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Charged cluster model in the low pressure synthesis of diamond

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Abstract

Gas activation makes possible the synthesis of diamond without codeposition of graphite in the chemical vapor deposition (CVD) diamond process, though its exact role is not clear. Charged carbon nuclei clusters, which are expected to form in the gas phase, are suggested to be responsible for the formation of diamond. When the carbon cluster is sufficiently small, the capillary pressure built up inside the cluster can be high enough to make diamond more stable than graphite. The number of carbon atoms in the cluster that reverses the stability between diamond and graphite increases sensitively with increasing surface energy ratio of graphite to diamond. The gas activation process produces charges such as electrons and ions, which are energetically strong heterogeneous nucleation sites for the supersaturated carbon vapor, leading to the formation of charged nuclei clusters. Once the carbon clusters are charged, the surface energy of diamond can be reduced by electrocapillarity while that of graphite cannot because diamond is dielectric and graphite is conducting. The evolution of graphitic soot and diamond on the iron and the silicon substrates, respectively, can be approached based on the charged cluster model. The charged cluster model is further supported by the result that the insulating quartz block beneath the iron substrate enhances the initiation of diamond on soot.

1. Introduction

The low pressure synthesis of diamond has been intensively studied [1,2] since gas activation processes such as hot filament [3,4] and plasma [5,6] were used. It is widely believed that the gas activation process produces atomic hydrogen, although the exact role of the atomic hydrogen is not universally agreed upon [2,7]. The most popular explanation is the atomic hydrogen hypothesis [3,4], which is based on the fact that the atomic hydrogen etches graphite much faster than diamond. The atomic hydrogen hypothesis is contradictory to the thermodynamic concept [7,8] although the role of the atomic hydrogen as reducing the surface energy of diamond compared to that of graphite, which was suggested by Badziag et al. [9], is thermodynamically sound.

The fundamental question in the CVD diamond process is how diamond is formed dominantly over graphite from the gas phase or directly from the solid compact while graphite is known to be more stable. In order for diamond to be more stable than graphite, the pressure should be higher than thousands of megapascal based on the well-established phase diagram of carbon [10]. On a thermodynamic basis, the most convincing answer to this question is that the

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capillary pressure inside a sufficiently small carbon cluster can be high enough to make a diamond cluster more stable than a graphite cluster. Badziag et al. [9] and Hwang et al. [8,11] showed that nanometer-sized diamond can be more stable than graphite.

Gas activation by hot filament and plasma is known to be essential to the successful synthesis of diamond [1,2]. From a thermodynamic point of view, gas activation can affect some parameters that are related to the stability of the small carbon particles in such a way that diamond is more stable than graphite.

On the other hand, gas activation by plasma or hot filament produces charges such as ions and electrons. These charges are known to be strong heterogeneous nucleation sites for the supersaturated species in the gas phase [12,13]. The so-called "ion-induced nucleation" is well known in the Wilson cloud chamber [14,15] and the bubble chamber [16] experiments. If this charge-induced nucleation takes place, charged nuclei will form in the gas phase and the deposition behavior will be quite different from conventional nucleation and growth on the substrate surface.

In this paper, we will analyze in detail the theoretical and experimental aspects on the charged cluster model, which is a new concept in the CVD diamond process. The term, "cluster" in this paper refers to particles normally containing more than a few hundred atoms so that the crystal structure is defined and the macroscopic concept of the thermodynamic property such as the surface energy can be applied.

2. Stability of small diamond and graphite clusters

When a cluster gets smaller, the surface free energy term tends to become dominant over the bulk term. Because of the small molar volume of diamond compared to that of graphite, for a sufficiently small carbon cluster diamond can be more stable than graphite [8,9,11]. Fig. 1 illustrates that the stability between diamond and graphite can be reversed for the carbon cluster containing less atoms than the number at the intersection of two curves. The number of atoms in the cluster that reverses the stability between diamond and graphite can be obtained by equating the free energy changes of two clusters. In the classical nucleation theory [17,18], the free energy change associated with the formation of a solid particle containing "n" atoms from the vapor phase is expressed as

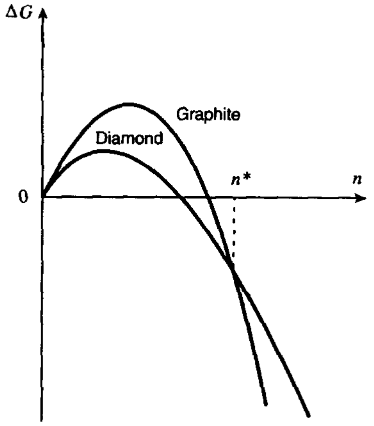

Fig. 1. Two schematic curves of Gibbs free energy versus the number of atoms for graphite and diamond.

$$\Delta F = -n\mu + (4\pi)^{1/3}(3\Omega)^{2/3}\sigma n^{2/3}, \tag{1}$$

where μ is the bulk free energy change per atom associated with the transfer of an atom from the vapor to the solid phase, σ is the specific surface energy, and Ω is the atomic volume. The number of atoms at the intersection of two curves is expressed as [11]

$$n^* = 36\pi\left(\frac{\sigma_{\text{dia}}\Omega_{\text{dia}}^{2/3} - \sigma_{\text{gra}}\Omega_{\text{gra}}^{2/3}}{\Delta\mu^{\text{dia}\to\text{gra}}}\right)^3, \tag{2}$$

where σ_{dia} and Ω_{dia} are, respectively, the specific surface energy and the atomic volume of diamond and σ_{gra} and Ω_{gra} those of graphite. These equations are based on the assumptions of spherical shape of the cluster, isotropic surface energies [19] and constant molar volumes [20].

