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Unusual dependence of diamond growth rate on methane concentration in hot filament chemical vapor deposition

HFCVD에서 메탄 농도 및 필라멘트 온도에 따른 다이아몬드 박막 성장속도의 이상 변화

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Abstract

Unusual dependence of diamond growth rate on methane concentration in hot filament chemical vapor deposition

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Diamond synthesized utilizing chemical vapor deposition process has long been studied, in order to exploit superior thermal, mechanical, and optical properties of diamond. Thorough understanding of growth mechanism of CVD diamond is therefore an important task to enhance deposition speed of diamond and to develop new applications of CVD diamond. Considering thermodynamic paradox encountered when explaining the formation of CVD diamond in atomic growth, theory of charged nanoparticles suggested that
diamond nanoparticles are generated in the gas phase and become building blocks for diamond film.

In chapter 1, an odd phenomenon occurring in CVD diamond deposition process is introduced, which cannot be explained with conventional understanding on chemical vapor deposition. In hot filament chemical vapor deposition, growth rate of diamond film is proportional to the amount of methane injected. However, when the temperature of the filament is low, the growth rate is inversely proportional to methane concentration. To investigate this behavior, nanoparticles existing in the gas phase were directly captured with TEM grid, in order to see if there is any change when the filament temperature is lowered, since they become building blocks for diamond film. Furthermore, surface condition of the filament and its emission of electricity was investigated to understand environmental factors of the formation of charged nanoparticles. As methane concentration increases and filament temperature decreases, the filament gets poor in charging clusters nearby, and therefore the growth rate of diamond plummets.

In chapter 2, typical CVD diamond deposited utilizing hot filament chemical vapor deposition is analyzed with transmission
electron microscope. Significant difference in crystal structure appeared between inner and outer part of deposited diamond. Diffraction pattern of injected electron beam through whole bulk and TEM image obtained at the edge of the bulk have shown different crystallographic information. Diamond deposited in CVD system was confirmed to have lonsdaleite structure on the outer surface.

________________________________________________________

keywords : theory of charged nanoparticles; nanodiamonds; diamond deposition; HFCVD; electron emission; lonsdaleite

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Chapter I. Unusual dependence of diamond growth rate on methane concentration in hot filament chemical vapor deposition

I.1 Introduction

Diamond synthesized by chemical vapor deposition has been studied by a number of scholars in 20\textsuperscript{th} century. Synthesizing diamond utilizing chemical vapor deposition (CVD) process has huge advantages since diamond is generated in much lower pressure and temperature compared to conventional method: high pressure-high temperature diamond growth process. Carbon phase diagram shows that processing condition of CVD diamond is positioned deeply inside stable region of graphite phase [1], leading many scholars to wonder how CVD diamond is formed.

It is widely believed that crystal growth in chemical vapor deposition process occurs in atomic scale, saying that atoms sit on the most energetically unstable site of the crystal to lower total energy of
the system. This is called the terrace-ledge-kink (TLK) model [2-4]. However, it is well known fact that in synthesis of CVD diamond, when graphite substrate is used, graphite etching occurs while diamond is deposited on it. Normally, graphite is more stable than diamond, making simultaneous etching of graphite and deposition of diamond impossible. In short, it is thermodynamic paradox. A successful theorem should clearly explain how does this phenomenon take place.

Hwang et al. suggested different theorem upon deposition behavior of CVD diamond, named the theory of charged nanoparticles (TCN), which basically states that diamond nucleation occurs in different place [5-8]. To be specific, in hot filament chemical vapor deposition (HFCVD), formation of nanodiamonds occurs in the gas phase near the filament, and these nanodiamonds become building blocks for diamond film on substrate. Though this model contains few unrevealed assumptions, it does not encounter thermodynamic paradox stated above in explaining the deposition of CVD diamond. We believe that nanodiamonds are generated near the hot filament by nucleation of carbon atoms decomposed from injected methane gas, and stabilized by being negatively charged with electrons emitted from the hot filament. It has been reported that excess charge in diamond cluster stabilizes
diamond phase by lowering its Gibbs free energy of formation compared to that of graphite phase [9].

