Investigation of Diamond Nucleation under Very Low Pressure in Chemical Vapor Deposition.

Qijin Chen

State Key Laboratory of Surface Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, 100080, China
Department of Physics, University of Chicago, 5720 S. Ellis Ave., Chicago, IL 60637
(* The corresponding address. Email: qchen@rainbow.uchicago.edu)
(March 24, 2022)

Diamond nucleation under very low pressure (0.1-1.0 torr) was obtained at very high nucleation densities and very rapid rates using hot-film chemical vapor deposition (HFCVD). The density on mirror-polished silicon was as high as $10^{10}-10^{11}$ cm$^{-2}$, equivalent to the highest density in a microwave-plasma CVD system. That on scratched silicon substrates was up to $10^9$ cm$^{-2}$, 1-2 orders of magnitude higher than that obtained under conventionally low pressure (tens of torr, $10^7-10^8$ cm$^{-2}$). Also, the density on scratched titanium substrates was as high as $10^{10}$ cm$^{-2}$. The samples were characterized using scanning electron microscopy (SEM) and Raman spectroscopy. The mechanism is investigated in detail, revealing that, under very low pressure, very long mean free path of the gas species, strong electron emission from the hot filament, and high efficiency of decomposition of hydrocarbon species by the filament greatly increase the concentration of reactive hydrocarbon radicals and atomic hydrogen on the substrate surface, and therefore, dramatically enhance the nucleation eventually. This work has great practical applications and theoretical significance.

I. INTRODUCTION

Nucleation is the first step of diamond growth in chemical vapor deposition (CVD) under low pressure. Great progress has been made in this respect. In the early days of diamond research using CVD, diamond was deposited using diamond seeds as nuclei, or directly on a single-crystal diamond. In 1982, diamond seeds were no longer needed to get diamond nuclei owing to the work of Matsumoto et al. However, the density was too low to lead to continuous films. Later on, nucleation was found to be effectively enhanced by scratching the substrate surface, which has been one of the major methods for nucleation enhancement since then. For the most intensively studied silicon substrate, the nucleation density is up to $10^7-10^8$ cm$^{-2}$, whereas it is no more than $10^4$ cm$^{-2}$ for unscratched, mirror-polished silicon. In addition, various other pretreatment methods of the substrate have also been tried and showed varying degrees of nucleation enhancement, such as predeposition of non-diamond carbon including graphite, amorphous carbon, diamond-like carbon, and even coating with pump oil. However, all these methods result in unoriented nucleation, and therefore, become invalid in achieving epitaxy of diamond on hetero-substrates. The problem of achieving high-density nucleation on mirror-polished single-crystal Si has to be solved for this purpose. Breakthrough in this regard arose owing to Jeng et al in microwave plasma CVD (MPCVD). They obtained local, oriented nucleation with a density up to $10^7$ cm$^{-2}$ by negatively biasing the substrate. In 1990, Yugo et al obtained an (unoriented) nucleation density up to $10^9-10^{10}$ cm$^{-2}$ using a similar method. Up to date, the highest density achieved using this method is $10^{10}-10^{11}$ cm$^{-2}$, as reported by Stoner et al. In 1993, Jiang et al reported observation of oriented nucleation using negative bias. So far, high-density nucleation of diamond on Si in a MPCVD system is no longer a problem. In an HFCVD system, similar bias method had been tried on mirror-polished substrates for a long time without success until recently. Using a similar negative bias in their HFCVD system, Zhu et al reported that the nucleation enhancement took place only at the edge of the sample. Chen and Lin achieved high density of oriented nucleation using an electron-emission-enhancement (EEE) method with and without a bias to the substrate, demonstrating an EEE mechanism.

On a Ti substrate using the scratching enhancement under normally low pressure, it has been reported that nucleation takes place only after a long carburization process with a very poor density, which usually leads to serious hydrogenation of the substrate.