$\Delta\mu^{\text{dia}\to\text{gra}}$ is the free energy change per atom between diamond and graphite, which is always negative. At a substrate temperature of 1200 K and a chamber pressure of 2700 Pa, the free energy difference between diamond and graphite in Eq. (2) is estimated to be -1.1201×10^{-20} J/atom by the Thermo–Calc program [22]. Based on the reported surface energies of diamond and graphite [19], the two curves intersect at $n^* \approx 351$. Thus, under the assumptions made here, for the cluster containing less than 351 atoms, diamond is more stable than graphite. In order for n^* in Eq. (2) to be positive, $\sigma_{\text{dia}}\,\Omega_{\text{dia}}^{2/3}$ should be smaller than $\sigma_{\text{gra}}\,\Omega_{\text{gra}}^{2/3}$, which is satisfied for the reported related data within errors of the estimation. It can be said that for a carbon cluster containing less than n^* atoms, diamond is more stable than graphite, which is similar to Badziag et al.'s statement [9]: "Nanometer-sized diamond is more stable than graphite".

The chemical potential is the criterion for the spontaneous transfer of atoms between phases even when the system deviates from equilibrium. The number of atoms at which the chemical potential of carbon is the same between diamond and graphite clusters has a form similar to Eq. (2) and is expressed as [8]

$$n^{\dagger} = \frac{32\pi}{3}\left(\frac{\sigma_{\text{dia}}\Omega_{\text{dia}}^{2/3} - \sigma_{\text{gra}}\Omega_{\text{gra}}^{2/3}}{\Delta\mu^{\text{dia}\to\text{gra}}}\right)^3. \tag{3}$$

The same expression as Eq. (3) is also derived by the condition that the slopes of the two curves in Fig. 1 are the same. While n^* is the critical number of atoms for which the graphite cluster becomes more stable than the diamond cluster, $n^{\dagger}$ is the critical number of atoms for which the addition of one atom to a cluster is more favorable for a graphite cluster than for a diamond cluster. n^* is larger than $n^{\dagger}$ by a factor of 27/8.

If the critical nucleus of the carbon cluster formed from the gas phase is smaller than $n^{\dagger}$, nucleation of diamond will be dominant over that of graphite. And if the graphite cluster contains less than $n^{\dagger}$ atoms, it can directly transform into the diamond cluster by thermal fluctuation. Roy et al.'s [21] report on the direct solid-state transition from nanometer-sized, non-diamond carbon compacts into the diamond compacts can be approached by Eq. (3).

The estimated values of n^* and $n^{\dagger}$ have some uncertainties because of the assumptions made in the derivation. Even when the equilibrium shapes of diamond and graphite are considered in the derivation, the exact estimation is still difficult because of the lack of reliable surface energy data on each facet of the equilibrium shape especially for the small cluster. However, Eqs. (2) and (3) show that the formation of the metastable diamond phase can be approached based on a thermodynamic analysis if the capillary effect of the small particles is considered. These equations also show that the parameters related to the stability change between the small diamond and graphite clusters are the specific surface energies (σ), atomic volumes (Ω) and the free energy difference between diamond and graphite ($\Delta\mu^{\text{dia}\to\text{gra}}$).

3. The role of gas activation

There is no doubt that the gas activation makes possible the dominant formation of diamond over graphite. From the thermodynamic point of view, this means that gas activation makes diamond more stable than graphite at least in the nucleation stage. That is, the dominant formation of diamond can be achieved by increasing n^* in Eq. (2) or $n^{\dagger}$ in Eq. (3). In this respect, the gas activation process seems to increase n^* in Eq. (2) or $n^{\dagger}$ in Eq. (3). It should be examined how the gas activation process can affect the parameters in Eqs. (2) and (3) in order to increase n^* or $n^{\dagger}$.

Among the parameters in Eqs. (2) and (3), the specific surface energies of diamond and graphite are the only parameters that can be varied by the processing condition; molar volumes and the free energy difference between diamond and graphite are not expected to be affected by the processing condition. We will examine the effect of the surface energy variation on $n^{\dagger}$ in Eq. (3).

At a substrate temperature of 1200 K and a chamber pressure of 2700 Pa, which is one of the typical conditions in the CVD diamond process, the free energy difference between diamond and graphite in Eqs. (2) and (3) is estimated to be -1.1201×10^{-20} J/atom [22]. For the reported data of the molar volumes, 3.410×10^{-6} M^3/mol and 5.405×10^{-6} M^3/mol [20] and the surface energies 3.7 J/M^2 and 3.1 J/M^2 for diamond and graphite [19], respectively, $n^{\dagger}$ in Eq. (3) is estimated to be 104, which is comparable to that contained in the critical nucleus. If the surface energy of diamond is assumed to decrease to 3.6, 3.5, 3.4, and 3.3, $n^{\dagger}$ increases to 177, 279, 413 and 584, respectively. The number 584 is equivalent to nanometer-sized carbon clusters.

The validity of these numerical estimations will depend on the validity of the assumptions made in deriving Eq. (3) and of the available related data. However, the estimation will give the physical concept on the capillarity effect of the small carbon cluster and the possibility that the minor modification of the surface energies can reverse the stability between the small diamond and graphite clusters.

