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Role of Charge Produced by the Gas Activation in the CVD Diamond Process

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Charged carbon clusters which are formed by the gas activation are suggested to be responsible for the formation of the metastable diamond film. The number of carbon atoms in the cluster that can reverse the stability between diamond and graphite by the capillary effect increases sensitively with increasing the surface energy ratio of graphite to diamond. The gas activation process produces charges such as electrons and ions, which are energetically the strong heterogeneous nucleation sites for the supersaturated carbon vapor, leading to the formation of the charged clusters. Once the carbon clusters are charged, the surface energy of diamond can be reduced by the electrical double layer while that of graphite cannot because diamond is dielectric and graphite is conducting. The unusual phenomena observed in the chemical vapor deposition diamond process can be successfully approached by the charged cluster model. These phenomena include the diamond deposition with the simultaneous graphite etching, which is known as the thermodynamic paradox and the preferential formation of diamond on the convex edge, which is against the well-established concept of the heterogeneous nucleation.

Key words : Diamond, Graphite, Charge, Nucleation, Capillary effect, Thermodynamics

I. Introduction

Although the low pressure synthesis of diamond has been intensively studied, the underlying principle for the formation of the metastable diamond is not understood yet.[1,2] Understanding the mechanism on the chemical vapor deposition (CVD) process of diamond should be the first step for the systematic approach of the process and for the application of its principle to other systems. The fundamental question in the low pressure synthesis of diamond[1,2] is how the metastable diamond forms dominantly over the stable graphite in the presence of the gas activation

One of the most popular explanation is the atomic hydrogen hypothesis suggested by the pioneering Russian scientists[3] in this field. According to the atomic hydrogen hypothesis, the kinetics of etching of graphite by atomic hydrogen is much higher than that of diamond, which makes possible the dominant formation of the metastable diamond over the stable graphite. This atomic hydrogen hypothesis is equivalent to saying that kinetics can go against thermodynamics, leading to the violation of the 2nd law of thermodynamics. In spite of this weak point, the atomic hydrogen hypothesis is strongly supported by the experimental observation[4,5] that diamond deposits on the graphite substrate while the graphite substrate etches simultaneously. The experimental observation that the less stable diamond deposits and the stable graphite etches is definitely against the thermodynamic concept and are known as the thermodynamic paradox.[2]

We previously suggested the charged cluster model,[6] which was based on the capillary effect of the small cluster. This model could successfully explain the diamond deposition with the simultaneous graphite etching without leading to the thermodynamic paradox.[7] The purpose of this paper is to describe the role of charge, which induces the gas phase nucleation and stabilizes the diamond cluster over the graphite one.

II. Capillary Effect of the Small Cluster

Any irreversible process such as the CVD diamond process should satisfy the 2nd law of thermodynamics. The CVD diamond process is the precipitation of diamond from the gas phase chemical reaction. The precipitation is the phase transition from gas to solid, in which the nucleation of the solid carbon from the gas phase is involved. In the nucleation stage, the high capillary pressure is built up inside the embryonic clusters. We previously showed that this capillary pressure is high enough to make diamond more stable than graphite in the nucleation stage and that the dominant nucleation of diamond over graphite is possible.[8,9]

From the view point of this capillary approach, the CVD diamond process is identical to the phenomenon of

the dominant formation of the metastable phase over the stable one when the stability is reversed in the nucleation stage. Zirconia particle is one example: the metastable tetragonal zirconia particles are formed dominantly over the stable monoclinic zirconia particles when they are precipitated from the liquid phase or the gas phase.[10] This phenomenon is relatively well-established based on the capillary effect of the small zirconia particle.[11] The dominant nucleation of the metastable phase over the stable one is general. Most of liquid droplets, when nucleated from the vapor phase, can be formed below the melting point. This phenomenon is known as the Ostwald stage rule.[12] A theoretical interpretation of this phenomenon was given by Stranski and Totomanow[13] based on the capillary effect in the nucleation stage.