We report in this paper another completely different nucleation method and investigate its mechanism. Usually, the pressure for nucleation ranges from tens of torr to above one hundred torr, the same as that for growth. Under this condition, high-density nucleation can not be obtained on mirror-polished Si surface without the use of bias or EEE method. The density on a scratched sample is only $10^7-10^8$ cm$^{-2}$. In contrast, as reported below, under very low pressures (0.1-1.0 torr), nucleation can be achieved on mirror-polished Si substrates with a density as high as $10^{10}-10^{11}$ cm$^{-2}$, equivalent to the highest value in MPCVD. For scratched substrates, the density is also 1-2 orders of magnitude higher than that under normal pressures. On a scratched Ti wafer, the density can also be as high as $10^{10}$ cm$^{-2}$. The nucleation progresses at a much higher speed with a more uniform distribu-
tion across the sample. This method has its own special merits, e.g., high uniformity and rapidity, in comparison with other nucleation enhancing methods and has great significance in diamond deposition.

This work is mainly taken from Sec. 4.2 of the author’s thesis. We did not notice the paper by Lee et al until after its publication. However, part of the experimental conditions and results were not properly reported, and the discussion was very incomplete and only partly correct. In view of this and the availability of ref. 19, we deem it appropriate to publish it on a more widely spread journal. As the normal pressure (10^{-1}-10^{-2} torr) is conventionally referred to low pressure, we call the pressure (0.1-1.0 torr) in our experiments very low pressure, to show the difference.

II. EXPERIMENTS

Our experiments were carried out in an HFCVD apparatus as reported in ref. 21. To repeat briefly, a φ140 mm and 500 mm long fused silica tube was used as the deposition chamber. Coils of φ0.2 mm tungsten wires were used as filaments. The substrates were Si and Ti wafers in the size of 8 × 10 mm^2, mounted on a copper platform under the filament during the experiments. The filament temperature was measured with an optical pyrometer, while the substrate temperature was measured with a thermocouple (Pt-PtRh). The source gas was methane diluted in hydrogen. Part of the substrates were mirror-polished Si wafers without any nucleation enhancing pretreatment, while the others were scratched with 0.5-1.0 μm diamond powders. All samples were chemically cleaned with acetone in an ultrasonic bath for >10 min, to remove oil, diamond residues after scratching, and other dirties on the substrate surface before loaded into the deposition chamber. In addition, the mirror-polished Si samples were also cleaned subsequently with deionized water and rinsed in a 30 vol. % HF solution to remove possible surface oxide. Typical experimental parameters for nucleation are listed in Table I. The pressure used, 0.1-1.0 torr, was one to two orders of magnitude lower as compared with normal conditions. Specific parameters of each experiment and the growth conditions will be mentioned where appropriate. The as-deposited samples were characterized with scanning electron microscopy (SEM) and Raman spectroscopy.

| Parameters          | Notations | values   |
|---------------------|-----------|----------|
| Flow rate (sccm)    | F         | 70-100   |
| CH₄ concentration (vol.%) | [CH₄]   | 1.0-3.0  |
| Pressure (torr)     | p         | 0.1-1.0  |
| Filament temperature (°C) | T_f     | 2050-2150|
| Substrate temperature (°C) | T_s    | 800-900  |
| Nucleation time (min)| t         | 1-10     |

*a sccm denotes cubic centimeter per minute at STP.

III. RESULTS

Figure 1 shows the SEM image of the diamond nuclei on a scratched Si(100) substrate after 10 min nucleation under the conditions as follows. p = 1 torr, [CH₄] = 1.5 vol.%, T_f = 2150°C, T_s = 800°C, F = 100 sccm, t = 10 min. The density was 2 × 10^9 cm^{-2}.

Figure 2 shows the Raman spectrum of the sample in Fig. 1. The characteristic peak of diamond at 1332 cm^{-1} is very clear, confirming the formation of diamond during the nucleation process.

FIG. 1. SEM image of the nuclei on a scratched Si(100) substrate under very low pressure. p = 1 torr, [CH₄] = 1.5 vol.%, T_f = 2150°C, T_s = 800°C, F = 100 sccm, t = 10 min. The density was 2 × 10^9 cm^{-2}.