Therefore, our group has long been studying the existence of nanodiamonds in the gas phase in HFCVD system, and their relationship to the formation of CVD diamond. Jin-Woo Park reported that existence of nanodiamonds in the gas phase has been confirmed, and that those particles are negatively charged [10]. However, still remaining problem is revealing relationship between the nanodiamonds and the formation of CVD diamond.

In general, CVD process consists of introducing precursor into vacuum chamber, decomposing the precursor using heat or plasma to obtain ionized atoms of interest, and finally depositing the atoms on substrate material as thin film. In the theory charged nanoparticles, one step is added: decomposed atoms forms nanoclusters in the gas phase, and these nanoclusters are deposited on substrate. In either cases, growth rate of film on substrate is proportional to the amount of precursor introduced. In case of our experiments on depositing diamond utilizing HFCVD system, it has been reported by Jin-Woo Park, that as methane concentration in the system increases from 1% to
3%, growth rate of diamond film increased correspondingly [11], as shown in Fig. 1-1.

However, odd phenomenon was observed when temperature of the filament was lowered. When the filament temperature was lower than usual case (2000°C), dependence of diamond growth rate on methane concentration was inversed. That is, the growth rate of diamond in 1% methane concentration was higher than that in 3% methane concentration [11], as shown in Fig. 1-2. It can also be interpreted as, diamond growth rate has drastically decreased only in 3% methane concentration as the filament temperature went down. Believing that understanding this phenomenon would provide an important key in revealing the secret of CVD diamond, we investigated this experimental result further. Based on the theory of charged nanoparticles, we have built a plausible hypothesis that matches with theoretical and experimental results.
Fig. I-1 Field Emission Scanning Electron Microscopy (FESEM) images of diamond microparticles deposited on silicon substrate for 8 hours when filament temperature was 2100°C. Methane concentration of (a) and (c) is 3%, and that of (b) and (d) is 1%. (a) and (b) are low magnification images and (b) and (d) are high magnification images. Reprinted with permission from [11]. Copyright 2016 Seoul National University.
Fig. 1-2 (a) and (b) are low magnification images, and (c) and (d) are high magnification images of diamond microparticles deposited for 4 hours on silicon substrate when filament temperature was below 2000°C, in methane concentration of 1% for (a) and (c), and 3% for (b) and (d). Reprinted with permission from [11]. Copyright 2016 Seoul National University.
I.2 Experimental Procedure

I.2.1 Diamond film deposition

Though diamond deposition is not a main subject of this article, the experimental procedure of depositing diamond with the hot filament CVD system will be explained to help readers understand our experiments.

The hot filament CVD reactor is shown schematically in Fig. 1-3. The filament consists of three tungsten wires of 0.5mm diameter, twisted together to a 9-turn coil of 8-mm diameter. Small piece of silicon wafer (0.5cm x 0.5cm) is put closely under the filament to raise its temperature during the deposition process. Chamber is sealed, evacuated to its base pressure (10⁻³torr), and maintained at this condition for a few minutes. Next, we gently increase DC current flow through the filament, to raise its temperature to around 2100°C. Distance between the hot filament and the silicon substrate is 5-7mm, so its temperature increases as the filament temperature increases, up to around 950°C. Methane gas mixed with hydrogen gas is introduced through showerhead above the hot filament. At the same time, vacuuming power is lowered to achieve working pressure (20torr).
inside the chamber. When the temperature of the filament, temperature of the substrate, and the pressure is all set, we measure time as deposition time.

As methane molecules pass through the hot filament, it decomposes into carbon atoms and various carbon-hydrogen compounds, and some of them gathers to nucleate into carbon clusters. These carbon clusters are stabilized in diamond phase, thanks to electrons emitted from the hot filament. As mentioned above, excess charge in carbon clusters makes diamond phase more preferable [9]. These charged nanodiamonds are deposited on silicon substrate and form diamond film.

