished, untreated Si. Even on a diamond-scratched Si substrate the nucleation density achieved has been typically in the  $10^7$ – $10^8$ - $\text{cm}^{-2}$  level. Contrary to conventional wisdom, we show in this paper that very-low-pressure conditions can, indeed, be advantageous for diamond nucleation. Using a pressure of  $\text{H}_2/\text{CH}_4$  as low as 0.1 Torr in a HF-CVD system, we obtained on an untreated, mirror-polished Si a diamond nucleation density as high as  $10^{10}$ – $10^{11}$   $\text{cm}^{-2}$ . This value is equivalent to the highest level ever obtained on a negatively biased Si in a MP-CVD system. To our knowledge, such a nucleation density represents the highest level ever reported for HF-CVD growth. We suggest that the technique presented here will have important use in the practice of diamond growth.

### II. EXPERIMENT

Diamond nucleation and growth were conducted in a typical HF-CVD system. A  $\phi 140$ -mm and 500-mm-long fused silica tube was used as the growth chamber. Si substrate was held on a Mo holder, and tungsten hot filaments were hung at a distance of 6 mm above the substrate. The gas mixture of hydrogen and methane was used as source, with a flow rate of 100 SCCM (SCCM denotes cubic centimeter per minute at STP). The ratio of  $\text{CH}_4/\text{H}_2$  was kept at 2% during the nucleation step. The temperature of the W filament was measured by an optical pyrometer. Substrate temperature was between 800 °C and 850 °C as measured by a thermocouple. The pressure of the growth chamber was kept at 1 or 0.1 Torr

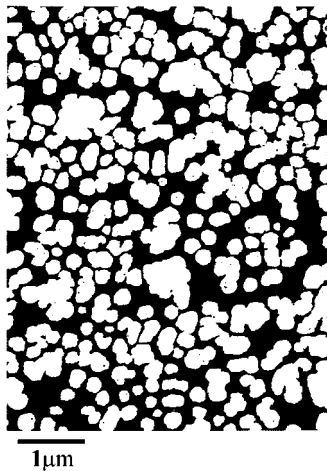


FIG. 1. SEM micrograph of Si (100) scratched by 0.5- $\mu\text{m}$  diamond powder and nucleated under the following conditions:  $p = 1$  Torr,  $\text{CH}_4/\text{H}_2 = 2\%$ ,  $T_f = 2150$  °C, and  $T_s = 800$  °C.

for nucleation and at 20–50 Torr for growth.

Except for one substrate which was scratched by 0.5- $\mu\text{m}$  diamond powder, all other substrates were pieces from a mirror-smooth Si wafer without being polished by diamond powder. Before loading into the growth chamber every Si substrate was cleaned in an ultrasonic bath sequentially for 10 min each with acetone, ethanol, and deionized water, then etched for 1 min in a 30% HF solution, and finally rinsed with deionized water. As we had noticed that surface cleaning was very essential for achieving high-density nucleation, the cleaning process of the Si substrate was carried out carefully. The results of nucleation and growth were examined by scanning electron microscope (SEM) and Raman spectroscopy. The nucleation density was estimated from the number of particles observed on SEM micrographs.

### III. RESULTS

Figure 1 shows the SEM micrograph of diamond nuclei grown for 10 min on a Si (100) substrate which was prepolished by 0.5- $\mu\text{m}$  diamond powder. The following parameters for nucleation were used: pressure  $p = 1$  Torr,  $\text{CH}_4/\text{H}_2 = 2\%$ , filament temperature  $T_f = 2150$  °C, and the substrate temperature  $T_s = 800$  °C. The nucleation density of  $2 \times 10^9 \text{ cm}^{-2}$  achieved was one to two orders of magnitude higher than the highest density ( $10^7 - 10^8 \text{ cm}^{-2}$ ) obtained on a similarly treated substrate using conventional pressure which is typically several tens of Torr. Moreover, Fig. 1 shows a very uniform distribution of nuclei and no evidence of accumulation of nuclei at the scratched traces.

