Experimental approach to the mechanism of the negative bias enhanced nucleation of diamond on Si via hot filament chemical vapor deposition

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The mechanism of the negative bias enhanced nucleation of diamond on silicon has been studied by a set of experiments using hot filament chemical vapor deposition. Nucleation enhancement was achieved for experimental configurations either with or without the application of a negative bias to the mirror-polished Si substrates. The obtained nucleation density ranged from 10^8 to 10^{10} cm^{-2}. The as-deposited films were characterized by scanning electron microscopy and Raman spectroscopy. Our results demonstrate that the electron emission from the diamond coating the substrate holder, which is speculated to greatly increase the concentration of atomic hydrogen and dissociated hydrogen radicals on/near the substrate surface is responsible for the nucleation enhancement during the bias pretreatment. *© 1996 American Institute of Physics.* [S0021-8979(96)01014-6]

I. INTRODUCTION

Diamond films have been deposited from the gas phase at subatomsphere by various chemical vapor deposition (CVD) methods.[1–3] Owing to the promising applications of thin diamond films in electronics, many efforts have been made to achieve heteroepitaxy of diamond films on silicon wafers, which requires high density nucleation on primitive mirror-polished Si. However, the nucleation mechanism is still not quite clear, though many efforts have been made on it. Nevertheless, methods have been developed to enhance nucleation. The most successful one is the negative bias enhanced nucleation method in microwave plasma CVD (MPCVD). By this method, Yugo *et al.*,[4] Stoner *et al.*,[5] and Jiang *et al.*[6,7] acquired a high density nucleation on mirror-polished Si and, subsequently, got epitaxially oriented diamond films.[6–8] In hot filament CVD (HFCVD), Chen *et al.*[9,10] recently used a similar method and achieved high density nucleation and epitaxially oriented growth on mirror-polished Si. Zhu *et al.*[11] and Stubhan *et al.*[12] also got high density nucleation on mirror-polished Si by HFCVD. On the other hand, the role of the negative bias has led to controversy, though lots of mechanisms have been advanced. The most popular one is the positive ion bombardment first advanced by Yugo *et al.*[4] However, there is only a very small amount of ions in the HFCVD system,[13,14] yet the negative bias nucleation method is also successful. Moreover, there are other experimental results against the ion bombardment interpretation. For example, Katoh *et al.*[15] obtained a high density nucleation even using a positive bias in MPCVD. What is the true mechanism for the widely used negative bias nucleation method?

In this article, the authors report an experimental study on the mechanism of the negative bias enhanced nucleation. High density nucleation was achieved either with or without a negative bias to the substrate using HFCVD. Our results demonstrate that the true mechanism for the biased nucleation is not the positive ion bombardment but the electron emission from the diamond coating on the Mo substrate holder.

II. EXPERIMENT

Our experimental device was a typical HFCVD system. A ϕ 140 mm and 500 mm long fused silica tube was used as a deposition chamber. A Mo plate was placed on a copper platform of ϕ 80 mm to support samples. ϕ 0.2 mm tungsten wires winding into coils 2.5 mm in diameter were used as filaments. Their temperature was measured by an optical pyrometer. Well polished $8\times10–10\times15$ mm^2 and 0.5-mm-thick *p*-type (001) silicon wafers were used as substrates. Cooling water was also used to adjust the substrate temperature. The temperature of the substrates was measured by a thermocouple (Pt-PtRh). The source was diluted CH_4 in hydrogen. The substrates were chemically cleaned with acetone in an ultrasonic bath for 10 min, followed by 1 min rinse in 30 vol % HF solution. Several groups of experiments were done using different configurations as shown below. The experimental parameters are listed in Table I.

For experiment 1, we used the setup shown in Fig. 1. The Mo plate, which was used to support the samples, had been predeposited with a thin diamond film (not including the area directly beneath the Si samples, in order to keep good electrical contact between the sample and the Mo plate). Figure 1 gives the schematic configuration of the experimental apparatus and electrodes viewed along the direction in parallel with the filament. The paths of the electrons are also shown schematically. The filament, etc., are not drawn proportionally in size. During the nucleation stage, a dc bias of −220 V relative to the filament was applied to the Mo sample supporter and, thus, the substrate with an emission current of 280–300 mA. The nucleation stage lasted for

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TABLE I. Experimental conditions.