FIG. 2. Raman spectrum of the sample shown in Fig. 1. The characteristic peak of diamond at 1332 cm^{-1} is very clear, confirming the formation of diamond during the nucleation process.
As it turned out, it was not as easy to get high-density nucleation on a mirror-polished substrate as on a scratched one under 1.0 torr. Thus the pressure was further lowered. Figure 3 shows the SEM photo of a mirror-polished Si(100) wafer after 10 min nucleation under the following conditions. $F = 70$ sccm, $[\text{CH}_4] = 2$ vol. %, $p = 0.1$ torr, $T_f = 2150^\circ$C and $T_s = 850^\circ$C. The nucleation density was as high as $10^{10}$-$10^{11}$ cm$^{-2}$, comparable to the highest density attained in MPCVD using negative bias method. Obviously, it was much higher than that on the scratched substrate as shown in Fig. 1. As the nuclei in Fig. 4 were too tiny, the layer of nuclei was very thin. It is difficult to characterize that sample with Raman spectroscopy. To investigate whether diamond nuclei had indeed formed or only a pure non-diamond carbon layer formed, subsequent growth was tested. Figure 5 shows the SEM image of a Si(100) sample after 5 min nucleation under the same conditions as for Fig. 3 and a subsequent overnight growth at a normally low pressure. To eliminate amorphous carbon in the nuclei more effectively, a lower CH$_4$ concentration was used. The conditions for growth were as follows. $F = 100$ sccm, $[\text{CH}_4] = 0.7$ vol. %, $p = 20$ torr, $T_f = 2000^\circ$C and $T_s = 800^\circ$C. As is obvious in Fig. 4, the diamond micro-crystals had very good crystallinity with an average size of 0.5 $\mu$m and a density of $10^9$ cm$^{-2}$, which is comparable to the nucleation density on the scratched substrate as shown in Fig. 1. This value was lower than the nucleation density in Fig. 3, which can be attributed to the much larger size of the diamond crystallites than that of the initial nuclei; a uniform size of 0.5 $\mu$m would imply a density of only $4 \times 10^8$ cm$^{-2}$. The Raman spectrum corresponding to Fig. 4 is

$$\text{Intensity (arb. unit)}$$

| Raman Shift (cm$^{-1}$) | 1100 | 1450 | 1800 |
|-------------------------|------|------|------|
| Diamond                |      |      |      |

FIG. 3. SEM image of a mirror-polished sample after 10 min nucleation under very low pressure. $p = 0.1$ torr, $F = 70$ sccm, $[\text{CH}_4] = 2$ vol. %, $T_f = 2150^\circ$C, $T_s = 850^\circ$C. The density was as high as $10^{10}$-$10^{11}$ cm$^{-2}$.

FIG. 4. SEM picture of the diamond film on a mirror-polished Si(100) substrate after 5 min nucleation plus subsequent overnight growth. The conditions used were the same as in Fig. 3. The growth conditions were: $F = 100$ sccm, $[\text{CH}_4] = 0.7$ vol. %, $p = 20$ torr, $T_f = 2000^\circ$C, $T_s = 800^\circ$C. The density was $3 \times 10^4$ cm$^{-2}$.

FIG. 5. Raman spectrum of the sample in Fig. 4. The quality of the diamond film was pretty high.
shown in Fig. 5, demonstrating a very high quality of the diamond; the diamond peak was very strong while that of non-diamond phase was very weak.

Normally speaking, the nucleation density was only $10^4$ cm$^{-2}$ on a mirror-polished single-crystal Si substrate without pretreatment, as shown in Fig. 6, which was deposited under a usual pressure of 100 torr. The nucleation density was only $3 \times 10^4$ cm$^{-2}$, several orders of magnitude lower than that for Fig. 3.

In brief, on a scratched Si substrate, the density of $10^9$ cm$^{-2}$ was obtained under the very low pressure as compared with the one of only $10^7$-$10^8$ cm$^{-2}$ under the normally low pressure. On an unscratched, mirror-polished Si substrate, $10^{10}$-$10^{11}$ cm$^{-2}$ was achieved in contrast with $10^4$ cm$^{-2}$ for the normal pressure. This demonstrates that using very low pressure is a very effective method for high-density nucleation on both scratched and unscratched substrates.