Experimental variables and how to manage them are as follows. The filament temperature is measured by 2-color pyrometer, and is adjusted by controlling DC current supplier. The temperature of the substrate is obtained by thermocouple installed next to the substrate, and is modified by changing the distance between the substrate and the filament. Methane concentration of the system is controlled by changing ratio of the amount of flow between hydrogen gas and methane gas, with mass flow controller (MFC). For example, 3% methane concentration means 3sccm (standard cubic centimeter per
minute) of methane gas was injected along with 97sccm of hydrogen gas. Total pressure of the system during deposition was always at 20torr, and total flow of hydrogen and methane gas mixture was also maintained at 100sccm.
Fig. I-3 Schematic image of HFCVD chamber for diamond deposition. Filament is connected to copper electrodes, and DC current flows through the filament to raise its temperature up to 2300°C.
I.2.2 Capturing nanodiamonds

In order to investigate why the dependence of diamond growth rate on methane concentration was inverted as filament temperature was lowered below 2000°C, various approach had been made. Based on the theory of charged nanoparticles, we hypothesized that huge difference in nanodiamonds existing in the gas phase would be observed. As mentioned in the introduction, existence of nanodiamonds and their property of being negatively charged have been reported by Jin-Woo Park [10]. Since these nanodiamonds become building blocks of diamond film, we assumed that drastic decrease of diamond growth rate upon decreasing filament temperature in 3% methane concentration may have been resulted from huge difference or degradation of nanodiamonds in the gas phase. Therefore, experiments on directly capturing these nanodiamonds have been conducted for each processing conditions, for filament temperatures below 2000°C and above °C, and for methane concentration of 1% and 3%.

In order to capture nanodiamonds during the actual diamond deposition process, we installed capturing apparatus on side wall of the chamber, as shown in Fig. 1-4. This is the same capturing apparatus
Jin-Woo Park used for capturing nanodiamonds [10]. TEM gird (a sample holder used for transmission electron microscope) is placed on small hole of quartz plate so that membrane of the TEM grid is not attached to the quartz plate. TEM grid is initially pulled back into small room extended from the chamber wall. After setting all processing conditions for diamond deposition, TEM grid is pushed into the deposition zone, right below the hot filament. Ambient temperature at capturing zone was around 550°C. Reason we did not captured nanodiamonds at position where ambient temperature is 900°C, which is the same as temperature of silicon substrate in actual diamond deposition process, is that TEM grid cannot withstand high temperature. It can survive at 600°C for only 10-15 seconds, and longer exposure or higher temperature burns out the membrane of TEM grid. After capturing nanoparticles with TEM grid, it has been analyzed with TEM (Tecnai F20 and JEM-2100F).
**Fig. I-4** Schematic image of HFCVD chamber installed with capturing apparatus. Capturing apparatus consists of stainless iron body with quartz plate at the tip of it, for holding TEM grid at high temperature.
I.2.3 Current measurement and filament surface investigation

It is important to know how much carbon clusters near the hot filament are negatively charged, since the excess charge in the carbon clusters affects whether they remain as diamond or transform into graphite. For this, thermionic emission current from the filament was measured. Using the capturing apparatus, an in-situ measurement of current while deposition process was possible. An iron plate with size of 1.25 x 1.15cm$^2$ was used as probe, and it was welded to tungsten wire with 0.5mm diameter. The wire was in contact with feedthrough installed at the bottom of the chamber, and finally connected to picoammeter (Keithley 6487). Probe was movable as capturing apparatus, enabling the probe to avoid unwanted exposure to the hot filament. Thermionic emission current was measured at the same position as the capturing experiments, since too high temperature can cause phase transformation of the iron probe or generation of large thermoelectricity inside the probe. Also, tungsten wire can change its phase by absorbing carbon and thus change its electric resistance during the measurement if ambient temperature is too high.
In addition, surface morphology of the filament used for the experiments was observed with optical microscope. On the surface of the filaments used in high methane concentration, precipitates could be observed with naked eyes. Since they can affect the charging ability of the filament, the amount of precipitates and their chemical composition were investigated with optical microscope (ZEISS Axio Lab.A1) and energy-dispersive X-ray spectroscopy (EDS) installed in FESEM (ZEISS Merlin compact), respectively.