For a mirror-polished Si (100) substrate after 10 min nucleation the SEM morphology is shown in Fig. 2. The parameters for nucleation were  $p = 0.1$  Torr,  $\text{CH}_4/\text{H}_2 = 2\%$ ,  $T_f = 2150$  °C, and  $T_s = 850$  °C. Compared to Fig. 1, the increase in nucleation density is dramatic and the nucleation density attained was around  $10^{10} - 10^{11} \text{ cm}^{-2}$ . This value is comparable to the highest level reported to date, which was obtained in a MP-CVD system using a negative substrate bias. This result shows clearly that nucleation density obtained at 0.1 Torr was higher than that at 1 Torr, in spite of

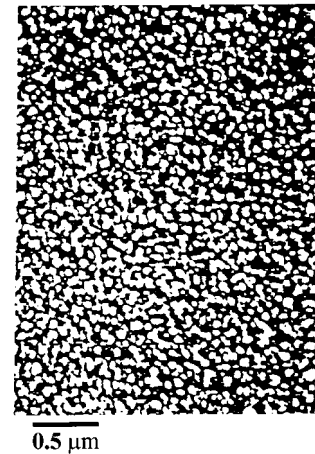


FIG. 2. SEM micrograph of a mirror-polished Si (100) nucleated under the following conditions:  $p = 0.1$  Torr,  $\text{CH}_4/\text{H}_2 = 2\%$ ,  $T_f = 2150$  °C, and  $T_s = 850$  °C.

the fact that the latter sample was scratched by diamond powder, which is known to enhance nucleation.

Figure 3 depicts the Raman spectrum of the sample shown in Fig. 2. The characteristic Raman peak of diamond at  $1332 \text{ cm}^{-1}$  is prominent, showing that diamond was indeed formed on the Si substrate. The broad band at  $1540 \text{ cm}^{-1}$  corresponds to a nondiamond phase such as amorphous carbon and/or graphite, which usually is deposited during the initial stage of diamond growth.

The present result suggests that the high pressure of several tens of Torr or above, although suitable for diamond growth, may not be conducive for achieving high-density nucleation of diamond on mirror-polished Si substrates. Figure 4 shows the nucleation result for a sample nucleated 20 min under the following conditions:  $p = 100$  Torr,  $\text{CH}_4/\text{H}_2 = 0.7\%$ ,  $T_f = 2150$  °C, and  $T_s = 850$  °C. The nucleation density here is only about  $3 \times 10^4 \text{ cm}^{-2}$ . In comparison with Figs. 1 and 2, it is clear that nucleation density obtained at 0.1 Torr is higher than those at 1 and 50 Torr. We thus conclude that very low pressure is indeed an effective method for obtaining high nucleation density of diamond on mirror-polished Si surfaces.

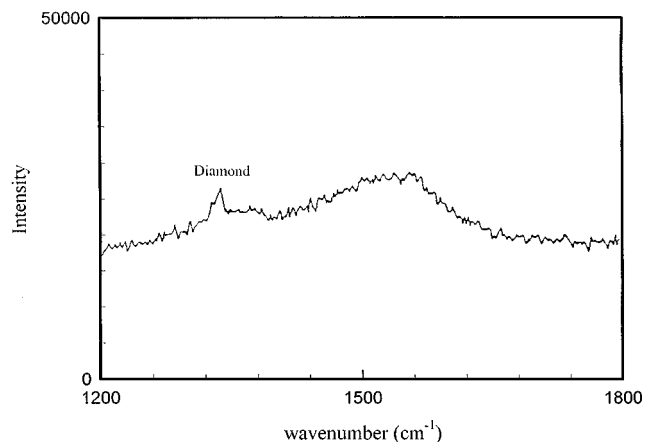


FIG. 3. Raman spectrum of the diamond sample shown in Fig. 2.