To demonstrate more clearly the nucleation rate, we studied the development of nucleation process with the nucleation time. Figure 7(a)-(d) show the SEM image of the nuclei on scratched substrates under the same nucleation parameters but with different nucleation time of 1 min, 2.5 min, 5 min and 10 min. To ensure the uniformity of the scratches on the samples, all of them were cleaved from a large Si wafer after scratching. The nucleation parameters were: $F = 70$ sccm, $[\text{CH}_4] = 3$ vol. $\%$, $p = 1$ torr, $T_f = 2100$-$2150^\circ$C, and $T_s = 850$-$900^\circ$C. Since the time was very short, it was difficult to adjust the filament and substrate temperatures to be exactly the same. Nonetheless, Fig. 7(a)-(d) show consistently
progress of the nucleation process. The size of the nuclei grew rapidly, while the nucleation density, which was approximately $3 \times 10^8 \text{ cm}^{-2}$, almost attained its final value during the first minute without much increase later on. Fig. 7(c) shows a sample after 5 min nucleation under the same condition plus 10 min subsequent growth under normal pressure. The growth parameters were: $F = 70 \text{ sccm}, [\text{CH}_4] = 3 \text{ vol.} \%, T_f = 2050^\circ \text{C}, T_s = 850^\circ \text{C}$. A magnified SEM picture reveals that the crystalline shape was beginning to be clear, as shown in Fig. 7(d). The size of the diamond particles was larger that that before growth (Fig. 7(c)), but much smaller than that for 10 min nucleation only (Fig. 7(d)), implying that the deposition rate of carbon, including diamond and non-diamond, was much higher under the low-pressure nucleation conditions above. This was one of the reasons why the nucleation progressed so rapidly, as will be discussed below.

Apart from Si substrates, very-low-pressure method was also applied to other substrates. Figure 8 shows the SEM image of nuclei on a scratched polycrystalline Ti substrate after 2 min nucleation under very low pressure ($p = 1 \text{ torr}$). The density was measured to be $1.5 \times 10^{10} \text{ cm}^{-2}$. A magnified SEM picture reveals the size of the nuclei began only after an intermediate TiC layer grew to as thick as 50 $\mu \text{m}$, with a very poor density, which was lower than that on a scratched Si substrate under normal pressure. Therefore, the very low pressure method works not just for Si substrates.

**IV. DISCUSSIONS**

As demonstrated clearly above, the very low pressure was responsible for the nucleation enhancement. To make full use of this method, a complete understanding of its mechanism is necessary. Generally speaking, the carbon ad-atoms may diffuse into the substrates at high temperatures while the substrate atoms may diffuse out. To nucleate, it is critical to generate supersaturation of carbon atoms/radicals on the substrate surface. Upon saturation of carbon and/or hydrocarbon species, graphite, amorphous carbon and diamond particles begin to form, depending on experimental conditions. On the other hand, the role of atomic hydrogen is also critical. A sufficient amount of atomic hydrogen is necessary to (i) extract the H atoms from the substrate surface to create active nucleating sites, to (ii) suppress the formation of carbon in $sp^2$ phase (i.e., non-diamond carbon) to ensure the formation of carbon in $sp^3$ phase (i.e., diamond), and to (iii) help eliminate possible oxide layers on the substrate surface, which is usually regarded as a hindrance against nucleation. The reason that only very poor nucleation is obtained on a mirror-polished substrate under normal conditions is mainly because of (i) the lack of enough nucleating sites and (ii) the low concentration of reactive hydrocarbon radicals and atomic hydrogen. Therefore, to get high density nucleation, enough amount of nucleating sites have to be created first, and then sufficiently large concentrations of reactive hydrocarbon radicals and atomic hydrogen have to be provided. For a Ti substrate, the easy formation of a TiC layer usually precedes the formation of diamond nuclei. This makes the supersaturation of carbon and/or hydrocarbon species on the substrate surface even more important. Based on these observations, several factors help explain the nucleation enhancing effect of very low pressure, as follows.

First, under very low pressure (0.1-1.0 torr), the mean free path, $\lambda$, of the molecules and radicals of the source gas is 1-2 orders of magnitude higher than that under normal pressure (tens of torr), as the mean free path is in inverse proportion to the pressure at equilibrium. Furthermore, the probability for a molecule to move a distance $x$ without collision is $e^{-x/\lambda}$, which is an exponential relationship. The concentrations of reactive hydrocarbon radicals and of atomic hydrogen decrease exponentially with increasing transportation distance. The molecules are decomposed in the neighborhood of the hot filament, whereas the nucleation and deposition takes place at a distance. Part of the decomposed radicals recombine through collisions, which is not favorable to deposition. The mean free path can be estimated as follows. The temperature is not uniform between the filament (2300-2400K) and substrate (1100K). For an estimate, let us take $T = 1700 \text{K}$ as an average. Since quite different sizes, and thus the mean free paths also differ much. Take $r_0 = 1.0 \text{ Å}$ as the radius of the background gas species in average since the gas is mainly composed of molecular hydrogen. Then we have

$$\lambda = \frac{r_0}{\sqrt{2 \pi m}} \frac{1}{d}, \quad \text{where} \quad d = r + r_0$$