From these analyses, it can be said that the stability between diamond and graphite especially in the nucleation stage would be critically affected if the surface energies of diamond and graphite are modified by any means in the processing condition. Surface energy modification seems to be the most probable role of the gas activation in the successful processing of diamond. The possibility that the gas activation can modify the surface energy will be examined in the following section.

4. Modification of the surface energy of diamond and graphite

For a given temperature and pressure, there are two ways that the surface energy can be modified by the processing conditions. One is the adsorption of the neutral species, which is described by the Gibbs adsorption equation [23], and which might result in the unbalanced reduction of the surface energy between diamond and graphite. In relation to this category of surface energy modification, Badziag et al. [9] suggested that the adsorption of the atomic hydrogen produced in the CVD diamond process reduced the surface energy of diamond more than that of graphite. Since this possibility was already suggested by Badziag et al. [9], we will not explain the details of this. In this paper, we suggest another possibility of the adsorption of the charged species, which is equivalent to the electrocapillarity effect described by Lippmann's equation [24]. The electrocapillarity arises when an external field is applied to a polarizable interface [25].

In electrochemistry, the electrode to which the electron passes easily is called non-polarizable and the excess charge is not built up to the electrode [25]. Conversely, when the transfer of electrons is difficult, application of a potential from outside will build up charge at the interface. In this case, the interface is called polarizable [25]. Since graphite is conducting and the charge tends to be uniformly distributed over the conducting bulk, the interface of the graphite cluster is expected to be non-polarizable. However, diamond is dielectric and the charge on the diamond cluster tends to be localized at the interface. The interface of the diamond cluster is expected to be polarizable; it will have an electrocapillary effect when the diamond cluster is charged. The surface energy of the diamond cluster can be decreased by the presence of charges while that of the graphite cluster cannot. This situation is another possibility of the unbalanced reduction of the surface energy between diamond and graphite. Both effects of adsorption and electrocapillarity can be favorable for the dominant formation of diamond and might be additive to each other in the CVD diamond process. By purely theoretical analyses, it is difficult to decide which is the more dominant factor. It needs to be experimentally verified which the dominant factor is. Our suggestion of modification of the surface energy by charges is based on the experimental observations implying that the stability between diamond and graphite is directly affected by the presence and absence of charges. These experimental results will be presented in a later section.

5. Nucleation behavior in the presence of charges

CVD diamond processing is the precipitation of solid carbon from the gas phase reaction. This precipitation takes place when the activity of carbon in the gas phase is higher than that of the solid phase. The thermodynamic analysis under CVD diamond process conditions shows that the activity of carbon in the gas phase is higher than that of both graphite and diamond [26,27]. That is, carbon in the gas phase is supersaturated with respect to both graphite and diamond. In the presence of supersaturation, the solid carbon phase will be nucleated and the nucleation will take place at the site of the lowest nucleation barrier. The surface of the substrate is normally regarded as a favorable site for nucleation. When charges are present in the chamber, however, the possibility of nucleation on charges in the gas phase cannot be ruled out.

In the gas activation processes of the CVD diamond such as the plasma and hot filament methods, abundant ions or electrons are produced. Note that the filament of refractory metals is being used as the electron source. Therefore, the gas activation process is characterized by producing abundant ions or electrons. Ions are known to be strong heterogeneous nucleation sites. Ion-induced nucleation was manifested by Wilson's cloud chamber [14,15] and the bubble chamber [16] experiments, where the ion-induced nucleation is utilized in locating the track of high energy particles. In these experiments, the accelerated high energy particles collide into a supersaturated medium and produce ions, which become the site of nucleation, marking the track of high energy particles. The nucleation barrier is reduced markedly in ion-induced nucleation [12,13]. Since electrons would play the same role in inducing nucleation as ions, charge-induced nucleation will be the more general term.

Especially when the supersaturation is appreciable in the presence of charges, the nucleation barrier vanishes and the stable nuclei are formed spontaneously [12,13]. In the case of water condensation from the vapor, for example, the nucleation barrier was estimated to vanish at the supersaturation ratio of 3.32 by Castleman et al. [13]. The possibility of charge-induced nucleation in the gas phase is the key point of the charged cluster model in this paper.

6. Charged cluster model

If this charge-induced nucleation takes place, charged nuclei will form in the gas phase and the deposition behavior will be quite different from conventional nucleation and growth on the substrate surface. When charges are not involved or negligible compared to the amount of the precipitating solid, the nuclei in the gas phase continue to coarsen into the macro-particles by coagulation or by Ostwald ripening. When the charges are abundant, as in the case of the gas-activated CVD diamond process, coarsening of the charged nuclei will be limited by the balance between the surface energy and the Coulomb energy. Thus, the charge density and the equilibrium amount of precipitation of the solid carbon in the gas phase determines the size of the charged nuclei. If the amount of charges produced in the process is relatively small compared to that of the precipitating carbon in the gas phase, the size of the charged nuclei will be large, diminishing the capillary effect and adversely affecting the stability of diamond over that of the non-diamond carbon. This dependence of the cluster size on the charge density and the amount of precipitation might be related to the following three well-known experimental observations in the CVD diamond process.

First, when the concentration of the hydrocarbon is increased relative to hydrogen in the CVD diamond process, the non-diamond phase is evolved [1,2]. Second, the growth rate of the diamond film is roughly proportional to the production of the charges [28]; a higher growth rate can be achieved by a higher plasma density. Third, Sommer et al. [29] reported that the thermodynamic condition of the filament coated by solid carbon corresponds to the formation of the non-diamond formation on the substrate. The coating on the filament will reduce the emission of electrons, which will decrease the charge density and then increase the size of the clusters for the given gas composition. These three observations can also be explained by the atomic hydrogen approach. It remains to be solved which is the more dominant factor between the charge and the atomic hydrogen.