Parameters	Experiments 1 and 2	Experiment 3	Experiments 4 and 5
Flow rate (sccm)	200	200	200
CH_4 concentration (vol %)	2.0	2.0	2.0–4.0
Filament temperature (°C)	2000	2000	2000
Substrate temperature (°C)	850	750–800	700–750
Filament–substr. dist. (mm)	6	10	10
Pressure (Torr)	30–40	30–40	30–40
dc bias/voltage (V)	−220	−250	250–300
Emission current (mA)	280–300	200–250	150–200
Nucleation time (min)	8–10	15–20	15–25

8 min, then the sample was taken out of the chamber for scanning electron microscopy (SEM) observation. After that, it was reloaded into the chamber for 20 min deposition. The growth conditions are: CH_4 concentration 1.2 vol %, filament temperature 2000 °C, substrate temperature 800 °C, and flow rate 200 sccm.

For experiment 2, the configuration was nearly the same as that in experiment 1 except that the Si substrate was electrically insulated from the Mo supporter by an intermediate thin ceramic plate (0.5 mm in thickness).

For experiment 3, the configuration is a little modified, as shown in Fig. 2. On one side of the sample, the Mo supporter was covered with a thin ceramic wafer or simply a clean Si wafer so that there was no electron emission from this side. Meanwhile, directly over the ceramic (or Si) or wafer, a tungsten wire (~1 mm in diameter) was placed in parallel with the filament as another anode besides the filament.

The configuration for experiment 4 is shown in Fig. 3. The substrate was not biased. Instead, the dc voltage was applied between the two W electrodes, which were covered with diamond films. Both the filament and the substrate were electrically dc floating. The paths of the electrons are also shown schematically in Fig. 3.

For experiment 5, the substrate was set to the same dc voltage as the filament, while the two electrodes were negatively biased relative to them, as shown in Fig. 4.

III. RESULTS AND DISCUSSIONS

A. Experiments with a negative bias to the substrates

Figures 5(a) and 5(b) show the SEM images of the sample surface from (a) the outer area to (b) the inner area after 8 min nucleation in experiment 1. According to the visible nuclei, the nucleation density is measured to be $\sim 10^{10}$ cm^{-2} and 5×10^{8} cm^{-2} for Fig. 5(a) and Fig. 5(b), respectively. This indicates that the density in the outer section of the sample is much higher than in the inner section. Obviously, nucleation proceeded from outer to inner of the sample surface in this experiment, as is similar to the Stoner *et al.* results on the substrate of β-SiC by MPCVD.[16] This phenomenon could be easily observed since our apparatus was transparent.

As reported by Stoner *et al.*,[16] during the bias nucleation stage, the diamond film coating the Mo sample holder emitted electrons around the Si wafer. In our experiments, the electron emission was easily observed to be kept clearly out of the sample, since the gas presented an easy-to-observe blue color (or purple if the filament was suddenly switched off) within 2–3 mm directly over the diamond coating owing to the collision between the electrons and the gas. As will be discussed below, this electron emission plays a critical role in diamond nucleation in the negative bias case. The farther away from the electron flux, the lower the nucleation rate. This accounts for the higher nucleation rate in the outer area of the sample.

Figure 6 shows the SEM pictures of (a) the outer and (b) the inner area of the as-grown diamond film after 20 min deposition. The diamond particles are well faceted, indicative of high crystallinity though they are still extremely small (0.2 μm or smaller in average). The density of the diamond grains is almost the same for Figs. 6(a) and 6(b), as measured to be $\sim 5\times 10^{9}$ cm^{-2}, greater than the density of the visible nuclei Fig. 5(b). This suggests that the actual nucleation density is higher than what Fig. 5(b) shows because most nuclei in the inner part are so small that they cannot be detected by

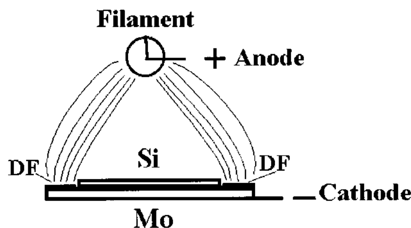


FIG. 1. Schematic diagrams of the configuration of the experimental apparatus and electrodes for experiment 1 viewed along the direction of the filament. The paths of the electrons are also shown schematically. DF denotes diamond films.

