

TOPICAL REVIEW

Charged nanoparticles in thin film and nanostructure growth by chemical vapour deposition

To cite this article: Nong-Moon Hwang and Dong-Kwon Lee 2010 *J. Phys. D: Appl. Phys.* **43** 483001

View the [article online](#) for updates and enhancements.

You may also like

- [\(Invited\) Role of Charges in Non-Classical Crystallization of Thin Films and Nanostructures in the Plasma CVD Process](#)
Nong-Moon Hwang
- [Thermal plasmas for nanofabrication](#)
Masaya Shigeta and Anthony B Murphy
- [Effects of catalyst-generated atomic hydrogen treatment on amorphous silicon fabricated by Liquid-Si printing](#)
Hiroko Murayama, Tatsushi Ohyama, Akira Terakawa et al.



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

TOPICAL REVIEW

Charged nanoparticles in thin film and nanostructure growth by chemical vapour deposition

Nong-Moon Hwang and Dong-Kwon Lee

National Research Laboratory of Charged Nanoparticles, Department of Materials Science and Engineering, Seoul National University, Sillim-dong, Gwanak-gu, Seoul 151-744, Korea

Received 2 August 2010, in final form 12 October 2010

Published 18 November 2010

Online at stacks.iop.org/JPhysD/43/483001

Abstract

The critical role of charged nanoclusters and nanoparticles in the growth of thin films and nanostructures by chemical vapour deposition (CVD) is reviewed. Advanced nanoparticle detection techniques have shown that charged gas-phase nuclei tend to be formed under conventional processing conditions of thin films and nanostructures by thermal, hot-wire and plasma CVD. The relation between gas-phase nuclei and thin film and nanostructure growth has not been clearly understood. In this review it will be shown that many films and nanostructures, which have been believed to grow by individual atoms or molecules, actually grow by the building blocks of such charged nuclei. This new growth mechanism was revealed in an attempt to explain many puzzling phenomena involved in the gas-activated diamond CVD process. Therefore, detailed thermodynamic and kinetic analyses will be made to draw the conclusion that the well-known phenomenon of deposition of less stable diamond with simultaneous etching of stable graphite should be an indication of diamond growth exclusively by charged nuclei formed in the gas phase. A similar logic was applied to the phenomenon of simultaneous deposition and etching of silicon, which also leads to the conclusion that silicon films by CVD should grow mainly by the building blocks of charged nuclei. This new mechanism of crystal growth appears to be general in many CVD and some physical vapour deposition (PVD) processes. In plasma CVD, this new mechanism has already been utilized to open a new field of plasma-aided nanofabrication.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Particle generation in the gas phase during chemical vapour deposition (CVD) has been a big issue in microelectronic processing because the particles might contaminate the device, affecting the yield, performance and reliability [1]. The source of contamination from the processing chamber has become increasingly important compared with that from a clean room as the feature size shrinks. Great effort has been made to prevent and minimize particle formation in the gas phase of a CVD reactor. In the microelectronic industry, the levels of particle contamination in the reactor have been monitored with either a wafer surface scanner or an *in situ* particle monitor (ISPM) sensor.

However, scientists began to find out that particles tend to be formed by nucleation in the gas phase inevitably during many thin film processes by CVD. In particular, in the plasma-enhanced CVD (PECVD) process, the generation of particles is relatively well known because the particles are frequently large enough to be visible to the naked eye. The particle-containing plasma is called a ‘dusty plasma’, which has been studied extensively for the last two decades [2–6].

Studies on the generation of particles in a non-plasma CVD process such as thermal CVD have been relatively rare because their size is generally much smaller than the wavelength of visible light and thereby invisible to the naked eye. A study on particle generation in thermal CVD was initiated by Adachi *et al* [7, 8], who used special apparatus for

nanoparticle detection, such as condensation particle counter (CPC) and differential mobility analyzer (DMA). To our understanding, the purpose of their study was to find out the processing conditions of film deposition where nanoparticles were not generated in the gas phase. However, what they found out was that the thin film processing condition where particles are not generated is rather difficult to find. After Adachi *et al*'s work, the generation of nanoparticles in the gas phase in the thermal CVD process has been studied mainly by scientists in the field of aerosol science and technology [9–15].

Crystal growth based on an atomic process is well established and described by the terrace, ledge and kink (TLK) model, where the atom adsorbs on a terrace, diffuses to a ledge and finally becomes incorporated in the crystal lattice at the kink [16, 17]. The selective accommodation of atoms at the kink results in atomic self-assembly, which produces a crystal structure with almost perfect regular arrays of atoms. This atomic self-assembly arises from the fact that the interaction between the atom and the crystal is repulsive on the terrace but attractive exclusively at the kink. However, if the building block becomes larger than an atom and its size increases progressively as a dimer, trimer, tetramer and so on, the self-assembly would become increasingly difficult. If the building block contains more than hundreds of atoms, the attraction would be dominant between the building block and the terrace of the growing surface. Then, the self-assembly would fail completely and a typical porous skeletal structure of diffusion-limited aggregation (DLA) would be produced.

Therefore, if gas-phase nuclei are electrically neutral, they tend to land randomly on the film. If the building block is electrically charged, however, the situation changes drastically because landing of the charged building blocks makes the growing surface charged and then the interaction between the charged building block and the charged growing surface has both van der Waals attraction and electrostatic repulsion. If the balance between the two is properly made, the charged building block would undergo self-assembly, producing a highly regular array of building blocks. This situation is similar to colloidal crystallization [18] except that the temperature is much higher in the CVD process, which appears to be favourable for dense and epitaxial crystallization.

According to our study for the past 15 years, many films and nanostructures prepared by CVD, which were believed to grow by individual atoms or molecules, actually grow by the self-assembly of charged nanoparticles formed in the gas phase, possibly combined with oriented attachments [19–22]. The epitaxial crystallization of charged nanoparticles on the growing surface is favoured with decreasing nanoparticle size and increasing substrate temperature. The grown films can hardly be distinguished from those grown by an atomic unit. This might be why people in the CVD community have believed the growth of thin films to occur by atomic units. To distinguish this new mechanism from the conventional atomic growth mechanism, it will be called the 'theory of charged nanoparticles' (TCN).

Exclusively, atomic growth in CVD is possible if the supersaturation is made low enough to inhibit the gas-phase nucleation. Then high quality films, which might

be comparable to those prepared by atomic layer deposition (ALD), can be obtained. However, the film growth rate would be typically less than a few nm/h, which is unacceptably low in many commercial CVD processes. This might be why most commercial CVD processes are done under the condition where the charged gas-phase nuclei are generated; the film growth rate by charged nanoparticles is typically more than two orders of magnitude higher than that by atomic growth. The quality of thin films assembled by charged nanoparticles may be poorer than that grown by atoms but fairly good to be used in many commercial applications.

More than 40 years ago, a concept similar to TCN was suggested by Glasner *et al* [23–26] during their study on the crystal growth of KBr and KCl in the presence of Pb^{2+} in an aqueous solution. In this case, nanometre-sized nuclei are formed in the solution and become the building blocks of the crystal. They confirmed the formation of these invisible nuclei in the solution by a thermal method, where the heat generated during cluster precipitation from the solution is measured. They showed that an almost perfect crystal grew by orderly packing or self-assembly of these nuclei with perfection of a crystal increasing with decreasing size of nuclei. Their suggestion was so revolutionary at that time that it received severe criticism [27] and has been neglected in the crystal growth community. Sunagawa [28, 29], who used to work with Glasner, made a similar suggestion that the growth unit of synthetic diamond is not an atom but a much larger unit.

More recently, a similar concept has been suggested in the plasma CVD process by Cabarrocas [30, 31], Vladimirov and Ostrikov [32], and Nunomura *et al* [33]. In the silane plasma CVD process, incorporation of crystalline silicon nanoparticles into the films produced a so-called polymorphous structure, which has better stability and electrical properties than amorphous films [30, 31]. Moreover, the building block of nanoparticles is utilized to synthesize various nanostructures by the plasma-aided nanofabrication technique [34, 35].

In the non-plasma process such as thermal and hot-wire CVD (HWCVD), however, the growth of thin films and nanostructures by charged nanoparticles has been much less known than in the plasma CVD process mainly because charged nanoparticles are invisible. As predicted by TCN, the generation of hypothetical charged nuclei has been confirmed experimentally in many CVD systems such as diamond [36–38], ZrO_2 [39], Si [40–42], carbon nanotubes [43, 44], ZnO nanowires [45] and silicon nanowires [46]. However, experimental confirmation on the generation of charged nanoparticles in the gas phase is not sufficient to say that the charged nanoparticles become a major building block of films and nanostructures grown by the CVD process. Therefore, the proof that films and nanostructures should grow by the charged gas-phase nuclei becomes crucial to the validity of the new growth mechanism. This proof turned out to be provided by the well-known puzzling phenomena of simultaneous diamond deposition and graphite etching during diamond CVD using the C–H system [47] and simultaneous deposition and etching of silicon during Si CVD using the Si–Cl–H system [48].

The purpose of this paper is to review the development and the application of the new crystal growth mechanism of

TCN with a building block of charged nanoparticles in the CVD process. Since this mechanism was developed in an attempt to explain many puzzling phenomena occurring in the low-pressure synthesis of diamond by CVD, the detailed thermodynamic and kinetic analyses will be provided with respect to the metastable growth of diamond. The focus will be on the thermodynamic paradox of simultaneous diamond deposition and graphite etching. After proving by a rigorous thermodynamic analysis that diamond and silicon CVD films should grow exclusively by charged nanoparticles, the easy microstructural criterion which distinguishes between atomic and nanoparticle depositions will be sought. For this, nanostructured films such as a cauliflower structure and nanocrystallites embedded in an amorphous matrix, which are frequently produced especially at a low substrate temperature in the CVD or even some physical vapour deposition (PVD) processes, will be analysed based on the conventional crystal growth theory in order to show that such microstructures cannot be formed by atomic growth. Finally, some applications based on this new mechanism will be introduced in the thermal, hot-wire and plasma CVD processes.

2. Charged nanoparticles as a building block of diamond crystals in gas-activated CVD

2.1. Dominant formation of metastable diamond over stable graphite

Since the low-pressure synthesis of diamond was reported by Derjaguin and Fedoseev [49] and by Spitsyn *et al* [50] in HWCVD and by Matsumoto *et al* [51] in plasma CVD, its underlying principle and process have been intensively studied [52, 53]. Although its process has been relatively well established [54, 55], its underlying principle has not been clearly understood [52, 56]. The fundamental question is why diamonds can be synthesized at a low pressure where graphite is more stable. The formation of a metastable phase is not limited to the CVD diamond but is observed in many systems [57–61]. For example, when nucleation from supercooled water vapour takes place below the freezing point of water, water is nucleated first and then, after appreciable growth, is transformed to ice [57]. Such phenomena, which had been observed so commonly in many solutions by Ostwald, were called ‘Ostwald stage rule’ [62]. On the other hand, metastable tetragonal zirconia is nucleated dominantly over stable monoclinic zirconia when precipitated from the gas phase or the solution [58, 59]. In these cases, a clear answer was made as to why the metastable phase is formed dominantly over the stable one.

The formation of the metastable phase is explained by the capillary effect of the small particles, particularly in the nucleation stage [58, 59]. The capillary pressure built up in the nuclei can be so large that the high-pressure phase of a smaller molar volume tends to become more stable than the low-pressure phase of a larger molar volume. If the capillary effect is roughly applied to the low-pressure synthesis of diamond with the spherical particle with a radius (r) of 1 nm and an isotropic diamond surface energy (σ) of 3.7 J m^{-2} [63], the

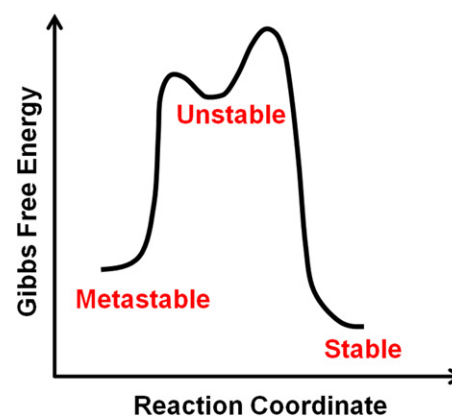


Figure 1. Thermodynamic and kinetic description of the metastable phase formation.

pressure (P) built up in the particle given by the Laplace equation ($P \cong 2\sigma/r$) becomes 7400 MPa. Under such a capillary pressure, the stability of diamond may be comparable to that of graphite.

The general concept of the metastable phase formation is schematically shown in figure 1 in terms of thermodynamics and kinetics. Since the Gibbs free energy of the stable phase is lower than that of the metastable phase, the driving force for the formation of the stable phase from the unstable one is higher than that for the formation of the metastable one. However, the kinetic barrier is a more important factor that determines the dominance of the formation since the formation of the stable and the metastable phases is a kinetically parallel process. Usually, such a kinetic barrier corresponds to the nucleation barrier.

Then, a question arises as to whether this general concept can also be applied to the formation of metastable diamond at a low pressure. To check this possibility, the nucleation barrier should be compared between graphite and diamond. The free energy of nucleation consists of the driving force for precipitation and the surface energy of the nucleus. For rough comparison, we will use the reported values of 3.7 J m^{-2} and 3.1 J m^{-2} , respectively, for isotropic surface energies of diamond [63] and graphite [64]. It should be noted that the surface energy of diamond is higher than that of graphite. And the driving force for the precipitation of diamond from the gas phase is smaller than that of graphite. Therefore, the free energy of diamond is higher than that of graphite in all ranges of radius as shown in figure 2(a). It appears that diamond becomes increasingly less stable than graphite as the size gets smaller. Judging only from figure 2(a), the diamond formation cannot be explained by the conventional approach of metastable phase formation. However, figure 2(a) can be misleading because the comparison of the free energy between diamond and graphite should not be made with respect to the radius but with respect to the number of atoms as shown in figure 2(b) [65]. It should be noted that even though the surface energy of diamond (3.7 J m^{-2}) is larger than that of graphite (3.1 J m^{-2}), the molar volume of diamond ($3.41 \text{ cm}^3 \text{ mole}^{-1}$) is much smaller than that of graphite ($5.405 \text{ cm}^3 \text{ mole}^{-1}$) and the surface energy multiplied by the molar area for diamond ($8.38 \times 10^{-4} \text{ J}$) is smaller than that of graphite ($9.55 \times 10^{-4} \text{ J}$).

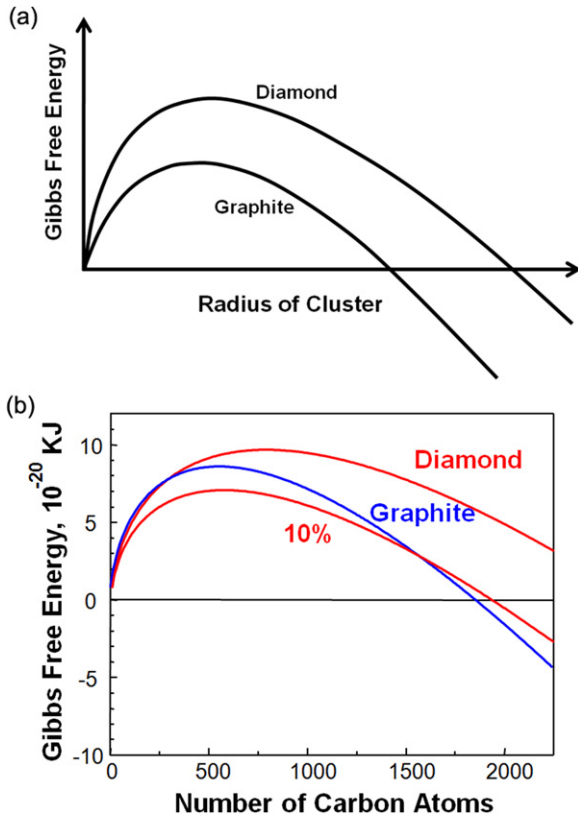


Figure 2. (a) Dependence of Gibbs free energy on the radius of diamond and graphite nuclei. (b) Dependence of Gibbs free energy on the number of atoms for diamond and graphite. Reprinted with permission from [65]. Copyright 1997 Elsevier.

The number of atoms at which the free energies of diamond and graphite intersect as shown in figure 2(b) can be derived as [66]

$$n^* = 36\pi \left(\frac{\sigma_{\text{dia}}(\Omega_{\text{dia}})^{2/3} - \sigma_{\text{gra}}(\Omega_{\text{gra}})^{2/3}}{\Delta\mu^{\text{dia} \rightarrow \text{gra}}} \right)^3, \quad (1)$$

where σ^{dia} and σ^{gra} are the surface energies of diamond and graphite, Ω^{dia} and Ω^{gra} the atomic volumes of diamond and graphite, respectively, and $\Delta\mu^{\text{dia} \rightarrow \text{gra}}$ the free energy change per atom between diamond and graphite. n^* for equation (1) is 351 for the reported surface energies, 3.7 J m^{-2} and 3.1 J m^{-2} of diamond and graphite, respectively. $\Delta\mu^{\text{dia} \rightarrow \text{gra}}$ is calculated to be $-1.2101 \times 10^{-20} \text{ J/atom}$, which is the chemical potential difference between diamond and graphite at 927°C .

In figure 2(b), the nucleation barrier of diamond is slightly larger than that of graphite, indicating that graphite would nucleate more dominantly than diamond. However, the difference of the nucleation barrier between diamond and graphite is only small. If the nucleation barrier of diamond was slightly smaller than that of graphite, diamond synthesis in the gas phase would be much easier than now. For example, oxygen-deficient combustion of oxyhydrocarbon materials such as fuel and wood could have produced diamond particles instead of graphitic soot particles.

In reality, graphitic or amorphous carbon is obtained without gas activation by a hot wire or a plasma. Gas activation

is necessary for the low-pressure synthesis of diamond. If we assume that the role of gas activation might be to reduce the surface energy of diamond, the nucleation of diamond can be more dominant than that of graphite. For example, if the surface energy of diamond is reduced by 10%, n^* in equation (1) becomes 1784 at 927°C . And the nucleation barrier of diamond becomes lower than that of graphite as shown in figure 2(b). Hwang *et al* [67] suggested that the stability of diamond nuclei relative to that of graphite nuclei in the gas-activated CVD process comes from the negative charge, which will be explained later in more detail.

Although quantitative values such as n^* in equation (1) estimated in this thermodynamic analysis may have some uncertainties because of the assumptions made, the overall concept would be valid. This analysis tells that the dominant nucleation of metastable diamond can be explained in a capillary concept similar to the dominant nucleation of metastable tetragonal zirconia. The difference between diamond and tetragonal zirconia is the size of the nuclei, where the stability changes between stable and metastable phases. This number is estimated to be 351 for diamond and graphite as shown in figure 2(b) but estimated to be more than hundreds of thousands of atoms for tetragonal and monoclinic zirconia [59]. This would be why the dominant formation of metastable tetragonal zirconia is a rule rather than exception but the dominant formation of metastable diamond is only possible under a special condition such as gas activation.

The size dependence of the stability between diamond and graphite has been studied experimentally by Fedosayev *et al* [64] and Bundy *et al* [68]. They observed that the nanodiamond that initially formed with a grain size below 3 nm transforms into graphite at a larger size. This problem was approached theoretically by many scientists [69–73]. Although the quantitative estimations of these treatments might not be valid, one clear conclusion can be drawn: the stability of diamond relative to that of graphite increases with decreasing size.

In the diamond CVD community, however, the ‘atomic hydrogen hypothesis’, which was suggested by Derjaguin *et al* [49, 74] and is quite different from the conventional approach of metastable phase formation, has been the most popular explanation. According to the atomic hydrogen hypothesis, atomic hydrogen, which is produced by gas activation such as a hot wire or a plasma, etches graphite much faster than diamond and therefore the low-pressure synthesis of metastable diamond is possible.

2.2. Atomic hydrogen hypothesis revisited

In order to understand the historical background as to why the atomic hydrogen hypothesis was suggested, we need to have some information about the old low-pressure synthesis of diamond by thermal CVD without gas activation, which was extensively studied by Eversole [75, 76] and Angus *et al* [77]. In this process, diamond seeds were used under the condition where the gas mixture of methane and hydrogen was decomposed by thermal CVD [77]. The implicit idea of this process is that even though diamond is less stable than graphite,

less stable diamond can grow on pre-existing diamond seeds because graphite needs to nucleate on them whereas diamond need not. In other words, only a growth barrier exists for diamond to grow on diamond seeds whereas an appreciable nucleation barrier exists for graphite to grow on them.

The idea is sound both thermodynamically and kinetically. However, this idea is valid only if the gas-phase nucleation does not take place. Once the gas-phase nucleation takes place, the nuclei would have a graphite structure. If the nuclei land on the diamond seeds as graphite debris, the entire surface of diamond seeds would be covered with graphite because the growth rate of graphite is much higher than that of diamond. Then, diamond cannot be grown any longer and the surface layer of graphite should be etched for further diamond growth. Therefore, the process is cyclic: deposition of diamond and etching of graphite.

If the supersaturation is too high, an avalanche of gas-phase nucleation would take place. If the supersaturation is too low, the growth rate of diamond would be too low. An optimum supersaturation can be made between the two extremes to produce the maximum growth rate of diamond. The obtained growth rate turned out to be $\sim 10 \text{ \AA h}^{-1}$, which is quite impractical for commercial applications. This is why this cyclic process of diamond synthesis had been studied only by a few scientists.

In order to increase the growth rate of diamond in this cyclic process, Derjaguin and Fedoseev [49] tried to increase the etching rate of graphite using atomic hydrogen. To produce atomic hydrogen, they used hot tungsten wires. While synthesizing diamond using hot wires, some unexpected results were obtained [49, 74, 78]. First, they could increase the growth rate of diamond more than 100 times as high as that of the old diamond CVD process. Second, they did not need to use the diamond seeds any more. They attributed such unexpected changes to atomic hydrogen, which etches graphite preferentially over diamond. This is our understanding on the background how the atomic hydrogen hypothesis was suggested.

However, the atomic hydrogen hypothesis has a critical weak point in that the irreversible transfer of carbon atoms violates the second law of thermodynamics [47, 56, 79]. The CVD process is thermodynamically an open system in that the deposited film, which is a system, exchanges a material with the gas phase, which is a surrounding. This concept is also widely used in the dusty plasma research [32, 80]. The criterion for the irreversible transfer of atoms between the system and the surrounding is the chemical potential of the species. The chemical potential of an atom is the partial derivative of the Gibbs free energy of the system with respect to the number of corresponding atoms under a constant temperature and pressure [81]. As atoms transfer from the region with a high chemical potential to the region with a low chemical potential, the total Gibbs free energy is decreased.

Since graphite is more stable than diamond under the condition of gas-activated CVD according to the phase diagram of carbon [79, 82], the chemical potential of carbon in diamond is higher than that in graphite, which can be written by the following inequality:

$$\mu_C^{\text{dia}} > \mu_C^{\text{gra}}, \quad (2)$$

where μ is a chemical potential, the subscript 'C' represents carbon and the superscripts 'dia' and 'gra' represent diamond and graphite, respectively.

It should be noted that reversible etching and deposition can occur simultaneously whereas irreversible etching and deposition cannot. Reversible etching or deposition is not driven by the chemical potential difference and does not produce a net flux whereas irreversible etching or deposition is driven by the chemical potential difference and produces a net flux.

The atomic hydrogen hypothesis says that graphite is etched by atomic hydrogen much faster than diamond and therefore less stable diamond can be deposited. Etching of a condensed phase into a gas phase means that the chemical potential of the element in a condensed phase is higher than that in a gas phase. Therefore, the irreversible graphite etching can be written as

$$\mu_C^{\text{gra}} > \mu_C^{\text{gas}}, \quad (3)$$

where the superscript 'gas' represents the gas phase. Similarly, the irreversible diamond deposition can be written as

$$\mu_C^{\text{gas}} > \mu_C^{\text{dia}}, \quad (4)$$

In this paper, etching and deposition refer to the irreversible process and those words will be used without the adjective 'irreversible'.

According to the atomic hydrogen hypothesis, inequations (3) and (4) should be simultaneously satisfied and can be written as

$$\mu_C^{\text{gra}} > \mu_C^{\text{gas}} > \mu_C^{\text{dia}}, \quad (5)$$

Inequation (5) produces the inequality of

$$\mu_C^{\text{gra}} > \mu_C^{\text{dia}}, \quad (6)$$

which says that diamond is more stable than graphite, being definitely contradictory with inequation (2).

According to the second law of thermodynamics, it is quite clear that if stable graphite should be etched, less stable diamond should be etched also. But this clear statement is contradictory with equation (5). The atomic hydrogen hypothesis implicitly assumes that the unbalanced etching rate between graphite and diamond can change the stability between graphite and diamond; it neglects the fact that the thermodynamic stability is not affected by kinetics. Simple thermodynamic analyses described above show that the atomic hydrogen hypothesis has a critical weak point.

Then, why is it so popular and widely accepted in the diamond CVD community? Vakil [83] measured the total solid carbon mass including the graphite substrate in gas-activated diamond CVD. The diamond content continuously increased while the total solid carbon mass continuously decreased by etching of the graphite substrate. The atomic hydrogen hypothesis was strongly supported by the experimental fact that diamond is synthesized with simultaneous etching of graphite [83–85]. These well-organized experiments seem to be regarded as evidence for the atomic hydrogen hypothesis. Considering such experimental observations, some people have a good reason to say that the atomic hydrogen hypothesis is not a hypothesis but an experimental fact.

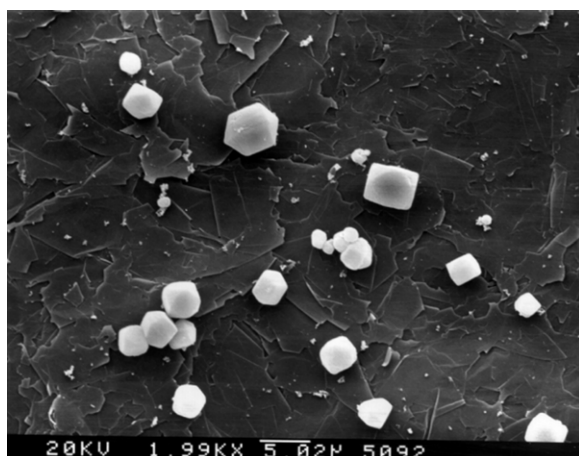


Figure 3. Microstructure showing diamond deposition with simultaneous graphite etching. Diamond was deposited on the graphite substrate at a hot wire temperature of 2100 °C and a substrate temperature of 1050 °C. The mass of the graphite substrate was 43.21 mg before deposition and 37.06 mg after deposition, being decreased by 6.15 mg although the diamond crystals were deposited on the graphite.

2.3. Diamond deposition with simultaneous graphite etching: thermodynamic paradox or not?

Figure 3 shows the microstructure of diamonds, which were deposited on a graphite substrate for 2 h under 2700 Pa at a wire temperature of 2100 °C and a substrate temperature of 1050 °C with a gas mixture of 1%CH₄–99%H₂. Comparing the mass of the graphite substrate before and after deposition, a mass of 6.15 mg was decreased during deposition although the diamond crystals were deposited on the graphite. Therefore, figure 3 reproduced the well-known result of diamond deposition with simultaneous graphite etching.

If the phenomenon of diamond deposition with simultaneous graphite etching is transcribed into the thermodynamic language, the two inequations (3) and (4) should be satisfied simultaneously, which leads to inequation (5). Again, the final conclusion of inequation (6), which says that diamond is more stable than graphite, is contradictory with inequation (2) dictated by the well-established phase diagram of carbon. This phenomenon can be represented by the diagram of figure 4, which shows the relative magnitude of carbon chemical potentials of diamond, graphite and gas, based on the implicit assumption that the irreversible carbon flux is delivered by individual atoms. Figure 4 shows that among the three phases of diamond, graphite and gas, diamond is the most stable phase with graphite being the least stable one.