From the view point of the charge-induced nucleation, the role of the gas activation such as the hot filament and the plasma is to provide charges. Another method that can provide charges would be the CVD process by the gas mixture containing halogen elements, which have high electron affinity. In relation to this, Patterson et al. [30] reported the successful synthesis of diamond without conventional gas activation by using halogen-containing gases with a maximum temperature of 900°C. They [31] further claimed the successful synthesis of diamond by halogen-containing gas mixtures, which do not contain any hydrogen.

Involvement of charges in the CVD diamond process is also strongly implied by the fact that the deposition behavior is markedly affected by the applied bias [32], which is called the electron-assisted CVD process. Previous reports [32,33] and the experience in our laboratory tell that the stability of diamond is favored by a positive bias on the substrate while that of the non-diamond carbon is favored by a negative one. These facts imply that the stability of the charged nuclei might be affected by the sign of the charge and the negative charge would favor the stability of diamond. This phenomenon seems to be closely related to the well-established fact that the nucleation behavior in the presence of charges depends on the sign of the charge [34,35]. Unfortunately, the present theory and the available related data are not sufficient to make any quantitative prediction on the sign dependence of the stability between diamond and non-diamond clusters.

Based on the established concept of sign dependence in nucleation [36] and the phenomenological implication that a negative charge stabilizes the diamond cluster, we suggest the following possibility. According to the electrochemistry of the surface, all surfaces have an electrical double layer [37]. The surface is either positively or negatively electrified. If the presence of charges increases the intrinsic electric field of the electrified surface, the surface energy will decrease and vice versa. This effect would be much more marked when the surface is polarizable. If the surface of the uncharged diamond cluster is negatively electrified, the attachment of the negative charges on the surface will decrease the surface energy while that of the positive ones will increase it. And thus, the presence of negative charges, which are believed to be supplied from the hot filament or the plasma, will be critical to the stability of the diamond cluster.

Surfaces of the diamond and the graphite clusters would be polarizable and non-polarizable, respectively, since diamond is dielectric and graphite is conducting. Therefore, unbalanced reduction of the surface energy between diamond and graphite is expected by the presence of charges. It should be noted that in the capillary analysis of the previous sections, the unbalanced reduction of surface energy between diamond and graphite can increase markedly the size of clusters that stabilizes diamond over graphite. Thus, the diamond cluster can be stable when it is charged and it can transform to the graphite cluster when the charge is removed. These aspects will be described in detail in a later section.

Another feature of the charged cluster model is that the diamond film grows not by the atomic unit but by the cluster unit. Charged clusters would behave like a stable colloid suspension and remain invisible since they are expected to be of the nanometer size. Gas phase nucleation of diamond powder particles was already reported in an RF plasma by Mitura [38] and in DC arc plasma by Chonan et al. [39]. We think that the powder particles that they observed are the product of appreciable growth from charged clusters and are expected to be much larger than individual nanometer-sized charged clusters.

According to the charged cluster model, the charges produced by the gas activation process affect the CVD diamond process in two ways: one is to maintain the small size of the charged clusters so that the capillary effect may favor the stability of diamond and the other is the electrocapillary effect, by which the surface energy of the diamond cluster is decreased by the presence of the, presumably, negative charges. Although it will be difficult to experimentally confirm the presence of invisible charged clusters in the gas phase, charged clusters are predicted not only by the energetics of the charge-induced nucleation but also by the unusual phenomena of the CVD diamond process, as will be explained in the following sections.

7. Geometrical effect on the formation of diamond

The geometrical effect on the formation of the CVD diamond has been confirmed by well-designed experiments [40,41]. Dennig and Stevenson [40] and Ramesham and Ellis [41] have observed the formation of diamond particles on the well-defined geometry of a silicon substrate prepared by photo-etching and concluded that the preferential site for initiation of diamond was along the convex edge or at the apex. On the other hand, the theoretical analysis of the geometric effect on the nucleation [42,43] is well established and predicts that the convex edge or the apex is the least favorable site for nucleation. Since we believe that the contradiction between experimental observation and the theoretical analysis about the preferential site for the diamond initiation is important in relation to the growth mechanism, we will theoretically analyze the geometrical effect on the nucleation in more detail in the case of diamond initiation on the substrate.

Fig. 2a–2c show the three different substrate ge-

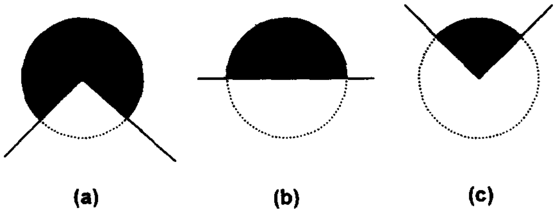

Fig. 2. Three different substrate geometries for heterogeneous nucleation with a contact angle of 90°: (a) the convex edge with an angle of 270°, (b) the flat substrate with an angle of 180° and (c) the concave edge with an angle of 90°.

ometries: the first represents the convex edge, the second the flat surface and the third the concave edge. The angles of the substrate in Figs. 2a–2c are 270°, 180° and 90°, respectively. For simplicity, the contact angle of the diamond particle with the substrate is assumed to be 90°; otherwise, an analytical expression cannot be obtained. The observed contact angle of the ball-like diamond on the silicon substrate is ~ 100°. For further simplicity, a spherical shape with isotropic surface energy is assumed for the diamond particle. These assumptions would not affect the main conclusion of the analysis.

