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Effect of methane concentration on size of charged clusters in the hot filament diamond CVD process

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Abstract

Negatively charged clusters of 3000–18 000 atomic mass units, which had been predicted by the charged cluster model, were experimentally confirmed under typical process conditions of hot-filament diamond CVD using gas mixtures of 1–5% CH_4 and H_2. The cluster size increased with increasing methane concentration. Under conditions for the generation of small clusters containing a few hundred carbon atoms, high-quality diamond films were deposited while under conditions for the generation of larger clusters ($> \sim 1000$ atoms), a cauliflower structure was obtained. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is generally believed that the growth unit of a crystal or a thin film is either an atom or a molecule. However, the possibility that a crystal can grow by clusters containing hundreds to thousands of atoms was first suggested by Glasner et al. [1] in their study on aqueous KBr and KCl crystal growth in the presence of Pb^{2+} ions. Their suggestion was so revolutionary that it received severe criticism [2]. Sunagawa [3] made a similar suggestion that the growth unit of synthetic diamond is not an atom but a much larger unit, which has not been taken seriously in the diamond community.

Based on theoretical and experimental analyses of the diamond CVD process, Hwang et al. [4–7] suggested a charged cluster model (CCM). The CCM is very similar to the suggestions made by Glasner et al. [8–11] and by Sunagawa [3]. In the CCM, charged diamond clusters containing hundreds to thousands

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of atoms are suspended like colloidal particles in the gas phase and become the growth unit of a diamond film. They reported that the stability of diamond can increase by the high capillary pressure inside the nanometer-sized cluster and further by charge, which makes a strong ion-induced dipole interaction for the dielectric diamond cluster [12]. The CCM is a completely new paradigm of crystal growth.

Recently, the existence of these hypothetical clusters was experimentally confirmed in a hot filament reactor with a gas mixture of 1.5% CH_4–98.5% H_2 using a Wien filter method [13]. In the CCM, the size of diamond clusters was suggested to increase with increasing methane concentration in the process using the gas mixtures of methane and hydrogen. Small diamond clusters tend to land epitaxially on a growing diamond surface, leading to diamond crystals with well-defined facets while large clusters tend to land non-epitaxially, leading to a cauliflower or ball-like diamond structure.

In order to confirm the predictions of the CCM, the correlation between cluster size and methane concentration was investigated by measuring the energy and mass distributions of clusters in a hot filament diamond CVD reactor. The effect of cluster size on the microstructure evolution of diamond films was also studied by in situ diamond deposition near the orifice for gas sampling during the measurement of energy distribution of clusters.

2. Experimental procedure

The general experimental procedure is similar to that reported by Homann et al. [14,15], who measured the energy and mass distribution of charged soot in their study on the combustion and flame of a mixture of various gaseous hydrocarbons and oxygen. A three-chamber system with two-stage differential pumping, as shown in Fig. 1, was used in study. With this system, the hot filament reaction chamber pressure was 800 Pa while the measuring chamber was maintained at less than 0.0013 Pa. The gas adjacent to the substrate for diamond deposition in the hot filament reactor was extracted through a sampling orifice of 1.2 mm diameter to the second chamber and then through a skimmer of 2.0 mm diameter to the measuring chamber. The orifice was made of aluminum, which connected to a water-cooled brass plate. The distance between the filament and the orifice was 5 mm. The filament temperature was 2373 K.

The kinetic energy of the charged clusters ejected from the reactor was measured by an ion energy analyzer. In the measuring chamber, a repelling voltage was applied to the grid above the current detector. The current variation was measured on the detector with concurrent scanning of the repelling voltage. An