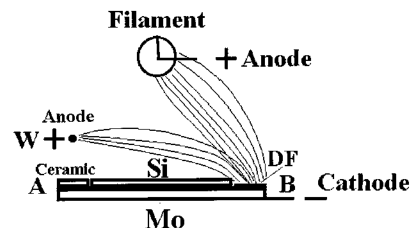


FIG. 2. Schematic diagram of the experimental configuration and corresponding paths of the electrons for experiment 3, viewed along the direction of filament. Side A was covered with a ceramic (or clean Si) wafer. Part of the electrons fly directly over the sample. DF denotes diamond films.

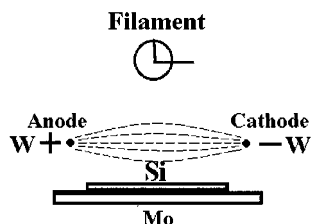


FIG. 3. Schematic diagram of the configuration for experiment 4. The W electrodes were covered with diamond films. The substrate and the filament were both electrically dc floating. The paths of the electrons are shown by the dashed lines.

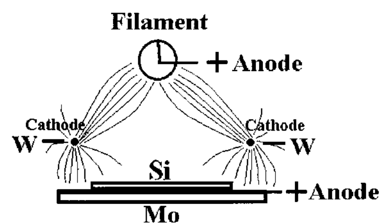
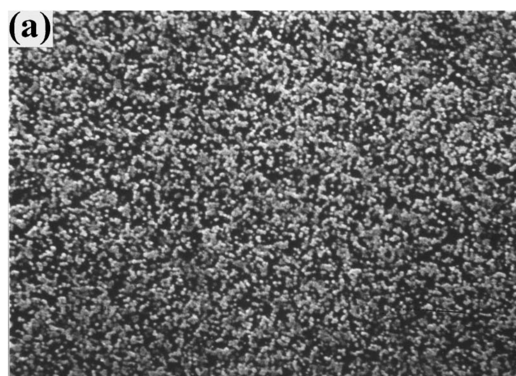


FIG. 4. Schematic diagram of the configuration for experiment 5. The two electrodes were cathodes while the filament was an anode. The substrate was electrically connected to the filament. Part of the electrons impacted onto the substrate. Also shown are the electron paths.

our SEM; they formed later than the visible ones in Fig. 5. The nucleation density is estimated to be quite uniform across the substrate surface. The film thickness is measured by SEM to be about 0.2 μm, just approximately the same as the size of the diamond grains. The film looked green after deposition. Contrary to the Zhu *et al.* report,[11] we got nucleation enhancement across the sample surface by simply biasing the substrate. The Raman spectrum of the as-grown film shows an evident diamond peak at 1333 cm^{-1} though the film is very thin. Meanwhile, the broad nondiamond peak is very weak, indicative of the high quality of the film.

As of today, the mechanism of diamond nucleation is not yet clear. Regarding the role of negative bias in MPCVD, Yugo *et al.*[4] argued that the negative bias accelerated the ions in the plasma to the substrate surface and, thus, enhanced the reactions causing diamond nucleus generation.



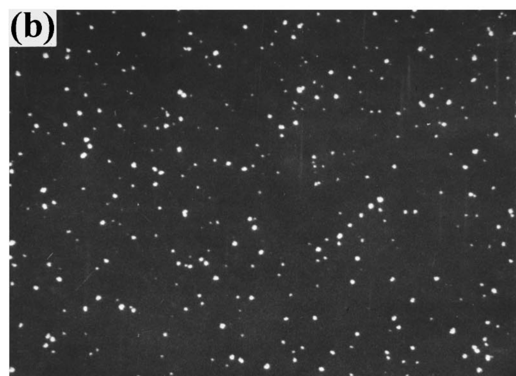
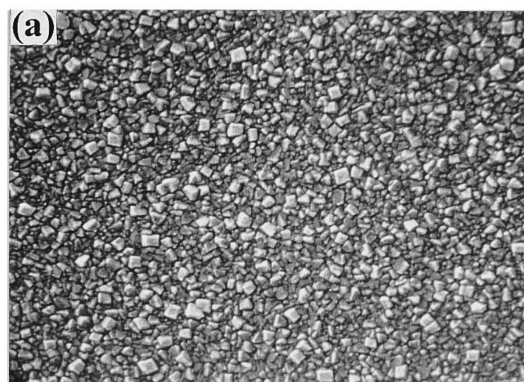