This is a very interesting situation where the experimental observation is contradictory with the second law of thermodynamics. Great care and attention must be paid to disentangle such a paradoxical problem. It should be recalled that historically, a great discovery was often made from such a big contradiction. Since the second law of thermodynamics cannot be violated, there must be something wrong in our application of the second law to the experimental observation.

In order to see clearly the direction of an irreversible transfer of carbon atoms allowed by the second law of

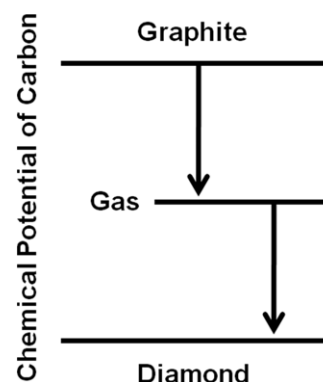


Figure 4. Diagram of chemical potentials of carbon for diamond, graphite and gas, related to the direction of carbon flux according to diamond deposition with simultaneous graphite etching based on atomic deposition.

thermodynamics, the chemical potential diagrams are drawn in figure 5 for the three possible stabilities among diamond, graphite and gas under a low pressure. Figures 5(a), (b) and (c) show the direction of the carbon flux delivered by individual atoms when the chemical potential of carbon in gas is highest, between diamond and graphite and lowest, respectively. Figure 5(a) shows that if less stable diamond should deposit, stable graphite should deposit also. Figure 5(b) also shows that graphite deposition with simultaneous diamond etching is possible, which is opposite to the experimental observation of diamond deposition with simultaneous graphite etching. Finally, figure 5(c) shows that if stable graphite should etch, less stable diamond should also etch.

Because of the unbalanced etching rate between diamond and graphite, the etching rate of graphite can be much higher than that of diamond, whose aspect is represented in figure 5(c) by thickening the line of graphite etching. Any case of figures 5(a), (b) and (c) does not allow for diamond deposition with simultaneous graphite etching. Therefore, it is quite obvious that the experimental observation appears to be contradictory with the second law of thermodynamics.

In approaching such a puzzling problem, something, which appears to be absurd or strange, should be identified. In the experimental observation of diamond deposition with simultaneous graphite etching, one strange thing is that in the gas-activated diamond CVD, we supply methane concentration high enough to deposit the condensed phase of carbon, which can be diamond, graphite or other carbon allotropes such as amorphous carbon, C₆₀ or carbon nanotubes. Then, why does graphite etch away into the gas phase under the condition that the thermodynamic driving force is clearly for deposition of graphite?

In order to understand this situation, the CVD phase diagram of the C–H system shown in figure 6(a) should be examined [47]. In figure 6(a), the diamond and graphite lines indicate the solubility of carbon in the gas phase in equilibrium with diamond and graphite, respectively. The metastability of diamond with respect to graphite is represented by the fact that the diamond line is inside the graphite line. For example, outside the graphite line, the single phase of gas is

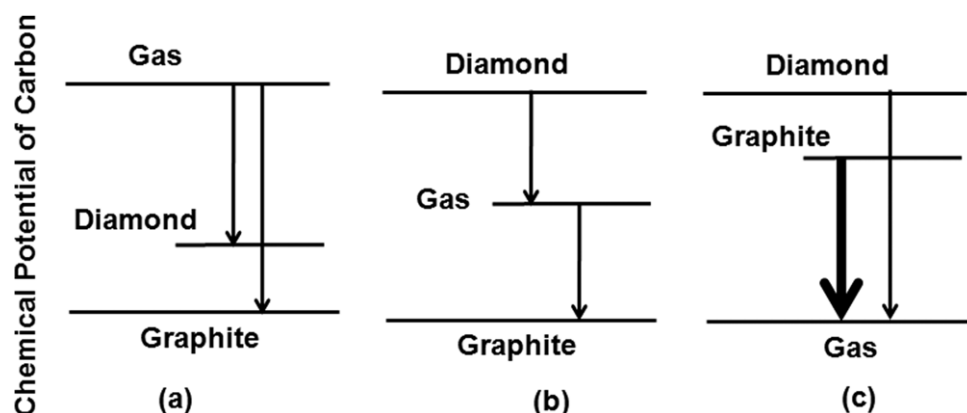


Figure 5. The direction of carbon atoms allowed by the second law of thermodynamics when the chemical potential of carbon in gas is highest (a), between diamond and graphite (b) and lowest (c).

stable and inside this line, the two phases of gas and graphite are stable with diamond being metastable inside the diamond line. The composition of 1%CH₄–99%H₂, which corresponds to the atomic fraction of carbon, 0.00493, falls in the two phase region of gas + solid below ~1730 °C and ~2030 °C, respectively, for diamond and graphite. This composition is shown as the vertical line in figure 6(a). The methane concentration range, typically used in the CVD diamond process, is 0.5–3%. In this composition range, the driving force is for deposition of both graphite and diamond in the substrate temperature range 730–1070 °C.

The notable feature in the CVD phase diagram of the C–H system in figure 6(a) is that the solubility of carbon in the gas phase is minimal around 1230 °C and then increases with decreasing temperature. The increase in carbon solubility with decreasing temperature below ~1230 °C indicates that the equilibrium amount of carbon in the gas phase increases with decreasing temperature. This aspect can also be revealed by the temperature dependence of the equilibrium amount of precipitation of solid carbon from the gas mixture of 1%CH₄–99%H₂ at 2700 Pa as shown in figure 6(b) [47]. The equilibrium amount of solid carbon, which is maximal at ~1230 °C, decreases with decreasing temperature below ~1230 °C.

Considering figure 6, the experimental fact of graphite etching under the condition of the driving force for deposition can only be explained by assuming that gas-phase nucleation occurs in the diamond CVD reactor. If gas-phase nucleation does not occur with the gas mixture of 1%CH₄–99%H₂, the carbon concentration in the gas phase would be represented by the vertical line in figure 6(a). Under this condition carbon in the gas phase is supersaturated and thus the driving force is for the precipitation of solid carbon. If gas-phase nucleation occurs, however, the carbon concentration in the gas phase would follow the solubility line in figure 6(a).

Let us examine what would happen when gas-phase nucleation occurs in the CVD diamond reactor. In the reactor, there exists a steep temperature gradient between the hot wire and the substrate, which are only ~1 cm away from each other. In this steep temperature gradient, if the gas phase drifted from the high-temperature region near the wire towards the low-temperature region near the substrate, the gas phase should

etch solid carbon. The reason is that when the gas with a minimal solubility of carbon at ~1230 °C reaches the substrate at a lower temperature, the gas becomes deficient of carbon because its equilibrium solubility of carbon is much higher at a lower temperature as shown in figure 6(a). Similarly, if the gas-phase nuclei move from the high-temperature region near the wire towards the low-temperature region near the substrate, some of them should be etched because their equilibrium amount of precipitation is maximal at ~1230 °C and becomes much lower at lower temperatures as shown in figure 6(b).

Therefore, the driving force becomes for etching or for deposition, depending on whether gas-phase nucleation occurs or not. This aspect can be understood more clearly by the chemical potential diagram. If gas-phase nucleation does not occur, the chemical potential diagram would be figure 5(a), where the driving force is for deposition of both diamond and graphite. If gas-phase nucleation occurs, however, the chemical potential diagram would be figure 5(c), where the driving force is for etching of both diamond and graphite. If these analyses are correct, gas-phase nucleation should take place in the diamond CVD process. Therefore, the experimental verification of gas-phase nucleation in the gas-activated diamond CVD process is critical to the validity of the conclusion that etching of graphite in the diamond CVD process should be due to gas-phase nucleation.

2.4. Experimental verification of gas-phase nucleation in the diamond CVD process

Hwang *et al* [47,67,79,86] suggested that gas-phase nucleation was predicted not only by graphite etching but also by many other experimental results in the gas-activated diamond CVD process. In an effort to confirm experimentally the existence of gas-phase nuclei, Jeon *et al* [36] attached an energy analyzer combined with a Wien filter to the hot wire diamond CVD reactor. Because a relatively high vacuum (<~0.001 Pa) is required for Wien filter measurements but a moderate vacuum (800–4000 Pa) is used for diamond CVD, differential pumping was done through an orifice (1.2 mm $\varnothing$) and a skimmer (2 mm $\varnothing$) between the measuring chamber and the CVD reactor, where $\varnothing$ represents the diameter.

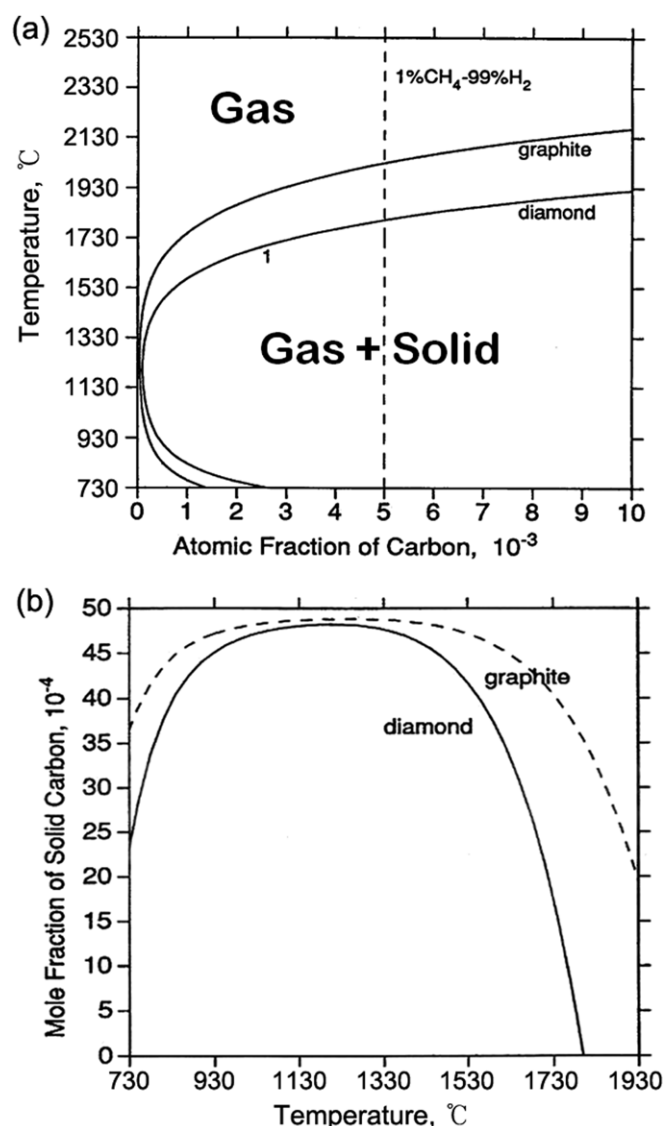


Figure 6. (a) The CVD phase diagram of the C–H system under 2700 Pa. The graphite and diamond lines indicate the maximum solubility of carbon in the gas phase. Outside this region, the single phase of gas is stable and inside this region, the two phases of gas + solid are stable. The vertical dashed line indicates the composition of the gas mixture of 1%CH₄–99%H₂, which is typically used in the gas-activated diamond CVD process. (b) The calculated temperature dependence of the equilibrium mole fraction of solid carbon under the same condition as (a). Reprinted with permission from [47]. Copyright 1996 Elsevier.

Using such a specially designed system, they could measure the size distribution of negatively charged carbon nanoparticles suspended in the gas phase as shown in figure 7 [36]. The measurement was done under the processing condition of a gas mixture of 1.5%CH₄–98.5%H₂, a reactor pressure of 800 Pa and a wire temperature of 2100 °C. The peak occurred at ~3000 atomic mass units, which corresponds to ~250 carbon atoms. Based on the negative current measured on the Faraday cup, they estimated the number density of negatively charged nuclei as ~10⁶ mm⁻³.

In a subsequent study, Jeon *et al* [38] observed that the size distribution of negatively charged gas-phase nuclei

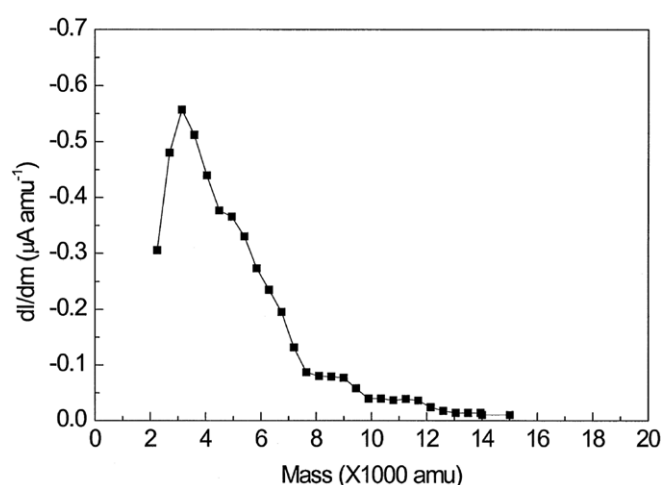


Figure 7. Mass distribution of negatively charged carbon nanoparticles suspended in the HWCVD reactor. The mass distribution was measured by the Wien filter combined with an energy analyzer after extracting the gas from the HWCVD reactor through the orifice into the measuring chamber. Reprinted with permission from [36]. Copyright 2000 Elsevier.

was affected by the methane concentration. Although the measurement of the size distribution confirms gas-phase nucleation, it does not tell which structure the gas-phase nuclei have. Using the oxyacetylene diamond CVD process, Ahn *et al* [37] tried to capture the hypothetical gas-phase nuclei on a silica amorphous membrane with a molybdenum grid placed on a water-cooled copper tube. They found that the gas-phase nuclei of ~1.5 nm captured on the amorphous membrane in a gas mixture of acetylene-to-oxygen ratio 1.04 were mostly amorphous with a few having a diamond lattice. Amorphous nuclei on an amorphous membrane do not necessarily mean that they have the amorphous structure in the gas phase. The small nuclei tend to accommodate their structure to the surface structure on which they land. Therefore, even though the gas-phase nuclei have a diamond structure, they can transform to the amorphous structure after landing on the amorphous membrane. The gas-phase nuclei larger than 5 nm captured at an acetylene-to-oxygen ratio of 1.09 were mostly graphite with a minor fraction of diamond.

There are many other reports on gas-phase nucleation in the diamond CVD process although these studies did not relate the gas-phase nucleation to the growth mechanism. Gas-phase nucleation in the diamond plasma CVD process was reported by Mitura in RF plasmas [87], Frenklach *et al* in microwave plasmas [88], Chonan *et al* in dc arc plasmas [89] and Gries *et al* in microwave plasmas [90]. The gas-phase nucleation in the diamond CVD process seems to be general.

2.5. Diamond deposition with simultaneous graphite etching: evidence of diamond deposition by gas-phase nuclei

Therefore, graphite etching can be understood by combining the C–H phase diagram of figure 6(a) and the experimental result of gas-phase nucleation, such as figure 7. The corresponding chemical potential diagram should be figure 5(c). According to figure 5(c), if stable graphite is etched

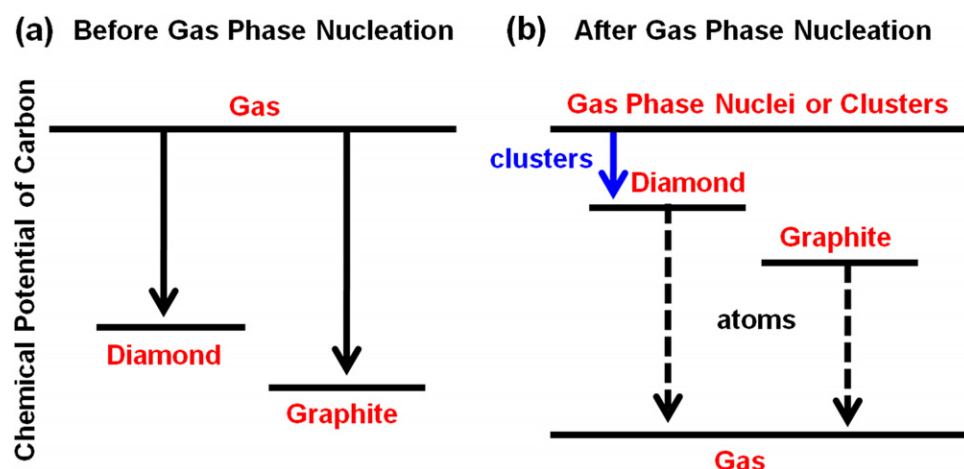


Figure 8. The chemical potentials of carbon in diamond, graphite and the gas phase before and after gas-phase nucleation. The arrows indicate the paradox-free direction of carbon flux.

as a result of gas-phase nucleation, less stable diamond should also be etched. However, this prediction of diamond etching is contradictory with experimental observation of diamond deposition as shown in figure 3. How can we solve this contradiction?

The only possibility that we can think of is that the contradiction comes from our implicit assumption that the building block for diamond deposition is an individual atom. The thermodynamic analysis of figure 5(c) predicts that diamond should be etched away atomically into a gas phase. If the gas-phase nuclei, which were experimentally confirmed as in figure 7, contribute to diamond deposition, the contradiction disappears. In this scenario, both diamond and graphite are etched away atomically but at the same time diamond is deposited by gas-phase nuclei. Macroscopically, what we observe is diamond deposition with simultaneous graphite etching. This scenario provides the paradox-free transfer of carbon flux for the phenomenon of diamond deposition with simultaneous graphite etching. Therefore, the puzzling phenomenon provides strong evidence that the diamond deposition should occur by the building blocks of gas-phase nuclei.

Figure 8 shows the paradox-free direction of carbon flux before and after gas-phase nucleation. Before gas-phase nucleation, the gas phase is supersaturated with respect to precipitation and has the driving force for deposition of both diamond and graphite (figure 8(a)). After gas-phase nucleation, however, the gas phase is undersaturated and has the driving force for etching of both diamond and graphite (figure 8(b)). Under such conditions the diamond gas-phase nuclei can contribute to deposition.

The diamond deposition by gas-phase nuclei may explain another puzzling phenomenon that the graphite substrate is good for initiation and growth of diamond in the gas-activated diamond CVD process [53]; most solid carbon is known to be a good initiator. Figure 3 shows a typical example of diamond formation on the graphite substrate. From the viewpoint of crystal growth based on atomic or molecular building blocks, graphite would be the worst substrate for diamond deposition, considering that diamond and graphite should compete with

each other in nucleation and growth. The reason why a diamond seed was used in the old diamond CVD process not using gas activation is that the growth barrier of diamond on a pre-existing diamond seed is lower than the nucleation barrier of graphite on diamond. For the same reason, the growth barrier of graphite on a pre-existing graphite substrate would be lower than the nucleation barrier of diamond on graphite because the graphite substrate would act as a graphite seed. On the other hand, this puzzling phenomenon can be explained if diamond grows by the deposition of gas-phase nuclei formed in the gas phase.

Then a question arises as to what the relative percentage of deposition flux would be between gas-phase nuclei and atoms. The atomic contribution to diamond deposition is negative because etching occurs atomically under the condition of gas-phase nucleation. This means that the flux for diamond deposition comes mainly from the gas-phase nuclei. In other words, diamond crystals grow mainly by the building blocks of gas-phase nuclei. From this conclusion, some additional information can be derived. First, most of the gas-phase nuclei should have a diamond structure. Second, they undergo perfect self-assembly into macro diamond crystals without leaving any void. Third, they should undergo epitaxial landing on the growing surface of diamond. Each of these aspects will be treated in more detail in the following sections.

2.6. Diamond deposition on a silicon substrate and graphitic soot deposition on an iron substrate

Another puzzling phenomenon in the diamond CVD process is that diamond films or crystals grow on a silicon substrate while highly porous and skeletal graphitic soot particles grow on an iron substrate under the same deposition conditions as shown in figure 9 [67]. Likewise, carbon nanotubes deposit on a palladium substrate [91] and on a nickel–chromium substrate [92]. These results imply that the deposition mechanisms of diamond, soot and carbon nanotubes should be closely related to one another. Therefore, if the growth mechanism of diamond and soot is understood, that of carbon nanotubes may also be understood.

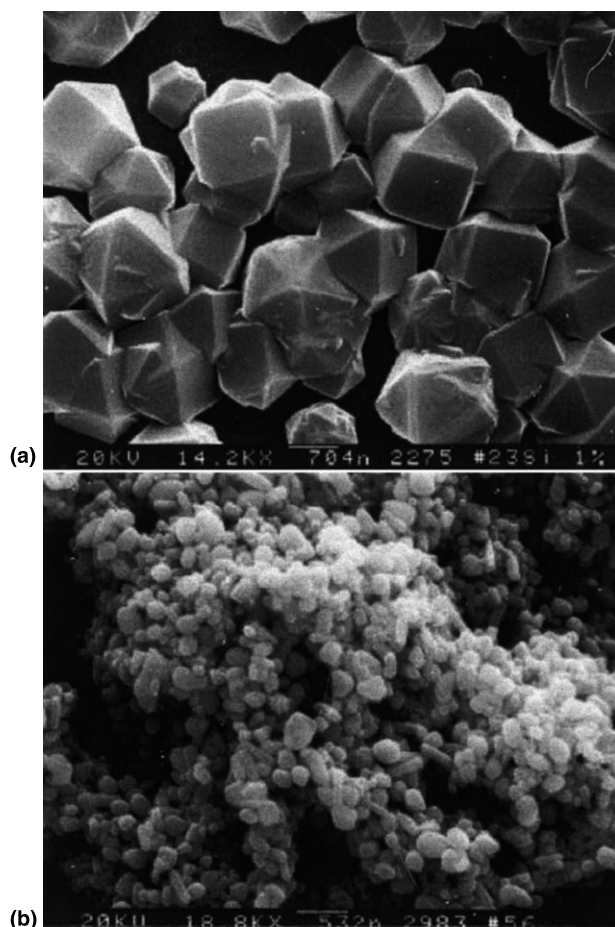


Figure 9. (a) Diamond deposited on a silicon substrate and (b) soot deposited on an iron substrate with 1%CH₄–99%H₂ gas mixture for 2 h at a substrate temperature of 990 °C under 2700 Pa (SEM): substrates were placed side by side during hot wire diamond CVD. Reprinted with permission from [67]. Copyright 1996 Elsevier.

Soot is porous and skeletal, being very fragile and weakly connected. It can be very easily rubbed by fingers, which means that the bonding between soot particles is not made by atomic or molecular bonding but by weak van der Waals bonding between particles. The morphology of soot is like the powder compacts formed by landing of particles, which were formed in the gas phase in the conventional CVD process [93]. This structure cannot be grown by atoms and molecules either through two-dimensional (2D) nucleation or on ledge-generating sources such as a screw dislocation. The microstructure of soot in the diamond CVD process is similar to that of soot observed in the combustion and flame process, where the formation mechanism of soot has been extensively studied [94–97]. 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 [96, 97]. In the field of combustion and flame, the formation of soot is explained by the ionic mechanism, which says that soot is aggregates of charged carbon nanoparticles after losing their charges [94–97].

If the formation mechanism of soot in the field of combustion and flame is applied to the soot formation in the diamond CVD process, charged carbon nanoparticles should

exist in the gas phase, which was already experimentally confirmed in the HWCVD process as shown in figure 7. Therefore, the porous and skeletal structure of soot on an iron substrate in figure 9(b) must be formed by landing of charged gas-phase nuclei. Then, a question arises as to how diamond crystals grow on a silicon substrate under the same conditions where such porous and graphitic soot grows on an iron substrate.

To explain such drastically different microstructure evolutions on silicon and iron substrates in figure 9, Hwang *et al* [67, 86] suggested a scenario called ‘charged cluster model’. In this scenario, negatively charged diamond nuclei are suspended in the gas phase like nanometre-sized colloidal particles. The stability of diamond comes from both the capillary effect and the negative charge. Therefore, if the charge is lost from the diamond nuclei, they transform immediately to graphite nuclei.

In order to understand the deposition behaviour of charged nanoparticles on silicon and iron substrates, the sedimentation behaviour of charged nanoparticles in colloid chemistry should be considered [98–100]. Since the growth of diamond and soot by the building block of charged nanoparticles is most similar to colloidal crystallization, its features will be explained. Nanoparticles have a random Brownian motion by their thermal energy. Sedimentation behaviour of colloids depends on the balance between van der Waals attraction and electrostatic repulsion. When the van der Waals attraction is dominant, they undergo random Brownian coagulation, which is called ‘flocculation’, producing a fractal structure by DLA [101].

When the electrostatic repulsion is dominant, they undergo slow flocculation or ‘deflocculation’, which produces a highly ordered structure by self-assembly. Self-assembly can be either two-dimensional (2D) or three-dimensional (3D), which has been clearly demonstrated in zeolite nanoparticles [102–104] and submicrometre latex particles [105–107]. In some cases, the assembly is so perfect that the resulting film becomes transparent [103, 105] or has a superlattice, which is investigated by small angle x-ray scattering [107]. In particular, when the particle size is of a few nanometres, the ordered assembly of particles under the dominant repulsive force generates a perfect crystal [108, 109]. Cu, Ag and Au monodisperse nanoparticles suspended in a solution were also shown to undergo self-assembly into a perfect superlattice such as face-centred cubic (FCC) [110–113].

When the charged diamond nuclei approach an iron substrate, the nuclei lose charge to the substrate because iron is a material with a high charge transfer rate which corresponds to the hydrogen evolution rate of electrode materials in electrochemistry [114]. The role of the charge transfer rate on the deposition of diamond will be dealt with in detail in section 2.8. The loss of charge to the iron substrate is expected to occur just before landing through a tunnelling process. After losing charge, the diamond nuclei transform to the graphite nuclei. The resultant neutral graphite nuclei aggregate randomly with each other, producing porous skeletal graphitic soot, which is typical of a fractal structure by DLA.

When the charged diamond nuclei approach a silicon substrate, however, the nuclei retain the charge even after

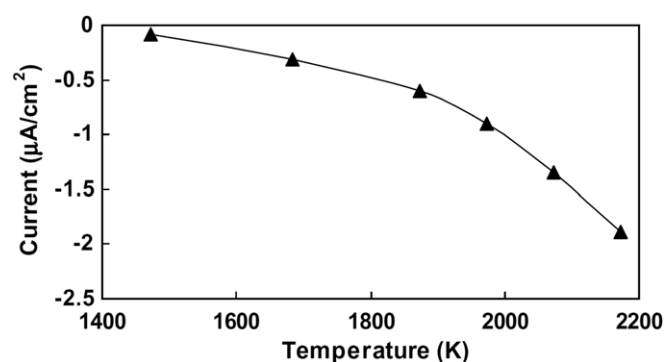


Figure 10. Measured electric current versus the wire temperature in the HWCVD reactor. Reprinted with permission from [43]. Copyright 2008 Elsevier.

landing. The charged diamond nuclei deposit by electrostatic self-assembly or colloidal crystallization, growing into diamond films or diamond crystals. The part most difficult to be convincing in this model, is the evolution of perfectly dense diamond crystals by the building block of gas-phase diamond nuclei, which implies that the nuclei grow epitaxially and leave no voids. It should be noted that self-assembly alone cannot explain such a crystal growth.

Some additional possibilities should be considered. One possibility is the temperature. In colloidal processing, the self-assembly is achieved mostly at room temperature and the individual nanoparticles have their own orientations in the superlattice and keep their identity. If the self-assembly is achieved at a relatively high temperature as in the thin film process, however, individual nanoparticles may undergo epitaxial coalescence on the growing surface and lose their identity. The second possibility would be the oriented attachment [19, 20], where nano- or microparticles rotate into epitaxial orientation before coming into contact. The third possibility is the ability of the accommodation of the small nanoparticles to the structure and orientation of the growing surface by epitaxial recrystallization because of their liquid-like property [115, 116].

