Theory of Charged Clusters as New Understanding of Thin Film Growth

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Abstract

A new theory of thin film growth was suggested, where charged clusters of nanometer size are generated in the gas phase and are a major flux for thin films. The existence of these hypothetical clusters was experimentally confirmed in the diamond and silicon CVD processes as well as in metal evaporation. These results imply new insights as to the microstructure control of thin films. Based on this new understanding, the low temperature deposition of crystalline and amorphous silicon can be approached systematically.

1. Introduction

It is generally believed that the growth unit of a crystal or a thin film is either an atom or a molecule. The atom first adsorbs on the terrace, diffuses to the ledge and finally becomes the crystal at the kink [1]. However, a drastically different way of film growth mechanism was suggested by Hwang et al. [2, 3]. The new mechanism is a theory of charged clusters (TCC), where nanometer-sized charged clusters are formed in the gas phase of many thin film processes and become a major growth unit of thin films.

If the source of film growth is exclusively a single atom or molecule, the film growth rate would be so low that the process would not be adopted in the commercial production lines. Under normal growth conditions, some clusters such as dimer, trimer and larger clusters tend to generate inevitably even in moderate vacuum. It should be noted that even by a molecular beam epitaxy (MBE) process, it is difficult to generate exclusively a single atom or molecule.

If the clusters are not charged or neutral, the cluster deposition begins to pose problems in preparing epitaxial growth or dense films especially when the substrate temperature is low or the cluster size is large. But the clusters do not pose any serious problems when they are electrically charged. Fortunately, the clusters generated without our notice in the thin film reactor tend to be charged by the mechanism of surface ionization [4] even in the absence of a charge-generating source such as plasma or hot filament. It should be noted that the clusters have much lower ionization potential and much higher electron affinity than a single atom or molecule. As a result, high quality films with a relatively high growth rate could be grown thanks to the spontaneous generation of the charged clusters in many thin film processes.

In this paper, some fundamental aspects of the TCC will be introduced and the implications of the TCC regarding thin film growth will be described.

2. Diamond CVD process

The TCC was originally developed to disentangle many puzzling phenomena in the growth of CVD diamond, which was difficult to approach by the conventional concept of atomic growth. For example, TCC can avoid the thermodynamic paradox in explaining the well-known phenomenon of simultaneous diamond deposition and graphite etching [5]. Besides, the TCC can explain satisfactorily the preferential formation of diamond particles on the apex over the valley of the substrate [2]. The relative easy formation of diamond on the graphite surface in the new diamond CVD process using the gas activation can also be successfully explained by the TCC [6]. In the old CVD diamond process not using the gas activation [7, 8], the diamond seed was used for growth of metastable diamond because the growth barrier of diamond on the diamond seed is lower than the nucleation barrier of graphite on the diamond seed. The formation of graphite debris on the seed led to the dominant growth of graphite, which covered the entire surface of the seed, which had to be etched for further diamond growth, requiring the cyclic etching process. Considering this fact, the relative easy formation of diamond on the graphite substrate is amazing from the viewpoint of atomic deposition while it can be understood by TCC, where diamond nuclei are formed in the gas phase and land on the graphite substrate. The TCC also explains the evolution of porous skeletal soot

on some transition metals such as Fe, Ni and Co and of diamond films on other substrates such as Si, W and Mo under the identical processing condition [2]. It should be noted that no theory of crystal growth based on atomic growth can explain the evolution of porous skeletal soot.

Charged clusters can be formed as a result of ion-induced nucleation especially in the plasma and hot filament CVD process. The fact that the ion provides a strong heterogeneous nucleation center was well established in the Wilson cloud and the bubble chamber experiments [9, 10]. In a Wilson cloud chamber experiment for the nucleation study [11, 12], the ion-induced nucleation was unavoidable because ions were continuously generated in the atmosphere by cosmic rays and natural radioactivity.