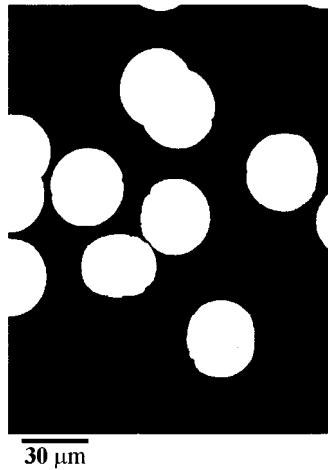


FIG. 4. SEM micrograph of a mirror-polished Si (100) nucleated under the conventional conditions:  $p=100$  Torr,  $\text{CH}_4/\text{H}_2=0.7\%$ ,  $T_f=2150$  °C, and  $T_s=850$  °C.

To further investigate the nucleation process under very low pressure, we grew diamond under the same conditions but with various nucleation times. All the substrates were pieces cleaved from one large Si(100) wafer. As mentioned above, all substrates were cleaned carefully and properly before loading into the growth chamber. Figures 5(a)–5(d) show the SEM micrographs corresponding to nucleation time of 1, 2.5, 5, and 10 min, respectively. Nucleation parameters were,  $p=1$  Torr,  $\text{CH}_4/\text{H}_2=2\%$ ,  $T_f=2100$  °C, and  $T_s=850$  °C. Comparing the SEM images in Fig. 5 we find that within the time range used in the present experiment, the nucleation density remained almost the same at about  $5 \times 10^8 \text{ cm}^{-2}$ , but the size of nuclei increases significantly with increasing nucleation time. For the sample nucleated for 10 min [Fig. 5(d)], the nuclei grew so large that a continuous diamond film was nearly formed.

The sample which was previously nucleated for 5 min [Fig. 5(c)] was allowed to grow an additional 10 min under the following conditions:  $p=20$  Torr,  $\text{CH}_4/\text{H}_2=1.5\%$ ,  $T_f=2050$  °C, and  $T_s=800$  °C. The SEM micrograph of this sample is depicted in Fig. 5(e). The average size of the nuclei in Fig. 5(e) is similar to or slightly larger than that in Fig. 5(c). Unlike that in Fig. 5(d), the film in Fig. 5(e) is far from being continuous. This indicates that the growth rate under low pressure (1 Torr) is fast compared to that at a high pressure of 20 Torr. The reason for this will be discussed below.

#### IV. DISCUSSIONS

The results in Sec. III show that high nucleation density of diamond was obtained on mirror-polished Si substrates under very low pressure (0.1 Torr). In addition, the growth rate at low pressure (1 Torr) can also be high. We propose and discuss the mechanism of the enhanced diamond nucleation as follows. It will be evident later that the validity of the following discussion is not very dependent on the detailed mechanism of nucleation and growth. For the ease of discussion, we make the assumption that the nucleation and growth rate depend, among other factors, on the concentration of the nucleating or precursor species on the growth