For hydrogen atoms, $r = 0.75 \text{ Å}, \lambda_H = 1.3/p \text{ mm}$; for hydrocarbon radicals, mainly $\text{CH}_x$, take $r = 1.6 \text{ Å}, then
The probability for a reactive hydrocarbon precursor to get to the sample without collisions are $e^{-x/\lambda_{CHx}} \approx 4 \times 10^{-73}$ (= 0), 2 $\times$ 10$^{-4}$, and 0.43 for $p = 20$ torr, 1 torr, and 0.1 torr, respectively. For atomic hydrogen, the probabilities are: $e^{-x/\lambda_H} \approx 4 \times 10^{-34}$, 0.02, and 0.68 for $p = 20$ torr, 1 torr, and 0.1 torr, respectively. This is an amazingly enormous difference. Therefore, the probability for the atomic hydrogen and reactive hydrocarbon radicals in the neighborhood of the hot filament to get directly onto the substrate surface without collision or recombination is dramatically increased under very low pressure by many orders of magnitude. On the other hand, as the flow rate of the source gas did not change with pressure in our experiments, the amount of atomic hydrogen and hydrocarbon radicals generated by the hot filament per unit time remained unchanged. Actually, the amount increased due to the effect mentioned as the third reason below. In contrast, the concentration of atomic hydrogen and reactive hydrocarbon species were greatly increased, leading to very high supersaturation of the hydrocarbon. Since the nucleation rate is roughly proportional to the amount of the reactive hydrocarbon species arriving at the substrate surface per unit time, both the density and the rate of nucleation were dramatically enhanced.

While the damages of the substrate surface resulting from scratching may serve as nucleating sites, there exist only a very small density of surface defects on the unscratched, mirror-polished substrates. Therefore, a much lower pressure (0.1 torr) was used in our experiments to get a much higher concentration of reactive hydrocarbon radicals and hydrogen atoms to create an enough density of nucleating sites, and finally an enough high nucleation density, based on the mean-free-path scenario. On the other hand, as nucleation preferentially occurs on the damages of a scratched sample surface, these damages may put an upper limit of the density of nucleation. There seems to be no such an upper limit for an unscratched sample. This is probably the reason why a much higher density was obtained on the mirror-polished substrate.

Next, very low pressure induced very strong electron emission from the hot filament with an emission current as high as 0.5-1.0 A. The electrons had a continuous energy distribution from 0 up to $\sim$80 eV. As discovered in earlier work, the emitted electrons collided with and disassociated various gas molecules or radicals, helped to generate more atomic hydrogen and hydrocarbon radicals, and increased the concentration of atomic hydrogen and hydrocarbon radicals near the sample.

Last, under lower pressure, the efficiency of decomposition of the gaseous species by the hot filament was higher. As reported by Setaka, lower pressure leads to a higher decomposition efficiency of hydrogen. For methane, a similar result is expected. This effect again helped to increase the concentration of atomic hydrogen and reactive hydrocarbon radicals on the substrate surface.

All of these factors account for the nucleation enhancing effect of the very low pressure in our experiments. Katoh et al studied the influence of the pressure on the bias enhanced nucleation in MPCVD, and reported that lower pressure led to a higher nucleation density, in agreement with our results.

Calculations have also been done by Spear et al on the fraction of carbon deposited as a function of pressure for a mixture of CH$_4$-H$_2$ at equilibrium. The result shows that fraction becomes higher under lower pressure while other conditions are the same, consistent with our argumentation above.

In comparison with the negative-bias enhancement method and/or the EEE method, either in MPCVD or HFCVD, the very low pressure is distinguished from its high uniformity and rapidity. For both the bias and EEE methods, nucleation usually takes place non-uniformly. Careful parameter control and enough long time are necessary to get a uniform sample. As shown in Fig. (a)-(f), nucleation with a highly uniform distribution occurred from the very beginning.