The Gibbs Free energy of the formation of the solid particle from the gas phase is expressed as

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

where n is the number of atom contained in the solid particle, $\Delta\mu$ the driving force per atom for precipitation from the gas phase, σ the surface energy, Ω the atomic volume. We can write this expression for graphite and diamond. By equating them and solving for n, the following expression can be derived.

$$n^* = 36\pi\left\{\frac{\sigma^{dia}(\Omega^{dia})^{2/3} - \sigma^{gra}(\Omega^{gra})^{2/3}}{\Delta\mu^{dia\rightarrow gra}}\right\}^3 \quad (2)$$

where σ^{dia} and σ^{gra} are the surface energies of the stable and metastable phases, Ω^{dia} and Ω^{gra} the atomic volumes, and $\Delta\mu^{dia\rightarrow gra}$ the free energy change per atom between diamond and graphite. The crucial difference between carbon and zirconia systems is the number of atoms inside the particle that reverses the stability between the stable and the metastable phase. Estimation by Eq. (2) indicates that the stability between graphite and diamond is reversed for the particle size less than one nanometer while the stability between the monoclinic and the tetragonal zirconia is reversed for the much larger size of thousands of nanometer. This difference might be related to the fact that the dominant formation of the metastable tetragonal zirconia cannot be avoided in the precipitation from the liquid or the gas phase while the dominant formation of diamond is achieved only when the gas activation is adopted. Eq. (2) indicates that in order to stabilize diamond over graphite, n* should be increased. The atomic volume and the free energy change between diamond and graphite in Eq. (2) are not affected by the processing condition. The surface energy is the only parameter that can be affected by the processing condition. With the reported values of the related parameters in Eq. (2), n* is estimated to be around 350 at 1200 K. This means that for the carbon cluster containing the carbon atoms less than n*, diamond is more stable than graphite. When the critical nucleus of the solid carbon contains atoms less than n*, nucleation of diamond would be dominant over that of graphite.

This analysis of the capillary effect of the small cluster indicates that the dominant formation of the metastable diamond over that of the stable graphite can be approached by considering the capillary effect in the nucleation stage. This analysis based on the capillary effect does not violate thermodynamics and, in this respect, seems to be more sound than the atomic hydrogen hypothesis.

III. Role of the Gas Activation

The gas activation process is essential to the successful synthesis of the CVD diamond. Unless the gas activation is adopted, graphite forms dominantly over diamond From the viewpoint of the capillary thermodynamics in the nucleation stage, the gas activation is to increase the stability of the diamond cluster over the graphite cluster. Stabilization of diamond can be achieved by increasing n* in Eq. (2). And n* can be increased by the surface energy modification in such a way that the ratio of the diamond surface energy to that of graphite decreases.

At the constant temperature and pressure, there are two ways that the surface energy can be modified by the gas activation: adsorption and electrocapillarity. The former is described by the Gibbs adsorption equation[14] and the latter by the Lippmann equation.[15] The electrocapillarity is effective for the polarizable interface when the interface is electrified. Thus, one possibility is that the gas activation produces the species such as atomic hydrogen, whose adsorption on diamond decreases the surface energy more than its adsorption on graphite does. The other possibility is that the gas activation produces charges, whose attachment on diamond decreases the surface energy more than its attachment on graphite does. These two effects may be additive. The first possibility was suggested by Badziag *et al.*[16] and the second one by Hwang *et al.*[6]

It might be true that the atomic hydrogen is produced by the gas activation but at the same time, it is evident that the gas activation produces charges. It should be noted that plasma itself is maintained by the continuous production of charges and the hot filament is used as the electron sources. Thermodynamic analysis of the CVD diamond process indicates that the activity of carbon in the gas phase is higher than those of both graphite and diamond. That is, carbon in the gas phase is supersaturated with respect to its precipitation. When there exists supersaturation in the presence of abundant charges, the charge-induced nucleation is energetically highly probable. The charge-induced nucleation is well established in the Wilson cloud chamber[17] and the bubble chamber[18] experiments, where the track of the high

energy particles is revealed by the growth of the nuclei formed by the ion-induced nucleation. 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 the high energy particles.

Phenomenologically, it is well established that the charges enhance the nucleation. And abundant charges are produced by the gas activation in the CVD diamond process. Therefore, it seems to be essential that the possibility of charge-induced nucleation should be considered in the CVD diamond process. We will use the classical equation by Volmer[19] and Thomson,[20] who first investigated the charge-induced nucleation and showed that vapor molecules form stable clusters about all gaseous ions.