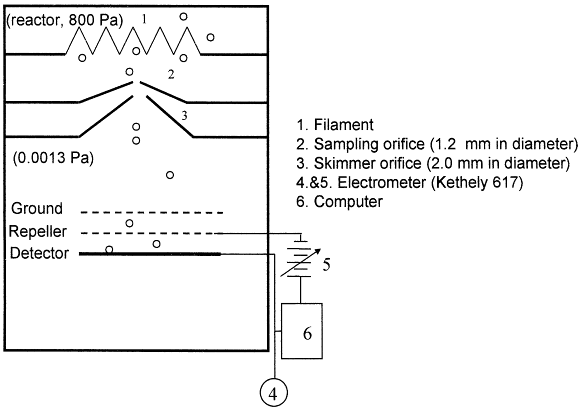

Fig. 1. Schematic diagram of the ion mobility analyzer used to measure the energy distribution of charged clusters. The system consists of three chambers. The top chamber is the hot filament reactor. The measuring chamber is at the bottom.

energy distribution of the charged clusters was obtained by differentiating the current with respect to the repelling voltage. The velocity of the ejected gases was measured by a Wien filter.

During these measurements, diamonds tended to coat near the hole of the aluminum orifice in the reactor. Presumably due to the Coulomb repulsion between the coated diamond at the orifice and the charged clusters, the current measured in the measuring chamber decreased markedly with processing time and the data was not reproducible. In order to avoid this, platinum was coated on the orifice. Another factor affecting the current signal on the detector is the negative electric bias on the filament with respect to the chamber. A stable current was obtained at a bias of −20 V, which was not high enough to trigger a DC glow discharge between the filament and the orifice.

3. Results

Fig. 2(a) shows the energy distributions of clusters formed using four different CH_4–H_2 gas mixtures, 1% CH_4, 1.5% CH_4, 3% CH_4 and 5% CH_4. Most clusters were negatively charged with a negligible amount of positively charged clusters in the hot filament diamond CVD reactor used in this study. This result implies that the source of charge originates from electron emission of the hot filament. In the diamond synthesis by the oxy-acetylene flame, however, both positive and negative clusters were measured [16]. Fig. 2 shows that clusters formed at low CH_4 concentrations (1% CH_4–99% H_2 and 1.5% CH_4–98.5% H_2) have low energy while those at high CH_4 concentrations (3% and 5% CH_4) have higher energy.

Following the scheme suggested by Gerhardt and Homann [15], the mass distributions in Fig. 2(b) were obtained from the energy distribution data in Fig. 2(a) based on the measured relations between the velocity and the cluster mass. Clusters of ~3000 amu were dominant for low methane concentrations (1% and 1.5% CH_4) while an appreciable number of large clusters, approximately ~18 000 amu, existed at higher methane concentrations (3% and 5% CH_4). If the negatively charged clusters measured in Fig. 2(b) consist of pure carbon, the clusters of ~3000 and ~18 000 amu contain ~250 and ~1500 carbon atoms, respectively.

The total negative current in the measuring chamber was 2–3 nA, which came through two orifices of 1.2 and 2.0 mm diameter. From these data, it is difficult to estimate the current in the reaction chamber because it is not known how much fraction of the flux from the first orifice goes through the second orifice. The total