FIG. 5. SEM images of the sample surface from (a) the outer to (b) the inner area after 8 min negative bias nucleation. CH_4 concentration 2.0%; substrate temperature 850 °C; filament temperature 2000 °C; and bias voltage −220 V.



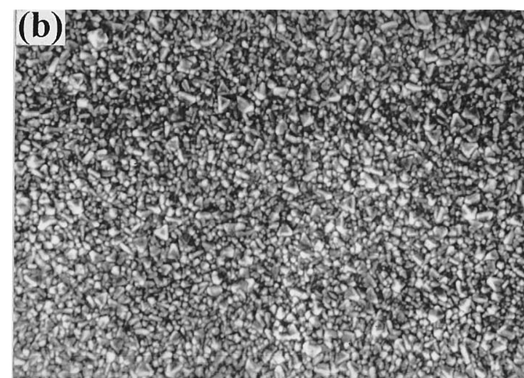


FIG. 6. SEM pictures of (a) the outer area and (b) the inner area of the as-grown diamond film after 20 min deposition. CH_4 concentration 1.2%; substrate temperature 800 °C; and filament temperature 2000 °C.

Jiang *et al.*[17] claimed that the bias-enhanced ion bombardment improved the adatom diffusion and was responsible for the diamond nucleation. Recently, there appeared some new reports supporting this point of view.[18,19] Compared with MPCVD, however, there exists a much smaller amount of ions in HFCVD.[13,14] Yet high density nucleation could be achieved within as short as 8 min in our experiments. So we can rule out the role of ions to a large extent. Katoh *et al.*'s success in positive nucleation using MPCVD[15] also supports this conclusion.

Stoner *et al.*[5] put forward some possible nucleation mechanisms at first. Shortly after that, they suggested the possibility that the enhanced nucleation results from an increased concentration of dissociated hydrogen and/or hydrocarbon radicals near the surface, caused by electron emission from the diamond on the Mo substrate holder.[16] In their recent work (Zhu *et al.*[11]), however, they again adopted the ion bombardment mechanism to interpret their experimental results in HFCVD.

There is little ionization in HFCVD, as early stated by Angus and Hayman.[13] However, there are still some other researchers who argued for the ion bombardment during the negative bias nucleation in HFCVD.[18,19] It seems they all took the supposition that there exists a large amount of positive ions in HFCVD. But where do the ions come from? Now we take a simple calculation on how a large amount of positive ions exists in a typical HFCVD system. Recently, Cherry and Whitmore[14] reported their work in the ionic contribution in HFCVD. The maximum bias current observed was less than 10 nA, three orders smaller than that in MPCVD (of the order of 10 mA) without the aid of electron emission from the diamond coating.[16] They regarded it as ion flux. However, under typical parameters (growth rate 1 μm/h, CH_4 concentration: 2 vol %, flow rate 100 sccm, and substrate area 1 cm^2), simple calculation demonstrates that, of the species that contribute to diamond growth, at most a small portion of 1×10^{-5} can be ionic, and that only a portion of 1×10^{-3} out of all the hydrocarbon species contribute to growth. Thus, of all kinds of species, at most a small portion of 1×10^{-10} can be ionic. How could such a small proportion play an important role in either nucleation or growth? In addition, the current is more likely to come from the electrons given off by the hot filament. Therefore, we firmly believe that there is a very small amount of positive ions in a typical HFCVD system, and that the ions play a negligible role in diamond nucleation in HFCVD.