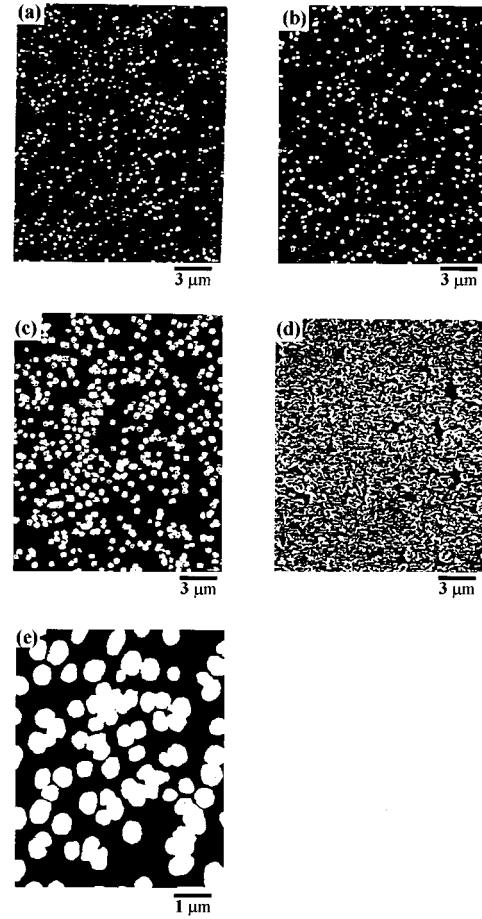


FIG. 5. SEM micrograph of a mirror-polished Si (100) nucleated for different times: (a) 1 min, (b) 2.5 min, (c) 5 min, (d) 10 min, and (e) 5 min plus an additional 10 min growth. The nucleation conditions are  $p=1$  Torr,  $\text{CH}_4/\text{H}_2=2\%$ ,  $T_f=2100$  °C, and  $T_s=850$  °C. The growth conditions for sample (e) are  $p=20$  Torr,  $\text{CH}_4/\text{H}_2=1.5\%$ ,  $T_f=2050$  °C, and  $T_s=800$  °C.

surface. The nature of these active species needs not be known for the analysis; although they are likely related to such active species as hydrocarbon radicals or atomic hydrogen. Further, we assume that the active species are thermally decomposed at or close to the filament and, to first order of approximation, its concentration  $m$  is proportional to the pressure  $P$  of its precursor or the reactant gas, i.e.,

$$m = k_d P, \quad (1)$$

where  $k_d$  is a constant. According to the kinetic theory of gases,<sup>12,13</sup> the mean free path ( $\lambda$ ) of the active species is inversely proportional to pressure according to the relationship

$$\lambda = \frac{kT}{\sqrt{2}\pi d^2 P}, \quad (2)$$

where  $k$  is the Boltzmann constant, and  $T$  and  $d$  are, respectively, the temperature and collision diameter of active species with the reactant gas. On the other hand, the probability  $\rho$  of active species traveling a distance of 1 without encountering collision is proportional to  $e^{-1/\lambda}$ , i.e.,  $\rho \propto \alpha e^{-1/\lambda}$ .

Using Eq. (2) and combining all the constants into  $B$ , we obtain

$$\rho \propto e^{-BP}, \quad (3)$$

where  $B = \sqrt{2} \pi d^2 l / kT$ . The concentration of active species that survives collisions and eventually arrives at the substrate surface is thus proportional to the product of Eqs. (1) and (3), giving

$$m \propto k_d P e^{-BP}. \quad (4)$$

Equation (4) shows that the concentration of active species first increases exponentially and finally decreases with decreasing pressure. Taking the derivative of Eq. (4) with  $P$  and setting it to zero, the optimum pressure at which maximum concentration of the species occurs is found to be  $(B)^{-1}$ . Using 0.5 cm for  $l$  (which is the nominal spacing between the hot filament and substrate used in a HF-CVD system),  $3 \times 10^{-10}$  m for  $d$ , the optimum pressure is estimated to be 0.02 Torr at 2400 K. The estimated optimum pressure is smaller but close to the pressure of 0.1 Torr which produced the highest nucleation density in the present work. At this point, it is important to note that the above discussion is independent of the nature of the nucleating species and thus applies equally well to hydrocarbon radicals or other nucleating species. Moreover, the same analysis also applies to the pressure dependence of growth rate provided the concentration of one specific species is the primary rate-determining factor for growth.

It is helpful to extract a physical interpretation of the above analysis. The mean free path  $\lambda$  at 0.1 Torr is 200–500 times that at 20–50 Torr [from Eq. (2)]. The latter value is the pressure range conventionally used for CVD diamond deposition. At 0.1 Torr,  $\lambda$  falls in the millimeter range, which is comparable to the spacing between the hot filament and substrate commonly used in a HF-CVD system. As the active species are generated at or near the filaments, they have to reach the substrate before initiating nucleation and/or growth. The fraction of these species that survives collision to arrive at the substrate increases remarkably when  $\lambda$  reaches a value comparable to the distance between the filament and substrate, i.e., millimeters, at very low pressure. The increase of  $\lambda$  with decreasing pressure leads to an increasing amount of these species impinging on the substrate, and thus creates a more favorable condition for diamond nucleation and growth. However, since the production of active species is proportional to the pressure, their concentration eventually will go through a maximum as the reactant pressure falls below a critical value. Once this critical value is reached, a further lowering in pressure will offset the favorable effect of increasing  $\lambda$ . Therefore an optimum pressure for inducing diamond nucleation (and growth) is expected. The present study shows that this optimum pressure is significantly lower than the tens of Torr which is commonly used in conventional CVD diamond growth.