I.3 Result

I.3.1 Capturing nanodiamonds

Fig. 1-5 and Fig.1-6 are TEM images of captured nanoparticles when the filament temperature was 1900°C and 2000°C, respectively. Results could be obtained only at 3% methane concentration, because at 1% methane concentration, TEM grid was burnt out so fast that capturing nanoparticles with TEM grid was impossible. Moreover, even when the membrane remained, particles were not observed, possibly because of their extremely small size (~1nm).
However, significant difference was observed between nanoparticles captured when the filament temperature was 2000°C and those when the filament temperature was 1900°C, as expected. Firstly, nanoparticles captured when the filament temperature was 2000°C were single crystalline nanoparticles with size 3-5nm. Measuring lattice parameters of each particle, we found that these particles had d-spacing values of 2.1Å, 2.2Å or 2.5Å. Since (111) plane of diamond structure has 2.07Å, 2.1Å can be estimated to (111) plane of diamond. 2.2Å may indicate (100) plane of lonsdaleite, also called as hexagonal diamond. Lonsdaleite is an allotrope of carbon, which has diamond structure as main matrix but occasional structural defect of hexagonal sequences [12]. Lastly, 2.5Å value has not been clearly determined. However, considering that only carbon atoms and carbon molecules exist in the gas phase, we assumed that these nanoparticles are another allotrope of carbon, named ‘non-diamond carbon’ particles. The percentage of appearance of each d-spacing values were 18%, 41%, 41% for 2.1Å, 2.2Å and 2.5Å, respectively.

On the other hand, nanoparticles captured when the filament temperature was 1900°C show completely different morphology as shown in Fig. 1-6. It has been observed that these nanoparticles were
polycrystalline, with size up to 12nm, which is far bigger than nanoparticles captured when the filament temperature was 2000°C. Since these nanoparticles become building blocks for diamond film deposition, we believe that this difference has contributed to severe decrease in growth rate of diamond in 3% methane concentration, when the filament temperature was lowered from 2000°C to 1900°C. Measurement of lattice parameters of these polycrystalline nanoparticles has shown that they also contain values of 2.1Å, 2.2 Å and 2.5Å, but all of them existing simultaneously in one cluster. Moreover, their percentages of appearance were 6%, 19%, 75% for, 2.1Å, 2.2 Å, and 2.5Å, respectively. Notice that the fraction of 2.1Å, which indicates diamond nanoparticles, has severely decreased.
Fig. 1-5 Carbon nanoparticle captured when the filament temperature is 2000°C. Single crystalline nanoparticle with lattice parameter 2.1Å, which indicates (111) plane of diamond, is marked with white circle. Size of the nanoparticle is around 4nm.
Fig. I-6 Carbon nanoparticle captured when the filament temperature is 1900°C. Polycrystalline nanoparticle containing lattice parameters of both 2.1Å and 2.5Å is marked with white circle. Size of the nanoparticle is around 12nm.
I.3.2 Current measurement and filament surface investigation

Fig. 1-7 shows the result of measuring thermionic emission current at each filament temperature in each methane concentration. The result clearly shows that thermionic emission increases with increasing filament temperature and decreases with increasing methane concentration. When temperature of the filament was 1900°C, the measured currents were -0.49μA/cm² for 3% methane concentration, and -7.10μA/cm² for 1% methane concentration. In this case, thermionic emission increased by 1300% when methane concentration was reduced from 3% to 1%. When temperature of the filament was 2000°C, the measured currents were -2.55μA/cm² for 3% methane concentration, and -9.39μA/cm² for 1% methane concentration. This is an increase of 268%. Lastly, when filament temperature was 2100°C, measured currents were -5.57μA/cm² for 3% methane concentration, and -17.3μA/cm² for 1% methane concentration. This is an increase of 210%.