Recently, electrostatic self-assembly has been studied extensively in a solution containing colloidal nanoparticles. For example, Tang *et al* [21] showed that CdTe nanowires were made from 3.4 nm or 5.4 nm nanoparticles in the colloidal solution. Zhang and Wang [117] suggested that the growth mode, such as 1D nanowires, 2D sheets and 3D films, depends on the balance between electrostatic energy and van der Waals interaction between charged nanoparticles. More details will be given in the section on carbon nanotubes. The concept of electrostatic self-assembly in a solution containing charged nanoparticles might also be applied to the diamond CVD process to understand the diamond film growth by the building blocks of charged gas-phase nuclei.

2.7. Formation mechanism of charged diamond nuclei in the gas phase during HWCVD

The generation of negative charge in the HWCVD reactor can be easily checked by measuring the current in the reactor. If the grounded electrode is placed ~ 1 cm below the hot

wire, where the substrate for deposition is usually placed, the charged species will collide with the electrode. And the charge colliding with the electrode will flow to the ground. The amount of charge colliding with the electrode can be measured as a current as shown in figure 10 [43]. Using this method, a negative current of more than $20 \mu\text{A cm}^{-2}$ is measured under typical processing conditions. The possible source of negative charges in the HWCVD reactor would be the electron emission from the hot wire. Since the pressure in the reactor is 2700 Pa, the mean free path is relatively short. Therefore, appreciable collisions of electrons with molecules will occur, producing negative ions. Then, to reduce the high electrostatic energy, ions will induce nucleation. Therefore, ions act as strong heterogeneous nucleation sites [118, 119]. This phenomenon is called ‘ion-induced nucleation’, which is well established in the famous Wilson cloud and the bubble chamber experiments [120, 121]. As a result, negatively charged nuclei would be formed in the gas phase.

On the other hand, the minimum methane concentration that can deposit diamond is $0.2\%\text{CH}_4\text{--}99.8\%\text{H}_2$. Here, the supersaturation ratio for nucleation was estimated to be 5 [65], which is too small to induce ion-induced nucleation. To explain the generation of negatively charged diamond nuclei even in such a case, a nucleation centre, which provides a lower nucleation barrier than an ion, appears to exist in the diamond CVD reactor. One possibility is that photo-excited molecules are formed by the hot wire and act as a centre for photo-induced nucleation [122, 123]. On the other hand, it should be noted that the bubble chamber experiment [121] cannot be explained by ion-induced nucleation because the electrostatic energy involved in bubble nucleation inhibits nucleation rather than inducing it. At the time of bubble chamber experiments, photo-induced nucleation was not discovered. Bubble nucleation might be more properly explained by photo-induced nucleation because photo-excited atoms or molecules accompanied in the ionizing environment.

2.8. Role of gas activation in the low-pressure synthesis of diamond

For the low-pressure synthesis of diamond, gas activation by a hot wire or a plasma is essential [52, 53]. Previously, the role of gas activation was believed to produce atomic hydrogen. This leads to the ‘atomic hydrogen hypothesis’, which has shown limited applicability to some specific processes in the previous section. One possible role of atomic hydrogen would be the unbalanced reduction of surface energy between diamond and graphite. Badziag *et al* [70] suggested that if hydrogenation occurs, nanometre-sized diamond becomes more stable than graphite. As shown in figure 2(b), 10% reduction of diamond surface energy is enough for the dominant nucleation of diamond over graphite, increasing n^* in equation (1) to 1784.

However, there are many reports that diamond could be synthesized without hydrogen [124]. For example, Yoshimoto *et al* [125] and Palnichenko *et al* [126] reported the low-pressure synthesis of diamond without hydrogen. Gruen *et al* [127] reported the synthesis of diamond by microwave discharges of C_{60} and Ar. Wesolowski *et al* [128] and

Lyutovich and Banhart [129] reported the transformation from graphite to diamond after heavy electron bombardment by transmission electron microscopy. In all these experiments one common fact is that an electric charge is involved in diamond formation. In addition, plasma or hot wire methods adopted in the low-pressure diamond synthesis produce abundant electric charge.

On the other hand, it is known that nanometre-sized diamonds exist in abundance in interstellar space [130, 131]. Their existence was confirmed in meteorites. Other materials coexisting in the meteorites do not have their high-pressure form and therefore, interstellar diamonds are thought to have nucleated under low pressures [69, 131]. Nuth [69] explained diamond formation under low pressures by a capillary effect. Considering that the interstellar space is a highly ionizing environment, the formation of interstellar diamonds might also be explained by the stabilization of diamond nuclei induced by charge.

Hwang *et al* [67] and Huh *et al* [91] reported that there exists a strong correlation between electrocatalytic property and the deposition of diamond or graphitic soot. Electrocatalytic metals are materials which have a high hydrogen evolution rate during an electrochemical reaction, which means that the charge transfer rate at the interface is high. 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 [114]. In these materials, Pd, Pt, Rh, Ir, Ni, and Fe produce soot whereas Au, W, Ag, Nb, Mo, Cu, Ta, Al and Ti produce diamond. Bi has too low a melting point to be used as a substrate. Therefore, substrate materials making soot in the CVD diamond process correspond to materials having a high charge transfer rate. These results strongly imply that the charge stabilizes diamond.

In order to further confirm the stabilization of diamond by charge, Hwang *et al* [67] compared the deposition behaviour between two iron substrates: one placed on a quartz and the other placed on a steel block. The iron substrate on an insulating quartz plate is electrically floating and the charge will be building up whereas the iron substrate on a steel block is electrically grounded. After 2 h of deposition, diamond grew on the initially formed soot on the iron substrate placed on the insulating quartz plate whereas soot continued to grow on the iron substrate placed on the steel block. These results suggest that the electric charge stabilizes diamond over graphite. Based on a density functional calculation, Park *et al* [132] studied the effect of charge on the stability of a diamond nanocluster surface and showed that a negative charge stabilized diamond over graphite and a positive charge stabilized the hydrogenated surface.

Considering all these, the role of gas activation may not be to produce atomic hydrogen but to produce negative charges. Abundant negative charges are generated by electron emission in the HWCVD process. Although some positive charges can be generated by the surface ionization or thermal charging during HWCVD, negative charges are much more dominant than positive ones. In the typical pressure range 800–4000 Pa with a relatively short mean free path, both positive and negative charges will collide with each other and the minor

positive charges will be removed. As a result, negatively charged nanoparticles would be suspended in the gas phase like a colloidal suspension. Because of Coulomb repulsion between like charges, charged nanoparticles can maintain their small size and thereby a high capillary pressure, which is a favourable condition for diamond stability.

The scenario becomes a little bit different in the gas-activated diamond CVD process using a plasma, where both negative and positive charges are generated in the same amount. In the plasma CVD process also, gas-phase nucleation would occur at the site of a low nucleation barrier, which can be photo-excited species or ions. Therefore, photo-induced or ion-induced nucleation is expected. Once nucleated, the nuclei soon become negatively charged because of the much higher mobility of electrons than that of ions; by attaching themselves to the nuclei, the electrons can reduce the energy of the work function of the nuclei. By this process, most nuclei are expected to be multiply charged whereas in the soft charging environment of the HWCVD process, most nuclei are expected to be singly charged. Multiple negative charges would be favourable for diamond stability as shown by Park *et al* [132]. This means that diamond nanoparticles of much larger size can be formed in the gas phase by plasma CVD than by HWCVD.

This possibility has been experimentally confirmed in some plasma CVD diamond processes as shown in figure 11 [90]. Figure 11(a) shows the transmission electron microscopy (TEM) image of diamond nanoparticles collected on the web of a holey carbon grid during microwave plasma-assisted CVD under the conditions of 56%CH₄–CO₂, microwave power of 700 W, inlet flow rate of 60 sccm, pressure of 1.33 kPa and plasma duration of 3 min [90]. The size of the diamond nanoparticles is from 25 to 40 nm while the size ranges from 15 to 100 nm depending on the synthesis condition, in particular the composition of C–H–O gas mixture. Figure 11(b) shows an enlarged high-resolution TEM (HRTEM) image of the diamond nanoparticles in figure 11(a). The size of diamond nanoparticles is 2–10 nm. Multiple charging will be favourable for a high power density plasma. This might be why microwave plasma-assisted CVD is more suitable in diamond synthesis than RF plasma-assisted CVD.

3. Characteristics in the deposition behaviour of charged nanoparticles

3.1. Effect of the nanoparticle size on the deposition behaviour

The size of the charged nanoparticles increases as the concentration of CH₄ increases. Figure 12 shows the measured mass distributions of negatively charged nanoparticles with gas mixtures of 1%CH₄–99%H₂, 1.5%CH₄–98.5%H₂, 3%CH₄–97%H₂ and 5%CH₄–95%H₂ at a wire temperature of 2100 °C and a reactor pressure of 800 Pa [38]. During the mass distribution measurements, diamonds were deposited *in situ*. For methane concentrations of 1% and 1.5%, the peak occurred at ~3000 atomic mass units. Under this condition, they could deposit high-quality diamonds with well-defined facets

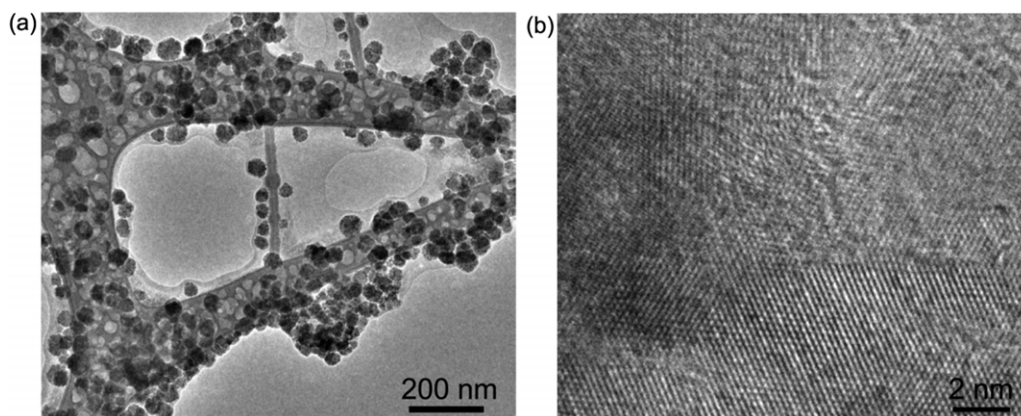


Figure 11. (a) TEM image of diamond nanoparticles collected on the web of a holey carbon grid (56% CH_4 - CO_2 , microwave power equals 700 W, inlet flow rate equals 60 sccm, pressure equals 1.33 kPa, plasma duration equals 3 min). (b) HRTEM image of diamond nanoparticles showing the individual diamond nanocrystals (2–10 nm) observed at a high magnification of (a). Reprinted with permission from [90]. Copyright 2010 IOP Publishing.

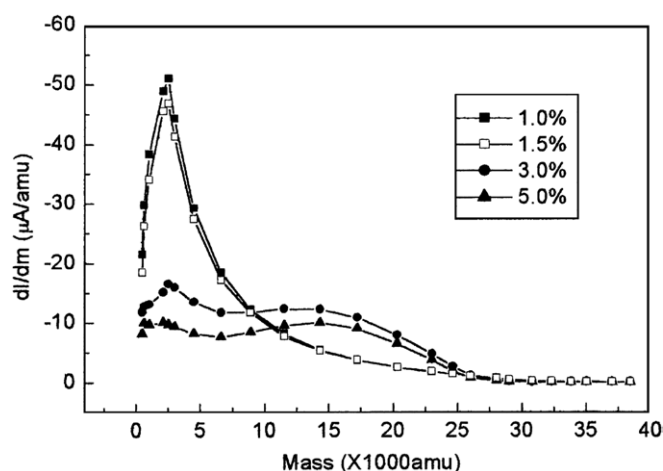


Figure 12. Mass distributions of negatively charged carbon clusters extracted from the HWCVD reactor using 1% CH_4 -99% H_2 , 1.5% CH_4 -98.5% H_2 , 3% CH_4 -97% H_2 and 5% CH_4 -95% H_2 gas mixtures, hot wire temperature of 2100 °C and reactor pressure of 800 Pa. Reprinted with permission from [38]. Copyright 2001 Elsevier.

as shown by the scanning electron microscope (SEM) image in figure 13(a). For methane concentrations of 3% and 5%, the size distribution became much broader with an appreciable number of gas-phase nuclei containing more than 1000 carbon atoms. Under this condition, they could deposit ball-like diamonds with numerous nanometre-sized nodules on the macroscopically spherical surface as shown in figure 13(b). This structure is often called a cauliflower structure because it looks similar to the vegetable cauliflower.

Diamond crystals shown in figure 13(a) look perfect at least in appearance and do not show any sign that they have grown by gas-phase nuclei. From the appearance alone, it would be almost impossible to tell whether they have grown by atoms or gas-phase nuclei. However, Sunagawa's analysis [28, 29] on the growth morphology of synthetic diamonds is worth noticing. According to the periodic bond chain (PBC) analysis by Hartman and Perdok [133–135], diamond has a flat (F) face on the (1 1 1) plane with three PBCs, a stepped

(S) face on the (1 1 0) plane with one PBC and a kinked (K) face on the (1 0 0) plane with no PBC [136]. The K face has no barrier for growth or atomic attachment whereas the F face has the highest barrier for growth. In other words, the K and F faces correspond to rough and singular interfaces, respectively. Therefore, the growth rate of (1 0 0) should be the highest and that of (1 1 1) should be the lowest, eventually leading to an octahedron shape closed by (1 1 1) surfaces.

All natural diamonds obtained by mining have the octahedral shape without exception although they tend to have a dissolution shape of the octahedron. However, most synthetic diamonds, regardless whether they are made by the high-pressure and high-temperature (HPHT) process or by the low-pressure CVD process, have a truncated octahedral or cuboctahedral shape as shown in figure 13(a). This indicates that the growth rate of the (1 1 1) surface is comparable to that of the (1 0 0) surface. Based on this fact, Sunagawa [28, 29] suggested that synthetic diamonds should not grow by individual atoms but by nanoparticles.

Also he pointed out additional evidence supporting his suggestion. One of them is the wavy macrosteps on the surface, which are widely observed in synthetic diamonds. The step of monoatomic height is usually wavy because its entropy term is dominant over its enthalpy term. However, the step with its height larger than a monoatom should be straight because its enthalpy term is dominant over its entropy term. The wavy macrosteps, if they are not formed by step bunching, indicate that the crystal grew by building blocks comparable in size to the step height.

A similar suggestion was made by Samotoin [137], who reported diamond morphology of spiral growth with a step height of ~ 8 nm. Polycrystalline diamond films were synthesized from a hydrocarbon gas activated by an arc discharge of continuous current. Based on the analysis of this morphology, he suggested that the growth unit of CVD diamond should be nanoparticles commensurable in size with the step height of ~ 8 nm. A building unit much larger than individual atoms was also suggested in the synthetic diamonds prepared by HPHT. Based on the TEM observation of the diamond morphology at the growth front, Yin *et al* [138]

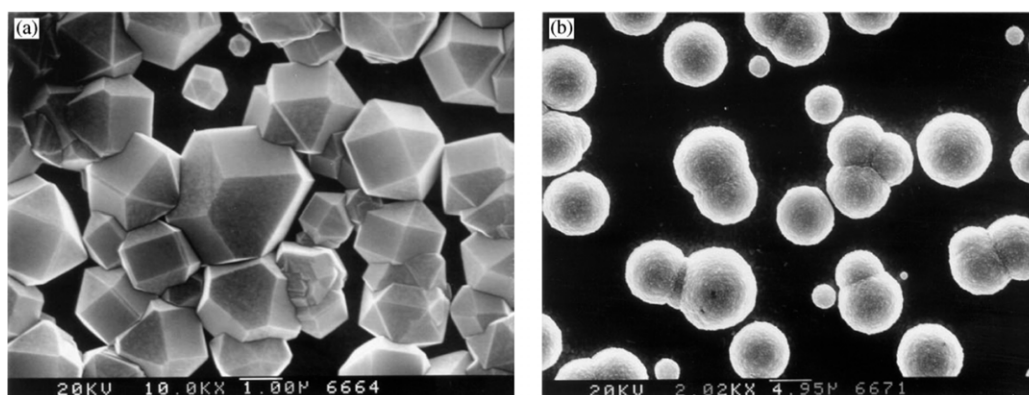


Figure 13. SEM images of diamond films deposited *in situ* during the measurement of mass distribution of charged clusters at 2100 °C wire temperature and 800 Pa reactor pressure: (a) 1%CH₄–99%H₂, (b) 3%CH₄–97%H₂. Reprinted with permission from [38]. Copyright 2001 Elsevier.

reported that the synthetic diamond by HPHT is formed through continuous dissolution of graphite in the molten catalyst to form a colloidal solution, transition of graphite to diamond under the action of the catalyst, diffusion of the diamond clusters to the growing diamond and collection or unification of the diamond subcritical clusters on the growing diamond crystal.

When the size of the charged nanoparticles is larger as in the case of higher methane concentration of figure 12, the microstructure of diamonds changes drastically. The cuboctahedron shape with well-defined facets in figure 13(a) is no longer evolved but the diamond shape becomes spherical as shown in figure 13(b). This means that small charged nanoparticles have a different attachment rate on each surface, resulting in an anisotropic growth rate and producing a polyhedral shape such as cuboctahedron diamonds in figure 13(a) whereas large ones have the same attachment rate, resulting in an isotropic growth rate and producing a spherical shape such as ball-like diamonds in figure 13(b). If the spherical diamond particle of figure 13(b) is observed with higher magnification, the surface is covered with numerous nanometre-sized nodules, which is a cauliflower structure.

No clear theory is available now to explain such a size effect of the charged nanoparticles on the microstructure evolution. The most satisfactory explanation on the size effect was made by Fujita [115, 116] who suggested that the property of nanoparticles changes abruptly at a specific size which was called the ‘magic size’. In the order of increasing size, particle coalescence, epitaxial recrystallization and diffusional sintering were suggested to take place. Fujita [115] estimated the magic size for several materials. The magic size of isolated particles was estimated to be 15–20 nm $\varnothing$ for FCC metals and alloys, 10–15 nm $\varnothing$ for body centred cubic (BCC) metals and alloys, 15–20 nm $\varnothing$ for Al₂O₃, and 3–5 nm $\varnothing$ for TiC and SiC, where $\varnothing$ represents the diameter of nanoparticles. For embedded particles, it is $\sim$ 2 nm $\varnothing$ for Si and $\sim$ 1 nm $\varnothing$ for diamond. The magic size for an isolated diamond particle is expected to be $\sim$ 2 nm $\varnothing$.

Nanoparticles smaller than the magic size deform and diffuse like a liquid phase and rapid coalescence takes place when the nanoparticles are in contact. In this case, it would be difficult to distinguish the building block for the resultant

crystal. The concept of magic size might be related to the melting point depression of nanoparticles [139, 140]. As the particle size becomes larger than the magic size, epitaxial coalescence will begin to fail. Then, twin or grain boundaries will form as if secondary nucleation takes place on the growing surface. As a result, the polycrystalline film will grow. As the frequency for the formation of the boundary increases, the grain size will decrease. The grain size will be minimal when all the particles have their individual orientations, leading to a cauliflower structure or a nanostructure. This aspect agrees with the experimental observation that as the particle size increases, the growth mode changes from the crystal with well-defined facets to the cauliflower structure.

In relation to the effect of particle size on the deposition behaviour of nanoparticles, Yoshida and his colleagues [141–145] made extensive studies on the epitaxial growth of films with a building block of nanoparticles by the method called thermal plasma flash evaporation. Using this method, they could deposit high-quality epitaxial YBa₂Cu₃O_{7-x} films with a growth rate as high as 16 nm s⁻¹ [144]. They called the related phenomenon ‘hot cluster epitaxy’. Using a microtrench fabricated on a Si wafer, they could estimate the size of the depositing nanoparticles to be about 0.3–10 nm [143]. They observed by scanning tunnelling microscopy (STM) that small 1–2 nm nanoparticles underwent epitaxial spiral growth, medium size 3 nm nanoparticles became epitaxial 2D nuclei, and large nanoparticles over 3 nm produced non-epitaxial island grains [144]. The starting material was powders of $\sim$ 1 μ m, which was continuously injected into a thermal plasma for complete evaporation and precipitation into nanoparticles above the substrate.

3.2. Nanocrystalline diamond and cauliflower structure

Polycrystalline and microcrystalline diamonds with highly faceted morphology have high surface roughness, which is disadvantageous for some applications [146, 147]. In this respect, nanocrystalline diamond (NCD) and ultrananocrystalline diamond (UNCD) are attractive because they have an extremely low surface roughness without deteriorating other properties. NCD and UNCD are successfully synthesized by various CVD techniques such as microwave plasma-enhanced chemical vapour deposition (MPCVD) and HWCVD

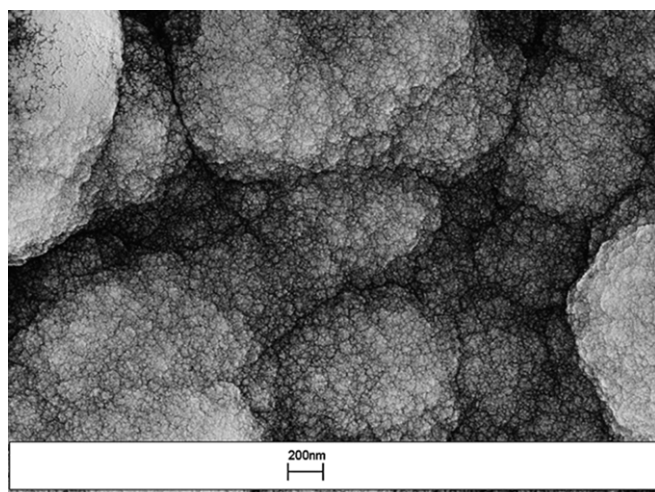


Figure 14. Ball-like or cauliflower structure which is the aggregation of diamond nanoparticles. Reprinted with permission from [152]. Copyright 2008 Elsevier.

[148–150]. NCD is synthesized commonly by using a high percentage of CH_4 in H_2 (5–20%). This NCD shows a cauliflower or ball-like structure which is composed of small NCDs [151, 152]. Figure 14 shows a typical cauliflower structure which is the aggregation of NCDs of 20–30 nm [152]. UNCD is composed of very fine NCDs of 3–5 nm [153].

Such a nanocrystalline structure is not unique to diamond but very general in thin films of other systems prepared, in particular, at low substrate temperatures by CVD, laser ablation and even some sputtering. For example, the Si cauliflower structure aggregated by 10 nm particles was grown by HWCVD [154], the ZrO_2 cauliflower structure by thermal CVD [39], the ZnO_2 cauliflower structure by combustion CVD [155], the TiN_x cauliflower structure by laser CVD [156] and the platinum cauliflower structure by RF sputtering [157].

As explained so far, the NCD structure is formed by the deposition of charged nanoparticles generated in the gas phase. Then, a question arises as to whether other nanocrystalline structures might also be formed by the deposition of charged nanoparticles or not. If they are also formed by charged nanoparticles, the thin film growth by charged nanoparticles would be a general mechanism. Therefore, it is important to analyse the evolution of cauliflower structures to check whether they can be deposited by atomic growth or not.

In order for nanometre-sized nodules to be formed on the surface by atomic growth, a 3D nucleation or secondary nucleation should take place on the growing surface. The frequency of secondary nucleation determines the grain size because the grain size decreases with increasing frequency of secondary nucleation. Therefore, the minimum grain size of films can be determined by the maximum frequency of secondary nucleation. It is worth estimating the theoretically possible maximum frequency of secondary nucleation based on the well-established theory of crystal growth.

The barrier for atomic attachment on the growing interface depends on the interface structure, which is either rough or singular [158]. The rough interface, which is atomically disordered and consists of numerous kinks, has no barrier

for atomic attachment. The growth kinetics is controlled by the slower process of diffusion, which often leads to dendritic growth. Most solid–liquid interfaces of metals are rough. This is why dendritic growth is so common during solidification of metals. In the case of the rough interface, secondary nucleation cannot occur because the nucleation process requires a finite degree of supersaturation but the supersaturation cannot be built up on the rough interface, which has a sticking coefficient of one with no barrier for atomic attachment. Therefore in the solidification of metals, which have no secondary nucleation on the growing surface, the grain size is determined by the impingement through the growth of independent nuclei.

The singular interface, which is atomically ordered, has an appreciable barrier for atomic attachment. Therefore, it needs ledge-generating sources such as screw dislocations or 2D nuclei for growth. Therefore, the growth mode of the singular interface depends on the supersaturation. At low supersaturation, the growth does not occur in the absence of defects such as screw dislocations. In this regime of low supersaturation, only defect-assisted growth can occur. As the supersaturation increases, 2D nucleation takes place. The onset of 2D nucleation is so abrupt that as the supersaturation increases, the rate of nucleation increases abruptly to a high value like a step function [158]. When the number of 2D nuclei is so high, a sufficient number of ledges of monoatomic height are formed on the surface. In this situation, even the singular interface has no barrier for atomic attachment, and the phenomenon is called ‘kinetic roughening’ [16]. Even though ice has a singular interface, snow crystals show typical dendritic growth, indicating the diffusion-controlled growth as if it had a rough interface. Therefore, a snow crystal is a good example of kinetic roughening.

Secondary nucleation on the singular interface can take place in a narrow supersaturation range higher than the onset of 2D nucleation and lower than the onset of kinetic roughening. In order to estimate the minimum grain size, which can be theoretically achieved in the thin film process, the frequency of secondary nucleation should be estimated with respect to the frequency of 2D nucleation, which is the maximum barrier of growth on the singular interface. According to the estimation by Hirth and Pound [158], the ratio of the 2D nucleation to secondary nucleation rate is typically $\sim 10^8$. This means that after the growth of hundreds of millions of atomic layers, one event of secondary nucleation can occur. This determines the minimum grain size of films achieved through the growth by atomic or molecular units. Even if the errors made in the estimation are considered, the predicted minimum grain size is at least larger than a few micrometres.

This means that the nanometre-sized structure cannot be formed by atomic or molecular deposition at least in the vertical direction. Microstructures similar to NCD and UNCD have also been observed during the synthesis of monodisperse microparticles in solution [159, 160]. The microparticles consisted of small crystalline subunits of nanoparticles like NCD and UNCD. The size of the crystalline subunits of final microparticles was the same as the size of the initial precursor [160]. An intensive study on the growth mechanism of the microparticles showed that they were formed not

by the attachment of atomic units but by the aggregation of nanocrystalline subunits [161, 162]. According to this analysis, the cauliflower structure, which is widely observed in many thin films prepared by CVD, laser ablation and even by some sputtering, is an indication that the building blocks of the films should be charged nanoparticles. And the analysis also implies that the growth by charged nanoparticles may be a general mechanism in many thin film processes.

Various microstructures from polycrystalline to UNCDs resulted from the complex landing behaviour of charged nanoparticles on the substrate. The important factors affecting the microstructure are the size of nanoparticles and the temperature of the substrate. These effects on the landing behaviour were investigated in gold nanoparticles by molecular dynamics (MD) simulations [163]. In the simulation, three nanoparticles of different sizes with 321, 1055 and 1985 atoms were deposited on an Au (001) surface at temperatures of 27, 427 and 727 °C.

At a low temperature of 27 °C, the nanoparticle of 321 atoms was deposited homo-epitaxially on a surface. The nanoparticle of 1055 atoms was deposited on a surface making a twin boundary inside the cluster at the same temperature. The nanoparticle of 1985 atoms was deposited on a surface making a grain boundary with the surface at the same temperature. At a low temperature, the epitaxial deposition is sensitive to the size of the nanoparticle. As the size decreases, the epitaxial deposition becomes more favourable. At a high surface temperature of 727 °C, all the nanoparticles of 321, 1055 and 1985 atoms were deposited homo-epitaxially on an Au (001) surface. As the substrate temperature increases, the epitaxial deposition becomes more favourable in spite of the quite large size of the nanoparticles.