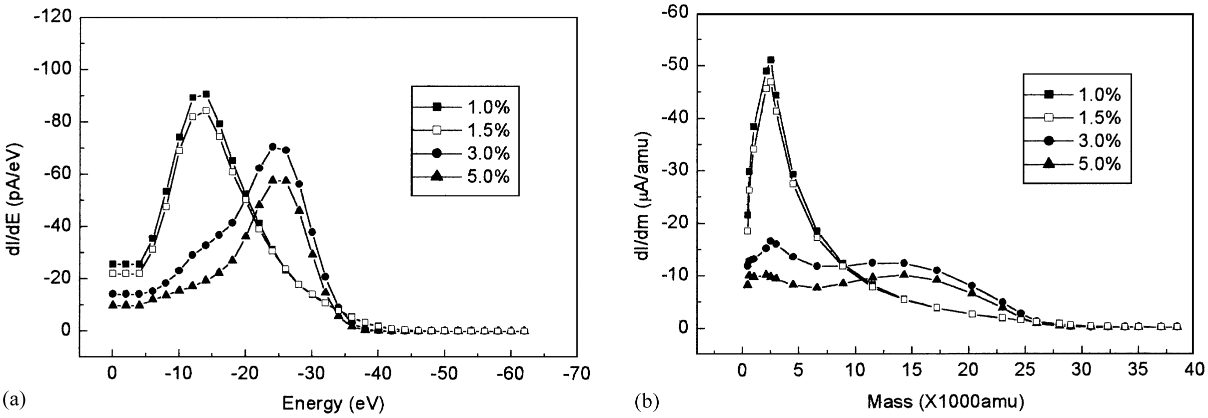

Fig. 2. (a) Energy and (b) mass distributions of negatively charged carbon clusters extracted from the hot filament reactor using gas mixtures of 1% CH_4–99% H_2, 1.5% CH_4–98.5% H_2, 3% CH_4–97% H_2, and 5% CH_4–95% H_2.

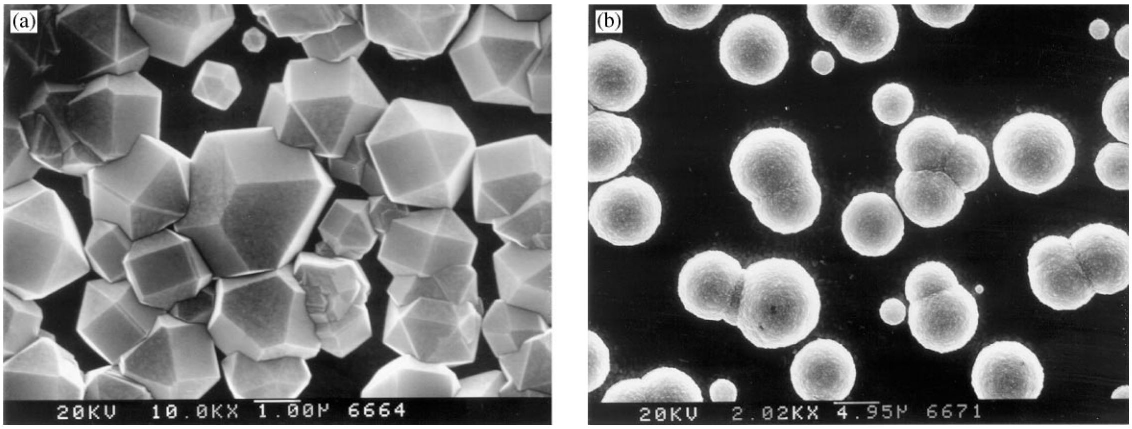

Fig. 3. SEM photographs of diamond films deposited in situ during the measurement of energy distribution of charged clusters at 2373 K, 800 Pa, for 1 h with (a) 1% CH_4–99% H_2 and (b) 3% CH_4–97% H_2.

negative current just below the first orifice was 200 nA. Since all of this current came from the first orifice of 1.2 mm diameter, the current in the reaction chamber is estimated to be $\sim$200 nA mm^{-2}. However, the current measured directly in the reactor was $\sim$20 µA mm^{-2}, which is about two orders of magnitude larger than that measured below the first orifice. The electrode used for current measurement in the reactor was the square stainless plate of 10 mm × 10 mm × 1 mm. A similar difference was also found in the oxyacetylene flame [17]. We are not sure about the origin of this difference. One possible origin is the fact that the charges are lost to the Pt-coated orifice and as a result, a large fraction of the charged cluster becomes neutralized. Another possible origin is the space charge effect [18] between the orifice and the detector. Therefore, the number density of charged clusters is $\sim 10^6$ mm^{-3} if based on the current measured below the first orifice and on the cluster velocity of $\sim 10^6$ mm s^{-1} measured by a Wien filter in the third chamber. But the value is $\sim 10^9$ mm^{-3} if based on the current measured in the reactor and on the thermal velocity of clusters of $\sim 10^5$ mm s^{-1} in the reactor. The number density of $\sim 10^9$ mm^{-3} would be more reliable because the current is directly measured in the reactor. The latter value of the number density will be used for estimation of the film growth rate in a later section.