When the condensed phase is dielectric like diamond, the interface would be polarizable. The interface of the charged dielectric cluster will form an electric double layer, which will decrease the interfacial energy. According to this analysis, the free energy of the charged cluster can be written as

$$\Delta G = -\frac{4\pi}{3} r^3 \Delta\mu + 4\pi r^2 (\sigma - \sigma_d) + \frac{(ze)^2}{2r}\left(1 - \frac{\varepsilon_g}{\varepsilon_c}\right) \tag{3}$$

where r is the radius of the cluster and $\Delta\mu$, the free energy change between the gas and the condensed phase. σ and σ_d are the surface energy of the neutral cluster and the decrease of the surface energy by the electrical double layer, respectively. z is the total number of charge and e, the unit charge. ε_g and ε_c are the dielectric constants of the gas phase and the condensed phase, respectively.

This equation indicates that the charge affects the surface energy term and introduces the Coulomb energy term. The surface energy modification by the electrocapillary effect at the electrical double layer imposed by the charge is described by the Lippmann equation, which is

$$\left(\frac{\partial \gamma}{\partial V}\right)_{\text{const comp}} = -q, \tag{4}$$

where γ is the surface energy, V, the potential difference and q, the charge density. In order to obtain the expression for the effect of the charge on the surface energy, the functional dependence of the charge density on the potential difference should be known. Since Eq. (4) indicates that the charged interface is capable of storing charge, the capacitance of an electrified interface can be defined. In order to simplify the treatment, the electrified interfaces will be treated as the parallel-plate condenser. In that case, the potential difference across the condenser is[15]

$$V = \frac{4\pi d}{\varepsilon} q, \tag{5}$$

where d is the distance between the plates and ε is the dielectric constant of the material between the plates. In the electrocapillary curve, the surface energy is maximum when the excess charge is zero. Thus, by substituting Eq. (5) into Eq. (4), the following expression can be derived.

$$\sigma = \sigma_{max} - \frac{\varepsilon}{4\pi d}\frac{q^2}{2} \tag{6}$$

This equation is the simplified expression for the effect of the excess charge at the interface on the surface energy. Eq. (6) indicates that the surface energy reduction depends on the dielectric constant at the interface and the ability to store the excess charge at the surface. Dielectric diamond is expected to be much more favorable than the conducting graphite in reducing the surface energy by charge. Thus, the charge will increase the stability of the diamond cluster over the graphite cluster.

Though we cannot make a quantitative estimation of the surface energy decrease of the diamond cluster by this simplified treatment, we can conclude that the charge produced by the gas activation can result in the unbalanced reduction of the surface energy between diamond and graphite in the way that favors the stability of the diamond clusters. In Fig. 1, we assumed the decrease of the diamond surface from 10% to 30% and compare the stability between the diamond and the graphite clusters. The unreduced diamond and graphite surface energies used in Fig. 1 are 3.7 J/M^2 and 3.1 J/M^2, respectively. The calculation is based on thermodynamic condition of 1%CH_4-99%H_2, 1200 K and 2700 Pa.

This reduction in the surface energy will reduce the nucleation barrier and this effect would be additive to the reduction of the nucleation barrier by the Coulomb energy. Fig. 2 shows the effect of the Coulomb energy term on the nucleation curve for the singly, doubly and triply

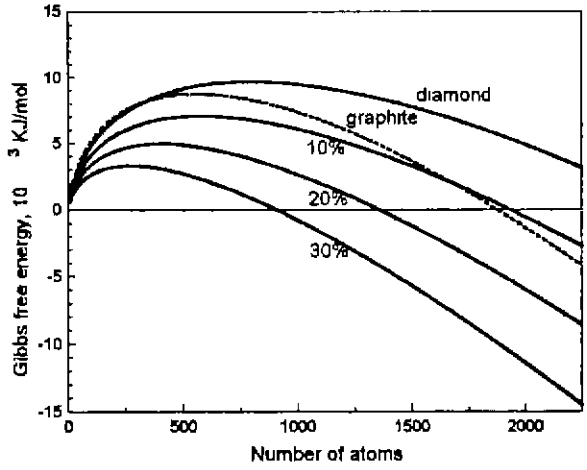

Fig. 1. Plots of the Gibbs free energy versus the number of atoms. Solid lines denote the free energies of diamond for 0%, 10%, 20%, and 30% reduction of the surface energy and a dashed line denotes the free energy of graphite.