These results agree with the concept of magic size suggested by Fujita [115, 116]. In this MD simulation, oriented attachment was not considered. In actual deposition by charged nanoparticles, the oriented attachment, where the charged nanoparticles are rotated into the epitaxial orientation on the surface before landing, is also expected to occur. Nevertheless, the deposition behaviour of nanoparticles by MD simulations is consistent with the experimental observations of diamond deposition with respect to the effect of the substrate temperature and the size of nanoparticles.

In diamond synthesis by gas-activated CVD, as the substrate temperature increases, the epitaxial growth is generally more favourable. Diamonds deposited at 600 °C were nanocrystalline with a grain size of 1.5–2 nm while perfect single-crystalline diamonds were grown at 750 °C [50]. Under microwave glow discharge conditions, polycrystalline diamonds were deposited at 800 °C while single-crystalline diamonds were deposited at 900 °C [164]. The size of diamond nanoparticles in the gas phase also affects the microstructure of diamonds as shown in figures 12 and 13. It is a well-established fact that NCD or cauliflower-like diamonds are generally deposited at high methane concentrations [150].

3.3. Nanocrystallites embedded in an amorphous matrix

A microstructure showing nanocrystallites embedded in an amorphous matrix is commonly observed in CVD films

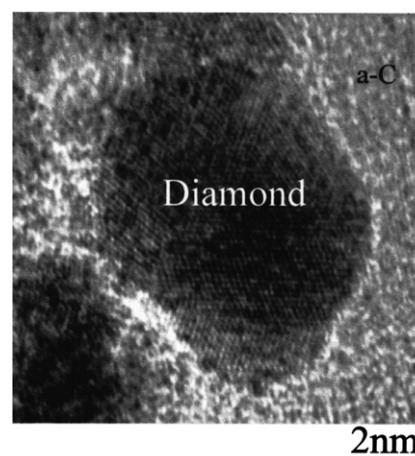


Figure 15. Plan view high-resolution TEM image of a nanodiamond embedded in an amorphous carbon phase. Reprinted with permission from [166]. Copyright 2002 American Institute of Physics.

particularly when deposited at low substrate temperatures. For example, it was observed that NCDs of a few nanometres were embedded in an amorphous matrix [165, 166]. Figure 15 shows a TEM image of a nanodiamond embedded in an amorphous carbon matrix [166]. The microstructure of nanocrystallites embedded in an amorphous matrix was reported in various materials such as Si, SiC, TiN, TiAlCN, ITO and GaAs by various processes such as sputtering, thermal CVD, HWCVD and PECVD [167–174].

Such microstructures are puzzling if approached by crystal growth based on atomic growth because definitely, the amorphous phase has a rough surface and the crystallites have a singular surface [175]. Nucleation cannot take place on the rough surface of an amorphous phase as explained earlier and the growth rate of the amorphous phase would be much higher than that of the crystallites. This means that crystallites embedded in the amorphous matrix cannot be formed by atomic growth but must be formed by landing of the crystalline nanoparticles from the gas phase or by crystallization from the amorphous phase through annealing at moderate temperatures.

An amorphous incubation layer is also the indication of growth by charged nanoparticles. When microcrystalline Si thin films are deposited at low temperatures either by PECVD or HWCVD, an amorphous incubation layer is always formed in the initial stage of the film growth on a glass substrate, until the microcrystalline structure sets in [176, 177]. Since the nucleation of a crystalline phase cannot take place on the amorphous phase, on which there exists no barrier for atomic attachment, the crystallites must have been formed by landing on the amorphous layer from the gas phase.

3.4. Low-temperature deposition of crystalline phase

Efforts to produce high-mobility polycrystalline silicon films on a low-cost glass substrate have been made extensively using, for example, excimer laser annealing [178, 179], solid phase crystallization [180], rapid thermal processing [181] and metal-induced lateral crystallization [182]. Since these

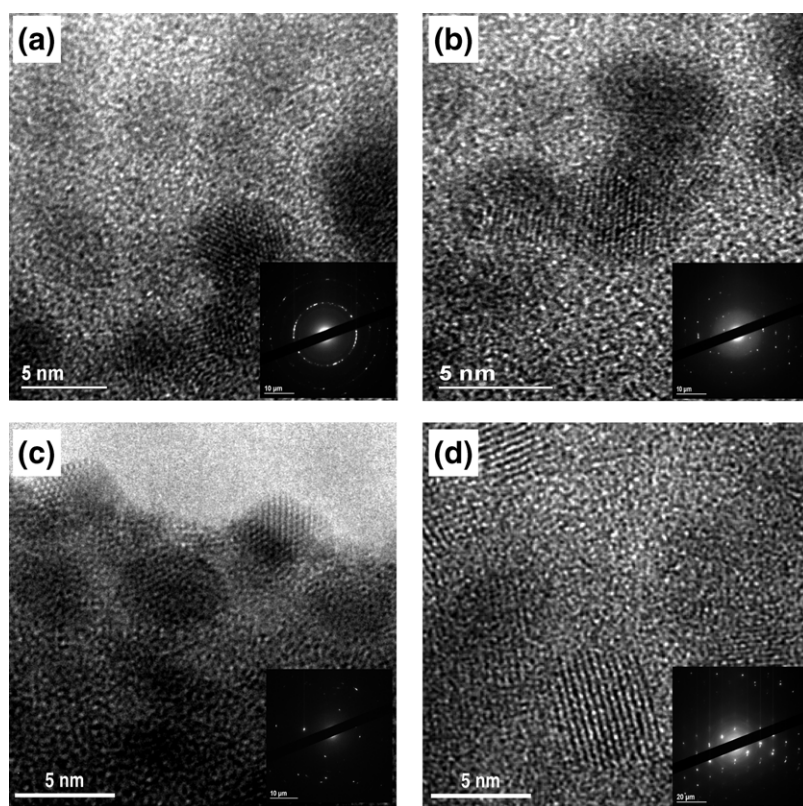


Figure 16. TEM images of silicon nanoparticles captured on the amorphous carbon membrane at room temperature during HWCVD with (a) 20%, (b) 15%, (c) 10% and (d) 5% SiH₄ at a wire temperature of 1560 °C. Reprinted with permission from [41]. Copyright 2008 Elsevier.

methods suffer from complex processing, which increases the production cost, the direct deposition of crystalline silicon on the glass substrate would be desirable. In relation to this possibility, the direct deposition of microcrystalline silicon films on a glass substrate below 400 °C has been reported using HWCVD [183–185] or plasma CVD [186].

However, the direct deposition of crystalline silicon films on a glass substrate at such low temperatures is unexpected and somewhat puzzling from the viewpoint of atomic growth because the growth of amorphous silicon is expected below 600 °C [93], considering the low diffusivity of silicon. It has not been understood why crystalline silicon can be deposited at such low temperatures if a hot wire or a plasma is used. As one possibility, Matsumura and Tachibana [187] suggested that atomic hydrogen produced during HWCVD increases the mobility of silicon. Recently, however, films containing crystalline silicon were shown to deposit on a flexible polymer substrate at temperatures even below 150 °C using HWCVD [188]. It is difficult to explain the direct deposition of crystalline silicon at such low temperatures through the mobility enhanced by atomic hydrogen. Another possibility is that crystalline silicon nanoparticles are formed in the gas phase in the high-temperature region near the hot wire and then incorporated into the films at low temperatures.

In order to confirm this possibility by capturing the hypothetical crystalline silicon nanoparticles formed in the gas phase, Lee *et al* [41] designed the HWCVD reactor, which is divided into three chambers by two-stage orifices. A different pressure was maintained in the three chambers

during the process by two-stage differential pumping. The working pressure of the first chamber (the HWCVD reactor) was maintained at 27 Pa under a flowing gas mixture of SiH₄ and H₂, with the pressure of the third chamber being maintained at 1.3×10^{-3} Pa during the process. The charged nanoparticles that were predicted to form in the first chamber of the hot wire reactor were extracted through the first and the second orifices into the third chamber, where the amorphous carbon membrane of the TEM grid at room temperature was placed for capturing these nanoparticles.

The TEM image of the crystalline silicon nanoparticles captured on the TEM grid membrane is shown in figure 16 [41]. The wire temperature was 1560 °C and the concentration of SiH₄ in the gas mixture of SiH₄–H₂ was varied as 20%, 15%, 10% and 5%. Clearly the crystalline silicon nanoparticles with the lattice fringe are revealed. The size of the crystalline nanoparticles decreased with decrease in SiH₄ concentration with 7–8 nm for 20% SiH₄ (figure 16(a)), 6–7 nm for 15% SiH₄ (figure 16(b)), 5–6 nm for 10% SiH₄ (figure 16(c)) and 4–5 nm for 5% SiH₄ (figure 16(d)). This effect of SiH₄ concentration on the nanoparticle size should be related to the increased amount of silicon precipitation in the gas phase with increasing SiH₄ concentration.

This result indicates that such a nanocrystalline structure can be deposited even at room temperature if the gas containing the charged nanoparticles is accelerated. The TEM images of figure 16 show not only crystalline silicon nanoparticles but also an appreciable amount of amorphous silicon without the lattice fringe. Such amorphous silicon must have been formed

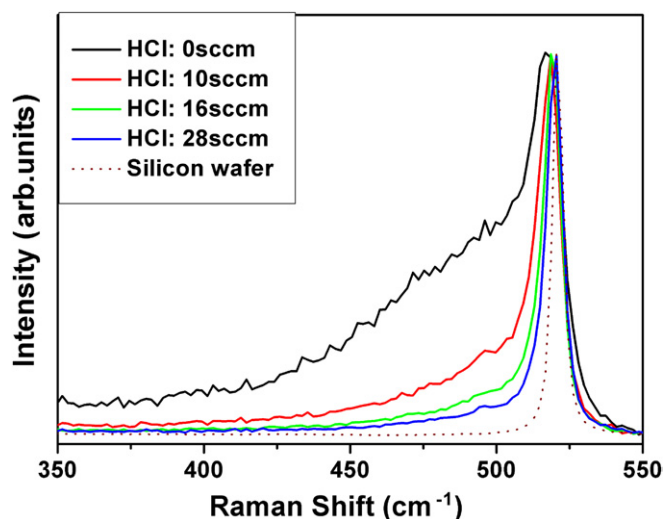


Figure 17. Raman spectra of the silicon films deposited at various HCl flow rates. The crystallinity of films increases with increasing HCl flow rate. Reprinted with permission from [189]. Copyright 2009 Elsevier.

in the low-temperature region near the substrate away from the hot wire.

Therefore, in order to minimize the deposition of amorphous silicon, the low-temperature precipitation of silicon should be inhibited. In other words, if the precipitation of silicon is allowed only in the high-temperature region and suppressed in the low-temperature region, exclusively crystalline nuclei may be formed with the nucleation of the amorphous phase inhibited. Then the fraction of crystalline silicon can be increased. By analysing the phase diagram of the Si–Cl–H system, Chung *et al* [189] suggested that HCl addition to SiH₄ satisfied this condition and showed that the crystallinity of silicon films increased with increasing HCl addition as shown in figure 17. As will be explained later (figure 29), the Si–Cl–H phase diagram has a retrograde solubility of silicon in the gas phase, which decreases with decreasing temperature below ~1100 °C. If gas-phase nucleation occurs, the driving force at low temperatures becomes for etching so that the precipitation of silicon is inhibited at low temperatures. Deposition was done on a glass substrate at 320 °C with the flow rate of 10%SiH₄–90%He gas being fixed at 100 sccm and the flow rate of HCl gas being varied at 0, 10, 16 and 28 sccm under a reactor pressure of 1333 Pa and at a wire temperature of 1600 °C. The Raman spectra in figure 17 clearly show that the crystallinity of silicon films increases with increasing HCl addition. As a reference, the Raman spectrum of a single crystal silicon wafer is shown as a dotted line.

As mentioned earlier, an amorphous silicon incubation layer, which is as thick as hundreds of nanometres, is formed on the glass substrate before crystalline silicon starts to form. The formation of such an amorphous silicon incubation layer has remained a serious problem for the thin-film transistor (TFT) applications of the direct low-temperature deposition of crystalline silicon because the thickness of the TFT should be typically less than ~200 nm. Chung *et al* [190] showed that the amorphous incubation layer could be reduced markedly or almost completely removed by HCl addition. This is an

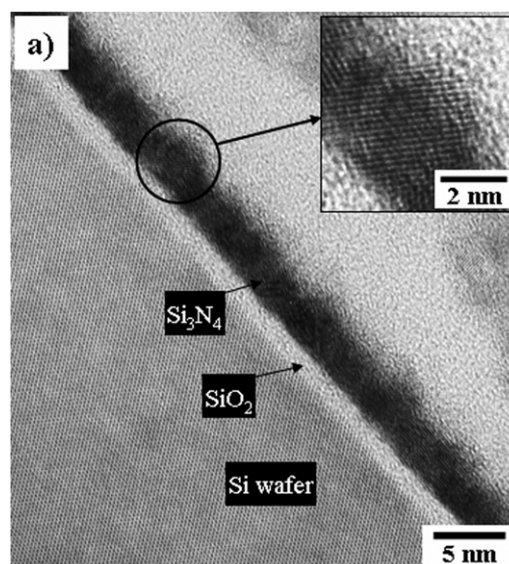


Figure 18. Cross-section view of the high-resolution TEM image of nanocrystalline silicon nitride deposited on a Si (100) wafer with a natural silicon oxide layer under the reactor pressure of 5333 Pa at the wire temperature of 1730 °C. Reprinted with permission from [191]. Copyright 2009 Elsevier.

example showing how new understanding of thin film growth by charged nanoparticles can be applied.

The concept of the low-temperature deposition of a crystalline phase can be applied to systems other than silicon. Kim *et al* [191] successfully applied this concept to the deposition of crystalline silicon nitride on a silicon substrate at 700 °C using HWCVD as shown in figure 18. If silicon nitrides are precipitated near the hot wire, the temperature would be high enough for the nanoparticles to have a crystalline phase. If these crystalline nanoparticles are carried to the substrate maintained at a low temperature, the low-temperature deposition of crystalline silicon nitride would be possible. However, in order to find out such a possibility of low-temperature deposition, the related phase equilibrium should be analysed in the steep temperature gradient between the hot wire and the substrate. Considering the phase equilibrium, the reactor pressure and the wire temperature were chosen to be 5333 Pa and 1730 °C, respectively, for deposition of the crystalline silicon nitride film shown in figure 18.

3.5. Growth mechanism of carbon nanotubes and nanowires

Before considering the growth mechanism of carbon nanotubes and nanowires in the CVD process, their growth mechanism in colloidal solutions will be introduced first because it has been studied extensively and well established in the field of colloidal crystallization. In particular, in the past decade, intensive studies on the evolution mechanism of complex nanostructures in colloidal solutions have been conducted. It was revealed that complex nanostructures such as nanowires, nanodendrites and nanoleaves are grown not by a classical crystal growth mode, which is via atom-by-atom additions, but by the oriented attachment of nanoparticles [19–22]. Tang *et al* [21] observed that CdTe nanoparticles were spontaneously reorganized into

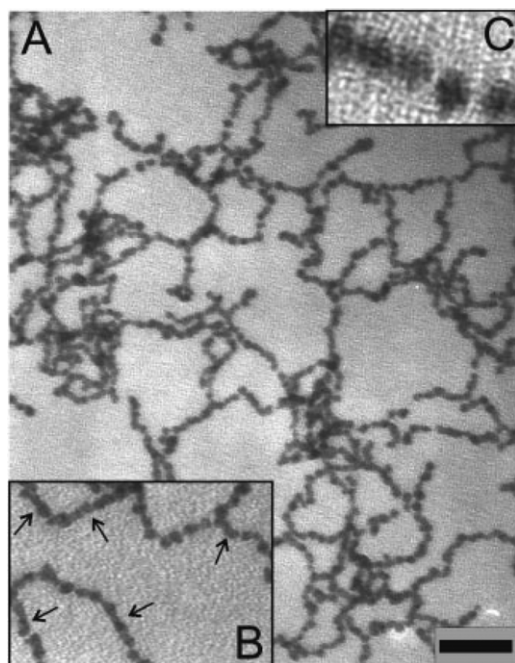


Figure 19. (a) TEM image of the intermediate state of nanoparticle–nanowire transition for 5.4 nm nanoparticles. (b) The enlarged portion of the chain, with short rods marked by arrows. (c) The high-resolution TEM image of the adjacent nanoparticles in the chain. Reprinted with permission from [21]. Copyright 2002 AAAS.

crystalline nanowires upon controlled removal of the protective shell of the organic stabilizer.

Figure 19 shows the intermediate step in the nanowire formation by oriented attachment of CdTe nanoparticles showing a pearl-necklace aggregate self-assembly [21]. The enlarged TEM image of figure 19(b) shows how the short nanorods are formed by coalescence of nanoparticles in the initial stage of nanowire formation. Therefore, the size of nanoparticles determines the diameter of nanowires. The formation of nanowires or necklace nanocrystal chains via the oriented attachment of nanoparticles has been reported for various materials such as Au, Ag, TiO₂, ZnS, CdTe, PbSe, ZnO and SnO₂ [22]. Moreover, more complex nanostructures such as nanodendrites, nanoleaves and nanomultipods were also synthesized by the oriented attachment of nanoparticles [192–194].

The oriented attachment of nanoparticles into various nanostructures was suggested to be induced by the balance between isotropic long-range electrostatic repulsion and isotropic short-range van der Waals attraction between the particles in the presence of short-range anisotropic dipolar attraction forces [117]. Nanoparticles can be self-assembled into 1D, 2D and 3D nanostructures depending on the balance between V_{elec} and V_{vdw} , which represent electrostatic repulsion and van der Waals attraction, respectively. For example, Zhang and Wang [117] suggested that the conditions of $V_{\text{elec}} < V_{\text{vdw}} < 2V_{\text{elec}}$, $2V_{\text{elec}} < V_{\text{vdw}} < 3V_{\text{elec}}$, and $3V_{\text{elec}} < V_{\text{vdw}}$ induce the growth of 1D nanowires, 2D nanosheets and 3D bulk, respectively. This oriented attachment mechanism is a recently established concept of particle-based crystallization

pathways in the field of colloid solutions. It can yield various morphologies of nanostructures that cannot be grown via a classical atom and molecule based crystallization mechanism.

The growth mechanism of carbon nanotubes and nanowires in the CVD process should also be approached by the self-assembly of charged nanoparticles formed in the gas phase because carbon nanotubes are simultaneously deposited under the condition of diamond deposition where charged nanoparticles are generated in the gas phase. Figure 20(a) shows the SEM micrographs of films grown on patterned Ni-coated Si substrates by HWCVD under a typical process condition of diamond deposition [195]. Figure 20(b) shows the high magnification SEM micrographs of the boundary area of figure 20(a). Carbon nanotubes were grown on the Ni-coated area and simultaneously a diamond film was grown on the masked area. This simultaneous deposition indicates that the growth source for carbon nanotubes and diamond should be the same. Therefore, the growth source of carbon nanotubes should be charged nanoparticles formed in the gas phase because carbon atoms are being etched atomically under this process condition as explained earlier. Since the growth of carbon nanotubes is mediated by Ni-catalyst particles in this case, the detailed growth mechanism needs further study. The nanotubes are randomly oriented with an average diameter of ~ 40 nm and a length of a few micrometres.

If an electric field is applied between the wire and the substrate, well-aligned nanotubes or nanowires can be grown. Figures 21(a) and (b) show the SEM micrographs of simultaneous growth of well-aligned carbon nanotubes on a Ni-coated Si substrate and well-aligned carbon nanocones or nanowires on a scratched Si substrate, respectively, under the same experimental conditions of figure 20 applying a dc bias voltage of 300–550 V between the wire and the substrate holder [195]. Sharp edges and apexes provide the highest electric field gradient and effectively attract the charged nanoparticles. Likewise, the electric field gradient is the highest at the tip of the nanotubes or nanowires. Therefore, the charged nanoparticles in the gas phase are effectively guided to the tip by the electric field and thus well-aligned nanotubes and nanowires could be grown.

Lee and Hwang [43] also studied the bias effect on the growth of carbon nanotubes in the HWCVD process. The mass of carbon nanotubes and nanoparticles deposited on the substrate biased at +25 V is found to be twice and ten times larger than the mass of carbon nanotubes or carbon nanoparticles deposited on the substrate biased at 0 V and –200 V, respectively. The field emission SEM (FESEM) images of the samples grown on the substrate at the applied biases of –200 V, 0 V and +25 V are shown in figures 22(a), (b) and (c), respectively [43]. Carbon nanotubes are observed to grow appreciably at an applied bias of +25 V, whereas they are not formed at the applied biases of 0 and –200 V, but carbon nanoparticles grow instead. This result of a positive bias promoting the growth of carbon nanotubes indicates that the growth flux of carbon nanotubes is negatively charged.

To confirm the existence of negatively charged graphite nanoparticles in the gas phase, Lee and Hwang [43] designed a two-chamber reactor, which is connected through an

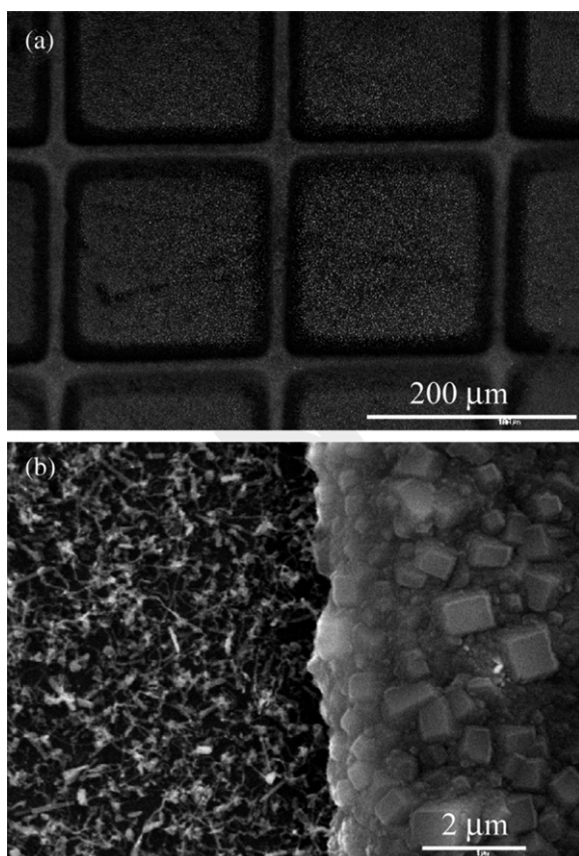


Figure 20. SEM micrographs of films grown on patterned Ni-coated Si substrates: (a) low magnification, (b) high magnification of the boundary area, where carbon nanotubes were grown on the Ni-coated area and simultaneously a diamond film was grown on the masked area. Reprinted with permission from [195]. Copyright 2004 Elsevier.

orifice for differential pumping. The first chamber is the deposition reactor and the second chamber is for capturing the nanoparticles being extracted through the orifice from the first chamber. Negatively charged graphite nanoparticles of ~ 5 nm were observed on the TEM grid applied with +25 V in the second chamber whereas none was observed on the TEM grid applied with -200 V.

There are many other experimental proofs that carbon nanotubes are grown by the self-assembly of charged nanoparticles formed in the gas phase. Du *et al* [196] observed the detailed morphology and structure in the intermediate stage of carbon nanotube growth by both floating CVD and detonation-assisted CVD. They observed by TEM that carbon nanoparticles with a size of 10–20 nm first form in the gas phase and then self-assemble into nanowires driven by an anisotropic interaction, and the nanowires finally develop into nanotubes as a consequence of particle coalescence and structural crystallization. Botti *et al* [197] synthesized carbon nanotubes directly from carbon nanoparticles. As-prepared carbon nanoparticles with a diameter of 50 nm were charged in a reservoir and introduced into the deposition chamber through a pipe. The charged carbon nanoparticles are passed through a nozzle, accelerated to about 30 m s^{-1} and then deposited by impaction onto a Si substrate without any metal

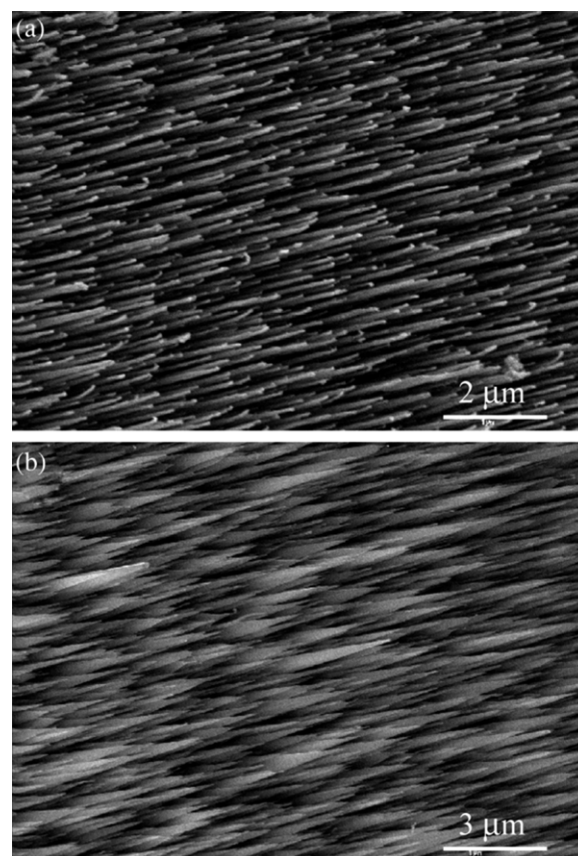


Figure 21. SEM micrographs of simultaneous growth of (a) well-aligned carbon nanotubes on a Ni-coated Si substrate and (b) well-aligned carbon nanocones on a scratched Si substrate with applied dc bias voltage of 300–550 V between the hot wire and the substrate holder. Reprinted with permission from [195]. Copyright 2004 Elsevier.

catalyst. Single-walled carbon nanotubes with a diameter of 50 nm, which corresponds to the size of a starting material of the carbon nanoparticles, were grown for 30 min. This result indicates that the charging of nanoparticles is essential for 1D growth of nanotubes. Although carbon nanoparticles in the gas phase are spontaneously charged in the CVD process, they should be electrically charged using an artificial charger when as-prepared carbon nanoparticles are used as the growth source.

The size distribution of charged nanoparticles can be measured using a DMA combined with a Faraday cup electrometer (FCE) [198, 199]. The schematic of DMA–FCE systems is shown in figure 23. In general, nanoparticles are electrically charged by an artificial charger before DMA measurement because DMA can measure only charged nanoparticles. However, if nanoparticles formed in the gas phase are spontaneously charged through contact ionization with the wall of the CVD reactor or by chemionization, DMA can measure the size distribution of self-charged nanoparticles without an additional artificial charger. Under the condition where carbon nanotubes are synthesized by thermal CVD, the distribution of charged nanoparticles in the gas phase was measured by DMA–FCE systems [44].

