

Very Low Pressure Nucleation of Diamond on Mirror-Smooth Silicon in Hot Filament Chemical Vapor Deposition System *

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Under very low pressure (0.1 Torr) the high density nucleation of diamond on mirror-smooth silicon in hot filament-chemical vapor deposition system was obtained. The nucleation density of order of 10^{10} – 10^{11} cm^{-2} was achieved, the same achievement which obtained in microwave plasma-chemical vapor deposition system with negative bias. In this paper the nucleation technique and the effect of low pressure on diamond nucleation were discussed in detail based on the molecular dynamics.

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Nucleation is the first step of diamond growth. During the early development of diamond growth by chemical vapor deposition (CVD) method, diamond seeds were used as nuclei.¹ Later, it was found that substrate scratching with diamond powder could greatly enhance nucleation.² Since then diamond scratching of substrate has become a common method for obtaining high density of nucleation. For Si, the most often used substrate, a nucleation density of 10^7 – 10^8 cm^{-2} can be achieved after careful scratching with diamond powder, whereas only 10^4 cm^{-2} nuclei can be obtained for a non-scratched Si.

By applying a bias voltage to substrate in a microwave plasma-chemical vapor deposition (MP-CVD) system, Jeng *et al.*³ obtained oriented nucleation with a density of about 10^7 cm^{-2} at a local area on a mirror-polished Si substrate. Later, Yugo *et al.*⁴ obtained a nucleation density as high as 10^9 – 10^{10} cm^{-2} by using similar approach. Currently, the highest nucleation density on Si was 10^{11} cm^{-2} reported by Stoner *et al.*⁵ In the hot filament-chemical vapor deposition (HF-CVD) system, another important method for diamond growth, however, high nucleation density has not been obtained on mirror-polished Si.

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 ($> 10^7$ cm^{-2}) has never been obtained on mirror-polished, untreated Si.

Contrary to the conventional wisdom, we wish to show in this paper that very low pressure condition can, indeed, be advantageous for diamond nucleation.

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Diamond nucleation and growth were conducted in a typical HF-CVD system. Tungsten hot filaments were hanged at a distance of 6 mm above the substrate. The mixed gas of hydrogen and methane was used as source, with a flow rate of 50 sccm. The ratio of CH_4/H_2 was kept at 2% for nucleation. The temperatures of the W filament and substrate were measured by an optical pyrometer and a thermocouple, respectively. The pressure of the growth chamber was kept at 0.1 and 1 Torr by a leak-valve for nucleation.

All the samples were cut from a mirror-smooth Si wafer without being polished by diamond powder. Before loading into the growth chamber every sample was cleaned in an ultrasonic bath sequentially for 10 min each with acetone, ethanol and deionized water, then etched in 30% HF solution for 1 min, and finally rinsed with deionized water. We noticed that surface cleaning was very essential for achieving high density nucleation of diamond, and thus the cleaning process was carried out carefully. The results of nucleation and growth were examined by scanning electron microscopy (SEM) and Raman spectroscopy.

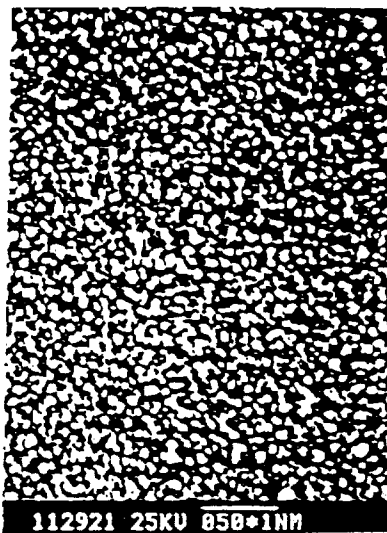


Fig. 1. SEM of diamond nuclei on mirror-smooth Si(100) substrate.

band at 1540 cm^{-1} corresponds to nondiamond phase such as amorphous carbon and/or graphite, which usually appeared during the initial stage of diamond growth.