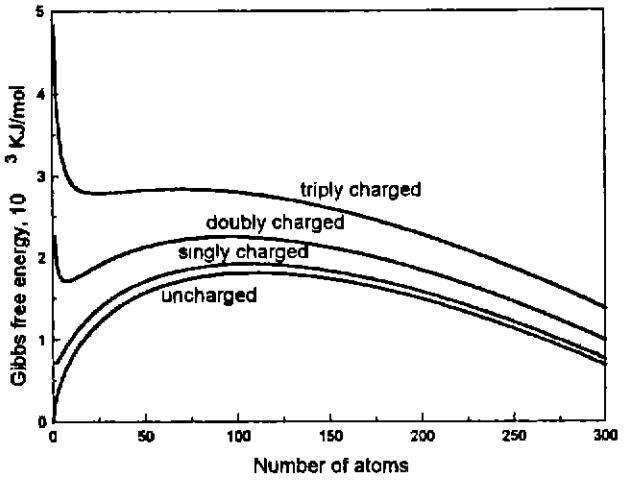

Fig. 2. Plot of the Gibbs free energy versus the number of atoms for the uncharged, singly charged, doubly charged, and triply charged clusters.

charged clusters, which are compared with that of the uncharged cluster. The surface energy, 2.59 J/M^3, which is the 30% reduction of the reported value, is used. And the supersaturation ratio used is 19.8, which is determined by the gas mixture of 1%CH_4-99%H_2 at 1350 K and 2700 Pa.[9]

Eq. (6) indicates that the surface energy is maximum when there is no excess charge at the surface. However, it is known that most of the surfaces are electrified more or less and the surface with no excess charge is rather exceptional. For example, the neutral water droplet is negatively electrified at the outer surface. Thus, the surface energy of the neutral cluster is not necessarily maximum. In this sense, the presence of charge can even increase the surface energy; this happens when the negatively electrified surface is attached by the positive charge. In this case, the surface energy will increase to its maximum then decrease with increasing amount of charge. Thus, the stability and the nucleation barrier of the charged cluster can be affected by the sign of the charge. Since it is known that the positive bias on the substrate favors the good quality diamond in the CVD diamond process,[21] the sign of the charged diamond cluster is expected to be negative. We expect that the positive cluster is the non-diamond phase and has a higher nucleation barrier. It is known that the pretreatment by the negative bias with the high methane concentration is known to induce the very high nucleation density of diamond.[22] This might be due to the formation of the non-diamond carbon layer, which can enhance the nucleation of diamond. It is known that any form of carbon enhances the nucleation of diamond. In the charged cluster model, the landing of the charged diamond cluster will enhance the formation of diamond on the substrate. This landing seems to be difficult because of the Coulomb repulsion. Any form of carbon, which consists of the same element as the diamond cluster, might have the high van der Waals attraction, and would enhance the landing of the charged diamond cluster in the gas phase.

If our expectation that the positive non-diamond cluster has the higher activation barrier is correct, the carbon supersaturation in the gas phase should be reduced in order to minimize the precipitation of the non-diamond cluster and maximize the precipitation of the negative diamond cluster with the small nucleation barrier. The supersaturation of carbon increases when the reactor pressure decreases for the fixed ratio of methane and hydrogen. The quality of diamond goes worse with decreasing the reactor pressure in agreement with our expectation. On the other hand, if the carbon supersaturation is increased for the same reactor pressure, the total amount of precipitation of carbon also increases, leading to the large cluster size. When the cluster size increases, two effects can result. First, the larger the cluster size, the less the rotational and vibrational entropy the cluster has, which makes it difficult to make the epitaxial sticking of the diamond cluster on the growing diamond film. It is known that the clusters below some magic size have the extraordinarily high diffusion rate.[23] If ideal epitaxial sticking fails, the defect formation such as twins or the stacking faults will form during growth by the growth unit of cluster. When the cluster size increase still further, the epitaxial sticking completely fails and each cluster will have the different orientation with others, which can result in the nano-crystalline structure. We believe that the evolution of the bad quality of the diamond film such as the cauliflower, the ball-like structures and the microcrystalline diamond, which are formed usually when the methane concentration is high, is due to the large cluster size.

IV. Behavior of the Charged Cluster

The coarsening behavior of the clusters would also be affected by the presence of charge. And this effect is also essential to the successful synthesis of the CVD diamond. If the charge-induced nucleation takes place in the gas phase, the coarsening behavior of the resultant charged nuclei would be quite different from that of the neutral clusters. The neutral clusters tend to coagulate each other, leading to the macro particles. However, the coagulation of the charged clusters tends to be prevented by the Coulomb repulsion. As a result, the charged clusters remain as the fine clusters and can maintain its high capillary pressure.