In the above calculations, we have assumed implicitly a thermodynamical equilibrium of the gases in the deposition chamber, which was not the situation in practice. There existed a compulsive flow due to the pump, which can be estimated using the equation of state of an ideal gas, $pV = nRT$, where $V$ is the gas flow rate in unit of m$^3$/sec, $n$ is the flow rate in unit of mole/sec, $T$ is the temperature in Kelvin, and $R = 8.314$ J/(mole.K) is a constant. Let $v$ denote the flow velocity of the gas in unit of m/sec, then $V = \frac{4\pi D^2 v}{p}$, where $D = 0.140$ m is the diameter of the chamber. Therefore, we have $v = \frac{4nRT}{pD}$.

As $T$ was not uniformly distributed in the chamber, it is appropriate to take cross-section between the filament and the substrate of the chamber as a better estimate, which was approximately 1000 K. Take the flow rate to be 100 sccm, i.e., $n = 100$ sccm = 7.44 $\times$ 10$^{-5}$ mole/sec, and plug in all the numbers, we get $v = 0.3/p$ m/sec, where $p$ is in unit torr. This velocity is negligibly small even at $p = 0.1$ torr (3 m/sec), as compared to the thermal velocity of the gas molecules, which is of the order 10$^3$ m/sec. As a matter of fact, the cross-section of the inlet of the source gases, which was at a distance of only several centimeters away from the filament, was much smaller than that of the whole chamber, the flow velocity between the filament and the substrate might be one order of magnitude higher. Even so, it was still only a first order perturbation to the thermal velocity. Accordingly, we expect that our estimate about the mean free path remains valid.
On the other hand, as the filament was close to the inlet of the gases, this compulsive flow velocity at very low pressure was very important in that it guaranteed that the amount of the reactive hydrocarbon radicals and atomic hydrogen getting to the substrate surface per unit time was proportional to the gas flow rate in this steady, non-equilibrium case, as opposed to being proportional to the pressure in a static, equilibrium case, which was a good approximation only for the case of normally low pressure. In the latter case, $v$ was really small so that the amount of hydrogen and methane decomposed by the filament was mainly proportional to the pressure, whereas in the former case, it was mainly proportional to flow rate. While both factors were present, it is believed that the former case dominated under the very low pressure in the experiments.

While the compulsive flow velocity did not make much difference in terms of the velocity distribution and the mean free path of the gas species, the energy distribution between the filament and the substrate might be far from equilibrium under very low pressure. As shown above, under normal pressure, the mean free path was so small, equilibrium did arise. On the contrary, under very low pressure, say, 0.1 torr, 40% of hydrocarbon and 70% atomic hydrogen could get onto the substrate without collisions, while they still had the energy from filament at $T = 2400$ K, more than twice that of the substrate, 1100K. Higher energy was believed to be able to enhance the mobility and reactivity of the ad-species on the substrate, and might therefore increase the nucleation rate.

One may have noticed that, under normal pressure for a scratched substrate, a considerably high density of nucleation is usually obtained regardless of the very small mean free path, as shown above. The reasons may be explained as follows. First, as most of the gas species are $\text{H}_2$ molecules, they do not likely result in loss of atomic hydrogen or hydrocarbon radicals in collisions. Only collisions between hydrogen atoms and/or hydrocarbon radicals may result in recombination and counter the effect of decomposition by the filament. The effective “mean free path” in terms of recombination will be larger. Thus, the probabilities for a hydrogen atom and a reactive hydrocarbon radical to get to the substrate surface are much higher than those calculated above, although they may undergo collisions. Second, Apart from $\text{CH}_x (x < 4)$ and $\text{C}_2\text{H}_x$, $\text{CH}_4$ also contributes in nucleation whose concentration is independent of the mean free path. It can occupy a vacant surface site, and help to form nuclei, though its role is much less important as compared with $\text{CH}_x (x < 4)$ and $\text{C}_2\text{H}_x$, etc. Third, part of the decomposition may take place in the neighborhood of the substrate, though the decomposition rate is very low, as the substrate temperature is far from high enough. While these contributions may lead to considerable nucleation density on a scratched substrate (at a low rate, though), they are not sufficient to lead to a high density on an unscratched, mirror-polished substrate.

As the substrate is usually covered with a surface oxide layer, which is disadvantageous to high-density nucleation, we see that, under very low pressure, a very high percentage of atomic hydrogen is transported onto the substrate from near the filament without collisions. This greatly helps to eliminate the surface oxide to make a clean substrate surface, presenting a nucleation enhancing effect.