Large difference in the amount of thermionic emission in 1% and 3% methane concentration appeared when the filament temperature is
1900°C. Moreover, when methane concentration was maintained the same, current emission increased exponentially as the temperature of the filament increased, following the law of thermionic emission by Richardson [15].

Reason for the difference in current emission in different methane concentrations seems to be caused by difference in surface condition of the filaments. Direct comparison of surface morphology of the filaments used in methane concentration of 1% and 3% is shown in Fig. 1-8. When methane concentration is 3%, carbon precipitates are observed on the surface of the filament, whereas the surface of the filament used in 1% methane concentration is clean. Fig. 1-9 shows that these precipitates have been confirmed as carbon chunks, possibly graphite.

Thermodynamic calculation has been done to explain the difference in surface conditions of the filaments, shown in Fig. 1-10. It has been confirmed that in methane concentration of 3%, carbon in the gas phase precipitates to solid state at temperature below 2300°C, whereas in 1% methane concentration, carbon precipitates on the filament at temperature below 2050°C. Though carbon precipitates were not found on the filament used in 1% methane concentration and temperature
below 2000°C, the calculation partly explain why carbon precipitates exist only on the filament used in 3% methane concentration. It needs to be concerned that the calculation was conducted assuming perfect carbon-hydrogen system without impurities that might activity of carbon in the gas phase, and that the result is only a reflection of thermodynamic stability, which does not consider kinetic barriers.
Fig. I-7 Measurement of thermionic emission current in the filament temperature of 1900°C, 2000°C and 2100°C in methane concentration of 1% and 3%, respectively. Light gray bars are the amount of currents in 1% methane concentration, starting with one on the left in filament temperature of 1900°C to one on the right in filament temperature of 2100°C. Dark gray bars are the amount of currents in 3% methane concentration.
Fig. I-8 Optical microscope image of surface of the filaments used in methane concentration of (a) and (b) in 1% and (c) and (d) in 3%.
Fig. I-9 (a) FESEM image of carbon precipitates on surface of the filament used in 3% methane concentration. (b) EDS data obtained from point#2, which is on one of the carbon precipitates. (c) EDS data obtained from point#3, which is on clean surface of the filament without carbon precipitates.
Fig. I-10 Thermodynamic calculation of equilibrium carbon precipitation for various carbon concentrations at temperature from 1800°C to 2400°C using Thermo-calc simulation. X-axis is temperature in Celsius and Y-axis is the equilibrium carbon precipitation in mole fraction.
I.4 Discussion

Difference in the amount of excess charge available for carbon clusters in the gas phase seems to have massive effect on their morphology, and eventually the growth behavior of CVD diamond. Comparing the charge emission amount of the filament at 1900°C and 2000°C in 3% methane concentration, it has increased by 420%. It is certain that clusters in the gas phase around the filament at 1900°C were far less charged. Lack of excess charge in nanoclusters lead to formation of non-diamond carbon nanoparticles rather than nanodiamonds, and their coagulation into polycrystalline nanoparticles. Since they were poorly charged, and thus electrostatic repulsion force among nanoparticles was weak, they were observed as coagulated polycrystalline nanoparticles in TEM image. Though nanoparticles existing in the gas phase in 1% methane concentration were not observed, considering tremendous amount of thermionic emission compared to that in 3% methane concentration, lots of stable nanodiamonds would have been formed, resulting in growth of facet diamonds as shown in Fig. 1-1 and Fig. 1-2.
Moreover, difference in surface condition of the filament used in 1% methane concentration and that was used in 3% methane concentration may also have brought huge effect, other than thermionic emission, on charging nanoparticles in the gas phase. The filament used in 3% methane concentration was covered with graphite, which has higher work function value than tungsten carbide. Literature value of work functions of tungsten carbide and graphite are 3.73eV and 4.84eV, respectively [13-14]. Work function value affects not only thermionic emission of the filament but also the extent of surface ionization.