The size of the individual charged clusters is determined by the relative amount of the total solid carbon and the total charges. The free energy change for the surface energy reduction drives the coarsening of the individual clusters but the free energy change for the Coulomb energy tends to maximize the surface area of the charged clusters in order to reduce the charge den-

sity and as a result, tends to minimize the size of the individual clusters. The size of charged clusters would be balanced between the surface energy and the Coulomb energy. The free energy of the 'N' clusters, which precipitated from the gas phase and have the monosized radius 'r', is composed of the surface energy term and the Coulomb energy term as

$$\Delta G = N 4\pi r^2\sigma + N\frac{(z/N)^2}{2r}\left(1-\frac{\varepsilon_g}{\varepsilon_c}\right) \tag{7}$$

with the following two constraints.

$$z = \sum_i e_i \tag{8}$$

and

$$V = N\frac{4\pi}{3}r^3, \tag{9}$$

where 'z' is the total charge of the system and 'V' the total volume of the precipitated clusters. Here we assume that the clusters are monosized and the total charge is equally distributed among the individual clusters. Though more exact solution for the distribution of the radii and the charge of the clusters can be evaluated numerically by the Lagrange method, the assumptions that we made here is for simplicity and for obtaining the analytical expression for the radius of the cluster which minimizes the Gibbs free energy. After eliminating 'N' from Eqs. (7) and (9), the following expression is obtained.

$$\Delta G = \frac{3V\sigma}{r} + \frac{2\pi r^2}{3V}z^2\left(1-\frac{\varepsilon_g}{\varepsilon_c}\right) \tag{10}$$

Eq. (10) indicates that the radius of the cluster should increase in order to minimize the surface energy term but should decrease in order to minimize the Coulomb energy term. By differentiating Eq. (7) with respect to 'r' and by setting the resultant equation zero, we find 'r' for the minimum of the Gibbs free energy, which is expressed as

$$r = \left(\frac{9V^2\sigma\varepsilon_c}{4\pi z^2(\varepsilon_c-\varepsilon_g)}\right)^{1/3} \tag{11}$$

and in terms of the number of atoms in the cluster, 'n',

$$n = \frac{3\sigma\varepsilon_c}{\Omega(\varepsilon_c-\varepsilon_g)}\left(\frac{V}{z}\right)^2 \tag{12}$$

In Eq. (12), Ω is the atomic volume. The number of atoms in the cluster increases to infinity when the dielectric constant of the condensed phase approaches that of the gas phase. Then, the Coulomb energy term disappears and only the surface energy term remains in Eq. (7). In this case, the Gibbs free energy becomes minimum when all the clusters coagulate into one large particle. 'n' in Eq. (12) is proportional to the surface energy and to the square of the ratio of the total cluster volume to the total charge.

By substituting Eq. (11) into Eq. (9), we can obtain the expression for the total number of the clusters as

$$N = \frac{z^2}{3V\sigma}\left(1-\frac{\varepsilon_g}{\varepsilon_c}\right) \tag{13}$$

The total number of the clusters is proportional to the square of the total charge for the given total volume of the clusters. These results indicate that the coarsening behavior and the size distribution of the charged clusters would be quite different from those of the neutral clusters. The charged cluster would not grow in an unlimited way but remain stable against the coagulation like a colloid suspension. These expressions are derived by considering only the Coulomb energy. The more advanced treatment considering the ion-induced dipole interaction[23] will be published elsewhere. From these analyses, we can say at least that while the flocculation of the neutral clusters would be fast, resulting instantaneously in the coarse particles, the flocculation of the charged ones would be slow.

In order to increase the stability of the diamond cluster, the size of the cluster should remain small during the process and this can be achieved by the presence of charge. In order to increase the growth rate of the diamond film, the total volume of the cluster should be large. But if the total volume of the charged clusters is large compared to the total charges, the size of the cluster will be large so that the diamond cluster will lose its stability and will transform into the non-diamond phase. Thus, in order to increase the growth rate of the good quality diamond film, the amount of charge as well as the amount of the carbon cluster in the gas phase should be increased. The amount of the charge can be increased by increasing the plasma density in the plasma CVD diamond process and the amount of the carbon cluster can be increased by increasing the carbon fraction in the input source gas or by increasing the CVD reactor pressure. It should be noted that these conditions are satisfied in the high density plasma CVD diamond process which achieves the high growth rate of the good quality diamond.[25]

