Influences of Melamine Flow Rate on the Growth Behavior of Nanocrystalline Diamond Films by Direct Current Plasma Chemical Vapor Deposition Method

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Abstract: In CH₄/H₂ atmosphere, Nitrogen-doped nanocrystalline diamond films were prepared by direct current hot-cathode plasma chemical vapor deposition (PCVD) method on the conditions of different flow rate of Melamine. While the flow rate of Melamine is 2sccm, the grain refining effect on the diamond films is obvious and the nanocrystalline grains protrude from the basis of the film which shape rough surfaces. The films are incompact, due to its large gaps and holes as well as defects, however the conductivity of these films are increased. The increasing flow rate of Melamine promotes the growth of (111) oriented.

1. Introduction
The thermal, optical, electrical and other important properties of diamond are related to its small amount of impurities. Nitrogen is a representative impurity in natural diamond and synthetic diamond. As diamond film is a polycrystalline material, there are a large number of non-diamond phases, grain boundaries and various defects, and C-N bond is easily formed at the grain boundaries, which provides an effective way to solve the problem of diamond n-type doping. Therefore, it is of great significance to study the influence of nitrogen doping on the growth characteristics of diamond films. In recent years, researchers have begun to try to add (NH₂)₂CO, N₂, NH₃ and other nitrogen-containing auxiliary components to traditional growth gas sources. Diamond film was prepared by changing technological parameters to study the existence form of nitrogen in diamond film and the influence of nitrogen on its structure and performance[1-5].

For example, Li Mingji from Jilin university studied the nitrogen impurities in nitrogen-doped diamond film [6]. Locher and Tang et al. found that a small amount of nitrogen had an effect on the <110> crystal surface of diamond film formed stably [7]. Chemov et al. reported that the high-current emission current density of nitrogen-doped diamond thin film cathode with nitrogen as the doping source was as high as 220A·cm⁻². Okano used (NH₂)₂CO as the nitrogen doped source to prepare nanodiamond film with high doping concentration and good field emission performance up to 10²⁰/cm³[8]. However, there are few studies on the preparation of diamond films by DC-PCVD method with nitrogen impurities, and the traditional N₂ and NH₃ doping sources are mainly used.
Melamine (C₃H₆N₆) contains 6 C - N key, 3 C = N, 6 N - H keys, considering its special molecular structure, this paper, by using DC-PCVD deposition equipment, CH₄ / H₂ as the reaction gas source, and ventilation with different flow of C₃H₆N₆ for diamond film preparation, studies the influence of nitrogen on diamond film surface on diamond film surface morphology, phase composition, crystal quality and the influence of resistivity, with expect to expand the types of nitrogen source of nitrogen doped diamond film and obtain better conductivity nitrogen doping nanodiamond film.

2. Experiment

The diamond film was deposited by DC-PCVD equipment, with the thickness of 0.5mm and the size of 10mm ×10mm mirror polished p-type Si (111) substrate as the substrate. To enhance the initial nucleation, the pretreatment method are as follows: firstly, manual grinding of 0.5 μm of diamond powder, secondly ultrasonic vibration of the mixture of 5μm of diamond powder and anhydrous ethanol to complete the surface scratches pretreatment. finally ultrasonic cleaning with anhydrous ethanol to remove the surface residues and backup after blower blow dry.

In the experiment, C₃H₆N₆ was brought into the reaction room by the following method: the H₂ gas path was divided into two branches, one of which directly entered the reaction room, and another one was shown in figure 1. The saturated methanol (CH₃OH) solution of C₃H₆N₆ was put into the liquid storage tank, and the CH₃OH vapor containing C₃H₆N₆ was brought into the reaction chamber with H₂ by means of slow bubbling of H₂. In the experiment, the flow rate of H₂ flowing through CH₃OH was regarded as the flow rate of C₃H₆N₆ entering the reaction chamber.

The substrate temperature monitored by infrared thermometer during the experiments is 950°C, the pressure in the reaction chamber is 13 KPa, CH₄ / H₂ flow rate is 6 sccm / 200sccm, by changing the added to the flow of C₃H₆N₆ diamond film was successfully prepared. The flow rate of C₃H₆N₆ corresponding to sample a, b, c and d was 0sccm, 1sccm, 2sccm and 4sccm respectively, and the deposition time was 6h.