For comparison we nucleated on mirror-smooth Si sample for 20 min under conventional condition: $p = 50\text{ Torr}$, $\text{CH}_4/\text{H}_2 = 0.7\%$, $T_f = 2150^\circ\text{C}$, and $T_s = 850^\circ\text{C}$. The nucleation density is only about $3 \times 10^4\text{ cm}^{-2}$.

To investigate the nucleation rate and incubation period under very low pressure, we grew diamonds under the same conditions but with various nucleation time. All the samples were pieces cleaved from one large Si (100) wafer. Figures 3 (a)–3 (d) show the SEM pictures corresponding to the nucleation time of 1, 2.5, 5, and 10 min, respectively. Nucleation parameters were as follows: $p = 1\text{ Torr}$, $\text{CH}_4/\text{H}_2 = 2\%$, $T_f = 2100^\circ\text{C}$, and $T_s = 850^\circ\text{C}$. Compared the

Figure 1 shows the SEM morphology of a typical mirror-smooth Si(100) substrate after 10 min nucleation. The parameters for nucleation were as follows: $p = 0.1\text{ Torr}$, $\text{CH}_4/\text{H}_2 = 2\%$, $T_f = 2150^\circ\text{C}$ and $T_s = 850^\circ\text{C}$. The nucleation density attained was around $10^{10}\text{--}10^{11}\text{ cm}^{-2}$. This value is equivalent to the highest level reported to date, which was obtained in a MP-CVD system using a negative substrate bias. To our knowledge, such a nucleation density represents the highest among data ever reported for HF-CVD growth in literature.

Figure 2 shows the Raman spectrum of this sample. In Fig. 2 the characteristic Raman peak of diamond at 1332 cm^{-1} is prominent, showing that diamond was formed indeed on Si substrate. The broad

SEM images in Fig. 3 we found that within the time range used in the present experiment, the nucleation densities remain almost the same at about $5 \times 10^8 \text{ cm}^{-2}$, but the size of nuclei increases remarkably with increasing nucleation time. In the sample nucleated for 10 min [Fig. 3 (d)] a continuous diamond film was nearly formed. The incubation period is very short, within 1 min. We can conclude that very low pressure is indeed an effective method for obtaining high nucleation density of diamond on mirror-polished Si substrate.

The enhancement of nucleation density, we believe, is due to:

1. The increase of the amount of atomic hydrogen and activated hydrocarbon near the substrate surface. Here we take atomic hydrogen as an example. As we know that atomic hydrogens play a very important role in low pressure diamond formation, however, they recombine and become hydrogen molecules very easily, then lose their activity. When the pressure keeps high, its mean free path becomes very short, about micron, for example under pressure of several tens of torr, thus atomic hydrogen decomposed by hot filament very soon be recombined in the way flying toward substrate, only a few can be survived and arrived at the substrate, while under very low pressures, the mean free path of atomic hydrogen increases, for example, at 0.1 Torr, approaches millimeter range which is comparable to the nominal spacing between the hot filament and substrate used in a HF-CVD system, so the fraction of these atomic hydrogens surviving recombination to arrive at the substrate will increase remarkably. Nevertheless, since the concentration of atomic hydrogen near hot filament is proportional to the product of decomposition efficiency and reactant pressure, thus were considered both factors: the mean free path and reactant pressure, the amount of atomic hydrogen near the substrate will eventually go through a maximum as the reactant pressure decreases to a certain value. We have taken calculation and gave a rough estimation of the optimum pressure (about 0.02 Torr) for diamond nucleation. As expected, the optimum pressure is considerably lower than the normal pressure used in conventional CVD diamond growth. The same consideration is also suitable for other activated hydrocarbon radicals.