V. Crystallization of the Charged Cluster into the Dense Film

The most difficult step in the charged cluster model is to explain how the charged diamond clusters crystallize into the 100% dense film. We will introduce the previous report on the evolution of the dense structure from the charged particles. Glasner and his colleagues[25-29] confirmed by the thermal method that the invisible nuclei were formed in the solution supersaturated with respect

to precipitation of KBr and KCl. They further confirmed by the Pb^{+2} content of the crystal that the final crystal was built up from these invisible nuclei. We think that the crystallization of the charged diamond cluster into the dense film is exactly the same phenomenon as that of Glasner and Tassa's. It was known that the addition of the lead compound retarded the nucleation and growth rate of KBr and KCl. Glasner and Kenat[26] measured the heat of crystallization by a systematic calorimetric study, which showed that the nucleation of KCl was enhanced rather than being suppressed by the presence of the lead ions. When no $PbCl_2$ was added, crystallization began at 7°C below the saturation temperature of KCl. On the other hand, in the case of 0.53 mg Pb^{+2} per 1000 g H_2O with 5.416 g of KCl, crystallization began at 4°C below the saturation temperature. From these measurements, they confirmed that the invisible nuclei of KCl were formed in the solution. Since the precipitation of KCl tended to be suppressed with increasing content of lead ions, they concluded that only the block nuclei exceeding the critical size would precipitate[26-29] Their most important conclusion was that the macro-crystal of KCl was formed by these block nuclei. They further observed that the perfection of crystallinity increased with increasing content of lead ions though the amount of precipitation was decreased. As will be explained below, these whole pictures suggested by Glasner and his colleagues are exactly the same as those of our charged cluster model.

Although the highest packing density of the monosized hard sphere is only 74%, 100% density can be achieved because the cluster is not a hard sphere but has the high vibrational and the rotational entropy. The sticking behavior of the charged clusters would be quite different from that of the neutral clusters. The interaction between the neutral clusters is dominated by the dispersion force (van der Waals attraction). On the other hand, both the attractive dispersion force and the Coulomb repulsion force are involved in the interaction between the charged cluster. Since the charged cluster is a kind of colloid suspension, the behavior of coagulation in the colloid system will be referred. In the colloid system, the behavior of the coagulation between the attraction-dominant and the repulsion-dominant particles is quite different; the first case is called the flocculation and the second the deflocculation.[30] When attraction is dominant, the particles undergoing the Brownian motion will stick to each other randomly, leading to a very porous packing. When repulsion is dominant, however, the particles cannot stick to each other randomly. Instead, they will highly selectively stick to the sites where the repulsive force can be overcome by the attractive force. These sites seem to be the corner, which is analogous to the kink site for atom. When the charged cluster selectively sticks to the corner, the highly ordered packing will be achieved. The porosity even after this ordered packing seems to be removed by the high vibrational and rotational motion of the small cluster, leading to the epitaxial sticking of the charged cluster.

As the size of the charged cluster increases, the vibrational and the rotational entropy decreases and the ideal epitaxial sticking will become difficult, leading to the formation of defects such as the stacking fault and the twin. When the size of the clusters increases further, the crystallinity will be lost, leading to the microcrystalline or the amorphous structure. Most of the atoms in the charged cluster are a part of the interface and when the epitaxial sticking is not achieved, the crystallinity will be lost. Another variable is the temperature. When the temperature is high enough, the vibrational and the rotational energy of the cluster will be high and the epitaxial sticking will be favored.

Another important factor is the charge transfer from the charged cluster. In order to continue the growth, the charge should be removed. In the system where the charge transfer is slow, the charge transfer can be the rate-determining step of the film growth. The charge can be removed along the growing surface to the earth or to the gas phase. The charge transfer to the gas phase will be enhanced by the CVD reactor pressure. When the plasma is in contact with the growing surface, the charge transfer to the gas phase will be relatively easy.

The time when the charge is transferred from the charged cluster would also be important. This is because when the charge is lost from the charged cluster, the electrocapillary effect by the charge will be lost and at the same time, the stability of diamond will be lost also. In that case, the diamond cluster can be transformed into the graphite cluster. This is important especially when the first diamond cluster lands on the substrate. In order to suppress the transformation, the temperature of the cluster should be low enough to suppress the thermal activation. Judging from the experimental observations, thermalization of the cluster with the substrate seems to be enough to suppress the thermal activation of the transformation.