The amount of current generated by thermionic emission is given by Richardson’s law of thermionic emission [15],

\[ J = A_G T^2 e^{-\frac{W}{kT}} \]

where \( J \) is the emission current density, \( T \) is the temperature of metal in Kelvin, \( W \) is the work function of the metal, \( k \) is the Boltzmann constant, and \( A_G \) is a constant related to material-specific correction factor [16]. Certainly, graphite coating on the tungsten filament reduces its thermionic emission, by reducing exposed area of tungsten filament,
and by binding electrons with higher work function value than that of tungsten carbide.

Moreover, graphite coating on the filament impedes surface ionization of carbon molecules in the gas phase, which occurs when these molecules directly collide on surface of the hot filament. The relationship between surface ionization and work function value of the surface materials is given by Saha-Langmuir equation [17],

$$\frac{n_+}{n_0} = \frac{g_+}{g_0} e^{\frac{W-V}{kT}}$$

where $\frac{n_+}{n_0}$ is the fraction of ionized molecules, $\frac{g_+}{g_0}$ is the fraction of statistical weights of the ionic and atomic states, $W$ is the work function of the filament, $V$ is the ionization energy of the element, $k$ is the Boltzmann constant and $T$ is the temperature of surface in Kelvin. The equation has various forms, but it can be interpreted that energy barrier for transferring electron between a molecule and a material is lowered when the molecule has great ionization energy or electron affinity. Among various carbon compounds existing in the gas phase in HFCVD system, C$_2$ molecule is known for its large electron affinity: 3.6eV [18]. Comparison of C$_2$ molecules’ probability of being
negatively charged upon collision on surface of tungsten carbide and that of graphite shows that it is a thousand times more probable for C$_2$ molecules to be negatively charged upon collision with tungsten carbide. C$_2$ molecules is known as common element generated when methane is decomposed in HFCVD system. Therefore, they can largely contribute in making nanodiamonds with excess negative charge in the gas phase.

All things considered, we can conclude that nanoparticles existing in the gas phase are more negatively charged in 1% methane concentration than in 3% methane concentration, and when the filament temperature is above 2000°C than when filament temperature is below 2000°C. Moreover, as filament temperature decreases in 3% methane concentration, massive change in morphology of nanoparticles has been observed. Lack of excess charge in the carbon clusters in the gas phase lead to formation of non-diamond carbon clusters, and polycrystalline clusters as shown in Fig. 1-6.

Since the deposition condition of CVD diamond is well known to be etching environment for graphite, these non-diamond carbon clusters are likely to be etched away, too. Diamond is also under etching condition, but its solid crystal structure makes the etching process very
slow and therefore does not affect. Eventually, only diamond nanoparticles existing in the gas phase are able to contribute to the formation of CVD diamond. Other non-diamond carbon clusters are etched away before reaching the substrate and do not contribute to the growth of diamond film. That is why the growth rate of diamond film is inversely proportional to methane concentration when filament temperature is lowered. Whereas the filament temperature did not matter much in low methane concentration, high methane concentration combined with low filament temperature made it hard for carbon clusters to be charged, bringing severe drought of nanodiamonds in the gas phase.