Zhu *et al.*[11] argued that the positive ions were generated by the hot filament and, thus, resulted in the nucleation enhancement in their experiments. However, the filament does not seem to have a considerable ability to generate positive ions. Instead, it has a strong ability to emit thermal electrons. Our further observations revealed that the electron emission (indicated by the blue color mentioned above) could still last rather long (say, 1 min, depending on the substrate temperature, etc.) even though the filament had been suddenly switched off and, thus, had lost its asserted ability to generate ions. On the other hand, if it is positive ions that had caused the blue color, then the location of the color should have been close to the filament instead of the Mo supporter. But in fact, it was just above the diamond coating on the Mo supporter. This is inconsistent with the positive ion bombardment interpretation.

Bearing in mind the existence of the threshold of the bias voltage, we arranged that part of the sample was nucleated and covered by a continuous film, over which there was no blue color. Then we switched the bias off and on. Now a blue color zone occurred directly over the film. Therefore, it is clearly electrons, not ions, that caused that blue color.

In MPCVD, things seem a little different. However, Stoner *et al.*[16] reported that they did not get nucleation enhancement using the same bias voltage but with a very small electron emission current in contrast with the enhancement with a large emission current. Compared with the large amount of ions already existing in the MPCVD system, the collision of the electrons with the gaseous species does not contribute much to the total ion amount and, hence, it is implausible that the ions play an important role in the enhancement of nucleation.

As for the substrate temperature increase during nucleation (see Stoner *et al.*[5]), we regard it as the Ohmic effect of the bias current through the Mo supporter. Our further experiments showed that a small increase of the bias voltage could result in a great increase of the emission current and, thus, a sharp increase of the substrate temperature (as high as 200 °C), while the energy of the ions changed very slightly. It is unlikely that the great increase of the substrate temperature results from the bombardment of the energetic ions.

In addition, our experimental study showed that the threshold bias voltage become lower as the substrate temperature went up. The emission intensity depended on the status of the diamond coating on the Mo supporter. This phenomenon again cannot be interpreted by ions.

Although it is not clear exactly how the electron emission enhances nucleation, our results demonstrate that, as once suggested by Stoner *et al.*,[16] it is plausible that the electron emission greatly increases the concentration of atomic hydrogen and dissociated reactive hydrocarbon radicals on/near the substrate surface and, therefore, enhances the nucleation. This is likely true for the biased nucleation in both HFCVD and MPCVD.

As mentioned above, nucleation proceeds from the edge to the center of the substrate because the electron emission is kept outside the sample. The electrons cause a higher concentration of the reactive hydrocarbon radicals and atomic hydrogen. Then these species transport to the surface of the sample via both gas phase diffusion and the diffusion along the substrate surface. The latter depends radically on the substrate temperature. The higher the temperature, the higher the diffusivity and, thus, the higher the nucleation rate and density. The surface diffusion is more important in the case of higher substrate temperature and/or of a large sample. At lower temperature and for larger sample, longer time will be needed for full nucleation across the sample. For example, when the substrate temperature falls to ~750 °C, it will take 30–60 min to achieve nucleation across a sample of 10×15 mm^2.

In order to verify our conclusion, we repeated the same experiment but with the Si substrate electrically isolated by

inserting a thin ceramic wafer between the Si and the underlying Mo electrode (i.e., experiment 2). As a result, the intermediate ceramic wafer did not make a considerable difference; we got the same thing as in experiment 1. This result does not agree with the McGinnis *et al.* report.[18] In our opinion, if a much smaller Si wafer is put on the center of a larger one, it will be difficult for the reactive hydrocarbon radicals, most of which are initially generated outside the larger wafer, to step up onto the surface of the smaller one by surface diffusion. Meanwhile, gas phase diffusion will not be so effective due to the large size of the underlying sample. Hence, only poor nucleation can be obtained on the smaller one, whether it is electrically isolated or not. On the other hand, if the ion bombardment mechanism were true, then as mentioned by Mao *et al.*,[20] a severe limitation of the bias nucleation method would be that it is unable to cope with the nucleation on insulating substrates, or generally, the electrically isolated substrates. Our experiments undoubtedly deny this supposition. We also successfully got a high nucleation density ($\sim 10^9$ cm^{-2}) on thermally oxidized mirror-polished Si using the configuration of experiment 1. This again supports the electron emission mechanism.

