New Mechanism of Thin Film Growth by Charged Clusters

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Abstract

The charged clusters or particles, which contain hundreds to thousands of atoms or even more, are suggested to form in the gas phase in the thin film processes such as CVD, thermal evaporation, laser ablation, and flame deposition. All of these processes are also used in the gas phase synthesis of the nanoparticles. Ion-induced or photo-induced nucleation is the main mechanism for the formation of these nanoclusters or nanoparticles in the gas phase. Charged clusters can make a dense film because of its self-organizing characteristics while neutral ones make a porous skeletal structure because of its Brownian coagulation. The charged cluster model can successfully explain the unusual phenomenon of simultaneous deposition and etching taking place in diamond and silicon CVD processes. It also provides a new interpretation on the selective deposition on a conducting material in the CVD process. The epitaxial sticking of the charged clusters on the growing surface is getting difficult as the cluster size increases, resulting in the nanostructure such as cauliflower or granular structures.

1. Introduction

It has been generally believed that the growth unit for crystals or thin films is an atom or a molecule. However, Glasner et al. [1-4] proposed a drastically different way of crystal growth by a two-step process in their study on the crystal growth of alkali halides from the aqueous solution in the presence lead ions. They claimed that the nanometer-size nuclei were formed in the

solution and they became the growth unit. They showed that a transparent crystal grew by these nuclei and that the crystal quality increased with decreasing size of nuclei. Although the tiny nuclei were invisible, they could detect the nucleation of them in solution by calorimetric measurements.

Similarly, nucleation in the gas phase can take place during the thin film process without our notice. Considering the amount of ions generated during the CVD process, the gas phase nucleation is highly probable. Currents of ~ nA, ~ μA and ~ mA per square centimeter are typically measured in thermal, hot filament and plasma CVD reactors, respectively, which correspond to the charge density of ~ 10^6, ~ 10^9 and ~ 10^{12} ions/cm^3. In the presence of such a large amount of ions, ion-induced nucleation [5] is highly probable. It is historically famous that the phenomenon of ion-induced nucleation was applied to Wilson cloud and bubble chamber experiments [6-8] to locate the track of the high energy particles. These are regarded as one of most contributing experiments in modern physics.

In addition to ions, abundant photo-excited species are generated in the hot-filament and the plasma CVD processes. Similarly, an appreciable amount of ions and photo-excited species is produced in thermal evaporation, laser ablation and flame deposition processes. Photo-excited species have been known to be more powerful than ions in inducing nucleation [9, 10]. The supersaturation needed for photo-induced nucleation was much smaller than that for ion-induced nucleation. In the processing environment where photo-excited species and ions are produced, photo-induced nucleation is expected to be the dominant mechanism. The photo-induced nucleation would produce the neutral nuclei in the gas phase. However, the nuclei is closer to the bulk than to the gas phase in physical property. The Ionization potential and the electron affinity of the nuclei would approach a work function value of the condensed phase. The ionization potential of the nuclei is comparable to that of alkali metals and the electron affinity is higher than that of the halogen elements. As a result, the nuclei would be easily ionized in the processing condition. Therefore, even the photo-induced nucleation would also produce the charged clusters.

The neutral clusters undergo Brownian coagulation and normally grow instantly into visible

size during the residence time in the CVD reactor. In the presence of abundant charges, however, the charged clusters exert Coulomb repulsion each other. In the aerosol science, a half life of the particles or clusters is defined as the time taken for the number density to be reduced by half [11]. Although a half life of neutral clusters is much shorter than the residence time in the CVD reactor, a half life of charged clusters would be much longer than the residence time. As a result, the charged clusters can maintain the nanometer size throughout the processing.

Recently, Hwang et al. [12, 13] suggested a charged cluster model in the thin film process, which is practically the same concept as the Glasner et al's proposal. In the model, the charged clusters, which might be induced by ions or by photo-excited molecules existing in the thin film reactor, exist in the gas phase. The charged clusters contain hundreds to thousands of atoms and are suspended in the gas phase like colloid suspension; Brownian coagulation is inhibited by the presence of charge. The high capillary pressure stabilize the diamond [14, 15] and further stabilization comes from the ion-induced dipole interaction at the cluster surface, which is stronger for dielectric diamond than for conducting graphite [16-18]. Normally, the charged nanometer size clusters are the major flux for thin films.

The charged clusters have high selectivity in landing on the growing surface. The selectivity comes from the presence of charge and is equivalent to the three-dimensional self-assembly of clusters. Besides, nanometer-size clusters smaller than Fujita's magic size have unusually high deformation and diffusion rates. The crystal with well-defined facets and the dense film can grow by the deposition of such clusters. Initially we developed the model while studying the growth mechanism of the diamond CVD process but it turned out to be general in many other thin film processes. The purpose of this paper is to describe the overall aspect of the charged cluster model in the thin film process.