I.5 Conclusion

We showed that charging effect of the hot filament in HFCVD system decreases as the filament temperature is lowered, and as methane concentration increases. In high methane concentration, significant difference in nanoparticles existing in the gas phase was observed when the filament temperature is lowered below 2000°C. Single crystalline nanodiamonds formed when the filament temperature
is above 2000°C could contribute in growing diamond film, whereas non-diamond carbon clusters formed when the filament temperature is below 2000°C could not. It resulted in severe decrease in growth rate of diamond as filament temperature was lowered. On the other hand, at low methane concentration, charging effect of the filament is enough to form nanodiamonds in the gas phase in both low and high filament temperature, resulting relatively mild change in growth rate of dimond film. As a result, dependence of growth rate of diamond appeared to be inversely proportional to methane concentration when the filament temperature was lowered.
Chapter II. Crystallographic investigation of diamond deposited on silicon substrate utilizing hot filament chemical vapor deposition

II.1 Introduction

Diamond synthesized utilizing chemical vapor deposition process has been used in various fields of study and industry. Crystallinity of CVD diamond have been mostly confirmed with Raman spectroscopy, and sharp peak at 1332cm\(^{-1}\) was an indicator of fine diamond. However, TEM analysis of CVD diamond showed interesting result, pointing that diamond synthesized in HFCVD process has complex structure than we thought.
II.2 Experimental procedure

Diamond microparticles were deposited on silicon substrate utilizing hot filament chemical vapor deposition. For fine crystallinity, methane concentration was set to 1%, and the deposition was done for 1 hours. Diamond deposited on silicon substrate was confirmed with scanning electron microscope, and then transferred to TEM grid. Procedure of transferring diamond is as follows. Several droplets of pure alcohol were dropped on silicon substrate deposited with microdiamonds. Next, TEM grid was rubbed on the wet surface of silicon wafer, so that microdiamonds can be mechanically detached from the silicon substrate and then attached to TEM grid as alcohol evaporates. Since diamond microparticles are thick, obtaining TEM image was available only at the edge of the microparticles. However, getting electron beam diffraction pattern of the whole bulk was still available, since exposure time can be lengthened to gather weak diffracted beam coming from relatively thick part of the microparticle.
II.3 Result and discussion

First, diffraction pattern obtained is shown in Fig. 2-1(b). Electron beam was injected into large fraction of diamond microparticle so that diffraction can occur in both the edge and the inside of microdiamond. Diffraction pattern is in agreement with patterns calculated by Carine crystallographic simulation to a certain extent. Since (111) and its family planes of diamond has lattice parameter of 2.06Å, and (220) and its family planes has lattice parameter of 1.26Å, the pattern obtained seems to match. However, two strange points exist here. First, lattice points corresponding to 1.8Å exist, though they should not appear normally. Diamond structures is a face centered cubic (FCC) structure with half of tetrahedral sites being filled with carbon atoms. According to diffraction selection rules, (200) plane, whose lattice parameter is 1.8Å in carbon FCC structure, belongs to forbidden reflection. That is, its intensity should be reduced to zero, by destructive interference with waves reflected from atoms at tetrahedral sites. Though this destructive interference can be reduced when double diffraction occurs in case of bulk crystal, (200) points on diffraction pattern appear too bright.
Fig. II-1 (a) Aperture image, showing area which electron beam was injected to. (b) Diffraction pattern obtained by electron beam injected in (a). Lattice parameters of each points are calculated.
Moreover, pale peaks appearing between bright peaks to make a long line in Fig. 2-1(b) may indicate the existence of other crystal structure, or stacking defects. Currently, we believe that it is resulted from structural defects.