Figures 24(a), (b), (c) and (d) show the FESEM images of carbon nanotubes synthesized at reactor temperatures

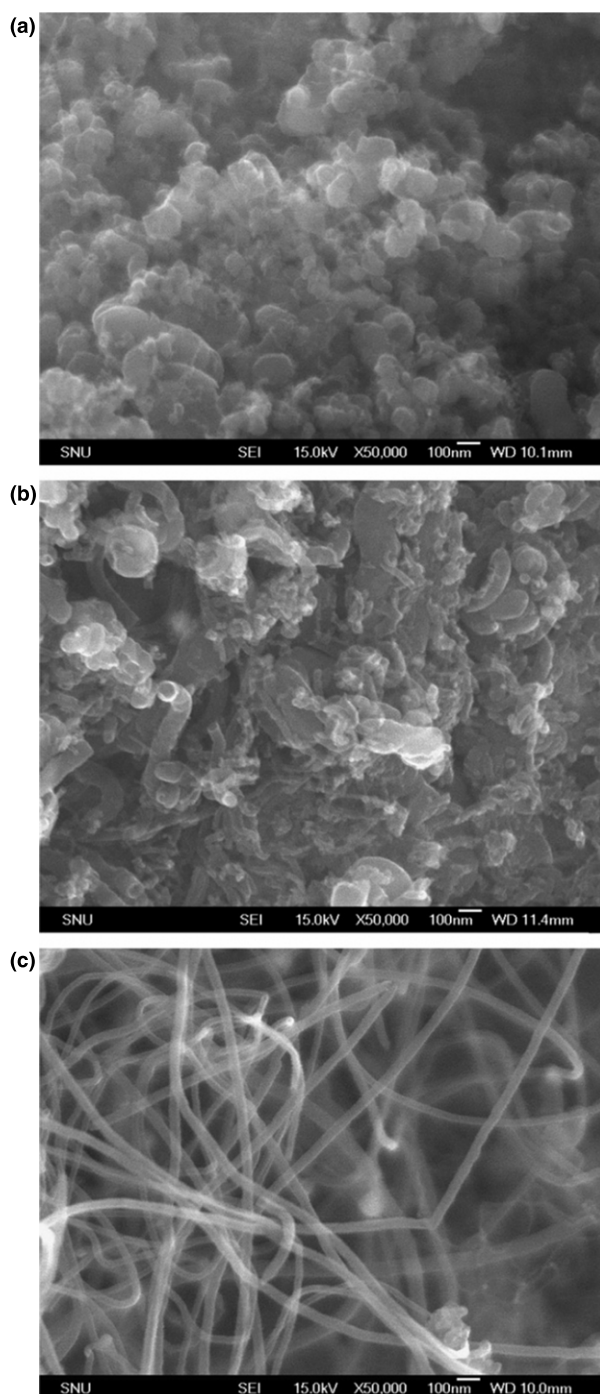


Figure 22. SEM images of carbon nanotubes and nanoparticles grown for 30 min on the stainless steel substrate at 600 °C at applied biases of (a) –200, (b) 0 and (c) +25 V under the conditions of 1900 °C wire temperature, 22 665 Pa reactor pressure and $\text{CH}_4 : \text{H}_2 = 10 : 40$ sccm with a distance of 1 cm between the wire and the substrate. Reprinted with permission from [43]. Copyright 2008 Elsevier.

of 950 °C, 990 °C, 1000 °C and 1010 °C, respectively [44]. No carbon nanotubes were synthesized at 950 °C. Carbon nanotubes with a diameter of 20 nm began to form at 990 °C. Carbon nanotubes with a diameter of 300 nm were synthesized at 1000 °C. Carbon nanotubes with a thinner diameter of 130 nm but with longer length were synthesized at 1010 °C.

Figures 25(a) and (b) show the size distribution of positively and negatively charged nanoparticles, respectively, generated in the gas phase at various reactor temperatures [44]. At 950 °C charged nanoparticles were not detected. Both positively and negatively charged nanoparticles were generated under the condition where carbon nanotubes were formed at 990 °C, 1000 °C and 1010 °C. This indicates that carbon nanotubes are formed only when charged nanoparticles are generated in the gas phase. As the reactor temperature increases, both number and size of positively and negatively charged nanoparticles increase. The size distribution of charged nanoparticles is highly correlated with the diameter of carbon nanotubes.

Figure 26 shows the effect of hydrogen addition on the microstructure evolution during the synthesis of carbon nanotubes at a CH_4 flow rate of 100 sccm and a reactor temperature of 1010 °C under atmospheric pressure [44]. Figure 26(a) shows typical carbon nanotubes grown without hydrogen addition. Figure 26(b) shows the drastically different microstructure evolution with hydrogen addition at its flow rate of 100 sccm. In the previous approach based on the atomic growth, the processing parameters are directly attributed to the microstructure change. That is, the hydrogen addition would have been directly correlated with the microstructure change from curved and thin carbon nanotubes in figure 26(a) to the straight and thick carbon nanorods in figure 26(b).

In the new understanding by TCN, however, the processing parameters are correlated with the size distribution of charged nanoparticles, which is again correlated with the final microstructure evolution. Therefore, information about the size distribution of charged nanoparticles is necessary for a better understanding of the effect of the processing parameters. Figure 27 shows the effect of hydrogen addition on the size distribution of both positively and negatively charged carbon nanoparticles. Without hydrogen, the number density and size are much larger than those with hydrogen addition. This means that the decrease in the number density and the size distribution should be responsible for the evolution of straight and thick nanorods in figure 26(b).

It should be noted that mainly negatively charged nanoparticles are formed in the gas phase of the HWCVD process as indicated by the bias effect of figure 22 whereas both positively and negatively charged nanoparticles are formed roughly in equal amounts in the gas phase of the thermal CVD process as shown by figures 25 and 27. This difference comes from the different charging mechanisms between HWCVD and thermal CVD. In the HWCVD process, some of the electrons emitted from the hot wire are attached to atoms or molecules and, as a result, negative ions are produced, which are thought to induce ion-induced nucleation. Finally, negatively charged nanoparticles are produced. In the thermal CVD process, however, nuclei would be formed first in the gas phase and then undergo contact ionization with the reactor wall, producing both positively and negatively charged nanoparticles. Another possibility for charging in the thermal CVD process would be that charged species are generated by chemionization during the decomposition of precursors and act as centres for ion-induced nucleation.

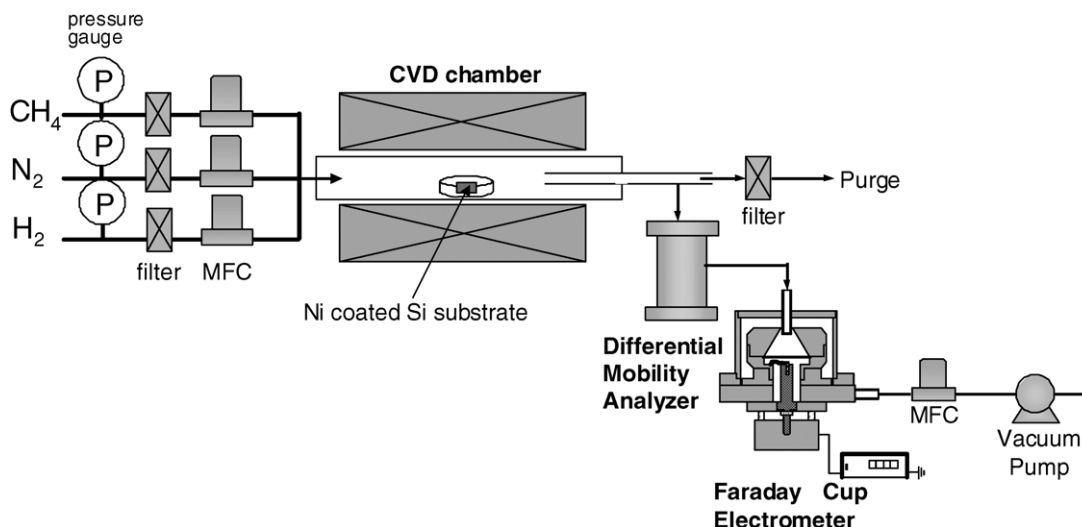


Figure 23. Schematic of experimental set-up for measurements of charged nanoparticles generated during the thermal CVD process.

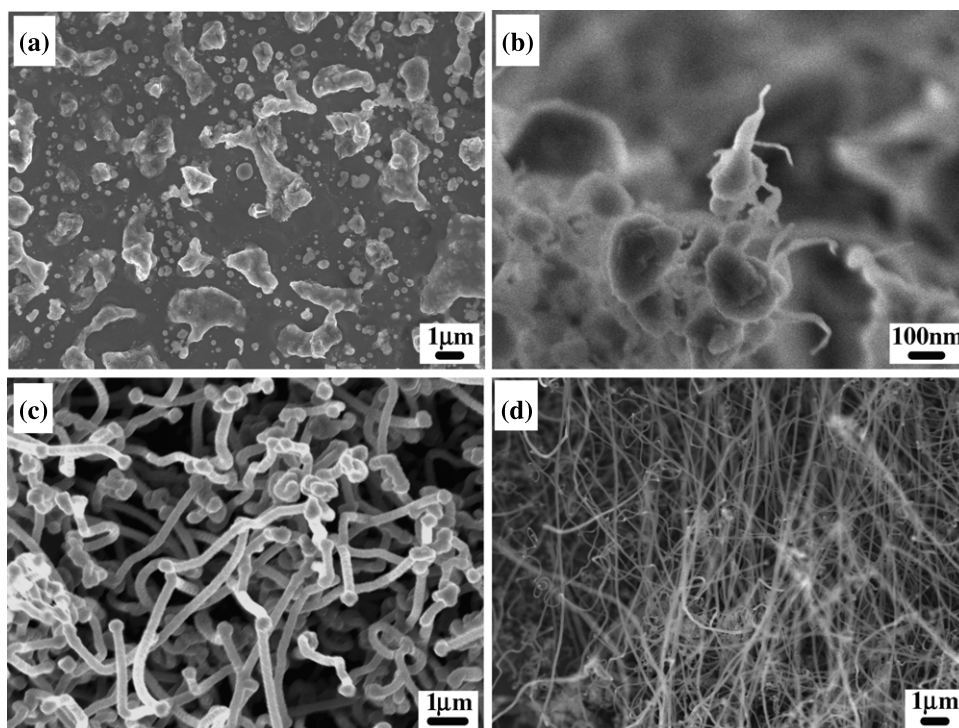


Figure 24. FESEM images of carbon nanotubes. The carbon nanotubes were synthesized at reactor temperatures of (a) 950 °C, (b) 990 °C, (c) 1000 °C and (d) 1010 °C. Reprinted with permission from [44]. Copyright 2009 Elsevier.

3.6. Simultaneous deposition and etching of silicon during CVD

In the silicon CVD process, the phenomenon of simultaneous deposition and etching of silicon is observed. In the selective epitaxial growth of silicon, the silicon tends to grow selectively on the conducting surface patterned on the insulating substrate [200]. Kumomi *et al* [201–203] prepared slightly conducting SiN_x patterned on an insulating SiO_2 substrate and deposited the silicon selectively on the SiN_x patterns using dichlorosilane and hydrochlorine. The microstructure evolutions are shown in figure 28 [202]. After 480 s, multiple fine particles were selectively formed on all

SiN_x patterns. However, after 720 s, one large particle, which was apparently distinguishable, emerged among the pre-existing fine particles on some of the SiN_x patterns, while other particles disappeared due to etching. After 960 s, almost the entire area of each pattern was covered with one large particle while a few SiN_x patterns were vacant, where all particles on these patterns had been etched away. After analysing this phenomenon, the authors [201–203] concluded that it could not be explained by a coarsening process such as Ostwald ripening, where large particles grow at the expense of small particles and, as a consequence, the average particle size increases while the total number of particles decreases during coarsening [204].

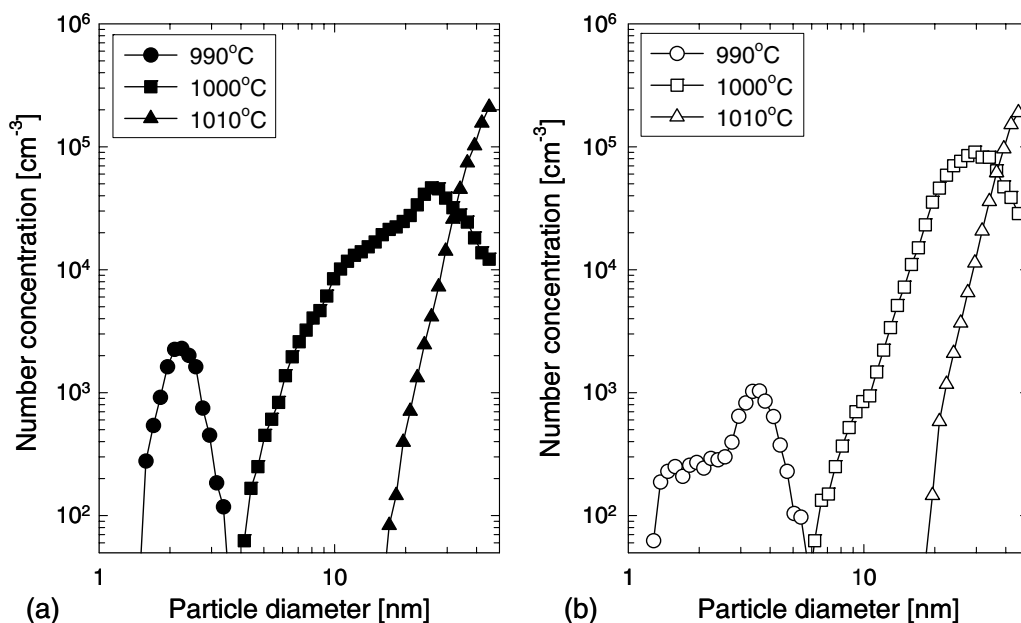


Figure 25. The size distribution of (a) positively and (b) negatively charged carbon nanoparticles at various reactor temperatures. Reprinted with permission from [44]. Copyright 2009 Elsevier.

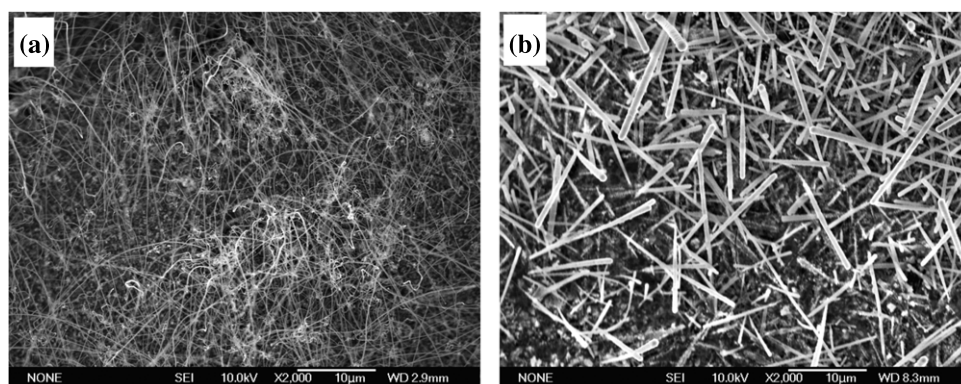


Figure 26. FESEM images of carbon nanostructures at H_2 flow rates of (a) 0 and (b) 100 sccm at a CH_4 flow rate of 100 sccm and a reactor temperature of 1010 °C. Reprinted with permission from [44]. Copyright 2009 Elsevier.

Hwang *et al* [205] did their own experiments to examine this phenomenon and observed a similar result. A gas mixture of 1% SiH_4 –2% HCl –97% H_2 was used with a substrate temperature of 950 °C and a reactor pressure of 19 998 Pa. The deposition behaviour was compared between conducting and insulating substrates. The silicon continued to deposit on the conducting substrate while numerous silicon particles deposited initially on the insulating SiO_2 and SiN_4 substrates and almost all of them are etched away with increasing deposition time.

Here, two irreversible phenomena of deposition and etching, which are in opposite directions, take place simultaneously. Irreversible deposition means that the chemical potential of silicon in the gas phase (μ_{Si}^{gas}) is higher than that of the solid (μ_{Si}^{solid}). And irreversible etching means that μ_{Si}^{gas} is lower than μ_{Si}^{solid} . Therefore, if we assume that two irreversible phenomena take place simultaneously in opposite directions, the inequality in chemical potentials leads to the thermodynamic contradiction.

As in the case of the C–H system for diamond CVD, the solubility of silicon in the gas phase of the Si–Cl–H system increases with decreasing temperature near the substrate temperature, as shown in figure 29 [48]. The numbers 10 and 0.1 in figure 29 represent the supersaturation ratio, which is defined as the ratio of the silicon partial pressure to its equilibrium vapour pressure. The equilibrium solubility line corresponds to the supersaturation ratio of 1. The solubility of silicon in the gas phase is 0.001 29 at 1100 °C. The solubility increases to 0.002 13 at a substrate temperature of 950 °C.

If silicon nucleates in the gas phase, the driving force at the substrate temperature changes for etching, because of the depletion of silicon in the gas phase. Under this situation, the silicon on the substrate will be etched away atomically into the gas phase with simultaneous deposition onto the substrate of silicon nanoparticles from the gas phase, which leads to the macroscopic observation of simultaneous deposition and etching of silicon. Therefore, the phenomenon of simultaneous deposition and etching of silicon dictates that silicon crystals

shown in figure 28 should grow by building blocks of gas-phase nuclei and simultaneously they should be etched by atomic units.

On the other hand, although the selective deposition has been widely used in semiconductor processing, the reason why the deposition is easy on the conducting substrate but difficult on the insulating substrate has remained without being understood. The selective deposition can be approached by the new understanding based on the building blocks of charged nanoparticles, which have much higher attracting image force on the conducting surface than on the insulating surface. It should be noted that the landing of nanoparticles on any surface is inhibited by the levitation force in the presence of a gas flow.

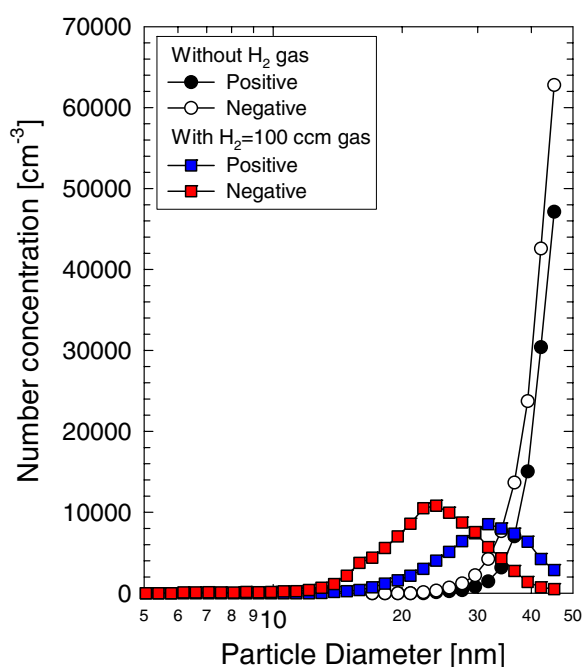


Figure 27. The size distribution of both positively and negatively charged carbon nanoparticles with H_2 flow rates of 0 and 100 sccm at a CH_4 flow rate of 100 sccm and a reactor temperature of 1010 °C.

The gas flow velocity is zero on the surface because of the friction and increases gradually away from the surface, which generates the levitation force. Since the neutral nanoparticles have no image force on the surface, their landing on the surface will be most inhibited by the levitation force. This is the effect of flow rate on the deposition behaviour of thin films in the CVD process approached by TCN. Therefore, the conventional explanations of the CVD process based on atomic deposition can be replaced by the new explanations based on TCN. Another example will be introduced in the next section.

3.7. Surface reaction-controlled and diffusion-controlled growth in the CVD process

In the CVD process, the temperature dependence of the film growth rate is divided typically into three regions. The growth rate increases with increasing temperature in a certain temperature range and then, above that range, the growth rate becomes relatively insensitive to the temperature increase and in some cases, the rate decreases with a further increase in the temperature [206–210]. This aspect is represented by the slopes in the plot of the logarithm of growth rate against inverse temperature. According to the standard classification [206–209], a higher slope in the lower temperature region indicates surface reaction-controlled growth and a lower slope in the higher temperature region indicates gas-phase diffusion-controlled growth. The negative slope in the high-temperature range is attributed to gas-phase nucleation [206, 210].

Jeon *et al* [39] studied the temperature dependence of the deposition behaviour of yttria-stabilized zirconia (YSZ) films prepared by CVD with varying evaporation temperatures of $ZrCl_4$ precursor between 250 and 550 °C. YCl_3 precursor and the substrate were at the same temperature of 1000 °C. The zirconia nanoparticles formed in the gas phase were confirmed by capturing them on the membrane TEM grid. The size was ~ 8 nm with the lattice fringe of zirconia. The deposition rate of the films decreased with increasing evaporation temperature of $ZrCl_4$, being $\sim 10 \mu m h^{-1}$, $\sim 5 \mu m h^{-1}$ and $\sim 1 \mu m h^{-1}$, respectively, at $ZrCl_4$ evaporation temperatures of 250 °C,

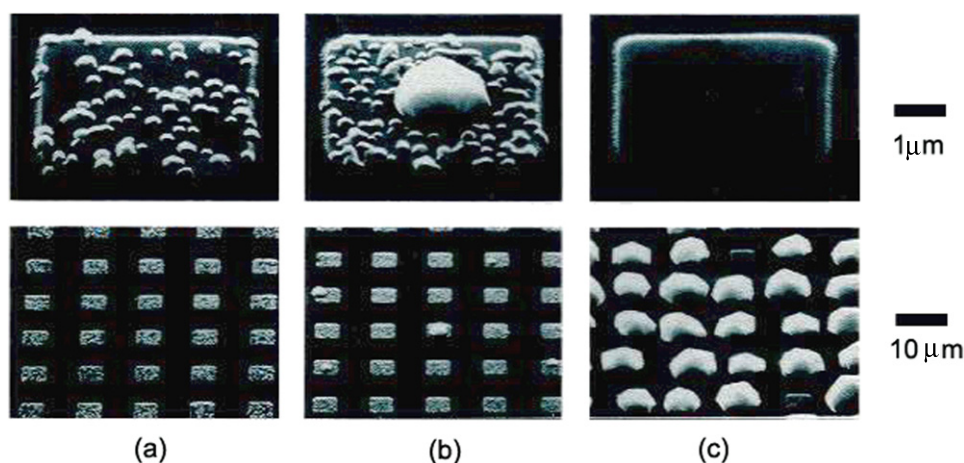


Figure 28. SEM micrographs of the Si-deposited surface at three deposition times. (a) At 480 s, multiple fine nanoparticles are formed selectively on all SiN_x portions. (b) At 720 s, a large nanoparticle emerges among the fine ones on some of the portions. (c) At 960 s, most portions were covered with a single large nanoparticle, but there are a few portions with no nanoparticle. Reprinted with permission from [202]. Copyright 1991 Materials Research Society.

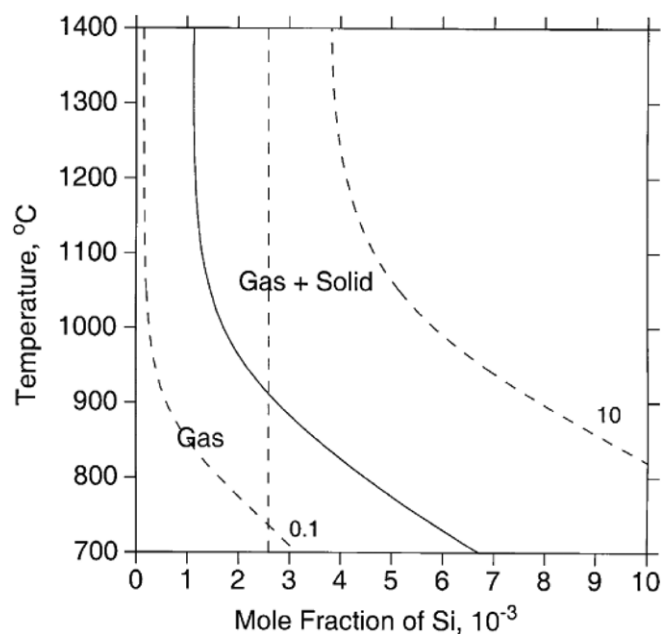


Figure 29. Temperature dependence of solubility of silicon (solid line) in gas phase in Si–Cl–H system (vertical dashed line represents composition used in the process): thermodynamic calculation was carried out under conditions of 19 999 Pa pressure and with 2.86 mol Cl and 201.06 mol H. Reprinted with permission from [48]. Copyright 1999 Elsevier.

350 °C and 450–550 °C. Considering that the evaporation flux of ZrCl_4 increases with increasing evaporation temperature, the decreased film growth rate with the increase in the evaporation temperature of ZrCl_4 is contrary to expectation. A cauliflower-shaped structure was developed at 250 °C and then gradually changed to a faceted-grain structure above 350 °C, implying that the size of charged YSZ nanoparticles decreased with increasing ZrCl_4 temperature.

If these results are explained by the conventional concept of molecular growth, the surface reaction-controlled growth in the low-temperature region of ZrCl_4 evaporation changes to gas phase diffusion-controlled growth or gas-phase nucleation in the high-temperature region. To understand the temperature dependence of the growth rate by the new concept, additional information about the temperature dependence of the electric current was obtained. The electric current increased with increasing evaporation temperature of ZrCl_4 almost linearly up to 450 °C. The current data indicated that the size of charged YSZ nanoparticles generated in the gas phase decreased with increasing evaporation temperature of ZrCl_4 . The small size of charged nanoparticles resulted in a low growth rate but produced angular grains with well-defined facets whereas the large size resulted in a high growth rate but produced a cauliflower-shaped structure.

Therefore, the surface reaction-controlled and gas phase diffusion-controlled growth in the conventional concept of atomic growth correspond, respectively, to large and small sizes of charged nanoparticles, which produce the cauliflower structure with a high growth rate and well-developed faceted grains with a low growth rate, respectively. For a given number of precursors, the size of nanoparticles decreases with

increasing amount of charging. Normally, the increase in the dissociation temperature of precursors increases the amount of charging, decreasing the size of charged nanoparticles. The small size of charged nanoparticles is favourable for epitaxial recrystallization, which can be explained by the concept of the magic size suggested by Fujita [115, 116] and was also shown by the size effect of nanoparticles on the deposition behaviour through MD simulations [163]. Therefore, the small size produces large grain size with well-developed facets but has difficulty in landing, leading to a low growth rate.

4. Generation of charged nanoparticles and their deposition in the thin film processes

4.1. Thermal evaporation

The thermal evaporation process is carried out in relatively high vacuum. Because of the long mean free path, atomic collision for clustering in the gas phase is much less frequent than in the CVD process. In the thermal evaporation process, the base pressure is normally less than 1.3×10^{-4} Pa, although the pressure can increase to 1.3×10^{-1} – 1.3×10^{-2} Pa during the evaporation process. Experimentally, it has been confirmed that charged nanoparticles are generated during thermal evaporation of metal wires in a heated tungsten basket [211–214]. Positively charged nanoparticles are dominant, which was confirmed by current measurements and bias experiments [211–214].

The generation of charged nanoparticles from hot surfaces was reported by Schmidt-Ott *et al* [215] as early as 1980 and was widely applied for the production of metallic particles [216–219]. Jeon *et al* [213, 214] attributed the source of positive charge to the surface ionization of evaporating metal atoms. However, Peineke *et al* [220] observed that wires of different purities and with purification by out-gassing at high temperatures led to pronounced differences in positive particle production. They attributed the positive charging to the surface ionization of impurity atoms with a low ionization energy [221]. This conclusion agrees with our further study on the source of positive charge during evaporation of metals in a tungsten basket. In the initial stage of heating, the surface layer is evaporated and an appreciable amount of positive charges is detected as an electric current. Once this surface layer is removed, negative charge tends to be dominant. As suggested again by Peineke *et al* [221], the source of negative charge appears to come from electrons emitted from the heated tungsten basket.