2. Gas Phase Nucleation in the CVD Process

Although the ion-induced and the photo-induced nucleation is phenomenologically well-established and the ions or the photo-excited species are abundantly produced in many thin film

processes, the possibility of the gas phase nucleation in the thin film process has long been neglected. Recently, however, the gas phase nucleation in the CVD reactor has been a big issue in the microelectronics since the particles can fail the semiconductor device [19]. For the processing of a giga bite memory chip, the attention shifted from the clean room to the clean reactor. The particle formation may originate from the reaction gases or from the reactor wall. Especially in the plasma CVD reactor, the particle formation is so general that it is called the dusty plasma [20-22]. In the dusty plasma, the negatively-charged clusters are suspended in the positively-charged plasma. Currently, the particle formation in the gas phase is regarded as being almost unavoidable in the plasma CVD process.

On the other hand, in pursuit of the good quality film, Adachi et al. [23-26] tried to find the SiO_2 CVD condition where the gas phase nucleation is prevented. The process is the atmospheric-pressure thermal CVD using tetraethylorthosilicate (TEOS). They used the aerosol sizing technique such as differential mobility analyzer (DMA) and the particle number counter to detect the particles nucleated in the gas phase. They observed that when the particles were not detected in the gas phase, the film did not grow either and further that the growth rate of the film increased with increasing number density of clusters. These behaviors were consistent for three different gas mixtures of the precursor and the carrier gas.

Okuyama et al. [27] also performed similar experiments. They observed that for the small particles of a few nanometers, the film surface was smooth while for the coarse ones larger than 10 nanometers, the film surface was irregular. Based on these observations, they made an important suggestion that the molecules and the particles codeposit in the film growth. Although they did not consider the role of charge, their suggestion is one of the very rare ones that the growth unit of the film can be the particle formed in the gas phase. But it is generally believed that the particles generated during the CVD process do not contribute to the film deposition [28]. The incorporation of the particles into the film is believed to impair the film quality significantly.

Homann et al. [29-33] measured the size distribution of the charged carbon clusters during their study on combustion of the hydrocarbon-oxygen flame. In measuring the size distribution,

they used three methods: energy analyzer, Wien filter and time of flight (TOF). The composition they used covers the ratio of C/O from 0.8 to 1.2. In all ratios, they measured the presence of the charged clusters though the cluster size increased with the ratio. It should be noted that the diamond films are made by the combustion flame when the ratio of C/O is close to unity [34].

Using the energy analyzer, we detected the charged clusters in a hot filament diamond CVD reactor under typical conditions that the diamond films are grown [35]. The clusters together with the other gases were extracted through the orifice and the skimmer to the measuring chamber under ~ 10^{-6} torr. Variation of the electric current at the detector was measured with varying repelling voltages. From the current data, the energy distribution was derived. Almost all clusters are negatively charged. From the energy distribution, the mass distribution can be estimated. Normally, the clusters contain hundreds of carbon atoms. By the energy analyzer, the energy distribution the mass distribution can be estimated but the phase identification of the clusters (graphite or diamond) could not be made.

We also observed the clusters captured on the grid for TEM observation during the oxyacetylene flame deposition of diamond [36]. We could observed diamond clusters as well as graphite clusters. The graphite clusters (3 ~ 4 nm) are generally larger than diamond clusters (~ 1.5 nm). For graphite clusters, the lattice image was easily observed while for diamond clusters, it was difficult to observe the lattice image. Only a few among the diamond clusters showed the lattice image. Dominance of diamond over graphite clusters was confirmed by the analysis of rings of the diffraction pattern. The difficulty in observing a lattice image of diamond clusters is attributed to the fact that most diamond clusters are smaller than the Fujita's magic size.

We observed the silicon clusters of 2 ~ 10 nm in the hot-filament CVD process [37]. The clusters at the filament temperature of 1800°C had almost a monosize distribution with the size of ~ 2 nm while at 1600°C, were larger and deviated a little from the monosize distribution with the size of 5 ~ 10 nm. We also made TEM observations on tungsten clusters during thermal evaporation coating of tungsten [38] and on ZrO_2 clusters during thermal CVD of ZrO_2 [39].

3. Effect of Gas Phase Nucleation on the Deposition Behavior in the CVD Process

If the gas phase nucleation takes place, the deposition behavior changes dramatically. The deposition behavior is affected by the temperature dependence of solubility, the presence of charge and the cluster size. In this section, we will analyze these three effects on the deposition behavior.

