Electron-emission-enhanced diamond nucleation on Si by hot filament chemical vapor deposition

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Diamond nucleation on mirror-polished Si was enhanced by electron emission using hot filament chemical vapor deposition. The nucleation density was \(10^8 \text{ cm}^{-2}\). The mechanism of diamond nucleation is carefully discussed. It is surmised that it is electron emission that is responsible for the enhancement of the diamond nucleation in our experiments. © 1996 American Institute of Physics.

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Great progress has been made in diamond synthesis by chemical vapor deposition (CVD) in the past several years. Owing to the alluring applications in electronics of epitaxial thin diamond films,\textsuperscript{1} many efforts have been made to get high density nucleation on mirror-polished Si, which is the most popular substrate for diamond deposition as of today. In microwave plasma CVD (MPCVD) system, negatively biasing the substrate has been proved an effective method to enhance the nucleation.\textsuperscript{2,3} However, the mechanism of this bias method is unclear. It is speculated by many researchers that the bombardment of the positive ions in the plasma is responsible for the enhanced nucleation.\textsuperscript{2,4} However, there is no direct evidence as yet.

In HFCVD, the difficulty in obtaining high nucleation density on mirror-polished Si has been resolved. Recently, we\textsuperscript{5} reported success in this regard by a negative bias nucleation method, which was similar to that used in MPCVD. In that paper, we speculated that the emission current from the diamond film coating the Mo substrate holder was responsible for the enhanced diamond nucleation in terms of the differences in the ion amounts between HFCVD and MPCVD system. Yet it may not be considered fully persuasive owing to the similarity of our method to that used in MPCVD. To make it clear, it is important to employ an innovative apparatus configuration in which there is electron emission and there can be no positive ion bombardment.

The purpose of this letter is to present such a new nucleation method, which serves as direct evidence for the electron-emission-enhancement (EEE) mechanism of the diamond nucleation on mirror-polished silicon. High density nucleation was achieved simply by electron emission. No bias was applied to the substrate. This work, in combination with our previous reports,\textsuperscript{5} demonstrates the validity of the EEE nucleation mechanism.

Our experiments were carried out in a conventional HFCVD apparatus as reported in Ref. 5 with a little modification in the layout of the dc electrodes. Two different settings were used, as shown in Figs. 1(a) and 1(b). In Fig. 1(a), the dc voltage was applied to the two tungsten electrodes. In Fig. 1(b), negative dc voltage was applied to the two W electrodes while the filament was dc grounded. All the dc electrodes were coated with diamond films, which were used to emit electrons during the nucleation stage. No bias was applied to the substrate. Both cases gave rise to no positive ion bombardment of the substrate surface. The source gases used were CH\(_4\) and H\(_2\). Mirror-polished 10\(\times\)15 mm\(^2\) p-type Si(100) wafers were used as the substrates. They were chemically cleaned with acetone in an ultrasonic bath for 10 min, followed by 1 minute’s rinse in 30% vol. HF solution. The experimental conditions are as follows: gas flow rate was 200 sccm; CH\(_4\) concentration, 3.5%; pressure, 30 torr; filament temperature, ~2000 °C; substrate temperature, 700–750 °C; dc voltage, 250–300V; electron emission current, 150–200mA.

Figure 2 shows the SEM image of a sample after 15 min nucleation using the dc voltage setting as in Fig. 1(a). The setting in Fig. 1(b) gave very similar results. The nuclei are well faceted. From this figure, the nucleation density was measured to be approximately \(10^8 \text{ cm}^{-2}\). Since the nuclei were relatively big, considering that neighboring nuclei may have combined, the actual density is probably a little higher.

In Ref. 5, we used the configuration in Fig. 3, where the substrate was negatively biased, to get high density nucleation. The density attained was \(10^9 \text{ cm}^{-2}\), greater than that in Fig. 2, because of the higher substrate temperature (800 °C) and the slightly larger emission current (200 mA) used.