An enormous amount of ions or charged species is generated in the plasma and the hot filament CVD processes. Why, then, shouldn't we consider the possibility of ion-induced nucleation in these processes? In the Wilson cloud chamber experiment, the amount of ions is very small compared to that of medium to precipitate. In the plasma or hot filament CVD process, however, the amount of ions is huge compared to that of the condensed phase to precipitate from the gas phase. The precipitated condensed phase should be divided into so many ions and the resultant size of individual charged nuclei is much smaller than the wavelength of the visible light so that we cannot see them. When the nuclei have mostly a unipolar sign, they do not coagulate due to Coulomb repulsion but are suspended like colloids of nanometer size. Besides, the charged nuclei of nanometer size make perfect films, which could hardly be distinguished from the films deposited by atomic or molecular unit.

3. Experimental confirmation of charged clusters

In order to confirm the existence of hypothetical charged clusters in the diamond CVD reactor, a Wien filter system combined with an energy analyzer was used [13]. For differential pumping, the system was divided into three chambers: upper, middle and lower. The upper chamber is a typical hot filament diamond CVD reactor under 6 torr. There was an orifice of 1.2 mm ϕ between the upper and the middle chambers. There was another orifice of 2.0 mm ϕ between the middle and the lower chambers. By this set-up, the upper chamber could maintain 6 torr while the lower or the measuring chamber could maintain less than 10^{-5} torr.

The atoms, molecules or clusters extracted from the upper chamber into the lower chamber can be detected as an electrical signal on the Faraday cup if they carry electric charge. If the charged particles go through the Wien filter, only those with a specified velocity go through the Wien filter while the particles with other velocities are deflected to the wall of the Wien filter.

Then the charge particles with selected velocity go onto the Faraday cup and its amount is measured as a current. But just before they reach the Faraday cup, they are under a repelling field from the grid applied with the repelling voltage. If the repelling voltage is 1 V, the charged particles with the kinetic energy less than 1 eV will be repelled. As a result, the current on the Faraday cup will decrease by the amount contributed by the charged particles with the kinetic energy less than 1 eV.

With increasing repelling voltage, the current will continue to decrease. Differentiation of this current with respect to the repelling voltage will give the energy distribution of charged particles. Since the velocity of the charged particles is given by the Wien filter, the mass distribution of charged particles can be determined. The result is shown in Fig. 1.
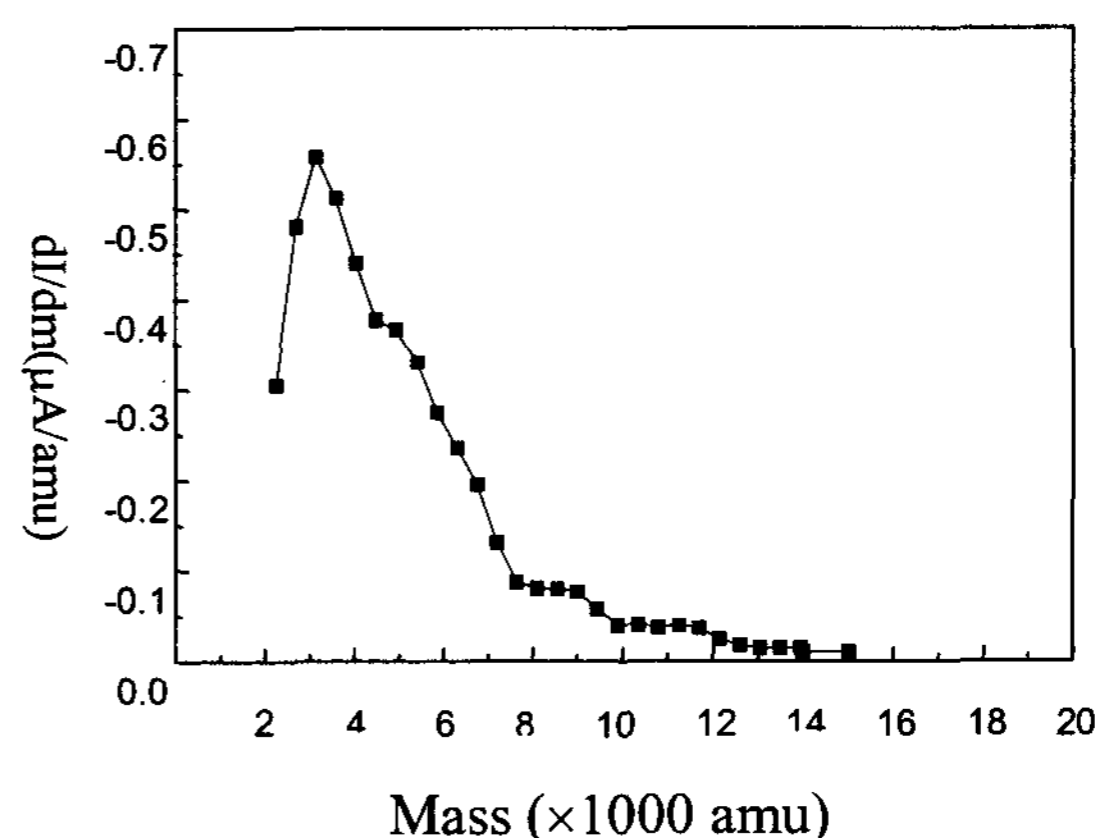