During the energy distribution measurements, diamonds were deposited in situ on a Mo substrate placed near the orifice with a substrate temperature of 1023 K. The diamond films deposited at 1% and 1.5% CH_4 showed good crystalline quality, while those at 3% and 5% CH_4 showed a ball-like or cauliflower-shape structure, as has been well established in the diamond CVD process [19]. Figs. 3(a) and (b) show the scanning electron microscopy (SEM) images after deposition for 1 h at 1% and 3% CH_4, respectively.

4. Discussion

4.1. New understanding of puzzling phenomenon of diamond deposition with simultaneous graphite etching

Figs. 2(a) and (b) clearly show the existence of negatively charged clusters under typical hot filament diamond CVD processing conditions as was also confirmed in the previous report by a Wien filter [13]. It can be argued that the existence of charged clusters does not necessarily mean that they are the major flux for diamond growth. In order to prove that the charged clusters formed in the gas phase are the growth unit of diamond, consider the most puzzling phenomenon taking place in the diamond CVD process: deposition of less stable diamond and simultaneous etching of stable graphite [20,21].

This phenomenon was explained by the atomic hydrogen hypothesis [22,23], which is based on the fact that atomic hydrogen etches graphite much faster than diamond [24–27]. The atomic hydrogen hypothesis contradicts the second law of thermodynamics. Deposition and etching are opposite irreversible processes, which cannot take place simultaneously. The driving force should be either for deposition or for etching but not for both. Therefore, if the driving force is for irreversible etching of stable graphite, it should be also for irreversible etching of less stable diamond. This phenomenon leads to a seeming contradiction with the second law of thermodynamics by conventional approaches where the deposition unit is assumed an atom, as was pointed out by Yarbrough [28].

Hwang and Yoon [5] suggested that this phenomenon is free of thermodynamic paradox if the diamond clusters nucleate in the gas phase and are the growth unit of diamond films. The phase diagram of the C–H system has a retrograde solubility of carbon in the gas phase in the temperature range of interest. Because of the retrograde solubility, the driving force is for deposition of both diamond and graphite before gas phase nucleation but the driving force changes for etching of both diamond and graphite after gas phase nucleation. In this case, both diamond and graphite etch away into the gas phase by the atomic unit but diamond clusters, which formed in the gas phase, deposit by the cluster unit. What is observed is the deposition of less stable diamond and simultaneous etching of stable graphite. This picture based on CCM is a theory that can explain the puzzling phenomenon without leading to thermodynamic paradox. Therefore, the charged clusters revealed in Figs. 2(a) and (b) should be the growth unit of diamond.

4.2. Growth rate estimated by the cluster number density in the gas phase

In order to see if the amount of charged clusters could provide a sufficient flux for the observed growth rate, we estimated the film growth rate by the cluster number density of $\sim 10^9\,\mathrm{mm}^{-3}$. The supply of carbon atoms per unit surface area and time, S, by clusters equals

$$\begin{aligned} S &= \frac{\text{number of carbon atoms}}{\text{surface area} \times \text{time}} \\ &= \text{gas velocity} \times \frac{\text{cluster size in amu} \times \text{number of clusters per unit volume}}{\text{atomic mass of C}}. \end{aligned} \tag{1}$$

The cluster size in amu measured in this study is ≈ 3000; the number of clusters per mm^3 $\approx 10^9$. The atomic mass of C is 12. The thermal velocity of clusters in the reactor is $\approx 1.0 \times 10^5\,\mathrm{mm}^2\,\mathrm{s}^{-1}$ according to the kinetic gas theory. It should be noted that the thermal velocity of clusters is about 10 times lower than the velocity of clusters ejected through the orifice, which is measured by a Wien filter. Putting these values into the above equation gives $S = 2.5 \times 10^{16}$ C atoms $\mathrm{mm}^{-2}\,\mathrm{s}^{-1}$. The growth rate of diamond from this carbon flux equals

$$R = \frac{S}{N}\,\frac{\text{atomic mass of C}}{\text{density of diamond}}, \tag{2}$$

where N is an Avogadro's number. Using the density of diamond, $0.0035\,\mathrm{g\,mm}^{-3}$, gives a growth rate of $\approx 500\,\mu\mathrm{m\,h}^{-1}$. The growth rate is based on the assumption that all the clusters in the gas phase contribute to the deposition. The growth rate observed in the diamond film deposition is much lower than this value. The growth rate of crystalline diamond in a hot filament CVD is generally a few $\mu\mathrm{m\,h}^{-1}$. For example, the film growth rate observed in this experiment (Fig. 3(a)) was $\approx 1\,\mu\mathrm{m\,h}^{-1}$. This analysis shows that the cluster flux in the gas phase is large enough to explain the observed growth rate of diamond.