The ratio of the activation energy for nucleation between the homogeneous and the heterogeneous nucleation is simply given by the ratio of the respective Wulff volume [44]. Since the Wulff volumes in Figs. 2a–2c are, respectively, three quarters, a half and a quarter of the complete sphere for the homogeneous nucleation, the activation energies for nucleation are, respectively, 0.75, 0.5 and 0.25 of that for the homogeneous nucleation. From this information, we can estimate the ratio of the nucleation rate between Figs. 2a–2c. The ratio of the nucleation rate between the homogeneous and the heterogeneous nucleations is expressed as

$$\frac{I_{\text{homo}}}{I_{\text{hetero}}} = \exp\left(- \frac{\Delta G^*_{\text{homo}} - \Delta G^*_{\text{hetero}}}{kT} \right), \tag{4}$$

where ΔG^*_{homo} and $\Delta G^*_{\text{hetero}}$ are the nucleation activation energies for the homogeneous and the heterogeneous nucleations, respectively. Since the pre-exponential factor, which varies by the order of 10^{16} depending on the consideration of the Lothe–Pound factor [45], is cancelled out, the ratio of the nucleation rate is relatively reliable compared to the absolute nucleation rate.

For Figs. 2a–2c, the ratios of the nucleation rate between the homogeneous and the heterogeneous nucleations are $\exp(-\Delta G^*_{\text{homo}}/4kT)$, $\exp(-\Delta G^*_{\text{homo}}/2kT)$, and $\exp(-3\Delta G^*_{\text{homo}}/4kT)$, respectively. ΔG^*_{homo} for nucleation of diamond from the gas phase is given by

$$\Delta G^*_{\text{homo}} = \frac{16\pi v^2 \sigma^3}{3(\Delta f^{\text{gas} \to \text{dia}})^2}, \tag{5}$$

where v and σ are the molar volume and the surface energy of diamond; and $\Delta f^{\text{gas} \to \text{dia}}$ is the driving force for precipitation of diamond from the gas phase. Thermodynamic calculations [27] show that for the mixture of 1% CH_4–99% H_2, the supersaturation ratio is maximum at 1300 K as ~ 20 and the maximum value increases to ~ 50 for the mixture of 3% CH_4–97% H_2. For a supersaturation ratio of 10, at a substrate temperature of 1200 K, a molar volume of 3.41×10^{-6} M^3/mol and a surface energy of 3.7 J/M^2, the ratios are estimated to be $\sim 10^{-124}$, $\sim 10^{-246}$, $\sim 10^{-369}$ for Figs. 2a–2c, respectively. For a supersaturation ratio of 100, the ratios are $\sim 10^{-31}$, $\sim 10^{-62}$, and $\sim 10^{-93}$.

Thus, for the supersaturation ratios of 10 and 100, the ratios of the nucleation rate between Figs. 2a–2c are $1 : 10^{123} : 10^{245}$ and $1 : 10^{31} : 10^{62}$, respectively. This marked difference in the nucleation rate comes from the exponential dependence of the nucleation rate on the activation energy. For this reason, the preferential nucleation at the concave site such as the crevice is well established in the phase transformation [46]. In this respect, the preferential initiation of the diamond particles at the convex site is against the well-established concept of nucleation. To our knowledge, no satisfactory explanation for the preferential initiation of diamond at the convex site is given yet.

On the other hand, this phenomenon can be approached by assuming the charge-induced nucleation of the diamond clusters in the gas phase. When gas phase nucleation takes place, the initiation of the diamond particles on the substrate is not by nucleation, but by landing of the charged nuclei. The charged nuclei are expected to land on the convex sites, which provide the highest electric field gradient. Thus, the convex site would be more favorable than the other sites.

8. Deposition of soot on iron substrate

We observe that soot is formed when iron (Fe) is used as a substrate. Iron substrate is known to be harmful to the processing of good quality diamond film. When the iron and the silicon substrates are placed side by side, a very porous soot structure is evolved on the iron substrate while the crystalline diamond is growing on the silicon substrate. We have confirmation by repeated experiments with the iron substrate that soot is always formed on the iron substrate, almost regardless of the processing conditions. The microstructures evolved on the silicon and iron substrates are shown in Fig. 3a and 3b, respectively. These specimens are prepared by a typical processing condition; the temperature of the tungsten filament is 2473 K, the substrate temperature 1263 K, the pressure 2700 Pa and 100 standard cubic centimeter per minute (sccm) of 1% CH_4–99% H_2 is supplied by a mass flow controller. The processing time is two hours.

Analysis of the Raman spectra shows that soot is graphitic. Composition is the same between soot on the iron substrate and diamond on the silicon substrate, but the crystal lattice and morphology markedly differ from each other. Since the two substrates are placed close to each other, the source in the gas phase making diamond on the silicon substrate is expected to be the same as that making soot on the iron substrate.

We find that the characteristics of soot in Fig. 3b are similar to those of soot commonly observed in the field of combustion and flame, where the mechanism of its formation has been intensively studied [47–50]. In this field, soot is regarded as aggregates of fine carbon particles nucleated and grown in the gas phase. The aspect of soot formation is known to be affected by the applied electric bias [48,49]. The formation of soot is explained by the ionic mechanism, which indicates that soot is aggregates of charged carbon clusters after losing the charges [47–50].