3-1. Paradoxical phenomenon of simultaneous deposition and etching in the diamond and silicon CVD processes

The temperature dependence of solubility in the gas phase for the material to deposit is related to the paradoxical phenomenon of simultaneous deposition and etching in the CVD process. For the temperature gradient of the reactor, we will assume that the substrate temperature is lower than the adjacent gas phase. This corresponds to the hot wall CVD reactor.

The solubility either decreases or increases with decreasing temperature around the substrate temperature. If the solubility decreases with decreasing temperature, the equilibrium amount of precipitation increases with decreasing temperature. In this case, in spite of gas phase nucleation, the driving force at the substrate is still for deposition. The deposition processes by clusters and atoms are kinetically parallel. The clusters and atoms will deposit simultaneously. In other words, co-deposition of clusters and atoms takes place. Normally, the dominant flux would be the clusters.

If the solubility increases with decreasing temperature around the substrate temperature, the equilibrium amount of precipitation decreases with decreasing temperature. And the gas phase nucleation will make the driving force at the substrate temperature for etching. In this case, the cluster will deposit but simultaneous etching will take place by the atomic unit. Macroscopically, deposition and etching will take place simultaneously. Since the cluster flux for deposition outweighs the atomic flux for etching, the net flux would be for deposition. Since we cannot distinguish between the cluster and the atomic transfer during or after the process, we cannot notice the difference and the phenomenon would look the same as the other deposition process.

In some cases, however, the phenomenon of simultaneous deposition and etching is revealed. The famous example would be the deposition of the less stable diamond and the etching of the stable graphite in the diamond CVD process [40, 41]. Also in the silicon CVD process, it was observed that the silicon particle deposited on some parts but on other parts, the silicon particles etched away simultaneously [42-44]. These phenomena would lead to the thermodynamic paradox if the second law of thermodynamics is applied based on the assumption that the deposition and the etching take place only by the atomic unit [45, 46]. The systems in which the solubility increases with decreasing temperature around the substrate temperature are C-H and Si-Cl-H. In the case of the diamond CVD process by oxyacetylene flame, the solubility itself decreases with decreasing temperature. However, there is the gradient of oxygen concentration when the process is done in air. Therefore, the oxygen concentration continuously increases from the inner flame to the other flame. Also in this case, the deposition flux is the clusters and the etching flux is atoms. It should be noted that in this case, the contribution to deposition comes solely from the cluster flux and the atomic flux makes the negative contribution to deposition. In this respect, this phenomenon of simultaneous deposition and etching is the proof that the perfect crystal can grow by the cluster unit.

Similar conclusions can be drawn for the case where the temperature gradient is opposite. In this case, the substrate temperature is higher than the adjacent gas phase, which is for the cold wall CVD process. In this case, the deposition by clusters and the simultaneous etching by atoms will take place for the system, where the solubility decreases with decreasing temperature. It should be noted that most systems have this type of temperature dependence of solubility.

3-2. Selective deposition

Here, the effect of charge on the deposition behavior will be described, focused on the selective deposition. The charged clusters will be selective in deposition; conducting materials are more favorable for landing of charged clusters than dielectric ones. This behavior can explain the well-known selective deposition in the CVD process [47], where the deposition is selectively done on the conducting area. The selective deposition is usually epitaxial with a pre-existing

material and called selective epitaxial growth (SEG).

If the gas phase is highly conducting, the selective deposition would not be favorable because the charge can be transferred relatively easily to the gas phase. We observed that the selectivity was maintained in a thermal CVD process of silicon but it was lost in a hot filament CVD process. The electric current in the hot filament reactor was ~ 1000 times higher than that in the thermal reactor. On the other hand, the electric current in a plasma reactor is ~ 1000 times higher than that of a hot filament reactor. It is expected that the selectivity would be worst in the plasma CVD reactor. This prediction is in agreement with the well-known fact that the change from SEG to non-SEG conditions is achieved by introducing the plasma to the reactor [47].

The selective can be enhanced if the selective deposition is done under the condition that the gas phase nucleation makes the driving force at the substrate for etching so that the deposition comes solely from the flux of clusters and the etching continues by the atomic flux. This condition is satisfied for the silicon SEG in the hot wall reactor using any gas mixtures of the Si-Cl-H system. The possible gas mixtures are SiH_4-HCl, $SiCl_4$-H_2 and SiH_2Cl_2-HCl.