The observed growth rate of diamond which is much lower than the rate estimated from the cluster deposition might be due to the fact that the charged diamond cluster is dielectric and has difficulty in landing on the growing surface of diamond because of Coulomb repulsion. The charge transfer might be a rate-determining step for deposition. The growth rate would increase if the charge removal is sufficiently fast. This ideal situation corresponds to the substrate with a high charge transfer rate (CTR) such as Fe, Co and Ni. The correlation between the charge transfer rate and the diamond deposition will be published elsewhere [29]. Although the substrates with a high CTR remove charge from the diamond clusters so quickly that the diamond clusters lose the stability gained by electric double layer [6,12] and transform into graphite clusters, the growth rate would be much higher than that of diamond films on the other substrates. The growth rate of soot on the substrates with a high CTR is about two orders of magnitude higher than that of the diamond films on the substrates with a low CTR at least in the initial deposition period. Such a high growth rate of soot implies that the rate-determining step for diamond growth might be the charge transfer rate. If this is true, it would be desirable for increasing the deposition rate that the gas phase adjacent to the growing surface of diamond is made conducting by plasma or by hot filament.

The charge transfer from the charged diamond clusters would be more difficult on the insulating substrates than on the conducting ones. The diamond deposition would be favorable on the conducting substrates over the insulating ones, which leads to selective deposition of diamond [30]. For better selectivity, the gas phase adjacent to the growing diamond surface should be made more or less insulating. It is well established that in the other CVD processes, the selectivity is lost when the plasma is introduced.

4.3. Microstructure evolution of diamond films grown by deposition of charged clusters

The CCM also suggested that the cluster size would increase with increasing methane concentration in the system using gas mixtures of methane and hydrogen. This suggestion is experimentally verified in Figs. 2(a) and (b). The CCM [7] further suggested that small clusters below Fujita's magic size [31,32] act like liquid and land epitaxially on the growing surface while large clusters tend to land non-epitaxially, retaining their individual orientations and leading to a cauliflower structure. According to Fujita, the magic size of diamond is 1–2 nm. The small clusters in Fig. 2(b) contain ~250 atoms which corresponds ~1 nm. Therefore, small clusters would act like liquid and grow epitaxially, producing diamond crystals with well-defined facets while large clusters act as secondary nuclei on the growing surface, resulting in a cauliflower, ball-like or nanocrystalline diamond structure. Comparison between Figs. 2 and 3 would reveal this aspect. Therefore, small clusters result in a large grain size while large clusters result in a small grain size. In order to make a nanostructure, large clusters should be deposited.

5. Possible implications of the CCM

For high methane concentrations of 3% CH_4–97% H_2 and 5% CH_4–95% H_2 in Fig. 2(b), large clusters coexist with small clusters. Large clusters tend to retain their orientation, leading to formation of nanocrystalline diamonds while small clusters contribute to a size increase by epitaxial growth. An increase in the methane concentration will increase the fraction of large clusters, leading to a decrease in grain size. The extreme case would be the absence of hydrogen, where mainly large clusters are expected.

In relation to this, Gruen et al. [33–35] reported the synthesis of nanocrystalline diamond films using Ar–C_{60} (fullerene) or Ar–CH_4 microwave plasma. Comparing their gas mixture with those in Fig. 2, the methane concentration is extremely high. According to the CCM, their conditions are expected to generate mainly large diamond clusters. The concentration of CH_4 in Ar–CH_4 microwave plasma cannot be increased much because the high concentration may increase the cluster size to such an extent as to decrease the capillary effect and thereby to decrease the stability of diamond with respect to other carbon allotropes.