We also obtained TEM image from the edge of diamond microparticles, where thickness is small so that electron beam can transmit. The TEM image is shown in Fig. 2-2(a), and fast Fourier transformation (FFT) of the image is shown in Fig. 2-2(b). FFT information has shown different pattern from that was obtained in the whole bulk. Lattice parameters and plane angles are largely different from that of normal diamond. In fact, it is in agreement with diffraction pattern of lonsdaleite, with error range less than 5%. Lonsdaleite is known to have fifty-fifty portion of diamond structure and hexagonal structure. The fact that diffraction pattern obtained from the whole bulk was in agreement with normal diamond while FFT information obtained from the edge of the bulk is in agreement with lonsdaleite means that lonsdaleite is dominant on the surface of these microdiamonds. This may indicate that the surface of diamond particle is stabilized by forming lonsdaleite structure.
Fig. II-2 (a) TEM image of the edge of diamond microparticle. (b) FFT information obtained from (a). Lattice parameters for each point are calculated.
II.4 Conclusion

It has been confirmed that seemingly facet diamond films or microdiamonds have lonsdaleite structure on their surface. Possibility is opened to variety of cases, but it may be a middle stage of forming $sp^2$ bonding on the surface of diamond. Further investigation is needed to confirm why this structure is observed.
Bibliography


국문 초록

CVD 공정을 이용해 만들어지는 CVD 다이아몬드는 우수한 물성으로 인해 여러 분야에 걸쳐 이용되고 있다. 따라서 CVD 다이아몬드의 생성 원리를 이해하는 것은 CVD 다이아몬드의 공정 방법을 혁신 시킬 수 있을 뿐 아니라 이용 가치를 창출하는 데에 있어서도 매우 중요하다. 그러나, CVD 다이아몬드의 형성을 기존의 원자 단위의 증착으로 설명하면 열역학적 모순에 부딪히게 된다. 다이아몬드의 생성과 흑연의 석각이 동시에 일어나기 때문이다. 열역학적으로 흑연이 더 안정한 물질이기 때문에, 이것은 불가능하다. 이 모순을 해결하기 위해, CVD 다이아몬드가 원자 단위로 증착되는 것이 아니라, 기상에서 생성된 다이아몬드 나노입자에 의해 증착 된다는 하전된 나노입자 이론이 제기되었다.

1장에서는 CVD 다이아몬드 공정 과정에서 발생하는 특이한 현상을 제시하고, 하전된 나노입자 이론에 입각한 가설을 세워 설명한다. 일반적으로 모든 CVD 공정에서, 박막의 증착

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속도는 주입하는 전구체의 양에 비례한다. 다이아몬드 증착의 경우 메탄 가스를 주입한다. 하지만, 현재 본 연구실에서 사용하는 핫와이어 CVD 장비에서, 유독 필라멘트의 높도가 낮을 때에 이러한 경향성이 반대가 되는 현상이 관찰되었다. 즉, 필라멘트의 온도가 평소에 사용하는 온도인 2000 도보다 낮을 때에, 메탄 농도를 증가시킬수록 다이아몬드의 증착 속도가 감소하는 현상이 관찰된 것이다. 이 현상의 원인을 알아내기 위하여, 필라멘트 온도별로 기상에 존재하는 나노입자를 포집하는 실험이 진행되었다. TEM 그리드를 이용하여 직접 필라멘트 밑에서 나노입자를 포집한 뒤, TEM 분석을 통하여 포집된 나노입자들이 필라멘트 온도가 높을 때와 낮을 때 어떻게 다를지 조사하였다. 또한, 기상의 나노입자가 얼마나 하전되고 있는지 알아보기 위하여, 필라멘트의 열전자 방출량과 필라멘트의 표면 성질을 분석하였다. 결과적으로, 메탄 농도가 높아지고 필라멘트 온도가 낮아지면, 기상에 있는 나노입자들이 잘 하전되지
않아서, 다이아몬드가 아닌 탄소화합물로 바뀌어 식각이 되어버리기 때문에 증착 속도가 느린 것으로 결론지었다. 2장에서는 전형적인 CVD 다이아몬드를 일반적인 라만 분광법이 아닌 TEM 분석을 이용하여 결정점을 확인하였다. 예상 외로, CVD 다이아몬드는 내부는 다이아몬드 결정 구조를 갖고 있으나, 표면에서는 론스달라이트 구조의 내부와는 다른 탄소의 결정 구조를 이고 있는 것으로 확인되었다.