Therefore, it can be said that the surface impurity layer of the tungsten basket plays a major role in producing the positive ions, which might act as a centre for clustering, producing the positively charged nanoparticles. The interesting fact is that the film grown under the generation condition of positively charged nanoparticles has a higher growth rate as well as a smoother surface than that grown under the condition where charged nanoparticles were not generated. Jeon *et al* [213] compared the copper films grown at different evaporation temperatures of 950 °C and 1300 °C. No current higher than the noise level of ~ 10 pA mm^{-2} was detected at an evaporation

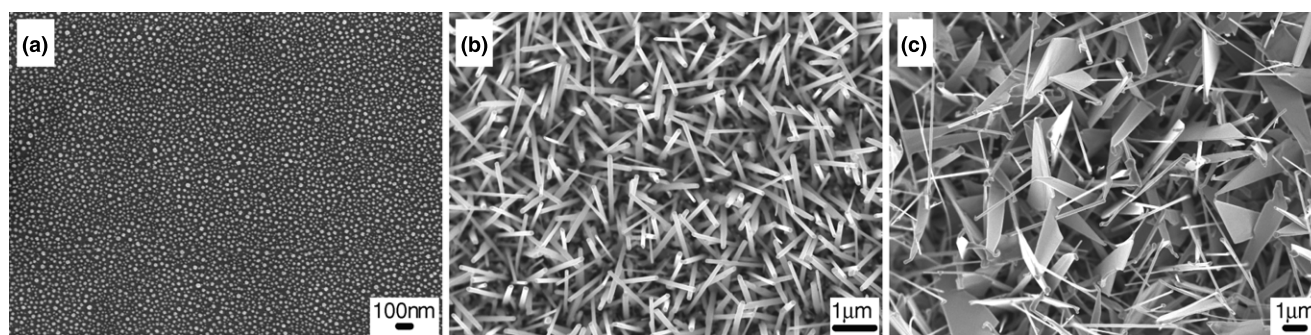


Figure 30. FESEM images of ZnO nanowires and nanosheets at reactor temperatures of (a) 800 °C, (b) 900 °C and (c) 1000 °C. Reprinted with permission from [45]. Copyright 2009 AAAR.

temperature of 950 °C, whereas more than 100 pA mm^{-2} was detected at 1300 °C. The film growth rate for 950 °C was about 300 times lower than that for 1300 °C. Therefore, the film deposited for 140 min at 950 °C has a similar thickness to the film deposited for 7 min at 1300 °C. Although the growth rate was extremely low at the evaporation temperature 950 °C, the film morphology was much worse than that evaporated at 1300 °C. These results imply that charged nanoparticles might produce denser and smoother films than the mixture of atoms and neutral nanoparticles. Considering this, the surface impurity layer of the tungsten basket plays a beneficial role in depositing high-quality films.

The quality of films would be best if films are deposited exclusively by individual atoms. However, the deposition condition exclusively by individual atoms is rather difficult to achieve during thermal evaporation or other PVD methods and normally small clusters such as dimers, trimers and tetramers tend to be formed. If the mean free path for the atomic collision is 1 m and the distance between the evaporation source and the substrate is 20 cm, the probability for an atomic collision is 0.2. This probability is not small. If one mole of atoms is evaporated, a number of collisions as frequent as $\sim 10^{23}$ will occur. This simple estimation indicates that the generation of clusters is difficult to avoid.

Therefore, the flux for deposition during thermal evaporation or other physical methods can be individual atoms, neutral nanoparticles and charged nanoparticles. The film quality in terms of surface morphology is expected to be best when exclusively individual atoms contribute to deposition, the second best when charged nanoparticles contribute to deposition and the worst when neutral nanoparticles contribute to deposition. Therefore, if the formation of neutral nanoparticles is unavoidable due to relatively poor vacuum of the reactor, intentional charging would be beneficial for improving the film quality. To our understanding, the improvement of film quality achieved by additional ionization in the processes, so-called ionized sputtering, ion-assisted deposition and ionized PVD, comes at least in part from such a charging effect.

4.2. Thermal CVD

Motivated by the possibility that the growth of films and nanostructures by charged nanoparticles might be general

in the CVD process, Kim *et al* [42, 44–46] set up a CVD reactor equipped with the DMA–FCE system and checked whether charged nanoparticles were generated or not during the synthesis of films and nanostructures by CVD. Under the condition where ZnO nanowires were synthesized by thermal CVD, the distribution of charged nanoparticles in the gas phase was measured by the DMA–FCE system without an additional artificial charger [45]. Figures 30(a), (b) and (c) show the FESEM images of ZnO nanostructures at reactor temperatures of 800 °C, 900 °C and 1000 °C, respectively [45]. At 800 °C no ZnO nanostructure was formed and only gold nanoparticles, which were formed from a gold film deposited for a catalyst, were shown. At 900 °C ZnO nanowires were synthesized with a diameter of $\sim 100 \text{ nm}$. At 1000 °C ZnO nanowires and nanosheets were synthesized. The distribution of charged nanoparticles was measured under the conditions of figure 30. Figures 31(a) and (b) show the size distribution of positive and negative nanoparticles, respectively, with different reactor temperatures [45]. At 800 °C no charged particles were measured, where no ZnO nanostructure was formed. At 850 °C both positive and negative nanoparticles were measured. As the reactor temperature increased, the number density of both positive and negative nanoparticles increased. The number density of the positive nanoparticles was somewhat higher than that of the negative nanoparticles. Under the conditions where negative and positive nanoparticles were generated in the gas phase, ZnO nanowires and nanosheets were synthesized. As the number density of the charged nanoparticles increased, ZnO nanostructures changed from nanowires to nanosheets.

From the present experimental results, it cannot be definitely decided whether the charged nanoparticles are mainly involved, partly involved or hardly involved in the growth of ZnO nanowires and nanosheets. However, a huge number of charged gas-phase nuclei imply that the role of catalytic gold nanoparticles should be reconsidered because the charged nanoparticles must have been formed without the help of the catalytic gold particles, which had been believed to enhance the decomposition of precursor gases. It should be noted that catalytic gold nanoparticles are not essential for the growth of ZnO nanowires because ZnO nanowires can be grown even without gold nanoparticles.

Considering the total surface area of charged nanoparticles, which is much larger than the area of the substrate, the additional supersaturation for further precipitation of ZnO

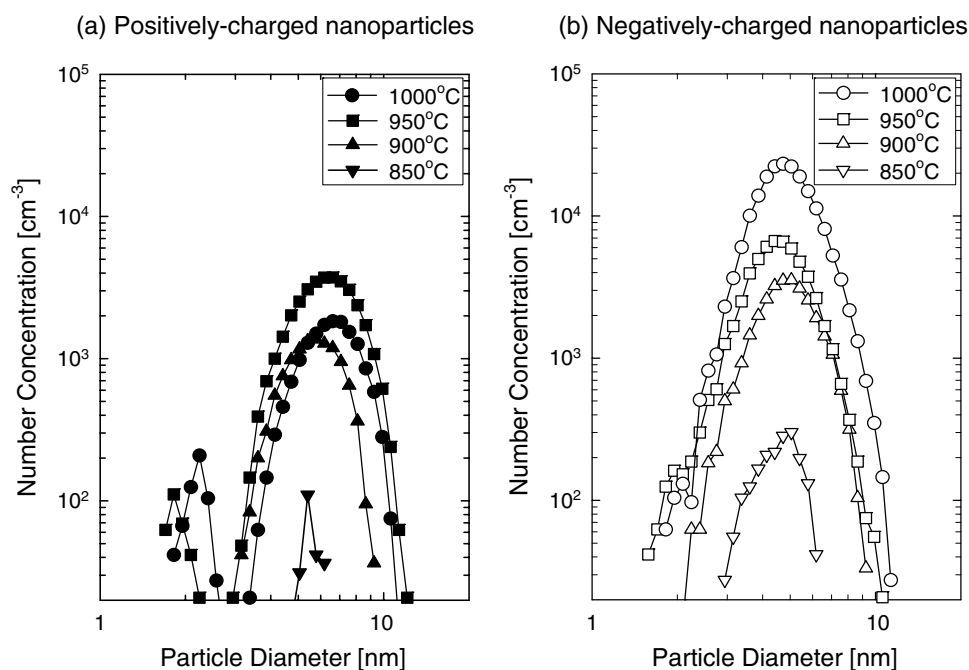


Figure 31. The size distribution of (a) positively and (b) negatively charged ZnO nanoparticles at various reactor temperatures. Reprinted with permission from [45]. Copyright 2009 AAAR.

from the gas phase would be negligibly small. Then, the molecular flux for the growth of ZnO nanostructures would be rather negligible, whereas a huge amount of ZnO flux is available from the charged nanoparticles generated in the gas phase. Considering these facts, it is more probable that the charged nanoparticles, instead of individual molecules, should interact with the catalytic gold particles to produce the ZnO nanowires. It should be noted that under the condition where charged nanoparticles were not generated, ZnO nanowires and nanosheets did not grow.

Normally, it is much easier to grow ZnO nanowires in the presence of catalytic metal particles than in their absence. If this fact is approached by TCN, the image field made by charged nanoparticles is much stronger with the metal particles than that with the ZnO nanowires. Therefore, charged ZnO nanoparticles selectively land on the metal particle on the tip of the growing nanowires. In the presence of the charged nanoparticles formed in the gas phase, the role of the catalytic metal particles is to provide a strong electrostatic attraction between the charged nanoparticles and the metal particles. In the absence of catalytic metal particles, such a difference in the image field is absent but still the selective landing of charged nanoparticles can occur because the electrostatic interaction depends on the relative position between the charged nanoparticle and the charged wire. If the charged nanoparticle approaches the nanowire in the axial direction, the interaction tends to be attractive, whereas if the charged nanoparticle approaches the nanowires in the radial direction, the interaction tends to be repulsive. This anisotropic interaction also comes from the image field. This concept was used to explain the growth of silicon nanowires in the absence of catalytic metal particles by TCN [222].

Figure 32 shows the FESEM images of Si nanowires grown at hydrogen flow rates of (a) 5, (b) 10 and (c) 15 sccm

at a SiCl_4/H_2 molar ratio of 0.05 and a reactor temperature of 975 °C by thermal CVD [46]. The generation of charged nanoparticles was experimentally confirmed by the DMA-FCE system under growth conditions of figure 32 as shown in figure 33 [46]. As the reactor temperature was increased, the size distributions of both positively and negatively charged nanoparticles shifted to smaller size and their number concentration increased. Figures 32 and 33 show that Si nanowires were grown under the conditions where small charged nanoparticles of ~30 nm were produced in the gas phase whereas a film consisting of nanoparticles with a size of ~100 nm was formed instead of nanowires under the conditions where the charged nanoparticles of ~100 nm were produced in the gas phase.

Figure 34 shows the FESEM images of silicon films grown at reactor temperatures of (a) 500 °C, (b) 600 °C, (c) 700 °C and (d) 800 °C with a SiH_4 flow rate of 10 sccm of helium-diluted silane of 10% SiH_4 –90% He for 30 min with nitrogen gas supplied as a carrier gas at a flow rate of 1000 sccm [42]. Under the conditions of figure 34, charged nanoparticles were generated as shown in figure 35. It should be noted that the SiH_4 concentration used in this experiment was made to be very low because if SiH_4 concentration typically used in silicon CVD was supplied, the number of charged nanoparticles was so large that it exceeded the detection limit of the DMA-FCE system. This means that the generation of charged silicon nanoparticles is almost unavoidable in the silicon CVD using SiH_4 .

There are two possible mechanisms for the formation of charged nanoparticles in thermal CVD. One is that ions are formed first by chemionization during decomposition of precursors in the reactor and nanoparticles are formed in the gas phase by ion-induced nucleation. The other possible mechanism is that nucleation takes place first and then the

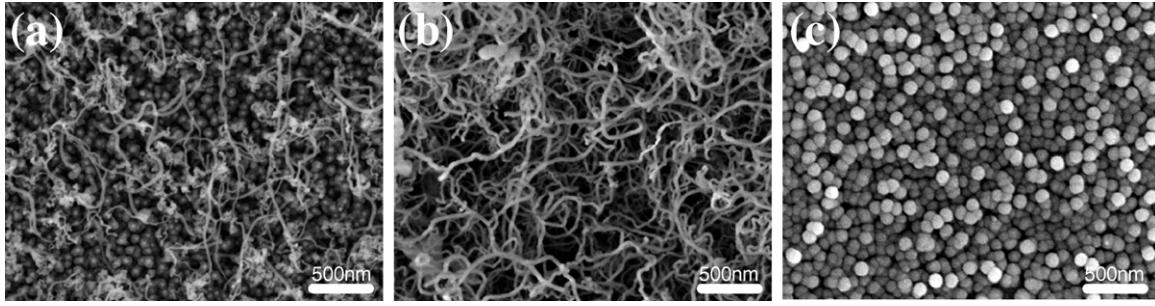


Figure 32. FESEM images of Si nanowires and nanoparticles at hydrogen flow rates of (a) 5, (b) 10 and (c) 15 sccm at a SiCl_4/H_2 molar ratio of 0.05 and a reactor temperature of 975 °C. Reprinted with permission from [46]. Copyright 2010 American Chemical Society.

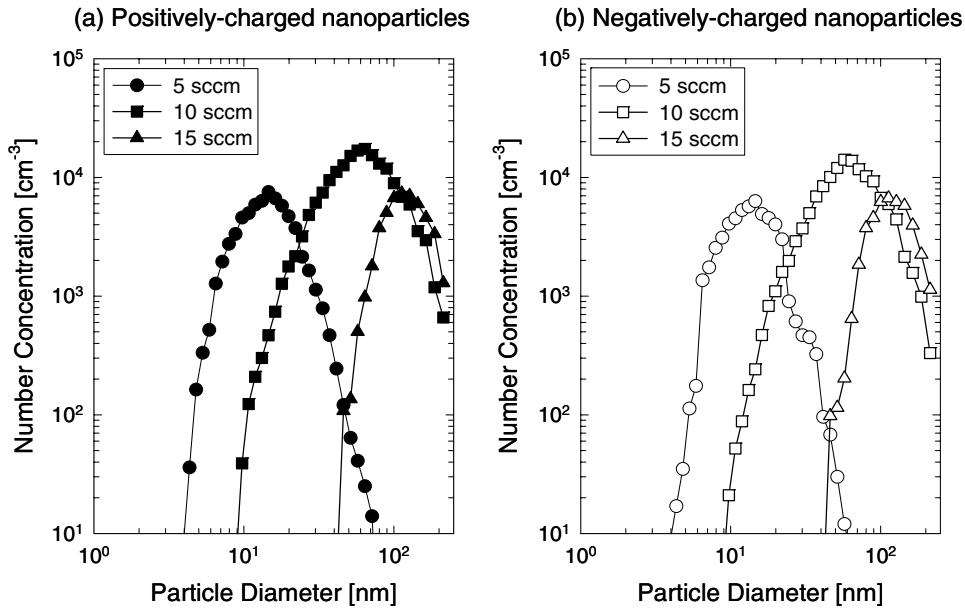


Figure 33. Size distribution of (a) positively and (b) negatively charged nanoparticles at hydrogen flow rates of 5, 10 and 15 sccm at a SiCl_4/H_2 molar ratio of 0.05 and a reactor temperature of 975 °C. Reprinted with permission from [46]. Copyright 2010 American Chemical Society.

nuclei undergo surface ionization on any surface such as the quartz tube of the reactor. Magnusson *et al* [223] reported similar thermal charging of gold nanoparticles during reshaping at a high temperature with the charging behaviour depending on the materials of the reactor tube.

If the silicon nuclei undergo surface ionization on the quartz reactor wall, positive and negative surface ionizations are described by the following Saha–Langmuir equations, respectively [224]:

$$\frac{n^+}{n^0} = \frac{g^+}{g^0} \exp\left(-\frac{\text{IP} - \text{WF}}{kT}\right), \quad (7)$$

$$\frac{n^-}{n^0} = \frac{g^-}{g^0} \exp\left(-\frac{\text{WF} - \text{EA}}{kT}\right). \quad (8)$$

In these equations, n^0 , n^- and n^+ indicate the numbers of neutral, negative and positive species, respectively. g^0 , g^- and g^+ mean the statistical weights of neutral, negative and positive species, respectively, and the ratio of them g^+/g^0 and g^-/g^0 in the equations is close to one. IP, EA, WF and k are the ionization potential and electron affinity of nanoparticles,

work function of the quartz wall and Boltzmann constant, respectively.

In this mechanism, IP and EA of nanoparticles generated in the gas phase and WF of the reactor wall are the important factors in determining the polarity of charged nanoparticles. IP and EA of nanoparticles, which depend on the size of nanoparticles, would approach the work function of bulk silicon as the size of nanoparticles increases. The difference between (IP-WF) and (WF-EA) in the above equations would make the difference between the number concentrations of positively and negatively charged nanoparticles.

Understanding the generation of charged nanoparticles with their subsequent deposition into films will give lots of benefits in optimizing the CVD process. Let us introduce how this new understanding can be applied to the deposition of GaN films for light-emitting diode applications in the metal organic CVD (MOCVD) process. One of the authors (NMH) was requested to solve the problem encountered when the MOCVD reactor was scaled up from a small quartz reactor to a large stainless steel reactor. The problem was that the consumption of trimethylgallium (TMG) in a stainless steel reactor was much higher to produce the same quality GaN

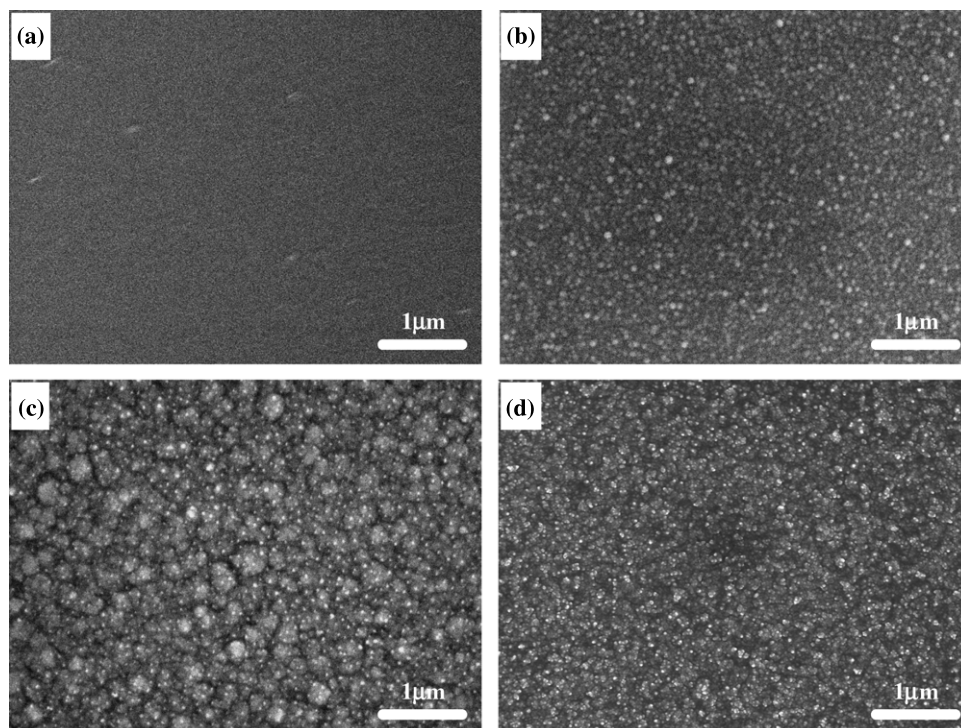


Figure 34. FESEM images of silicon films at reactor temperatures of (a) 500 °C, (b) 600 °C, (c) 700 °C and (d) 800 °C with a SiH₄ flow rate of 10 sccm. Reprinted with permission from [42]. Copyright 2010 American Institute of Physics.

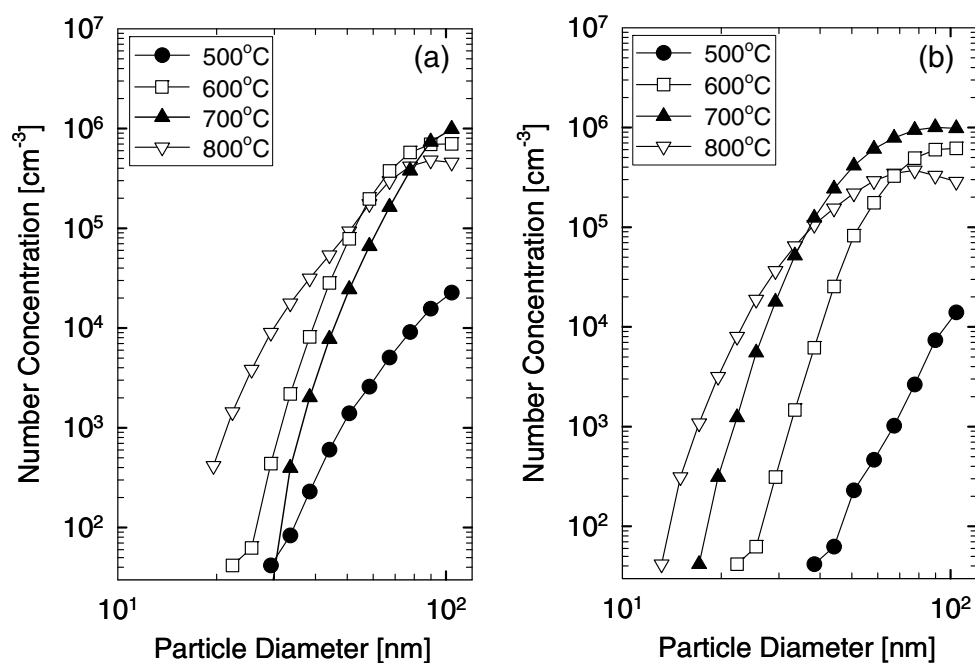


Figure 35. The size distribution of (a) positively and (b) negatively charged nanoparticles at various reactor temperatures with a SiH₄ flow rate of 10 sccm. Reprinted with permission from [42]. Copyright 2010 American Institute of Physics.

film than that in a quartz tube reactor. From the viewpoint of TCN, there are many differences between stainless steel and quartz reactors. First, the loss of charged GaN nanoparticles to the conducting stainless steel wall will be much larger than that to the insulating quartz wall. Second, a much larger amount of electric charge will be lost to the conducting stainless steel wall than to the insulating quartz wall. As a result,

charged nanoparticles of much larger size will contribute to the deposition of the GaN film in the stainless steel reactor, which will degrade the film quality. In order to obtain GaN film of the same quality as being obtained in the quartz reactor, a much higher flow rate of TMG is required to decrease the mean residence time in the reactor, which will decrease the size of the charged GaN nanoparticles. Therefore, the advice was

that an insulating lining should be made inside the stainless steel reactor. Following the advice, the requester installed the insulating lining on the inner side of the stainless steel reactor and solved the problem.

4.3. HWCVD

In thermal CVD, both positive and negative nanoparticles are generated. Nanoparticles of one polarity will attract those of the other polarity and after coalescence or coagulation, they become neutral. Neutral nanoparticles will be attracted to charged ones because of the image charge. As these processes continue, the size of charged nanoparticles continues to increase. For this reason, the size of charged nanoparticles tends to be large as shown in figures 25, 27, 31, 33 and 35, which is in contrast with the small size of diamond charged nanoparticles generated in the HWCVD process shown in figures 7 and 12. The diameter of charged nanoparticles generated during thermal CVD is larger by more than an order of magnitude than that during HWCVD. This means that the number of atoms in a charged nanoparticle in the former is larger by more than three orders of magnitude than that in the latter.

The reason why the size of charged nanoparticles in the HWCVD process is much smaller than that in the thermal CVD process is that nanoparticles generated in the HWCVD process are dominantly negatively charged. In other words, thermal CVD provides a bipolar charging environment whereas HWCVD provides a unipolar charging environment. Since the interaction between negative nanoparticles is repulsive, the collision frequency is markedly reduced and as a result the small size can be maintained. Dominance of the negative charge would be due to the unbalanced generation of positive and negative charges from the hot wire. Negative charges would be from electrons emitted from the hot wire, which is described by the Richardson–Dushman equation [225, 226]. Positive charges would be from the positive surface ionization of gas species on the hot wire. The amount of negative charge is much larger than that of positive charge. When the reactor pressure is higher than ~ 133 Pa in the HWCVD process, the collision frequency between positive and negative particles would be so high that positive nanoparticles will disappear and exclusively negative nanoparticles would exist. In general, nanoparticles in HWCVD are dominantly negatively charged and tend to be unipolarly charged. This is often the case, but not always. For example, applying a bias to the hot wire can drastically change the charging behaviour. Details will be discussed later.

Unipolar charging by HWCVD has both advantage and disadvantage. Since the small size of charged nanoparticles is favourable for epitaxial recrystallization, high-quality films can be deposited by HWCVD at relatively low temperatures. When only negative nanoparticles exist, however, the deposition on an insulating substrate such as glass is limited by the removal of the negative charges, which would build up on the insulating surface. In this case, the removal rate of the negative charge can determine the film growth rate. This aspect is shown in figure 36 [227]. The deposition was done

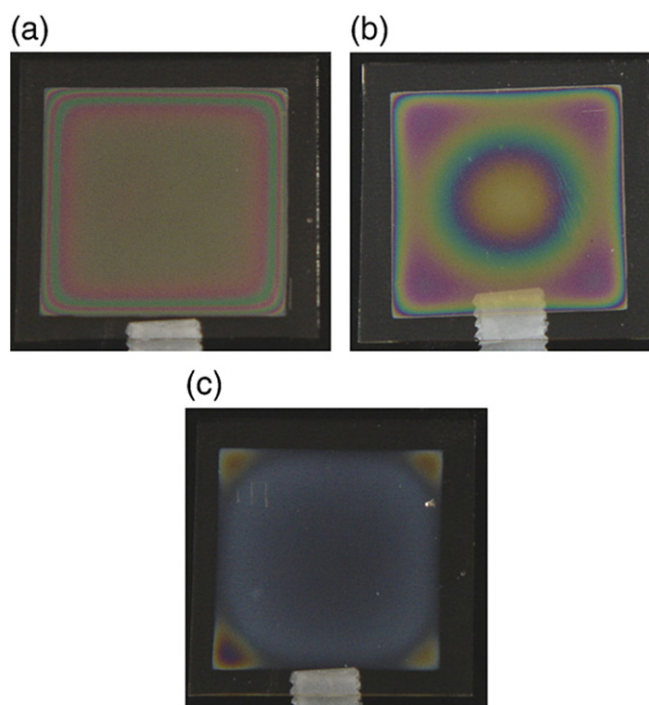


Figure 36. Photographs of silicon films deposited on glass for 4 min at wire temperatures of (a) 1590 °C (b) 1670 °C and (c) 1800 °C. The non-uniform deposition becomes more pronounced with increasing wire temperature. Reprinted with permission from [227]. Copyright 2007 Elsevier.

on glass under 67 Pa at a substrate temperature of 450 °C with a distance of 6.5 cm between wires and substrate with wires heated by an ac power supply.

The different deposition behaviour on glass according to the different wire temperatures of 1590 °C, 1670 °C and 1800 °C in figures 36(a), (b) and (c), respectively, might be related to the relative fraction of charged to neutral depositing flux; the amount of charged flux would increase with increasing wire temperature, which is indirectly confirmed by the observation that the amount of negative current increased with increasing wire temperature [40]. Therefore, the amount of neutral depositing flux would be minimal at the wire temperature of 1800 °C, in which case the centre of the substrate was hardly deposited. In figure 36(b), the deposition rate was minimal at the centre and maximal at the corners, which correlated well with the charge removal rate from the insulating substrate.

Such non-uniform deposition would become more pronounced as the size of the glass substrate increases. In order to avoid such non-uniform deposition on the insulating substrate, the generation behaviour of electric charges should be understood. Park *et al* [228, 229] studied the generation of electric charge during silicon HWCVD and found out that the electric field formed around the hot wires, which have the input and output potentials of +18 V and 0 V, respectively, provided by a dc power supply, interacted with the charged species generated from the hot wires.