When the diamond charged cluster loses its charge before its thermalization with the substrate, it can transform into the graphite cluster. This situation can take place for the substrate material which has the high charge transfer rate. We think that this happens for the substrate materials such as Fe, Ni, and Pt on which the graphite soot is formed. Fe, Ni and Pt are known as the electrode material having the high charge transfer rate in the hydrogen evolution reaction in the electrochemistry. We found out the very strong correlation between the substrate for the non-diamond formation and the electrode material having the high charge transfer rate. When the charge is lost from the charged cluster before it fits into the corner site, the random sticking is expected, leading to the porous graphite packing. As mentioned earlier, the very porous packing is expected

by the attraction-dominant charge-absent clusters while the densely ordered packing is obtained by the repulsion-dominant charge-retaining clusters. It should be noted that the soot evolved on the Fe, Ni and Pt is not only graphite but also very porous.

The first landing of the diamond cluster will determine the microstructure of the film such as smoothness of the surface. In the charged cluster model, the density of the particles which first land on the substrate corresponds to the nucleation density. One of the factors affecting this landing will be the electric image field which is formed as the charged cluster approaches the substrate. The gradient of this image field will be greatest for the sharp convex edge. The electric bias can enhance or retard the landing of the charged cluster on the substrate. It is well established in the CVD diamond process that the preferential site for the diamond formation is along the sharp convex edge[31,32] and the deposition behavior is affected by the applied electric bias.

Another factor affecting the landing on the substrate would be the magnitude of the attractive dispersion force between the charged cluster and the substrate. This force is normally expected to be greater for the homomolecule than for the heteromolecule, which means that any carbon-containing substrates will be good for the enhanced landing of the diamond charged cluster. It is also experimentally well established that the formation of diamond is enhanced on the carbon-containing substrate.

VI. Thermodynamic Paradox of Diamond Deposition and Simultaneous Graphite Etching

The charged cluster model predicts that the charge-induced nucleation should take place in the gas phase. The amount of the precipitated carbon clusters varies with the temperature because the solubility of carbon in the gas phase depends on the temperature. The temperature dependence of the solubility of carbon[7,33] indicates that the solubility is maximum at around 1500 K, at which the amount of the clusters will be maximum. In the hot filament CVD process, the temperature is highest at the filament and decreases toward the substrate. The substrate temperature ranges from 1000 K to 1300 K. Thus, a part of the clusters is expected to etch toward the substrate temperature by the atomic unit. Only an unetched portion of the clusters contributes to deposition. On the other hand, if the gas phase which has the minimum solubility at around 1500 K is supercooled to the substrate temperature, the gas is undersaturated with respect to carbon and will etch the solid carbon by the atomic unit. Thus, on the substrate surface, the deposition of diamond takes place by the cluster unit and etching of both diamond and graphite takes place by the atomic unit. From the macroscopic observation, the result is the diamond deposition with simultaneous etching of graphite if graphite is used as the substrate.

If the phenomenon of the diamond deposition with the simultaneous graphite etching is approached by the conventional nucleation and growth on the substrate, it leads to the thermodynamic paradox. The chemical potential is the universal criteria for the transfer of atoms between phases when the system deviates from the thermodynamic equilibrium. The diamond deposition and the simultaneous graphite etching mean that the chemical potential of carbon in diamond is lower than that in the gas phase and the chemical potential of carbon in graphite is higher than that in the gas phase. Therefore, the chemical potential of carbon in diamond is lower than that in graphite, which means that diamond is more stable than graphite, leading to the violation of the 2nd law. The only way that diamond can be more stable than graphite in the processing condition is the capillary effect when the small solid carbon particles are considered. But the graphite substrate has no appreciable capillary effect. Thus, in order to avoid the thermodynamic paradox, the gas phase nucleation of the diamond cluster is essential. It should be noted that unless the gas phase nucleation of the solid carbon took place, the driving force calculated in the C-H and the C-H-O systems[33] is not for etching but for deposition of the solid carbon at the substrate temperature for the thermodynamic condition of the process.

VII. Conclusion

In the CVD diamond process, the charge-induced nucleation is energetically favorable and as a result, the charged diamond cluster is expected to form. The various puzzling phenomena in the CVD diamond process, which cannot be explained by the conventional concept of nucleation and growth of diamond on the substrate, can be successfully approached by the charged cluster model.

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