Configuration shown in Fig. 2 was designed to further verify the electron emission mechanism. If, as proposed by Zhu *et al.*,[11] positive ions were generated near the filament, then the W anode, which has the same voltage as the filament but has no ability to generate ions, would exert a strong impulsive force on the ion flux. And then the expansion rate of the nucleation from side B to side A in Fig. 2 would decrease greatly. A group of experiments (experiment 3) were done using this configuration. On the contrary, the nucleation expanded from B to A much more rapidly. Uniform high density nucleation was obtained on both the Si sample and the ceramic (or Si) wafer on side A within 15–20 min, which could have taken one hour to achieve nucleation on such a large area under the same parameters using configuration in Fig. 1. The typical density for this type of experiments is $\sim 10^9$ cm^{-2}. This can be explained by the change of the electron path induced by the presence of the W anode (Fig. 2). Part of the electrons flowed directly through the above of the sample, generated a large amount of reactive species over it, and, thus, greatly reduced the effort for the species to diffuse from outside onto the sample. This effect was more salient at a relatively lower substrate temperature as the surface diffusivity was much lower. Actually, if the filament power was suddenly switched off during the nucleation, purple color could be seen both around the W electrode, the filament, and above the diamond coating on side B. This again demonstrates that the color is caused by electrons as opposed to ions. The electron emission mechanism is firmly grounded.

B. Experiments without a bias to the substrate

As further examination, we should be able to get similar high nucleation density with only electron emission but without a bias to the substrate. If we can, then our mechanism is justified. This is the motivation of experiment 4 (Fig. 3). Furthermore, in contrast with ion bombardment we introduced partly electron bombardment, onto the substrate in experiment 5 (Fig. 4) by setting the substrate to the same voltage as the filament. Using these two configurations, we got nucleation enhancement similar to those in the biased cases. The nucleation area expanded from near the cathode(s) to near the anode (Fig. 3) or to the middle of the sample (Fig. 4). We did not observe a considerable difference between the nucleation densities for these configurations; the electron bombardment in experiment 5 did not bring about a big change. Unfortunately, because of the presence of the W electrodes between the filament and the substrate, the filament–substrate distance could not be as small as we wanted and, thus, we could not get a very high substrate temperature for these configurations. In addition, the magnitude of the emission current was limited by the small diameter of the W electrodes. Due to the much lower substrate temperature and a relatively lower emission current, the typical nucleation density was $\sim 10^8$ cm^{-2}, less than that in Fig. 5. In order to make the experimental results comparable, experiments were conducted using configuration 1 while the substrate temperature and the emission current were similar to those in experiments 4 and 5. The resultant density was $\sim 10^8$ cm^{-2}, in good agreement with experiments 4 and 5. This explains the difference in density between experiment 1 and experiment 4 (or 5). Therefore, the results of experiments 4 and 5 present direct evidence for the electron-emission-enhancement nucleation mechanism. In addition to the Si substrate, we also tried highly oriented pyrolytic graphite substrate with these configurations, and got a nucleation density of $>10^8$ cm^{-2}, which was much higher than that obtained using a usual HFCVD configuration without electron emission enhancement ($\sim 10^5$ cm^{-2}).

Our experiments are very simple and easy to repeat. However, how exactly the electron emission enhances nucleation and what are the main factors remain unclear, though it is speculated that it increases the concentration of atomic hydrogen and reactive hydrocarbon radicals through collision with the gaseous molecules and species. For this purpose, strongly urged are careful measurements with a mass spectrometry of the change in the concentration of atomic hydrogen and various hydrocarbon species with the intensity and energy of the electrons.

IV. CONCLUSION

In summary, the mechanism of the negative bias enhanced diamond nucleation has been studied by a set of experiments. High density nucleation (10^8–10^{10} cm^{-2}) has been achieved on mirror-polished Si wafers either by applying a negative dc bias to the substrate or by only presenting an electron emission. Our results show clearly strong evidence against the positive ion bombardment interpretation. As a conclusion, we believe that it is the electron emission, which is speculated to increase the concentration of atomic hydrogen and reactive hydrocarbon radicals through collision with the gas, as opposed to the ion impact of the substrate surface, that enhances the nucleation in the case of negative bias nucleation in HFCVD and likely in MPCVD as well.

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