The surface morphology, crystal state and grain size of diamond film samples were observed by SEM; Laser Raman spectrometer was used to analyze the bonding state of carbon atoms and evaluate the crystal quality and phase purity of diamond film. The wavelength of Ar⁺ laser light source is 512.4 nm. Using X ray diffraction crystal structure of samples was analysed under 40 KV voltage, electric current 20 mA, scanning speed 4° / min, 0.02° step length; Hall test system was used to test the electrical properties of the samples.

3. Results and discussion

3.1. SEM analysis of diamond film

Figure 2 shows SEM images of samples (a), (b), (c) and (d), which are respectively high magnification images of C₃H₆N₆ flow at 0sccm, 1sccm, 2sccm and 4sccm (magnification rates are 80K), (e) and (f) are respectively low magnification images of C₃H₆N₆ flow at 2sccm and 4sccm (magnification rates are 10K). It can be seen from the high-magnification image that, with the increase of flow rate of
C$_3$H$_6$N$_6$, the surface morphology, crystallization state and grain size of diamond thin film samples all changed significantly. When the flow rate of C$_3$H$_6$N$_6$ was 1sccm, a large number of etching marks appeared on the grain surface, and the grain surface was not smooth and incomplete. When the flow rate of C$_3$H$_6$N$_6$ was 2sccm, the diamond changed from micr on-crystal to nanocrystalline, and the grain was obviously refined. The size was about 50nm, and the fine grain was prominent on the surface of the film, making the surface very uneven and roughness large. In addition, there are a large number of large gaps and voids in the film, which makes the density of the film very poor. According to the view put forward by C. Chang et al. CN as a growth accelerator for diamond, CN can extract hydrogen atoms adsorbed on the surface of diamond, thus creating more growth vacancies, inhibiting the growth of diamond grains and promoting their refinement. At the same time, a large amount of amorphous carbon phase and graphite phase were formed during the growth process, and were etched away by oxygen in CH$_3$OH, leaving a large number of etching marks, which led to obvious protrusion of grains. When the flow rate of C$_3$H$_6$N$_6$ increased to 4sccm, nanocrystals changed to micron crystals, but the crystallization quality was poor.

![Figure 2](image)

Figure 2. SEM micro graph of diamond films: C$_3$H$_6$N$_6$ flow: (a) 0scm; (b) 1sccm; (c) 2 sccm; (d)4sccm; (e) 2sccm; (f)4sccm.

As can be seen from the SEM images (e) and (f) with low magnification rate, the samples prepared when the flow rate of C$_3$H$_6$N$_6$ was 2sccm generally showed spherical "cauliflower" growth, with uneven size and large gap. Each "cauliflower" is formed by the agglomeration of a large number of diamond microcrystals. The doping amount of C$_3$H$_6$N$_6$ was 4sccm, and the surface was relatively smooth. "cauliflower" growth was occasionally observed locally, protruding on the membrane surface. The formation of cauliflower is due to the fact that hydrogen atoms detach from the surface of diamond crystal nucleus and leave carbon suspension bonds, which cannot be saturated by other hydrogen atoms in time, and the carbon suspension bonds bond with each other to form graphite phase with sp$^2$ structure. The existence of graphite phase will affect the formation of new diamond crystal nucleus, so that the growth of diamond is mostly concentrated on the nucleated grains. The formation of sp$^3$ structure on diamond surface is limited, and the growth process of crystal changes, resulting in the formation of "cauliflower" diamond with poor crystal shape. It is the growth of "cauliflower" that makes a large number of gaps in the membrane.

3.2. Raman analysis of diamond film

Figure 3 shows the Raman test result of the sample. It can be seen from the figure that the diamond characteristic peak is at 1332cm$^{-1}$, weak amorphous graphite-peak (D peak) is at 1355cm$^{-1}$ and single
crystal graphite peak (G peak). The half-height and width of the first-order Raman characteristic peak at diamond 1332 cm\(^{-1}\) can reflect the crystallization quality of diamond film [9]. An important basis for evaluating the quality and purity of diamond film is the ratio of peak strength of single-crystal graphite to peak strength of diamond [10]. After adding C\(_3\)H\(_6\)N\(_6\) of 2sccm, the characteristic peak of diamond at 1332cm\(^{-1}\) was significantly widened and decreased, indicating that grain refinement, increase of non-diamond carbon phase in the film and decrease of film quality was resulted from proper nitrogen incorporation. This is due to the presence of large amounts of C\(_3\)H\(_6\)N\(_6\) CN key, CN can extract the growth of diamond surface adsorption of hydrogen atoms to create more space, restrain the growth of the diamond grains, promoted the grain refinement, and too many CN bonds lead to surface hydrogen is extracted in great quantities, a lot of CN groups on the surface produced more suspension bond, in the absence of adequate methyl by adsorption, make diamond hanging bond refactoring and formation on the surface of graphite structure, affect the quality of the film [11]. When the flow rate of C\(_3\)H\(_6\)N\(_6\) increased to 4sccm, the diamond characteristic peak at 1332cm\(^{-1}\) was enhanced and the half-height and width were decreased, indicating that the quality of diamond film was improved. This is because the nitrogen is mixed by CH\(_3\)OH vapor carried into the reaction chamber, CH\(_3\)OH in plasma separating oxygen or various oxygen containing groups on sp\(^3\) bond has a strong inhibition and etching effect, making the secondary nucleation of diamond reduced, thereby reducing non-diamond phase content in the film, improving the quality of the crystal, this is consistent with the scanning electron microscope observation.