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FIG. 1. Schematic diagram of the electrode layout in the experiments, viewed along the filament. The W electrodes were covered with diamond films. (a) The dc voltage was applied between the two W electrodes; (b) The two W electrodes were used as the cathodes, while the filament was the anode.
Indeed, it is found that the nucleation density decreases with decreasing emission current and lower substrate temperature. One may note that there are two drawbacks in our present experimental configuration. One is that the electron emission current can not be large enough because of the small diameter of the tungsten electrodes (≤1 mm diameter when coated with diamond films). The other is that the substrate temperature can not be very high because the W electrodes are located between the filament and the substrate and therefore lead to a relatively large filament-substrate distance. However, our further experiments gave a similar density of ~10^6 cm^{-2} using the negative bias configuration (Fig. 3) at approximately the same substrate temperature and the same emission current as in this work. Therefore, our results demonstrate that the electron emission is an effective method for nucleation enhancement.

As of today, the most successful method to achieve high density nucleation on mirror-polished Si is reportedly the negative bias enhanced nucleation, mainly used in MPCVD systems. However, the mechanism for this nucleation enhancement is not yet clear. It has been attributed to the positive ion impact onto the substrate surface by many researchers owing to the existence of a large amount of ions in plasma in a MPCVD system. The ion impact hypothesis was first advanced by S. Yugo et al. They argued that the application of a negative bias to the substrate accelerated the ions in the plasma to the substrate surface, and thus increased active hydrocarbon species on/above the substrate surface and enhanced the reactions causing diamond nucleus generation. They also argued that accelerated ions removed amorphous carbon and increased the bond strength between diamond nuclei. B. R. Stoner et al. advanced several possible mechanisms based mainly on the ion impact hypothesis to interpret the nucleation enhancement by the negative bias method. X. Jiang et al. claimed that the bias-enhanced ion bombardment improved the adatom diffusion and was responsible for the diamond nucleation. Compared with MPCVD, however, there exists a much smaller amount of ions in HFCVD system. Yet one still can get high density nucleation by HFCVD using a similar negative bias and the scheme used in this letter. Therefore, it is believed that positive ion impact is not the true mechanism.

Recently, R. I. Cherry et al. reported their work on ionic contribution in HFCVD. The maximum bias current observed was less than 10 nA. They attributed it to an ion current mechanism. However, under typical parameters (growth rate: 1 μm/h; CH_4 concentration: 2% vol.; flow rate: 100 sccm, substrate area: 1 cm^2), simple rough calculation demonstrates that only 1×10^{-5} of the species which contribute to the diamond growth can be ionic, and that only 1×10^{-3} of the total hydrocarbon species contribute to growth. Thus only 1×10^{-10} of all kinds of species are ionic. How could such a little proportion play an important role in either nucleation or growth? In addition, the current likely comes from the electrons given off by the hot filament instead of the positive ions. Therefore, we firmly believe that there is only a very small amount of positive ions in a typical HFCVD system, and that the ions play a minor role in diamond nucleation in HFCVD.

In our previous report, we argued that it is the electron emission from the diamond coating on the Mo substrate holder that caused the diamond nucleation enhancement. In agreement, our present result shows direct evidence that electron emission alone is sufficient to enhance the diamond nucleation without biasing the substrate. The electrons accelerate in the dc electrical field, collide with and dissociate the hydrogen and hydrocarbon molecules and species, greatly increase the concentrations of atomic hydrogen and reactive hydrocarbon radicals, and eventually lead to the nucleation enhancement. The negative bias is only a superficial phenomenon, which may be misleading. As B. R. Stoner et al. revealed, negative bias alone can not bring about enhanced nucleation without electron emission.

W. Zhu et al. also reported nucleation enhancement by a slightly modified negative bias method in their HFCVD system. They argued that the hot filament generated the positive ions, and so they adopted the ion bombardment mechanism to interpret the results. They thought that the ions collide with the gas and led to a purple color. However, it should be observed that such a color can last for a relatively long time (e.g., 1 min or longer) after the filament is suddenly switched off and thus loses its asserted ability to generate ions. Meanwhile, the color always appears in contact with the diamond coating on the cathode but far from the anode. These phenomena contradict their argument. We believe that the color was caused by the collision between the electrons and the gas.

Our EEE method has also been tried on other substrates...
such as highly oriented pyrolytic graphite, oxidized Si surface. It always results in a high nucleation density.

In summary, high density nucleation on mirror-polished Si was achieved by electron emission in a HFCVD system. This result presents direct evidence for the electron-emission-enhancement nucleation mechanism. It is speculated that the EEE nucleation mechanism is also true for the negative bias nucleation by MPCVD.

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