As mentioned earlier, if the atomic flux is for etching of both diamond and graphite at the substrate during the diamond CVD process, diamond nucleation on the substrate should be achieved by landing of diamond clusters from the gas phase. Because these clusters are charged, their landing on the substrate will be affected by electric bias applied between the filament and the substrate. Therefore, the effect of electric bias on the nucleation behavior in the diamond CVD process can be approached in a new way by the CCM.

CVD diamond forms relatively easily on a graphite surface [20]. From the viewpoint of atomic growth unit, graphite is the most disadvantageous substrate for the diamond growth since graphite has no additional barrier for nucleation. Besides, the growth barrier of graphite would be much smaller than the nucleation barrier of diamond on graphite. Considering all these facts, it is amazing that graphite is a relatively favorable substrate for the diamond nucleation in the new diamond CVD process using gas activation. This phenomenon would be also very difficult to explain without assuming that pre-existing diamond clusters in the gas phase land on the graphite substrate.

In the CCM, charge is the most important factor that makes low-pressure diamond synthesis possible. Charge has two major effects. One is that charge inhibits the Brownian coagulation between clusters. As a result, charged clusters can maintain a nanometer size, which provides a high capillary pressure inside the cluster. This capillary pressure inside the carbon clusters of a few nanometers contributes a great deal to the stabilization of diamond over graphite [6]. The other effect of charge is to stabilize the dielectric diamond clusters over conducting graphite clusters by forming an electrical double layer at the cluster surface. The formation of porous skeletal graphitic soot on some transition metals was attributed to the removal of charge from the clusters. Once the diamond clusters lose charge near the transition metal surface, they lose stability and transform instantly to graphite clusters. Then, the neutral graphite clusters undergo the Brownian coagulation, resulting in a porous skeletal graphitic soot.

Therefore, an electric charge instead of hydrogen is essential to the low-pressure synthesis of diamond although the etching effect of hydrogen can be beneficial in decreasing cluster size. This hypothesis is supported by the recent report that diamonds were synthesized by graphite arc discharge in vacuum [36]. Yoshimoto et al. [37] reported the diamond growth by laser ablation in a hydrogen-free environment. Gruen et al. [33] could synthesize a diamond nanostructure by the discharge of C_{60} in Ar plasma in the absence of hydrogen or oxygen. All these processes produce electric charge. In relation to the stabilization of diamond by charge, a low-pressure mechanism [38,39] was suggested for the formation of interstellar diamond. The dominant formation of the metastable diamond over the stable graphite in space can also be explained by the charge effect [40] since the interstellar space is a moderately ionizing environment.

The CCM is a new paradigm of crystal growth, which applies not only to metastable diamond synthesis but also to many thin-film processes including some solution growth. The validity of the CCM was also verified in silicon CVD [41,42] and in thermal evaporation coating of Au [43]. It is difficult to verify the validity of the CCM in every case of thin-film growth. Usually, the final films look so perfectly dense and faceted that it is almost impossible to tell from the microstructure whether they were grown by the atomic unit or by the cluster unit.

We propose the cauliflower structure as a simple microstructural criterion for the deposition by charged clusters. The cauliflower structure, which is a nanostructure, is quite common in many thin-film processes including electrodeposition. The nanostructure in the thin film or electrodeposition process is more likely to form by landing of nanoclusters or nanoparticles formed in the gas phase or the solution as suggested in the CCM than by individual atoms or molecules. Since the nanostructure is so commonly observed in thin-film growth, crystal growth by charged clusters seems to be a general mechanism in many thin film processes and in some cases of solution growth.

6. Conclusions

In order to show that the CVD diamond growth is governed by the deposition of charged clusters instead of isolated molecules, the energy and mass distributions of negatively charged clusters were measured using varying methane concentrations in the hot filament CVD diamond reactor. The cluster mass increased with increasing methane concentration in agreement with the CCM. For the methane concentration of 1%, where small clusters were measured, high-quality diamonds with well-defined facets were deposited and for concentrations of 3% or greater, where large and small clusters coexist, poor-quality diamonds called cauliflower structures were deposited.

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