While our very low pressure led to impressive nucleation enhancement, however, we do not claim that the pressure should be arbitrarily low. As the very low pressure was realized by increasing the pump rate and/or decreasing the flow rate, the pressure could not be arbitrarily low. First, the capability of the pump was limited; it is difficult to get a high vacuum in the presence of gas feed. Second, at very low pressure, the deposition rate was roughly proportional to the flow rate, which should not be too low. Third, the mean free path should not be too long in the neighborhood of the filament, else the gas could not be effectively decomposed by the filament, as most gaseous species might not pass through the hot filament zone. Last, under too lower pressure, non-equilibrium effect would be more important, and the analysis above should be modified, accordingly. Therefore, there exists an optimum pressure which gives rise to the best result. Further experiments are necessary to optimize the experimental parameters.

It is appropriate to point out that the local pressure between the filament and the substrate was a little higher than the average of the whole chamber, however, the main conclusions, e.g., the much longer mean free path under the much lower pressure, etc, should remain valid.

Using the very low pressure technique, epitaxial nucleation on Si(111) substrates had been achieved and the serious problem of the formation of thick intermediate TiC layers and hydrogenation of very thin Ti substrates resulting from the long, slow, poor nucleation process has been solved. It also sheds light on the mechanism of diamond nucleation on a hetero-substrate, as it confirms that a high concentration of reactive hydrocarbon species and atomic hydrogen is necessary for nucleation.

V. SUMMARY

In summary, under very low pressure (0.1-1 torr), high density nucleation was achieved on mirror-polished Si substrates with a density as high as $10^{10}$-10$^{11}$ cm$^{-2}$, comparable to the highest value for MPCVD. For scratched Si substrates, the density was as high as 10$^{9}$ cm$^{-2}$, 1-2 orders of magnitude higher than that obtained under normal pressure (tens of torr). In addition to Si substrates, a density of as high as 10$^{10}$ cm$^{-2}$ was obtained on polycrystalline Ti substrates. Detailed study of the process of nucleation with increasing time revealed that nucleation progressed at a very high speed, the density getting to its final value within a very short time.
(1 min). Calculations demonstrate that, under very low pressure, the mean free path of the gas molecules and/or radicals is increased by 1-2 orders of magnitude, as a result, the probability for an hydrogen atom or an reactive hydrocarbon radical to transport from the filament to the substrate without collisions is dramatically, exponentially increased. On the other hand, very low pressure induces very strong electron emission with the electron energy up to 80 eV, adding to the dissociation of the gas species. Moreover, very low pressure favors a high efficiency for the filament to decompose the gas species. All these factors result in much higher concentrations of the atomic hydrogen and reactive hydrocarbon radicals on the substrate surface, leading to the drastically enhanced nucleation. This method solves the problem of getting high density of diamond nucleation on mirror-polished substrates in addition to the EEE method. It has great practical applications and theoretical significance. It is hoped that the very-low-pressure method can be extended for the growth stage, not just for nucleation. More work still needs to be done in this regard.

ACKNOWLEDGMENTS

The author thanks Z. Lin for various support as an advisor while this work was done, Y. Chen for collaboration on the very beginning of this work, Y.J. Yan, Q.L. Wu, and X. Kuang for operating the SEM, K. Zhu and Q. Zhou for their Raman spectroscopy service, and MRSEC at the University of Chicago for its computer facilities. This work is financially supported by Chinese Natural Science Foundation, 863 Program and Beijing Zhongguancum Associated Center of Analysis and Measurement.