**Figure 3.** Raman spectroscopy of diamond films.

**Figure 4.** XRD patterns of diamond films.
3.3. XRD analysis of diamond film

Figure 4 shows the XRD pattern of diamond film samples. You can see, there is sharp at 43.9 ° and 75.2 ° diamond (111), (110) crystal plane diffraction peak, 91.6 in weak diamond (311) crystal plane diffraction peak. With the increase of the flow rate of C_3H_6N_6, the diffraction peak intensity of (111) crystal surface decreased slightly, and the diffraction peak intensity of (110) crystal surface increased slightly. Table 1 shows the relationship between the relative strength ratio \( \frac{I_{(110)}}{I_{(111)}} \) of (110) crystal surface and (111) crystal surface with the flow rate of C_3H_6N_6. As can be seen from the table, the introduction of C_3H_6N_6 increases the ratio of \( \frac{I_{(110)}}{I_{(111)}} \), indicating that the introduction of C_3H_6N_6 promotes the growth of (110) surface. This is because the addition of a small amount of nitrogen impurities in the gas source will make the diamond film surface more show the (110) crystal surface [4].

| Nitrogen flow (sccm) | \( \frac{I_{(110)}}{I_{(111)}} \) |
|---------------------|-----------------|
| 0                   | 0.247           |
| 1                   | 0.361           |
| 2                   | 0.583           |
| 4                   | 0.541           |

3.4. Resistivity analysis

By Hall testing it was found that when C_3H_6N_6 flow is 2 sccm, diamond film resistivity by doping is decreased from 4.7 \( \Omega \cdot \text{cm} \) undoped to 9.3 \( \times \) 10^{-2} \( \Omega \cdot \text{cm} \), carrier concentration increased from 2.158 \( 4 \times 10^{17} \) cm^{-3} to 9.740 \( 8 \times 10^{18} \) cm^{-3}, with the result of conductive ability enhancement, carrier concentration increased. According to the analysis of SEM and Raman above, the improvement of conductivity is that on the one hand, a small amount of nitrogen incorporation promotes the refinement of grain and the increase of the proportion of grain boundary. However, there are many sp^2C-C bonds in grain boundary, and the impurities of grain boundary with conductive properties are connected to each other to form a conductive channel, which improves the conductivity. On the other hand, it may be due to the stable C-N in C_3H_6N_6, which is not easy to decompose under the action of plasma. As a carbon source, CN group also participates in the growth process of diamond film as a nitrogen source, forming a shallow donor level and improving the conductivity of the sample. When the flow rate of C_3H_6N_6 continues to increase, the resistivity increases due to the grain coarsening and the improvement of crystallization quality.

4. Conclusions

Diamond film was prepared with DC hot cathode PCVD equipment under CH_4/H_2 atmosphere at different flow rates of C_3H_6N_6. The conclusions are as follows:

(1) with the increase of flow rate of C_3H_6N_6, diamond film grains are firstly refined and then coarsened.

(2) due to the existence of a large number of CN bonds in C_3H_6N_6, hydrogen atoms adsorbed on the surface of diamond can be extracted to create more growth vacancies, which can inhibit the growth of diamond particles and lead to grain refinement. Therefore, nano-diamond film can be prepared by doping C_3H_6N_6 appropriately (with a flow rate of 2sccm).

(3) the refinement of grain and the shallow donor energy level formed by CN group can improve the conductivity of the sample.

(4) the introduction of C_3H_6N_6 promoted the growth of diamond film (110) crystal surface.
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