In this case, even though the silicon particles land on the insulating surface in the initial stage, they will etch away in a later stage because the charge will build up on the insulating surface with time. As the charge builds up with time, further landing of charged silicon clusters will have difficulty in landing on the insulating surface. Then, the etching driving force made by the gas phase nucleation will continue to etch the silicon particles deposited in the previous stage by the atomic unit. We observed this phenomenon [37, 48]. Silicon particles deposited on the insulating substrate initially but afterwards, all of them etched away. On the conducting substrate, however, silicon particles continued to deposit.

During epitaxial growth of silicon selectively on SiN_x periodically-patterned on SiO_2 substrate, Kumomi et al. [42-44] observed that initially many silicon particles deposited on SiN_x but afterwards, they etched away leaving one large silicon particle or none. Normally, one silicon particle grows while other ones etched away. This phenomenon can also be approached by the charged cluster model [49]. As mentioned earlier, deposition and simultaneous etching can be explained by the combined effects of gas phase nucleation and temperature dependence of

the silicon solubility in the gas phase of the Si-Cl-H system. Deposition in an initial stage and etching in a later stage can also be explained by the saturation of charge on the insulating (or semi-insulating) surface. The exclusive growth of one silicon particles can be explained by considering the Coulomb interaction between two approaching conducting charged particles, which is expressed as follows [50].

$$F = \frac{q_1 q_2 e^2}{4\pi\varepsilon_o d^2} - \frac{q_1^2 e^2 r_1 d}{4\pi\varepsilon_o \left(d^2 - r_1^2\right)^2} - \frac{q_2^2 e^2 r_2 d}{4\pi\varepsilon_o \left(d^2 - r_2^2\right)^2} + \cdots, \qquad (1)$$

where the sphere of radius r_1 has a net charge q_1 and the other of radius r_2 has charge q_2; d is the distance between the centers and $1/4\pi\varepsilon_o$ the permittivity. From eq. (1), if $r_2 >> r_1$ and thus $r_2 \approx$» d, the interaction between the large and the small particles charged with the same sign can be attractive. In this case, the attraction will increase as r_2 increases. This condition can induce the instability of growth in the condition that etching is predominant. If the cluster flux for deposition of a certain grain overcomes the etching flux and the grain starts to grow, its attraction with incoming charged clusters can be increased progressively, resulting in continued growth.

3-3. Effect of cluster size on microstructure evolution

In the charged cluster model, the microstructural evolution depends on the cluster size. As the cluster size increases, the growth mode changes from the crystal with well-defined facet to the cauliflower structure. According to Fujita [51, 52], the cluster property changes abruptly at the specific size, which was called the magic size. The magic size corresponds to the numbers of atoms in the cluster from 10^3 to 10^5, depending on the bonding mode and the bonding strength. In the order of the increasing cluster size, the particle coalescence, epitaxial recrystallization, and the diffusional sintering were suggested to take place.

The cluster smaller than the magic size deforms and diffuses like a liquid phase and the rapid coalescence takes place when the clusters are in contact. As a result, the epitaxial film can grow by these clusters. If the initial nuclei on the substrate have the different orientations one another, the continual epitaxial growth of each nucleus will lead to evolution of the columnar structure. As

the cluster size becomes larger than the magic size, the epitaxial coalescence will begin to fail. Then, the twin or grain boundaries will form and 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 clusters have their individual orientations, leading to a cauliflower structure or a nanostructure. The similar aspect was observed by Glasner et al. [3] in their growth of KCl and KBr from the solution.

According to our analysis, the cauliflower structure cannot be evolved by the atomic unit deposition. If the deposition is by the atomic unit, each bulge of the cauliflower structure should be formed by the three-dimensional nucleation on the growing surface. If so, the nucleation rate should be extremely high, for which a very high supersaturation is required. However, it is well established in the crystal growth that the kinetic roughening of the growing surface takes place at the supersaturation just higher than that for onset of two-dimensional nucleation. If the kinetic roughening takes place, the atoms from the gas phase easily find the kink sites and the supersaturation cannot be built up higher for the three-dimensional nucleation. In such a case, the growing surface acts like a rough interface and the growth process changes to diffusion-controlled dendritic or spherulic growth should take place as well established in the crystal growth [53]. For this reason, the grain size has a lower limit in the deposition by the atomic unit. And the cauliflower structure, which is a nanostructure, implies that the growth unit is clusters formed in the gas phase. In this respect, the cauliflower structure can be the evidence that the film grows by the mechanism of the charged cluster model.

4. Conclusions

The invisible nanometer charged clusters exist in the gas phase in some thin film processes including the CVD reactor. These clusters are the major flux for growth of the film. This mechanism can explain some unusual phenomena such as simultaneous deposition and etching, selective deposition and evolution of a cauliflower structure.

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