1 J. C. Angus, Y. Wang, and M. Sunkara, Annu. Rev. Mater. Sci. 21, 221 (1991); J. C. Angus, C. C. Hayman, Science 241, 913(1988)
2 J. C. Angus, H. A. Will and W. S. Stanko, J. Appl. Phys. 39, 2915(1968); D. J. Poferl, N. C. Gardner and J. C. Angus, J. Appl. Phys. 44, 1428(1973); S. P. Chauhan, J. C. Angus and N. C. Gardner, J. Appl. Phys. 47, 4746(1976)
3 J. J. Landers and J. Morrison, Surf. Sci. 2, 553(1964); J. Chem. Phys. 34, 1403(1961); B. V. Spitsyn, L. L. Bouilov, and B. V. Deryagin, J. Cryst. Growth 52, 219(1981)
4 S. Matsumoto, Y. Sato, M. Kamo and N. Setaka, Jpn. J. Appl. Phys. 21, Part 2, 183(1982); S. Matsumoto, Y. Sato, M. Tsutsumi and N. Setaka, J. Mater. Sci. 17, 3106(1982)
5 K. Mitsuda, Y. Kojima, T. Yoshida and K. Akashi, J. Mater. Sci. 22, 1557 (1987)
6 J. C. Angus, Z. Li, M. Sunkara, R. Gat, A. B. Anderson, S. P. Mehandru and M. W. Geis, in Proceedings of the 2nd International Symposium on Diamond Materials, edited by A. J. Purdes, J. C. Angus, R. F. Davis, B. M. Meyerson, K. E. Spear, and M. Yoder (The Electrochemical Society, Pennington, NJ, 1991), p.125
7 Z. Feng, K. Konovopoulos, I. G. Brown and D. G. Bogy, J. Appl. Phys. 74, 2841(1993)
8 A. A. Morrish and P. E. Pehesson, Appl. Phys. Lett. 59, 417(1991)
9 J. Singh and M. Vellaikal, J. Appl. Phys. 73, 2831(1993); K. V. Ravi and C. A. Koch, Appl. Phys. Lett. 57, 348(1992); K. V. Ravi, C. A. Koch, H. S. Hu and A. Joshi, J. Mater. Res. 5, 2356(1990)
10 D. G. Jeng, H. S. Tuan, R. F. Salat and G. J. Fricano, Appl. Phys. Lett. 56, 1968(1990)
11 S. Yugo, T. Kanai, T. Kimura and T. Muto, Appl. Phys. Lett. 58, 1036(1991)
12 B. R. Stoner, G.-H. M. Ma, S. D. Wolter and J. T. Glass, Phys. Rev. B45, 11067(1992)
13 X. Jiang, K. Schiiffmann, A. Westphal and C.-P. Klages, Appl. Phys. Lett. 63, 1283(1993)
14 W. Zhu, F. R. Sivazlian, B. R. Stoner and J. T. Glass, J. Mater. Res. 10, 425(1995)
15 Q. Chen and Z. Lin, Appl. Phys. Lett. 67, 1853(1995)
16 Q. Chen and Z. Lin, Appl. Phys. Lett. 68, 2450(1996)
17 Q. Chen and Z. Lin, J. Appl. Phys. 80, 797(1996)
18 S. S. Park and J. Y. Lee, J. Appl. Phys. 69, 2618(1996)
19 Qijin Chen, M.S. thesis, Institute of Physics, Chinese Academy of Sciences, 1995
20 S. T. Lee, Y. W. Lam, Z. Lin, Y. Chen and Q. Chen, Phys. Rev. B55, 15937(1997)
21 Q. Chen and Z. Lin, J. Mater. Res. 10, 2685(1995)
22 B. V. Spitsyn, L. L. Bouilov and B. V. Deryagin, J. Cryst. Growth 52, 219(1981)
23 M. Frenklach and H. Wang, Phys. Rev. B43, 1520(1991)
24 K. E. Spear, J. Am. Ceram. Soc. 72, 171(1989)
25 B. Sun, X. Zhang, Q. Zhang and Z. Lin, J. Appl. Phys. 73, 4614(1993)
26 The radii of hydrogen atoms and and carbon atoms differ from different sources. Also it depends on how they are determined. The covalent radii can differ from the Van der Waals radii by a factor of two. We take the average for estimate purpose. For hydrogen atoms and carbon atoms, they are 0.75˚A and 1.3˚A, respectively. Accordingly, the radii of H2 and CH4 are estimated to be 1.0˚A and 1.6˚A, respectively.
27 Due to different average velocities of hydrogen atoms and of hydrocarbon species, the factor √7 should also be modified accordingly. However, this is less important in comparison with the size of the gaseous species.
28 N. Setaka, J. Mater. Res. 4, 664(1989)
29 M. Katoh, M. Aoki and H. Kawarada, Jpn. J. Appl. Phys. 33, L194(1994)
30 B. R. Stoner and J. T. Glass, Appl. Phys. Lett. 60, 698(1992)
31 B. Sun, X. Zhang and Z. Lin, Phys. Rev. B57, 9816(1993); B. Sun, X. Zhang, Q. Zhang and Z. Lin, Appl. Phys. Lett. 62, 31(1993)
32 Q. Chen, Y. Chen, J. Yang and Z. Lin, Thin Solid Films 274, 160(1996)