2. The interaction of higher kinetic energy species with substrate, as a result of the longer mean free path under very low pressure, atomic hydrogen and hydrocarbon radicals will be able to reach the substrate surface without or with rare collision, thus the kinetic energy of these active species will be close to the local thermal energy of the hot filament (2150°C). Contrary under pressure of several tens of torr, because of diminishing mean free path of the active species, which is only several microns, these species will undergo many collisions before reaching the substrate surface. As a result, the kinetic energy of the impinging species is close

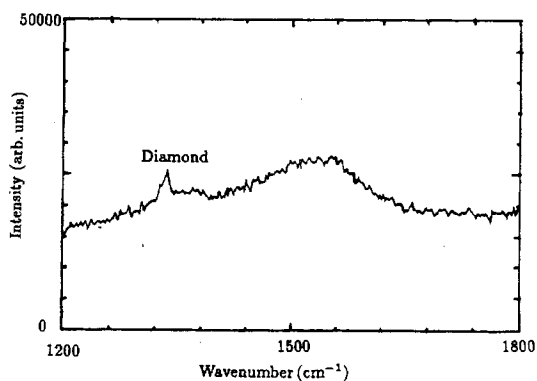


Fig. 2. Raman Spectrum of the sample after 10 min diamond nucleation on mirror-smooth Si(100) substrate under pressure of 0.1 Torr.

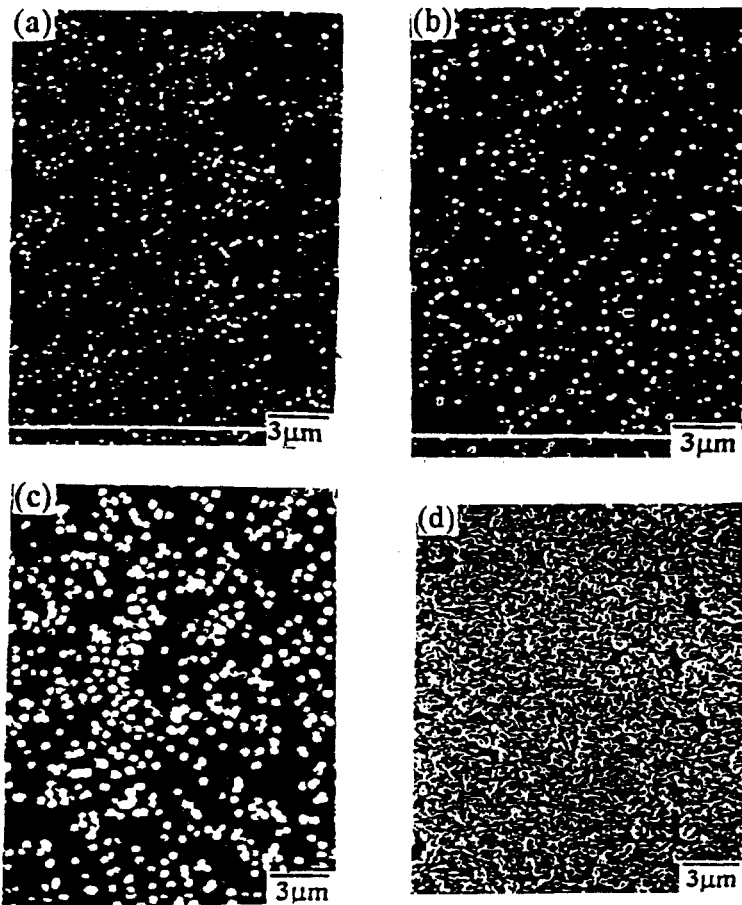


Fig. 3. SEM of diamond nuclei on mirror-smooth Si (100) substrate for nucleation time: (a) 1 min, (b) 2.5 min, (c) 5 min, and (d) 10 min, respectively.

to the thermal energy of the substrate, which is typically 850°C. Therefore the kinetic energy of the impinging species under very low pressure is about 2–3 times of that conventional pressure. Particles with a higher kinetic energy will exhibit larger surface mobility which promotes the congregation of the precursors and thus the nucleation process on substrate. Moreover, the bombardment of more energetic particles will lead to improved surface cleanness and increased likelihood of surface restructure or surface microstructure modification, giving rise to the conditions that are more favorable for diamond precursor adsorption, congregation and growth.

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