In the CVD diamond process, formation of graphite on the iron substrate, which has a catalytic effect in transforming diamond to graphite, can be explained. But what is normally expected is a graphite film rather than a porous compact of soot. From the point of crystal growth of the solid from the gas phase by the atomic unit, the carbon atom should find the kink site. The kink sites are provided by the rough interface. The graphite in the processing conditions of CVD diamond is expected to have a singular surface. The periphery of one atomic layer is known to be rough. This kind of rough interface of one atomic layer can be provided by two-dimensional nucleation or by ledge-generating sources such as screw dislocation. Neither the growth by two-dimensional nucleation nor by ledge-generating sources can produce such a porous compact of soot in Fig. 3b. The soot in Fig. 3b is very fragile and is weakly connected between the particles; it can be scrubbed by a finger. The bonding between the soot particles

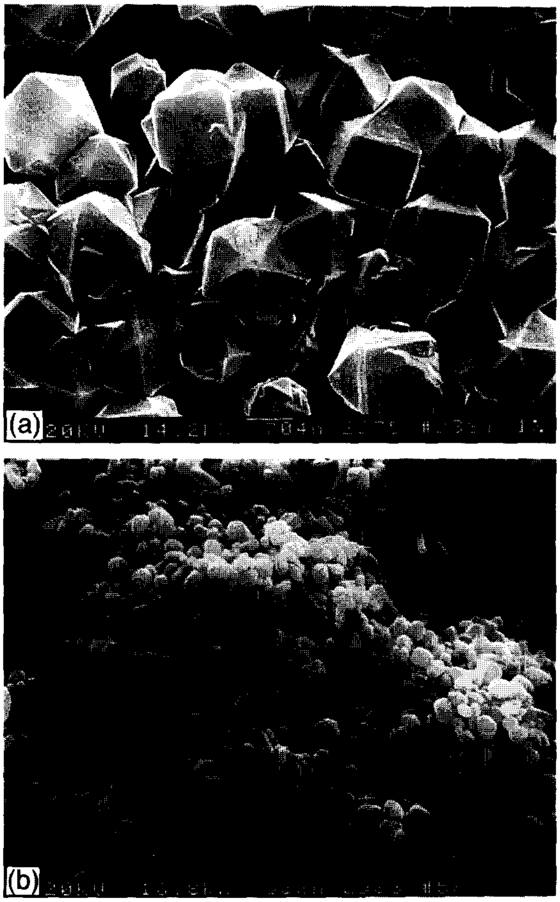

Fig. 3. SEM microstructures showing (a) diamond deposited on the silicon substrate and (b) soot deposited on the iron substrate for the gas mixture of 1% CH_4–99% H_2 for 2 h at a substrate temperature of 1263 K under 2700 Pa.

seems to be by the van der Waals force. The weak bonding between particles implies that the growth unit is of small particles rather than of the atom. The morphological feature of Fig. 3b resembles the powder compacts formed by landing of macro-particles, which were nucleated and grown in the gas phase in the conventional CVD process [51].

The growth rate of soot on the iron substrate in Fig. 3b is much higher than that of diamond on the silicon substrate in Fig. 3a in terms of their mass increase. The high growth rate of soot is difficult to interpret by the atomic hydrogen hypothesis because the graphite should be etched by the atomic hydrogen. If the soot is formed by the conversion from diamond, which grows by the atomic unit, the growth rate of soot on iron should not be higher than that of diamond on silicon. In the charged cluster model, the diamond charged cluster formed in the gas phase loses its charge to the iron substrate, which has a high charge transfer rate. This charge loss removes the surface energy reduction by the electrical double layer effect and makes diamond unstable with respect to graphite. Loss of charge also removes the Coulomb repulsion between the clusters and makes them stick randomly, resulting in a porous structure, which will be explained in more detail in a later section.

We found that the phase competing with diamond is not graphite in the processing conditions as long as the silicon substrate is used. Even when we use the 100% CH_4 gas, non-diamond amorphous carbon instead of graphite is formed on the silicon substrate. When the cluster is charged, the conducting graphite cluster, which has no benefit of surface energy reduction by the electrical double layer, cannot compete among the carbon allotropes in the stability of the small cluster. Note that in Fig. 1, we can draw the free energy curve of the other forms of carbon and can compare the stability of the small cluster of various carbon phases. But as long as the charge is lost on the iron substrate with a high charge transfer rate, graphite is the most stable phase.

Fig. 4 shows a stereoscopic microstructure taken at the edge of the iron substrate. We observe that such preferential growth of soot at the edge of the iron substrate is typical. As a result, the pinnacle of soot is developed at the edge. This result is strong evidence that the sources making soot should be charged. This tendency of soot to be formed preferentially on the convex edge might be the phenomenon similar to that of diamond to be formed preferentially on the convex edge.

Fig. 4. Stereoscopic view of the soot growing preferentially at the edge of the iron substrate. The deposition conditions were the same as those of Fig. 3.

9. Comparison of the microstructures on the iron substrates placed on quartz and steel blocks

The results in the previous section can be approached in the framework of the charged cluster model, in which it is presumed that the presence of charge on the cluster might be related to the stability of diamond and the evolution of soot on the iron substrate might be due to the quick losing of charge to the substrate. Based on these presumptions, we tried to examine the effect of electrical insulation of the iron substrate on the evolution of the microstructure. We made the iron substrate electrically floating by placing it on a quartz block. The evolved microstructure was compared to that on the iron substrate placed on a conducting steel block. We expected that once the charges were saturated in the electrically-floating iron substrate, further charge transfer would be suppressed or at least retarded by the insulating quartz layer.