Besides the direct effect discussed above, there are other more subtle influences of low pressure on diamond nucleation and growth. First, because of larger mean free path at low pressure, more atomic hydrogen and hydrocarbon radicals reach the substrate without or with few collisions, thus the kinetic energy of these active species remains close to the

local thermal energy of the hot filament (2150 °C). At 20–50 Torr, the mean free path is merely several micrometers and the species undergoes many collisions before reaching the substrate. Thus the final kinetic energy of the impinging species is close to the thermal energy of the substrate, which is typically 850 °C. As a result, the kinetic energy of the impinging species at very low pressure can be two to three times that at conventional CVD pressure. Species with a higher kinetic energy have a larger surface mobility which helps promote the aggregation of the precursors and thus increases nucleation and growth on substrate. In addition, the bombardment of particles with higher kinetic energy leads to improved surface cleanness and higher probability of surface reconstruction or microstructure modification, conditions which enhance surface adsorption and aggregation, thus nucleation and growth.

The Si surface is always covered by a thin oxide layer. The oxide layer hinders the adsorption, aggregation, and nucleation on the substrate surface. In a MP-CVD process the application of a negative bias to the substrate can accelerate and direct ions to the substrate surface, resulting in an efficient etching of the oxide layer. However, in a HF-CVD process using conventional gas pressure the amount of atomic hydrogen and/or ions reaching the substrate is reduced due to collision and recombination, thus the surface oxide layer is not removed effectively. A HF solution is frequently used to remove the Si oxide layer. In spite of this, an oxide-free Si surface cannot be ensured as Si is so easily oxidized that a patchily oxidized surface invariably results after Si is loaded in the growth chamber. Once inside the growth chamber, removal of the oxide layer on Si may be enhanced by lowering pressure, because with decreasing pressure more atomic hydrogen with higher kinetic energy is available to impinge and thus remove the oxide layer. Furthermore, at lower pressure oxide is also more easily decomposed and vaporized. More efficient removal of the oxide layer will lead to enhanced diamond nucleation.

Harris and Weiner<sup>14</sup> studied the pressure effect on the kinetics of diamond films grown by HF-CVD and reported that the relative growth rate increased with pressure between 9 and 20 Torr. This result appears to be at variance with the present findings and the reason for this apparent discrepancy is not clear. We note, however, that the present work deals with the beginning 15 min of growth, when two-dimensional growth dominates, whereas in the work of Harris and Weiner, the growth rate was measured after some hours of growth, when three-dimensional growth prevails.

## V. SUMMARY

Using an unusually low pressure of  $\text{H}_2/\text{CH}_4$  in a HF-CVD system, we obtained on mirror-polished Si substrate a diamond nucleation density as high as  $10^{10}$ – $10^{11}$  nuclei  $\text{cm}^{-2}$ . The mechanism for the enhanced nucleation at very low pressure was explained by the combinative effect of larger mean free path and increased concentration of active or nucleating species at the substrate. We estimated that the concentration of the active species at the substrate went through a maximum at a pressure of 0.02 Torr. As the mean free path increases with decreasing pressure, the active species undergo fewer collisions and thus suffer less loss of

energy during their transport to the substrate. Because of higher kinetic energy, these species are more effective in inducing surface aggregation and reconstruction as well as in removing surface oxide, which also promotes diamond nucleation. The present work suggests that the very low-pressure nucleation technique may have great prospects in diamond heteroepitaxy.

#### ACKNOWLEDGMENTS

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