As a result, the currents measured 1.5 cm below the input and output positions of the hot wires at 2000 °C heated by the dc power supply were $+4 \text{ nA cm}^{-2}$ and -544 nA cm^{-2} ,

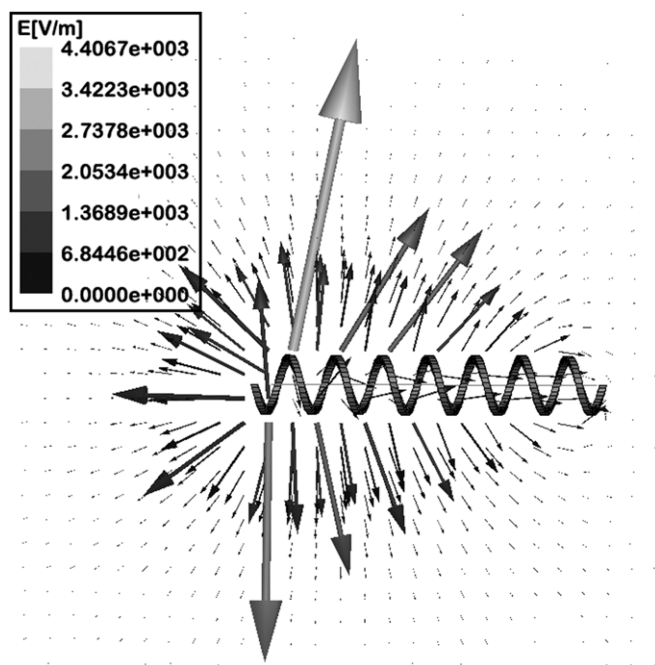


Figure 37. Electric field around the hot wire when the potential difference between the input and output positions of the hot wire is 18 V with the output potential of zero, being connected to the ground. Reprinted with permission from [228]. Copyright 2009 American Chemical Society.

respectively, and those 4.5 cm below the input and output positions were $+3 \text{ nA cm}^{-2}$ and -64 nA cm^{-2} , respectively. The sign of the current was different between the input and output positions of the hot wires, being positive and negative, respectively. In addition, as the distance from the wire was further away, the positive current increased at the input position and the negative current decreased in absolute value at the output position. The distribution of charged nanoparticles is different depending on the position, which can change the deposition behaviour of films at different positions in the reactor. These data imply that both positive and negative charges are generated but an appreciable fraction of negative charges was attracted to the electric field around the hot wires.

Figure 37 shows the electric field formed around the hot wire, which was calculated using the commercial software, Maxwell [230], considering the geometry of the reactor. The magnitude of the electric field is represented by both greyscale and magnitude of the arrow. Definitely, the electric field at the input position is much larger than that at the output position. The large positive electric field generated around the input position would attract the negative charge and repel the positive charge, leading to non-conservation of net charges.

By applying an additional bias to the hot wires with respect to the ground, the electric field around the hot wires can be controlled. For example, the additional biases of +25 V and -25 V applied to the hot wires produced $+2.38 \text{ nA cm}^{-2}$ and $-4.86 \times 10^4 \text{ nA cm}^{-2}$, respectively, 1.5 cm below the input position of the hot wires. Such an additional bias might be useful in controlling the generation and the deposition behaviour of charged nanoparticles in the HWCVD process. Under the processing condition of the non-uniform deposition

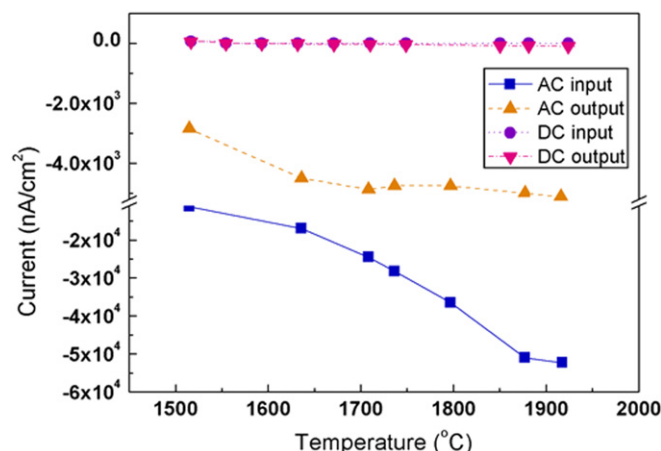


Figure 38. Temperature dependence of current measured 1.5 cm below the input and output positions of the hot wire for ac and dc powers. Reprinted with permission from [229]. Copyright 2010 Elsevier.

shown in figure 36, the additional bias of the negative voltage applied to the hot wires would supply positive charges to the substrate, discharging the built-up negative charges on the insulating substrate. The additional bias can be alternating with a variable duration and a variable magnitude of voltages.

Either ac or dc power supply is used to heat the wires in the HWCVD process. The ac power supply turned out to be worse with respect to non-uniform deposition, implying that the ac power supply should produce more dominant negative charges than the dc power supply. Park *et al* [229] compared the deposition behaviour and the generation of charges between dc and ac power supplies.

Figure 38 shows the measured currents for ac and dc powers with varying wire temperature, when the electrodes were placed 1.5 cm below the input and output positions [229]. Note that the Y-axis scales for ac and dc powers are different. The currents measured for the ac power were far more negative than those for the dc power at both input and output positions. For example, when the wire temperature was 1800°C , the currents measured 1.5 cm below the input position were $-3.65 \times 10^4 \text{ nA cm}^{-2}$ and -0.11 nA cm^{-2} , respectively, for ac and dc powers. In addition, the ac power produced a thin film with a higher crystalline fraction than the dc power.

In order to understand the generation behaviour of electric charges for the ac power, Park *et al* [229] measured the current using an oscilloscope. Figures 39(a) and (b), respectively, show the voltage of the ac power and the current measured on the electrode by an oscilloscope at the input position. In figure 39(a), the ac voltage oscillates at 60 Hz in the range -18 to +18 V. At the same time, the current in figure 39(b) also oscillates at 60 Hz as the ac voltage does. It is obvious that the current is affected by the oscillating electric field of the ac power. However, the amplitude of the current is not symmetric, oscillating between 0 and $-4 \times 10^{-3} \mu\text{A}$ although the ac voltage oscillates symmetrically with 0 V as a centre.

This result can be explained by the unbalanced generation of positive and negative charges from the hot wire. A relatively large number of negative charges or electrons is generated by thermal emission from the hot wire but a much smaller

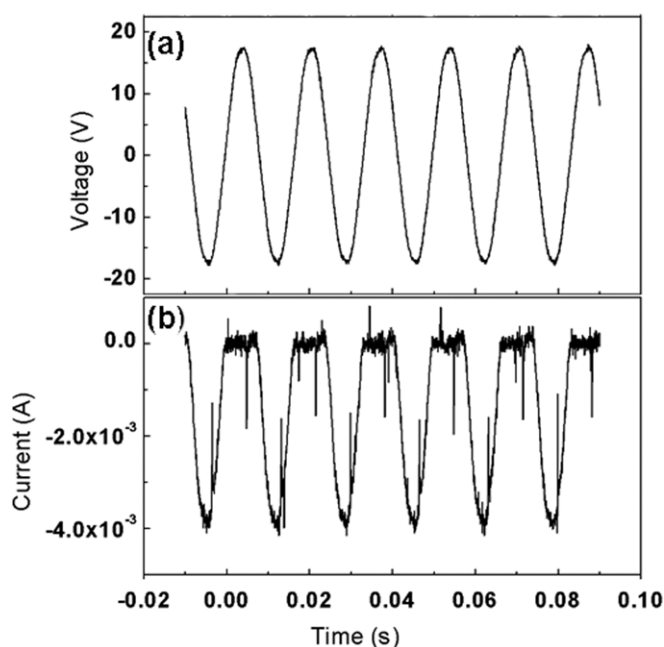


Figure 39. (a) Voltage oscillation with time measured by an oscilloscope at the input position of the hot wire under the ac power and (b) current oscillation with time measured by an oscilloscope on the electrode placed 1.5 cm below the input position of the hot wire. Reprinted with permission from [229]. Copyright 2010 Elsevier.

number of positive charges is generated by the positive surface ionization on the hot wire. When the hot wire exerts a positive potential, it will attract the negative charges and repel the positive ones. And the positive current measured on the electrode would be small because the number of positive charges generated by positive surface ionization would be small. When the hot wire exerts a negative potential, however, it will attract the positive charges and repel the negative ones. The measured negative current would be large because the number of negative charges generated by the thermal emission would be large.

Another factor that is responsible for the non-symmetric oscillation of the current in figure 39(b) would be the difference in the mobility between positive and negative charges. Most of the negative charges would be electrons, which must have much higher mobility than positive charges, which would be molecular or cluster ions. Electrons would respond to a given electric field much faster than molecular and cluster ions. This analysis explains why the current for the ac power in figure 38, which is the average value of such oscillating current as shown in figure 39(b), is much more negative than that for the dc power. This analysis also explains why the current is more negative below the input position than below the output position of the hot wire for the ac power, considering that the ac voltage is oscillating in the range -18 to $+18$ V at the input position of the hot wire whereas the voltage is zero at the output position.

As a result, the negative charge is more dominant for the ac power than for the dc power. This dominance of the negative charge would be responsible for the highly non-uniform deposition shown in figure 36, where the ac power was used. It is commonly observed that under the condition

producing a more negative current, a thin film with a higher crystalline fraction is deposited. Therefore, the thin films under ac power produced higher crystallinity than those under dc power. Also, thin films with a higher crystalline fraction could be deposited when a negative wire bias was applied to the hot wire for both ac and dc powers.

4.4. Plasma CVD

In the plasma CVD process, numerous electrons and positive ions are generated by the discharge process. Because electrons and ions have very high electrostatic energy, both of them try to reduce their energy by attaching themselves to any surface in the chamber. If an electron is incorporated into the surface of any bulk, the energy as much as the work function of the bulk would be reduced. If an ion is incorporated into the surface, the energy as much as the ionization energy minus the work function of the bulk would be reduced. Therefore, both electrons and ions have the high driving force to be neutralized by being attached to the bulk surface. However, the mobility of electrons is much higher than that of ions and as a result electrons tend to occupy most of the surface in the plasma reactor, leaving behind slow-moving ions in the plasma. As a result, the reactor surface has a negative potential and the plasma has a positive potential.

As the reactant gases are decomposed in the plasma, the supersaturation for precipitation of the depositing species builds up. The plasma environment provides numerous centres for photo-induced and ion-induced nucleation. Therefore, the generation of charged nanoparticles is difficult to avoid during PECVD [231]. Dominant anion-induced nucleation of Si:H has recently been confirmed by numerical simulations of particle generation mechanisms in silane-based discharges [232].

Initial nuclei may be neutral, positively charged or negatively charged. However, as nuclei grow, they tend to be negatively charged because the physical properties of nuclei would approach those of its bulk. That is, the ionization potential and the electron affinity of nuclei would approach the work function. Then, the electrons of high mobility would be attached to the nuclei, resulting in an energy reduction by the work function. Once the nuclei are negatively charged, they will be repelled from the negatively charged substrate after reaching the sheath boundary, being suspended like colloidal particles. If their residence time is sufficiently long in a so-called 'trap', which is characterized by a localized increase in the plasma potential arising from plasma non-uniformity [233, 234], they can grow larger than the wavelength of visible light. They can be observed by the naked eye, which is called 'dusty plasma'. Because of highly ionizing environment, the particles in the plasma tend to be multiply charged. For example, a particle of $1\text{ }\mu\text{m}$ has 10^4 negative charges [235].

Since the incorporation of these particles might result in device failure in microelectronic processing, the 'dusty plasma' has been studied extensively [32, 236, 237]. Various techniques have been developed to minimize the incorporation of such particles in the films [1, 238]. In most of these studies, the generation of particles in the gas phase has been regarded

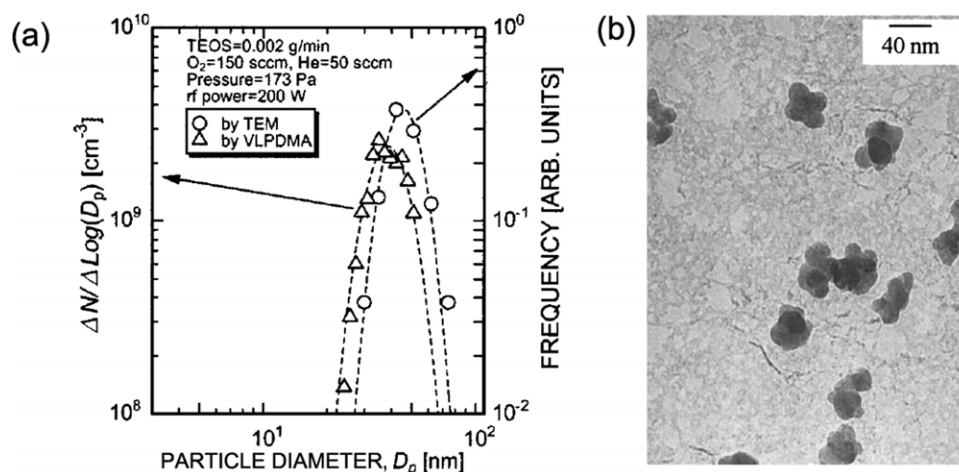


Figure 40. (a) Comparison of the SiO₂ nanoparticle size distributions measured by TEM and VLPDMA methods. (b) TEM image of the SiO₂ nanoparticles collected inside the PECVD reactor. Reprinted with permission from [248]. Copyright 2001 American Vacuum Society.

as being harmful by contaminating etching and deposition processes [239–243]. For example, for a-Si:H solar cells of high stability against light soaking, incorporating amorphous Si nanoparticles of 1–10 nm in size into a-Si:H films should be minimized because such incorporation tends to degrade the stability of the films [30, 244, 245].

Although charged particles of visible size may be harmful, those of nanometre size can contribute to film deposition mostly without doing any harm to the films. If the size of the particles decreases to a nanometre scale, the detection and size measurement of the particles during PECVD need special techniques, such as *in situ* laser light scattering [240–242, 246], *ex situ* electron microscopy [247] and *in situ* very low-pressure DMA (VLDMA) [248]. The size and number distribution of charged SiO₂ nanoparticles in the gas phase were *in situ* measured by VLDMA during the PECVD process as shown in figure 40 [248]. Figure 40(a) shows the size distribution of SiO₂ nanoparticles. The mean particle size was 40 nm. The captured nanoparticles on the TEM grid membrane showed that it was aggregation of several primary particles of 10–20 nm as shown in figure 40(b).

Cabarrocas *et al* [30, 31, 249, 250] suggested that these charged nanoparticles can be incorporated into films. They also suggested that polymorphous silicon films, which refer to a-Si:H matrix with silicon nanocrystallites produced in the gas phase, have improved transport properties and stability compared with a-Si:H films. Using radio-frequency PECVD at 13.56 MHz under conditions where nanocrystals are the primary contributors to film growth, Johnson *et al* [251] demonstrated that Ge nanocrystals generated in the gas phase land on a GaAs (1 0 0) wafer at 175 °C, adopting the orientation of the underlying lattice. This result is a typical example of epitaxial recrystallization of the charged nanoparticles.

Using the thermophoretic force arising from varying the near-substrate temperature gradient, Rutkevych *et al* [252] could selectively deposit or levitate carbon-based nanoparticles grown in a low-temperature reactive plasma of Ar–H₂–CH₄ gas mixture. When the nanoparticles were levitated in the plasma presheath, arrays of vertically aligned carbon nanotips were assembled, whereas the enhanced

deposition of the building units from the gas phase favoured the formation of polymorphous nanostructured films.

Vladimirov and Ostrikov [32] suggested that by controlling systematically fine clusters and particulates generated during PECVD, various nanostructures can be tailored, opening a new possibility for numerous challenging applications in fundamental science as well as in nanotechnology and other leading high-tech industries. Ostrikov [34] made an extensive review on the incorporation of gas-phase nuclei into nanostructures for a reactive-plasma-assisted nanoassembly process and indicated the importance of detection and control for a building block in plasma-aided nanofabrication. Cheng *et al* [253, 254] also reported that this concept could be applied to the low-temperature growth of a nanocrystalline SiC film.

The effect of surface morphology on the deposition behaviour of charged nanoparticles was numerically simulated in PECVD [255]. The electric potential of the surface affects the flux of charged nanoparticles, which is more dominant in the case of an insulating surface. Depending on the surface potential, the charged nanoparticles either deposit on the convex surface or fill up the concave surface. The sharp convex surface effectively attracted charged nanoparticle fluxes, whose phenomenon is closely related to the growth of nanotubes or nanowires. Studies in this field of plasma-aided nanofabrication are rapidly growing, which has recently been reviewed by Ostrikov and Murphy [35].

Barnes *et al* systematically studied the generation of TiO₂ charged nanoparticles in the gas phase and their deposition into films by RF plasma CVD [256] and dc magnetron sputtering [257, 258]. The RF power changed the distribution of the charged nanoparticles and film deposition. At a RF power of 90 W the powders, which are the aggregation of TiO₂ nanoparticles with a size of 9–15 nm, were deposited. The powders have poor crystallinity. At a RF power of 180 W highly crystalline TiO₂ films were deposited. During film growth, TiO₂ nanoparticles with a size of 7–12 nm in the gas phase were confirmed by TEM observation. The different deposition behaviour by RF power seems to be caused by the charging rates of RF power for nanoparticles. The electron

density of RF plasma increases as the RF power increases from 0 to 200 W [259]. Ti^+ ion flux also increased with increasing power, which increases the ionization efficiency in the RF plasma reactor. Therefore, as the RF plasma power increases, charging rates of nanoparticles increase. At the RF power of 90 W, TiO_2 nanoparticles might be poorly charged, which induces random landing of nanoparticles, resulting in porous microstructures. At the RF power of 180 W, most nanoparticles could be charged, which induces neat landing, resulting in well close-packed microstructures.

5. Other related processes

Considering the fact that charged nanoparticles tend to be generated in the gas phase during many CVD and some PVD processes, these processes can be used to produce nanoparticles. Actually, nanoparticles are synthesized using reactors very similar to CVD and PVD. For example, oxide-coated silicon nanoparticles [260], tungsten nanoparticles [261], copper and copper oxide nanoparticles [262] and zirconia nanoparticles doped with alumina [263] are synthesized in a reactor that is practically the same as a hot-wall CVD reactor. To decompose the precursor, plasma, flame and hot wire reactors can be used. For example, crystalline silicon nanoparticles [264] and silicon-carbide nanoparticles [265] are synthesized in the plasma reactor. The flame synthesis is the most successful commercial method to produce nanoparticles in large quantities. It is primarily used to produce oxide nanoparticles because the combustion reactor is in the oxidizing environment. Carbon black, titanium dioxide and silicon dioxide nanoparticles are synthesized by flame [266]. Recently, Si nanoparticles were successfully synthesized in the HWCVD reactor [267].

Similarly, nanoparticles are synthesized by thermal evaporation in a simple furnace reactor. Elemental nanoparticles such as Ag [268], Ga [269] and PbS [270], which have a relatively high vapour pressure, can be produced using this method. Pulsed laser ablation is used for materials that cannot readily be evaporated by heating or sputtering. By this method, magnetic oxide nanoparticles [271], titanium dioxide nanoparticles [272] and hydrogenated-silicon nanoparticles [273] can be synthesized. Spark discharge generation [274] and ion sputtering [275] methods are also used to synthesize nanoparticles.

Although the reactor for the gas phase synthesis of nanoparticles might be the same as that for film deposition, the processing conditions are a little bit different, largely because nanoparticle synthesis and film deposition differ in the final goal. For the synthesis of nanoparticles, the self-assembly and epitaxial recrystallization of charged nanoparticles should be minimized. For this, the temperature for collecting them should be minimized and the charge should be removed to make the nanoparticles electrically neutral. Although the presence of charge is not noticed in the synthesis of nanoparticles, the actual process is optimized unintentionally to remove electric charge from the nanoparticles. Otherwise, nanoparticles will coagulate or tend to form dense films.

For example, usually a stainless steel drum, which is often cooled by liquid nitrogen, is used with a scraper, which scrapes the nanoparticles from the stainless steel surface. The low temperature of the liquid-nitrogen-cooled stainless steel would exert a thermophoretic force and attract charged nanoparticles. The additional effect of low temperature is to minimize the thermal energy of nanoparticles to inhibit the tendency of aggregation, sintering and epitaxial recrystallization. It should be noted that stainless steel has a high charge transfer rate, being adequate for the removal of charge from the nanoparticles, which is favoured to obtain non-aggregated nanoparticles. If the stainless steel is coated with any dielectric material, the charge from the nanoparticles may not be removed properly and the charged nanoparticles may undergo self-assembly and deposit on the dielectric surface as dense films.

If many conventional CVD films grow by the charged nanoparticles which are generated unintentionally during the deposition process, films could be deposited also by intentionally generated charged nanoparticles. Electrospray [276] and aerosol depositions [277, 278] would be such a case. Although particle charging is obvious in electrospray deposition, it is not obvious in aerosol deposition. However, the particles are expected to be charged by contact charging among particles or by surface ionization with the wall on their passage to the outlet.

6. Conclusions

The generation of charged diamond nanoparticles in the gas phase, which had been predicted based on many puzzling phenomena such as diamond deposition on a silicon substrate and porous and skeletal graphitic soot deposition on an iron substrate, was experimentally confirmed. In order to explain another puzzling phenomenon of diamond deposition with simultaneous graphite etching without violating the second law of thermodynamics, it was concluded that the charged diamond nanoparticles should contribute mainly to the deposition of diamond films because both diamond and graphite should be etched atomically in the presence of gas-phase nuclei. This two-step growth of gas-phase nucleation with its subsequent deposition appears to be a general growth mechanism of thin films and nanostructures in many CVD and some PVD processes. In this new paradigm of crystal growth, the processing parameters such as pressure, temperature, and the flow rate of precursors and other gases should be correlated with the size, polarity and number density of charged nanoparticles, which again should be correlated with the microstructure evolution of films and nanostructures. The intentional control of electric charging in the film reactor would be important in controlling the deposition behaviour such as the growth rate, the quality and trench filling. The electrostatic energy, which is responsible for the self-assembly of charged nanoparticles into films and various nanostructures, is a new important parameter in the crystal growth by building blocks of charged nanoparticles. This new paradigm will complement and enhance the existing understanding of film and nanostructure growth.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean Government (MEST; No M10600000159-06J0000-15910). Fruitful discussions with Dr J Cahn at the National Institute of Standards and Technology, Professor M Hillert formerly at the Royal Institute of Technology, Professor I Sunagawa formerly at Tohoku University, Professor P Bennema formerly at Nijmegen University, Professor Yoshida at the University of Tokyo, Professor P Roca i Cabarrocas at Ecole Polytechnique, Professor K Ostrikov at CSIRO and Dr C S Kim at Seoul National University are greatly appreciated.

References

- [1] Selwyn G S and Patterson E F 1992 *J. Vac. Sci. Technol. A* **10** 1053
- [2] Boufendi L, Plain A, Blondeau J P, Bouchoule A, Laure C and Toogood M 1992 *Appl. Phys. Lett.* **60** 169
- [3] Howling A A, Sansonnens L, Dorier J L and Hollenstein C 1993 *J. Phys. D: Appl. Phys.* **26** 1003
- [4] Veprek S, Ambacher O, Rieger W, Schopper K and Veprek-Heijman M G J 1993 *Mater. Res. Soc. Symp. Proc.* **297** 13
- [5] Garscadden A, Ganguly B N, Haaland P D and Williams J 1994 *Plasma Sources Sci. Technol.* **3** 239
- [6] Stoffels E, Stoffels W W, Kroesen G M W and Hoog F J d 1996 *J. Vac. Sci. Technol. A* **14** 556
- [7] Adachi M, Okuyama K, Tohge N, Shimada M, Sato J and Muroyama M 1992 *Japan. J. Appl. Phys.* **31** L1439
- [8] Adachi M, Okuyama K, Tohge N, Shimada M, Sato J and Muroyama M 1993 *Japan. J. Appl. Phys.* **32** L748
- [9] Sloodman F and Parent J C 1994 *J. Aerosol Sci.* **25** 15
- [10] Rao N, Micheel B, Hansen D, Fandrey C, Bench M, Girshick S, Heberlein J and McMurry P 1995 *J. Mater. Res.* **10** 2073
- [11] Onischuk A A, Strunin V P, Ushakova M A and Panfilov V N 1997 *J. Aerosol Sci.* **28** 207
- [12] Swihart M T and Girshick S L 1999 *J. Phys. Chem. B* **103** 64
- [13] Girshick S L, Swihart M T, Suh S M, Mahajan M R and Nijhawan S 2000 *J. Electrochem. Soc.* **147** 2303
- [14] Nijhawan S, McMurry P H, Swihart M T, Suh S M, Girshick S L, Campbell S A and Brockmann J E 2003 *J. Aerosol Sci.* **34** 691
- [15] Na J, Kim T, Choi J B, Kim Y J, Shin Y H, Yun J Y and Kang S W 2010 *Electrochem. Solid State Lett.* **13** H248
- [16] Bennema P and Gilmer G H 1973 *Crystal Growth: An Introduction* ed P Hartman (Amsterdam: North-Holland)
- [17] van der Eerden J P 1993 *Handbook of Crystal Growth* vol 1a *Fundamentals 'Thermodynamics and Kinetics'* (Amsterdam: North-Holland)
- [18] Pieranski P 1983 *Contemp. Phys.* **24** 25
- [19] Penn R L and Banfield J F 1998 *Science* **281** 969
- [20] Banfield F, Welch S A, Zhang H, Ebert T T and Penn R L 2000 *Science* **289** 751
- [21] Tang Z, Kotov N A and Giersig M 2002 *Science* **297** 237
- [22] Zhang Q, Liu S J and Yu S H 2009 *J. Mater. Chem.* **19** 191
- [23] Glasner A and Kenat J 1968 *J. Cryst. Growth* **2** 119
- [24] Glasner A and Skurnik S 1968 *Israel J. Chem.* **6** 69
- [25] Glasner A and Tassa M 1974 *Israel J. Chem.* **12** 799
- [26] Glasner A and Tassa M 1974 *Israel J. Chem.* **12** 817
- [27] Botsaris G D and Reid R C 1967 *J. Chem. Phys.* **47** 3689
- [28] Sunagawa I 1987 *Morphology of minerals Morphology of Crystals* ed I Sunagawa (Tokyo: Terra Sci. Pub.)
- [29] Sunagawa I 1990 *J. Cryst. Growth* **99** 1156
- [30] Roca i Cabarrocas P 2000 *J. Non-Cryst. Solids* **266–269** 31
- [31] Roca i Cabarrocas P 2002 *Curr. Opin. Solid State Mater. Sci.* **6** 439
- [32] Vladimirov S V and Ostrikov K 2004 *Phys. Rep.* **393** 175
- [33] Nunomura S, Kita M, Koga K, Shiratani M and Watanabe Y 2005 *Japan. J. Appl. Phys.* **44** L1509
- [34] Ostrikov K 2005 *Rev. Mod. Phys.* **77** 489
- [35] Ostrikov K and Murphy A B 2007 *J. Phys. D: Appl. Phys.* **40** 2223
- [36] Jeon J D, Park C J, Kim D Y and Hwang N M 2000 *J. Cryst. Growth* **213** 79
- [37] Ahn H S, Park H M, Kim D Y and Hwang N M 2002 *J. Cryst. Growth* **234** 399
- [38] Jeon I D, Park C J, Kim D Y and Hwang N M 2001 *J. Cryst. Growth* **223** 6
- [39] Jeon I D, Gueroudji L, Kim D Y and Hwang N M 2001 *J. Korean Ceram. Soc.* **38** 218
- [40] Kim J Y, Kim D Y and Hwang N M 2006 *Pure Appl. Chem.* **78** 1715
- [41] Lee S S, Ko M S, Kim C S and Hwang N M 2008 *J. Cryst. Growth* **310** 3659
- [42] Kim C S, Youn W K and Hwang N M 2010 *J. Appl. Phys.* **108** 014313
- [43] Lee J I and Hwang N M 2008 *Carbon* **46** 1588
- [44] Kim C S, Chung Y B, Youn W K and Hwang N M 2009 *Carbon* **47** 2511
- [45] Kim C S, Chung Y B, Youn W K and Hwang N M 2009 *Aerosol Sci. Technol.* **43** 120
- [46] Kim C S, Kwak I J, Choi K J, Park J G and Hwang N M 2010 *J. Phys. Chem. C* **114** 3390
- [47] Hwang N M and Yoon D Y 1996 *J. Cryst. Growth* **160** 98
- [48] Hwang N M 1999 *J. Cryst. Growth* **205** 59
- [49] Derjaguin B V and Fedoseev D B 1977 *The Growth of Diamond and Graphite from the Gas Phase* (Moscow: Nauka)
- [50] Spitsyn B V, Bouilov L L and Derjaguin B V 1981 *J. Cryst. Growth* **52** 219
- [51] Matsumoto S, Sato Y, Tsutsumi M and Setaka N 1982 *J. Mater. Sci.* **17** 3106
- [52] Spear K E 1989 *J. Am. Ceram. Soc.* **72** 171
- [53] Angus J C and Hayman C C 1988 *Science* **241** 913
- [54] Kamo M, Sato Y, Matsumoto S and Setaka N 1983 *J. Cryst. Growth* **62** 642
- [55] Haubner R and Lux B 1993 *Diamond Relat. Mater.* **2** 1277
- [56] Yarbrough W A 1992 *J. Am. Ceram. Soc.* **75** 3179
- [57] Mason B J 1958 *Adv. Phys.* **7** 221
- [58] Ishihara K N, Maeda M and Shingu P H 1985 *Acta Metall.* **33** 2113
- [59] Garvie R C 1965 *J. Phys. Chem.* **69** 1238
- [60] Hori S, Yoshimura M, Somiya S and Takahashi R 1984 *Advances in Ceramics* vol 12 (Columbus, OH: American Ceramic Society)
- [61] Mutaftschiev B 1993 *Handbook of Crystal Growth* (Amsterdam: North-Holland)
- [62] Tammann G and Mehl R F 1925 *The States of Aggregation* (New York: Van Nostrand)
- [63] Belokurov B V 1960 *Zh. Fiz. Khim.* **34** 440
- [64] Fedosayev D V, Deryagin B V and Varasavskaja I G 1989 *Surf. Coat. Technol.* **38** 1
- [65] Choi K, Kang S J L, Jang H M and Hwang N M 1997 *J. Cryst. Growth* **172** 416
- [66] Hwang N M, Bahng G W and Yoon D N 1992 *Diamond Relat. Mater.* **1** 191
- [67] Hwang N M, Hahn J H and Yoon D Y 1996 *J. Cryst. Growth* **162** 55
- [68] Bundy F P, Bassett W A, Weathers M S, Hemley R J, Mao H U and Goncharov A F 1996 *Carbon* **34** 141
- [69] Nuth J A 1987 *Nature* **329** 589