For this experiment, we placed an insulating block of 3.3 mm thick quartz beneath the 1.5 mm thick iron substrate and compared the result with Fig. 3b, where a steel block was placed beneath the 1.5 mm

Fig. 5. SEM microstructure showing the evolution of diamond over soot on the iron substrate beneath which quartz was placed. The other deposition conditions were the same as those of Fig. 3.

thick iron substrate. All other experimental conditions are the same as those of Fig. 3. Since the quartz block also has a thermal insulating effect, the temperature of the substrate on the quartz block tends to be higher than that on a steel block for the same filament temperature. Thus, we were especially cautious not to make the substrate temperature higher than 1263 K, which is the substrate temperature chosen for Fig. 3. This was achieved by decreasing the filament temperature. In the preliminary experiment, we had confirmation that the decrease in the filament temperature retarded the initiation of diamond on the soot.

The result is shown in Fig. 5. The iron substrate on the quartz block shows the evolution of the diamond phase on the initially formed soot for the same processing time of two hours as that for Fig. 3b. That is, the formation of diamond on the initially formed soot on the iron substrate is enhanced for the substrate on the quartz block compared to that on the steel block. The diamond phase in Fig. 5 was also confirmed by Raman spectroscopy. More systematic results with varying thicknesses of the quartz block show the same trend [52]; the thicker the quartz block, the faster the evolution of diamond.

The quartz block has two possible effects: one is the thermal insulation and the other is the electrical insulation. Since we avoided the contribution to the enhanced initiation of diamond on soot from the effect of the thermal insulation of quartz, the effect of quartz is thought to come solely from the electrical insulation. By placing the quartz block beneath the iron substrate, the current from the hot filament to the conducting specimen holder was observed to be reduced from 80 to 5 μA. Since the current across the quartz block was negligible, the path of the current as much as 5 μA for the holder with the quartz block is expected to be the gas phase or the surface of the quartz.

The result of Fig. 5 indicates that the stability between graphite and diamond as well as the morphological difference between the porous soot and the dense diamond is affected by the electrical insulation of the substrate. We expect that the electrical insulation might suppress the charge transfer rate to the conducting specimen holder. Thus, the results imply that the stability of diamond and the evolution of the porous soot should be affected by the charge transfer rate.

10. Deposition mechanism of soot or diamond

Here, we will explain how the dense crystalline diamond can be evolved by the charged nanometer diamond clusters on the silicon substrate. We could approach this puzzling phenomenon in the framework of the charged cluster model.

The charged cluster resembles a colloid suspension in that they are charged and do not tend to coagulate due to Coulomb repulsion. Without the charges, the clusters will coagulate by van der Waals attraction between them. In a colloid system, Coulomb repulsion is a long-range force compared to the van der Waals attraction, which is also known as the dispersion force [25]. When two colloid particles overcome the barrier of their repulsion and become close enough, they will stick together.

The sedimentation behavior of the colloid particles is quite different depending on whether attraction or repulsion is dominant between particles. The colloid particles have a random Brownian motion. When attraction is dominant, the colloid particles do not have any selectivity in sticking to each other; they tend to stick randomly, resulting in porous packing and a low packing density. This behavior is known as the flocculated colloid packing [53]. When repulsion is dominant, however, the colloid particles tend to stick highly selectively; they tend to stick to the least-repulsive site, which is a kink corner, resulting in the dense and regularly-spaced packing. This behavior is known as the deflocculated colloid packing [53]. The repulsive dominant colloid particles are known to sediment so regularly that the final sedimentation tends to be the face-centered cubic packing or the body-centered cubic packing like the crystal structure. The regularity is so high as to be revealed by X-ray diffraction.

The charged diamond cluster suggested in this paper is expected to contain a few or several hundreds of carbon atoms. Thus, in the CVD diamond process the colloid suspension contains the charged clusters of approximately one nanometer. These clusters will behave like large molecules. These clusters are expected to collide into the substrate randomly by the Brownian motion. The force that attracts the charged clusters to the substrate should be of two kinds: one is the van der Waals attraction and the other is the Coulomb attraction, which is the image field on the substrate; the source of the image field is the charged cluster. The van der Waals attraction tends to be high between the materials of the same element or molecule. Thus, any carbon allotropes are expected to have a high attraction force for the charged diamond clusters. This expectation agrees with the previous observations that most of the carbon sources, if used for the substrate, are favorable to diamond formation [1]. The high attraction by the image field would be provided by the sharp edge on the substrate, which makes a high electric field gradient. We think that the soot pinnacle of Fig. 4 is the result of this attraction at the sharp corner. Another site of a sharp point would be the pre-existing clusters having landed on the substrate surface. In other words, once the charged cluster landed on the substrate, the cluster itself would provide the high electric field gradient, which again attracts the other charged clusters in the gas phase.

The deposition behavior after landing depends markedly on the charge transfer rate from the cluster to the substrate. When the transfer rate is high, as in the iron substrate, the clusters become neutral and only the attraction force between the clusters and the substrate remains and the clusters would become permanently attached. On the other hand, as soon as the cluster loses its charge, the cluster also loses the unbalanced reduction of surface energy by electrocapillarity. As a result, the diamond phase is no longer stable and the cluster would transform into a graphitic cluster. Combined with the high electric field gradient of the existing clusters and the high charge transfer rate, the cluster would grow like a whisker, finally resulting in the porous soot structure on the iron substrate. The final microstructure would resemble the porous packing in the attraction-dominant colloid suspension.