- [70] Badziag P, Verwoerd W S, Ellis W P and Greiner N R 1990 *Nature* **343** 244
- [71] Gamarnik M Y 1996 *Nanostruct. Mater.* **7** 651
- [72] Ree F H, Winter N W, Glosli J N and Viecegli J A 1999 *Physica B* **265** 223
- [73] Barnard A S, Russo S P and Snook I K 2003 *Phys. Rev. B* **68** 073406
- [74] Varnin V O, Derjaguin V V, Fedoseev D V, Teremetskaya I G and Khodan A N 1977 *Sov. Phys. Cryst.* **22** 513
- [75] Eversole W G 1962 *US Patent* No 3030187
- [76] Eversole W G 1962 *US Patent* No 3030188
- [77] Angus J C, Will H A and Stanko W S 1968 *J. Appl. Phys.* **39** 2915
- [78] Fedoseev D V, Varnin V P and Derjaguin B V 1984 *Russ. Chem. Rev.* **53** 435
- [79] Hwang N M, Hahn J H and Yoon D Y 1996 *J. Cryst. Growth* **160** 87
- [80] Ostrikov K, Denysenko I B, Vladimirov S V, Xu S, Sugai H and Yu M Y 2003 *Phys. Rev. E* **67** 056408
- [81] Gaskell D R 1995 *Introduction to the Thermodynamics of Materials* (Washington, DC: Taylor and Francis)
- [82] Whittaker A G 1978 *Science* **200** 763
- [83] Vakil H B 1989 *Proc. 1st Annual Diamond Technology Workshop* (Wayne State University, Detroit, MI)
- [84] Badzian A R, Badzian T, Roy R, Messier R and Spear K E 1988 *Mater. Res. Bull.* **23** 531
- [85] Salvadori M C, Brewer M A, Ager J W III, Krishnan K M and Brown I G 1992 *J. Electrochem. Soc.* **139** 558
- [86] Hwang N M and Kim D Y 2004 *Int. Mater. Rev.* **49** 171
- [87] Mitura S 1987 *J. Cryst. Growth* **80** 417
- [88] Frenklach M, Kematich R, Huang D, Howard W, Spear K E, Phelps A W and Koba R 1989 *J. Appl. Phys.* **66** 395
- [89] Chonan T, Uenura M, Futaki S and Nishii S 1989 *Japan. J. Appl. Phys.* **28** L1058
- [90] Gries T, Vandenbulcke L, Rouzaud J N and Persis S 2010 *Plasma Sources Sci. Technol.* **19** 025015
- [91] Huh J M, Yoon D Y, Kim D Y and Hwang N M 2005 *Z. Metallk.* **3** 225
- [92] Yang Q, Tang Y, Yang S L, Li Y S and Hirose A 2008 *Carbon* **46** 589
- [93] Pierson H O 1992 *Handbook of Chemical Vapor Deposition* (NJ: Noyes)
- [94] Calcote H F 1981 *Combust. Flame* **42** 215
- [95] Harris S J and Weiner A M 1985 *Ann. Rev. Phys. Chem.* **36** 31
- [96] Gerhardt P and Homann K H 1990 *J. Phys. Chem.* **94** 5381
- [97] Gerhardt P and Homann K H 1990 *Combust. Flame* **81** 289
- [98] Shaw D J 1970 *Introduction to Colloid and Surface Chemistry* (London: Butterworth Heinemann)
- [99] Velamakanni B V, Chang J C, Lange F F and Pearson D S 1990 *Langmuir* **6** 1323
- [100] Lange F F and Miller K T 1987 *Am. Ceram. Soc. Bull.* **66** 1498
- [101] Tang S 1999 *Colloid Surf. A* **157** 185
- [102] Cho G, Lee J S, Glatzhofer D T, Fung B M, Yuan W L and O'Rear E A 1999 *Adv. Mater.* **11** 497
- [103] Jung K T and Shul Y G 1997 *Chem. Mater.* **9** 420
- [104] Boudreau L C, Kuck J A and Tsapatsis M 1999 *J. Membr. Sci.* **152** 41
- [105] Feng J, Winnik M A, Shivers R R and Clubb B 1995 *Macromolecules* **28** 7671
- [106] Park Y J, Lee D Y, Khew M C, Ho C C and Kim J H 1998 *Langmuir* **14** 5419
- [107] Dingenouts N and Ballauff M 1999 *Langmuir* **15** 3283
- [108] Glasner A, Sarig S and Lamed Y 1972 *J. Cryst. Growth* **12** 173
- [109] Glasner A 1973 *Mater. Res. Bull.* **8** 413
- [110] Pileni M P 1997 *Langmuir* **13** 3266
- [111] Taleb A, Petit C and Pileni M P 1997 *Chem. Mater.* **9** 950
- [112] Pileni M P and Bunsen-Ges B 1997 *Phys. Chem.* **101** 1578
- [113] Boal A K, Ilhan F, DeRouchey J E, Thurn-Albrecht T, Russell T P and Rotello V M 2000 *Nature* **404** 746
- [114] Bockris J O M and Reddy A K N 1970 *Modern Electrochemistry* (New York: Plenum)
- [115] Fujita H 1991 *Ultramicroscopy* **39** 369
- [116] Fujita H 1994 *Mater. Trans. JIM* **35** 563
- [117] Zhang H and Wang D 2008 *Angew. Chem. Int. Edn* **47** 3984
- [118] O'Brien E F and Robinson G W 1974 *J. Chem. Phys.* **61** 1050
- [119] Castleman A W, Holland P M and Keesee R G 1978 *J. Chem. Phys.* **68** 1760
- [120] Wilson J G 1951 *The Principles of Cloud-Chamber Technique* (Cambridge: Cambridge University Press)
- [121] Peyrou C 1967 *Bubble and Spark Chambers* (New York: Academic)
- [122] Katz J L, Wen F C, McLaughlin T, Reusch R J and Partch R 1977 *Science* **196** 1203
- [123] Wen F C, McLaughlin T and Katz J L 1978 *Science* **200** 769
- [124] Hwang N M and Kim D Y 2000 *J. Cryst. Growth* **218** 40
- [125] Yoshimoto M, Yoshida K, Maruta H, Hishitani Y, Koinuma H, Nishio S, Kakihana M and Tachibana T 1999 *Nature* **399** 340
- [126] Palnichenko A V, Jonas A M, Charlier J C, Aronin A S and Issi J P 1999 *Nature* **402** 162
- [127] Gruen D M, Liu S, Krauss A R, Luo J and Pan X 1994 *Appl. Phys. Lett.* **64** 1502
- [128] Wesolowski P, Lyutovich Y, Banhart F, Carstanjen H D and Kronmuller H 1997 *Appl. Phys. Lett.* **71** 1948
- [129] Lyutovich Y and Banhart F 1999 *Appl. Phys. Lett.* **74** 659
- [130] Saslaw W C and Gaustad J E 1969 *Nature* **221** 160
- [131] Lewis R S, Ming T, Wacker J F, Anders E and Steel E 1987 *Nature* **326** 160
- [132] Park N J, Park S I, Hwang N M, Ihm J S, Tejima S and Nakamura H 2004 *Phys. Rev. B* **69** 195411
- [133] Hartman P and Perdok W G 1955 *Acta Crystallogr.* **8** 49
- [134] Hartman P and Perdok W G 1955 *Acta Crystallogr.* **8** 521
- [135] Hartman P and Perdok W G 1955 *Acta Crystallogr.* **8** 525
- [136] Hartman P 1973 *Crystal Growth: An Introduction* (Amsterdam: North-Holland)
- [137] Samotoin N D 2001 *Dokl. Earth Sci.* **381** 925
- [138] Yin L W, Li M S, Sun D S, Li F Z and Hao Z Y 2002 *Mater. Lett.* **55** 397
- [139] Qi W H and Wang M P 2002 *J. Mater. Sci. Lett.* **21** 1743
- [140] Lopeand A F and Rodriguez-Viejo J 2007 *Thermochim. Acta* **461** 82
- [141] Hayasaki K, Takamura Y, Yamaguchi N, Terashima K and Yoshida T 1997 *J. Appl. Phys.* **81** 1222
- [142] Takamura Y, Hayasaki K, Terashima K and Yoshida T 1997 *J. Vac. Sci. Technol. B* **15** 558
- [143] Terashima K, Yamaguchi N, Hattori T, Takamura Y and Yoshida T 1998 *Pure Appl. Chem.* **70** 1193
- [144] Takamura Y, Hayasaki K, Terashima K and Yoshida T 1998 *J. Appl. Phys.* **84** 5084
- [145] Yamaguchi N, Sasajima Y, Terashima K and Yoshida T 1999 *Thin Solid Films* **345** 34
- [146] Koidl P and Klages C P 1992 *Diamond Relat. Mater.* **1** 1065
- [147] Li J, Wang J, Yin M, Gao P, Chen Q, Li Y and He D 2008 *J. Cryst. Growth* **310** 4340
- [148] Gruen D M 1999 *Annu. Rev. Mater. Sci.* **29** 211
- [149] Auciello O and Sumant A V 2010 *Diamond Relat. Mater.* **19** 699
- [150] Butler J E and Sumant A V 2008 *Chem. Vapor Depos.* **14** 145
- [151] Lifshitz Y, Lee C H, Wu Y, Zhang W J, Bello I and Lee S T 2006 *Appl. Phys. Lett.* **88** 243114
- [152] Askari S J, Chen G C, Akhtar F and Lu F X 2008 *Diamond Relat. Mater.* **17** 294
- [153] Williams O A, Daenen M, D'Haen J, Haenen K, Maes J, Moshchalkov V V, Neslaek M and Gruen D M 2006 *Diamond Relat. Mater.* **15** 654

- [154] Hwang N M, Jeon I D and Kim D Y 2000 *J. Ceram. Process. Res.* **1** 33
- [155] Polley T A, Carter W B and Poker D B 1999 *Thin Solid Films* **357** 132
- [156] Gong Y, Tu R and Goto T 2009 *J. Alloys Compounds* **485** 451
- [157] Osipowicz A, Harting M, Hempel M, Britton D T, Bauer-Kugelmann W and Triftshaser W 1999 *Appl. Surf. Sci.* **149** 198
- [158] Hirth J P and Pound G M 1963 *Condensation and Evaporation* (Oxford: Pergamon)
- [159] Ocaña M, Serna C J and Matijević E 1995 *Colloid Polym. Sci.* **273** 681
- [160] Lee S H, Her Y S and Matijević E 1997 *J. Colloid Interface Sci.* **186** 193
- [161] Privman V, Goia D V, Park J and Matijević E 1999 *J. Colloid Interface Sci.* **213** 36
- [162] Robb D T, Halaciuga I, Privman V and Goia D V 2008 *J. Chem. Phys.* **129** 184705
- [163] Lee S C, Yu B D, Kim D Y and Hwang N M 2002 *J. Cryst. Growth* **242** 463
- [164] Kamo M, Yurimoto H and Sato Y 1988 *Appl. Surf. Sci.* **33–34** 553
- [165] Popov C, Kulisch W, Reithmaier J P, Dostalova T, Jelinek M, Anspach N and Hammann C 2007 *Diamond Relat. Mater.* **16** 735
- [166] Zhou X T, Li Q, Meng F Y, Bello I, Lee C S, Lee S T and Lifshitz Y 2002 *Appl. Phys. Lett.* **80** 3307
- [167] Hirasawa M, Ichikawa N, Egashira Y, Honma I and Komiyama H 1995 *Appl. Phys. Lett.* **67** 3483
- [168] Kamei T, Stradins P and Matsuda A 1999 *Appl. Phys. Lett.* **74** 1707
- [169] Shieh J and Hon M H 2002 *J. Vac. Sci. Technol.* **20** 87
- [170] Rajagopalan T, Wang X, Lahlouh B, Ramkumar C, Dutta P and Gangopadhyay S 2003 *J. Appl. Phys.* **94** 5252
- [171] Kim H K, Kim D G, Lee K S, Huh M S, Jeong S H, Kim K I and Seong T Y 2005 *Appl. Phys. Lett.* **86** 183503
- [172] Zhao H Y, Fan Q L, Song L X, Zhang T, Shi E W and Hu X F 2006 *Appl. Surf. Sci.* **252** 3065
- [173] Cheng Q, Xu S, Huang S and Ostrikov K 2009 *Cryst. Growth Des.* **9** 2863
- [174] Cheng Q, Xu S and Ostrikov K 2009 *J. Mater. Chem.* **19** 5134
- [175] Schaff J E and Roberts J T 1996 *J. Phys. Chem.* **100** 14151
- [176] Rath J K 2003 *Sol. Energy Mater. Sol. Cells* **76** 431
- [177] Lien S Y, Mao H Y, Wu B R, Horng R H and Wu D S 2007 *Chem. Vapor Depos.* **13** 247
- [178] Kim H J, Im J S and Thompson M O 1993 *Appl. Phys. Lett.* **63** 1969
- [179] Jin Z, Bhat G A, Yeung M, Kwok H S and Wong M 1998 *J. Appl. Phys.* **84** 194
- [180] Hatalis M K and Greve D W 1988 *J. Appl. Phys.* **63** 2260
- [181] Mercier J, Regolini J L, Bensahel D and Scheid E 1989 *J. Cryst. Growth* **94** 885
- [182] Lee S W, Jeon Y C and Joo S K 1995 *Appl. Phys. Lett.* **66** 1671
- [183] Matsumura H 2001 *Thin Solid Films* **395** 1
- [184] Mahan A H 2001 *Thin Solid Films* **395** 12
- [185] Schropp R E I 2001 *Thin Solid Films* **395** 17
- [186] Roca i Cabarrocas P, Fontcuberta i Morral A, Kalache B and Kasouit S 2003 *Solid State Phenom.* **93** 257
- [187] Matsumura H and Tachibana H 1985 *Appl. Phys. Lett.* **47** 833
- [188] Lee J I and Hwang N M 2008 *J. Cryst. Growth* **310** 3668
- [189] Chung Y B, Lee D K, Kim C S and Hwang N M 2009 *Vacuum* **83** 1431
- [190] Chung Y B, Lee D K, Lim J S and Hwang N M 2010 *Sol. Energy Mater. Sol. Cells* at press
- [191] Kim C S, Youn W K, Lee D K, Seol K S and Hwang N M 2009 *J. Cryst. Growth* **311** 3938
- [192] Zitoun D, Pinna N, Frolet N and Belin C 2005 *J. Am. Chem. Soc.* **127** 15034
- [193] Wen X, Xie Y T, Mak W C, Cheung K Y, Li X Y, Renneberg R and Yang S 2006 *Langmuir* **22** 4836
- [194] Liu J, Huang X, Li Y, Sulieman K M, He X and Sun F 2006 *Cryst. Growth Des.* **6** 1690
- [195] Yang Q, Xiao C, Chen W and Hirose A 2004 *Diamond Relat. Mater.* **13** 433
- [196] Du G, Feng S, Zhao J, Song C, Bai S and Zhu Z 2006 *J. Am. Chem. Soc.* **128** 15405
- [197] Botti S, Ciardi R, Terranova M L, Piccirillo S, Sessa V and Rossi M 2002 *Chem. Phys. Lett.* **355** 395
- [198] Knutson E O and Whitby K T 1975 *J. Aerosol Sci.* **6** 443
- [199] Moisala A, Nasibulin A G, Shandakov S D, Jiang H and Kauppinen E I 2005 *Carbon* **43** 2066
- [200] Kodas T T and Hampden-Smith M J 1994 *The Chemistry of Metal CVD* (Weinheim: VCH)
- [201] Kumomi H, Yonehara T, Nishigaki Y and Sato N 1989 *Appl. Surf. Sci.* **41–42** 638
- [202] Kumomi H and Yonehara T 1991 *Mater. Res. Soc. Symp. Proc.* **202** 83
- [203] Kumomi H and Yonehara T 1997 *Japan. J. Appl. Phys.* **36** 1383
- [204] Lifshitz I M and Slyozov V V 1961 *J. Phys. Chem. Solids* **19** 35
- [205] Hwang N M, Cheong W S and Yoon D Y 1999 *J. Cryst. Growth* **206** 177
- [206] Powell C F, Oxley J H and Blocher J M 1966 *Vapor Deposition* (New York: Wiley)
- [207] Vossen J L and Kern W 1978 *Thin Film Processes* (New York: Academic)
- [208] Shaw D W 1975 *Crystal Growth Theory and Techniques* (New York: Plenum)
- [209] Matthews A and Rickerby D S 1991 *Advanced Surface Coatings: A Handbook of Surface Engineering* (New York: Chapman and Hall)
- [210] Morosanu C E 1990 *Thin Films by Chemical Vapour Deposition* (Amsterdam: Elsevier)
- [211] Lee B S, Barnes M C, Kim D Y and Hwang N M 2002 *J. Cryst. Growth* **234** 599
- [212] Barnes M C, Jeon I D, Kim D Y and Hwang N M 2002 *J. Cryst. Growth* **242** 455
- [213] Jeon I D, Barnes M C, Kim D Y and Hwang N M 2003 *J. Cryst. Growth* **247** 623
- [214] Jeon I D, Kim D Y and Hwang N M 2005 *Z. Metallk.* **2** 186
- [215] Schmidt-Ott A, Schurtenberger P and Siegmann H C 1980 *Phys. Rev. Lett.* **45** 1284
- [216] Burtcher H, Scherrer L, Siegmann H C, Schmidt-Ott A and Federer B 1982 *J. Appl. Phys.* **53** 3787
- [217] Fernandez de la Mora J, de Juan L, Liedtke K and Schmidt-Ott A 2003 *J. Aerosol Sci.* **34** 79
- [218] Muller U, Schmidt-Ott A and Burtcher H 1987 *Phys. Rev. Lett.* **58** 1684
- [219] Nasibulin A G, Moisala A, Brown D P, Jiang H and Kauppinen E I 2005 *Chem. Phys. Lett.* **402** 227
- [220] Peineke C, Attoui M B and Schmidt-Ott A 2006 *J. Aerosol Sci.* **37** 1651
- [221] Peineke C and Schmidt-Ott A 2008 *J. Aerosol Sci.* **39** 244
- [222] Hwang N M, Cheong W S, Yoon D Y and Kim D Y 2000 *J. Cryst. Growth* **218** 33
- [223] Magnusson M H, Deppert K, Malm J O, Bovin J O and Samuelson L 1999 *J. Nanopart. Res.* **1** 243
- [224] Langmuir I and Kingdon K H 1925 *Proc. R. Soc. Lond. A* **107** 61
- [225] Richardson O W 1924 *Phys. Rev.* **23** 153
- [226] Wolf B 1995 *Handbook of Ion Sources* (Boca Raton, FL: CRC Press)
- [227] Song J H, Jo W and Hwang N M 2007 *Thin Solid Films* **515** 7446
- [228] Park S Y, Yang S M, Kim C S and Hwang N M 2009 *J. Phys. Chem. C* **113** 17011

- [229] Park S Y, You S J, Kim C S and Hwang N M 2010 *J. Cryst. Growth* **312** 2459
- [230] Cendes Z 1984–2009 *Maxwell 3D* 12th edn (Pittsburgh, PA: Ansoft)
- [231] Fridman A and Kennedy L A 2004 *Plasma Physics and Engineering* (New York: Taylor and Francis)
- [232] De Bleecker K, Bogaerts A, Gijbels R and Goedheer W 2004 *Phys. Rev. E* **69** 056409
- [233] Selwyn G S, Heidenreich J E and Haller K L 1990 *Appl. Phys. Lett.* **57** 1876
- [234] Selwyn G S 1993 *Japan. J. Appl. Phys.* **32** 3068
- [235] Goree J 1994 *Plasma Sources Sci. Technol.* **3** 400
- [236] Boufendi L and Bouchoule A 1994 *Plasma Sources Sci. Technol.* **3** 262
- [237] Ostrikov K, Vladimirov S V, Yu M Y and Morfill G E 2000 *Phys. Plasmas* **7** 461
- [238] Selwyn G S 1991 *J. Vac. Sci. Technol. B* **9** 3487
- [239] Spears K G, Robinson T J and Roth R M 1986 *IEEE Trans. Plasma Sci.* **PS14** 179
- [240] Watanabe Y, Shiratani M, Kubo Y, Ogawa I and Ogi S 1988 *Appl. Phys. Lett.* **53** 1263
- [241] Selwyn G S, Singh J and Bennett R S 1989 *J. Vac. Sci. Technol. A* **7** 2758
- [242] Watanabe Y 2006 *J. Phys. D: Appl. Phys.* **39** R329
- [243] Lieberman M A and Lichtenberg A J 2005 *Principles of Plasma Discharges and Materials Processing* (NJ: Wiley)
- [244] Staebler D L and Wronski C R 1977 *Appl. Phys. Lett.* **31** 292
- [245] Koga K, Inoue T, Bando K, Iwashita S, Shiratani M and Watanabe Y 2005 *Japan. J. Appl. Phys.* **44** L1430
- [246] Nunomura S, Kita M, Koga K, Shiratani M and Watanabe Y 2006 *J. Appl. Phys.* **99** 083302
- [247] Shiratani M, Kawasaki H, Fukuzawa T, Tsuruoka H, Yoshioka T and Watanabe Y 1994 *Appl. Phys. Lett.* **65** 1900
- [248] Seol K S, Tsutani Y, Fujimoto T, Okada Y, Takeuchi K and Nagamoto H 2001 *J. Vac. Sci. Technol. B* **19** 1998
- [249] Roca i Cabarrocas P 2004 *Phys. Status Solidi* **1** 1115
- [250] Roca i Cabarrocas P, Chaâbane N, Kharchenko A V and Tchakarov S 2004 *Plasma Phys. Control. Fusion* **46** B235
- [251] Johnson E V, Patriarche G and Roca i Cabarrocas P 2008 *Appl. Phys. Lett.* **92** 103108
- [252] Rutkevych P P, Ostrikov K, Xu S and Vladimirov S V 2004 *J. Appl. Phys.* **96** 4421
- [253] Cheng Q, Xu S, Long J and Ostrikov K 2007 *Appl. Phys. Lett.* **90** 173112
- [254] Cheng Q, Tam E, Xu S and Ostrikov K 2010 *Nanoscale* **2** 594
- [255] Rutkevych P P, Ostrikov K and Xu S 2007 *Phys. Plasmas* **14** 043502
- [256] Barnes M C, Gerson A R, Kumar S and Hwang N M 2003 *Thin Solid Films* **436** 181
- [257] Barnes M C, Gerson A R, Kumar S and Hwang N M 2004 *Thin Solid Films* **446** 29
- [258] Barnes M C, Kumar S, Green L, Hwang N M and Gerson A R 2005 *Surf. Coat. Technol.* **190** 321
- [259] Fukushima K, Kusano E, Kikuchi N, Saito T, Saiko S, Nanto H and Kinbara A 2000 *Vacuum* **59** 586
- [260] Ostraat M L, Blauwe J W D, Green M L, Bell L D, Atwater H A and Flagan R C 2001 *J. Electrochem. Soc.* **148** G265
- [261] Magnusson M H, Deppert K and Malm J O 2000 *J. Mater. Res.* **15** 1564
- [262] Nasibulin A G, Richard O, Kauppinen E I, Brown D P, Jokiniemi J K and Altman I S 2002 *Aerosol. Sci. Technol.* **36** 899
- [263] Srdic V V, Winterer M, Moller A, Miehe G and Hahn H 2001 *J. Am. Ceram. Soc.* **84** 2771
- [264] Bapat A, Perrey C R, Campbell S A, Carter C B and Kortshagen U 2003 *J. Appl. Phys.* **94** 1969
- [265] Rao N, Girshick S, Heberlein J, McMurphy P, Jones S, Hansen D and Micheel B 1995 *Plasma Chem. Plasma Process.* **15** 581
- [266] Hahn H 1997 *Nanostruct. Mater.* **9** 3
- [267] Scriba M R, Arendse C, Harting M and Britton D T 2008 *Thin Solid Films* **516** 844
- [268] Scheibel H G and Porstendorfer J 1983 *J. Aerosol Sci.* **14** 113
- [269] Deppert K, Bovin J O, Malm J O and Samuelson L 1996 *J. Cryst. Growth* **169** 13
- [270] Kruis F E, Goossens A and Fissan H 1996 *J. Aerosol Sci.* **27** S165
- [271] Shinde S R, Kulkarni S D, Banpurkar A G, Nawathey-Dixit R, Date S K and Ogale S B 2000 *J. Appl. Phys.* **88** 1566
- [272] Harano A, Shimada K, Okubo T and Sadakata M 2002 *J. Nanopart. Res.* **4** 215
- [273] Makimura T, Mizuta T and Murakami K 2002 *Japan. J. Appl. Phys.* **41** L144
- [274] Weber A P, Seipenbusch M and Kasper G 2001 *J. Phys. Chem. A* **105** 8958
- [275] Urban F K, Hosseini-Tehrani A, Griffiths P, Khabari A, Kim Y W and Petrov I 2002 *J. Vac. Sci. Technol. B* **20** 995
- [276] Salata O V 2005 *Curr. Nanosci.* **1** 25
- [277] Akedo J and Lebedev M 2000 *Appl. Phys. Lett.* **77** 1710
- [278] Akedo J, Lebedev M, Iwata A, Ogiso H and Nakano S 2003 *Mater. Res. Soc. Symp. Proc.* **778** 289