On the other hand, once the iron substrate is covered by the carbon cluster particles, the surface is no longer iron but a graphitic layer and the charge transfer kinetics will be affected. When the graphitic layer becomes thick, the iron would have a negligible effect and the resulting deposition behavior would be the same as if a graphite substrate were being used. Thus, the diamond would be evolved on the soot as the processing time goes on.

In the case of a silicon substrate, the charged cluster tends to land on the site having a sharp point such as a convex edge having a high electric field gradient. On the silicon substrate, however, the charge transfer rate is expected to be low. The charge seems to be maintained until the cluster becomes thermalized with the substrate, losing the high rotational and vibrational temperature of the cluster. Once the cluster is thermalized with the substrate, the temperature of the cluster might not overcome the activation barrier of the transformation from diamond to graphite. As a result, the diamond structure seems to be maintained even after the charge is transferred to the silicon substrate or to the gas phase.

As in the case of an iron substrate, the clusters attached on the substrate have a very high curvature and will exert a high electric field gradient, attracting the other clusters in the gas phase. Because of the slow charge transfer rate to the silicon substrate, the aspect of the charged cluster landing will resemble that of the repulsion-dominant colloid suspension. The highest packing density that can be achieved by the repulsion-dominant packing for the spherical hard sphere is 74%. There are two possibilities for the evolution of the dense diamond film by the clusters. One is that the diamond cluster is not spherical but faceted and the packing density of the faceted shape can be almost 100% if a proper arrangement is achieved. The other is that the cluster has a high rotational and vibrational entropy and it can stick almost homoepitaxially to the neighboring crystal as long as the temperature is sufficiently high.

The epitaxial sticking will be possible only for small clusters. For relatively large ones, it will be difficult. When the sticking is slightly non-epitaxial, twins or stacking faults will be evolved, which might be related to the TEM observations [54,55] of high densities of twins and defects in the diamond prepared by the gas-activated CVD process. When the sticking is highly non-epitaxial, a high angle grain boundary will be formed, resulting in polycrystalline growth.

When most of the clusters stick non-epitaxially due to the large size, the microcrystalline diamond, which is often called the cauliflower structure or the ball-like diamond [1,56], would be evolved. These microstructures evolved when the methane concentration is high and thus the cluster size is expected to be large.

In relation to the charge transfer rates, the data of the charge transfer rates for some materials are established in the field of the electrochemistry. In the case of the hydrogen evolution reaction, the electrode materials, in the order of decreasing charge transfer rate, are Pd, Pt, Rh, Ir, Ni, Fe, Au, W, Ag, Nb, Mo, Cu, Ta, Bi, Al and Ti [37]. We found that the substrate materials making soot in the CVD diamond process correspond to the materials having a high charge transfer rate in electrochemistry. The correlation is very high. Pd [57], Pt [57,58], Rh [57], Ir [57] Ni [58,59] and Fe [59] are the substrate materials making soot or a non-diamond phase while Au, W, Mo, Cu, Ta, Ag, Nb [4,57,60,61], Al [62] and Ti [63] are the substrate materials making diamond. Bi has too low a melting point to be used as a substrate.

Finally, we tried to find reports of crystal growth by the cluster unit in the literature. We found two of them. First, a situation very similar to the charged cluster model was described by Glasner and Tassa [64], who studied the effect of the halogeno-plumbate complex ions $[PbX_6]^{4-}$ on nucleation and crystallization of KBr and KCl solutions. By adding the halogeno-plumbate complex ions, they thought, at first, that the nucleation was suppressed because they could not observe the precipitation of KBr or KCl crystals. But they confirmed the invisible nuclei formation by a thermal method [64]. They referred to these invisible particles as bloc nuclei. They further suggested that the final crystals were built up from these bloc nuclei, which was proved by the Pb^{2+} content of the crystals.

Second, in studying the morphological evolution of the crystals Sunagawa [65] also suggested the possibility that the growth unit is neither atomic nor ionic but larger. Especially in line with the charged cluster model, Sunagawa suggested that the observed morphological differences among three types of diamond crystals, which are the natural, the high pressure synthetic and the CVD diamonds, were probably due to the differences in size of the growth unit.

11. Conclusion

From the nucleation energetics in the presence of charge and the phenomenological features in the CVD diamond process, we cannot rule out the possibility that charged nuclei should form in the gas phase. If charged nuclei form in the gas phase, the aspect of deposition would be drastically different from that by nucleation and growth on the substrate surface. Based on this possibility and other experimental implications, we suggested a charged cluster model, which has the following three features. First, the size of these clusters is balanced between the charge density and the amount of the precipitation of the solid carbon. Second, the unbalanced reduction of the surface energy between diamond and graphite can be achieved by the presence of charge. Third, the growth unit is not an individual atom but a cluster.

The previously reported characteristics of the CVD diamond process such as the dominant formation of diamond along the convex edge and the electric bias effect on the deposition can be explained consistently by the charged cluster model. The thermodynamic paradox of experimental observations that graphite was being etched while diamond was formed can also be approached successfully. The evolution of the porous graphitic soot on the iron substrate and the enhanced initiation of diamond on the graphitic soot on the iron substrate placed on a quartz plate can also be approached by the charged cluster model.

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