Fig. 1. Mass distribution of negatively charged carbon clusters extracted from the hot filament reactor for the gas mixture of 1%CH$_4$-99%H$_2$ under 6 torr at the filament temperature of 2100°C.

The cluster size increased with increasing methane concentration [14]. The diamond crystals with well-defined facets were grown for small clusters containing a few hundreds of atoms while the cauliflower-shaped or ball-like diamonds were grown for large clusters containing more than 1000 atoms.

The existence of clusters in the gas phase was confirmed in other systems, too. The clusters can be captured on the grid and observed by transmission electron microscopy (TEM). By this technique, clusters were observed by TEM in the CVD of silicon [15] and zirconia [16], and the thermal evaporation of gold [17] and copper [18].

4. Theory of film formation by charged clusters in the silicon CVD process

4.1 Simultaneous deposition and etching of silicon

Similar to the puzzling phenomenon of diamond deposition with simultaneous graphite etching in the

diamond CVD process, silicon particles were observed to deposit and etch simultaneously in the silicon CVD process [19-21]. This phenomenon can only be explained by the assumption that the silicon nuclei are formed in the gas phase with their subsequent deposition on the substrate while the silicon particles on the substrate etches away simultaneously [22, 23]. Since this phenomenon is critical to the theory of charged clusters in the silicon CVD process, it will be described in more detail.

In the experiment by Kumomi and Yonehara [20], the substrate temperature was 950°C with the pressure of 150 torr. The ratio of the supplied gas was SiH_2Cl_2 : HCl : $H_2 = 0.53 : 1.8 : 100$ with the flow rate of 102.33 l/min. In the initial stage (480 s) of their experiment, multiple fine particles were selectively formed on all SiN_x patterns on SiO_2. But in the intermediate stage (720 s), one large cluster, which is distinguishable, emerged among the pre-existing fine ones on some of the SiN_x portions. In the final stage (960 s), nearly the whole area of the portions was covered with one large particle while the other fine particles etched away, and a few portions were vacant, where all particles had etched away. This phenomenon indicates that the two irreversible processes of etching and deposition take place in directions opposite to each other. This phenomenon would violate the second law of thermodynamics if the deposition unit should be an atom.

This phenomenon can be explained in the same way as the experimental observation of diamond deposition and simultaneous graphite etching was explained [5]. The equilibrium solubility of silicon in the gas phase, which represents the boundary for deposition and etching, is shown in Fig. 2 under the processing conditions used by Kumomi and Yonehara [20]. The composition used by them is designated as the vertical dashed line.
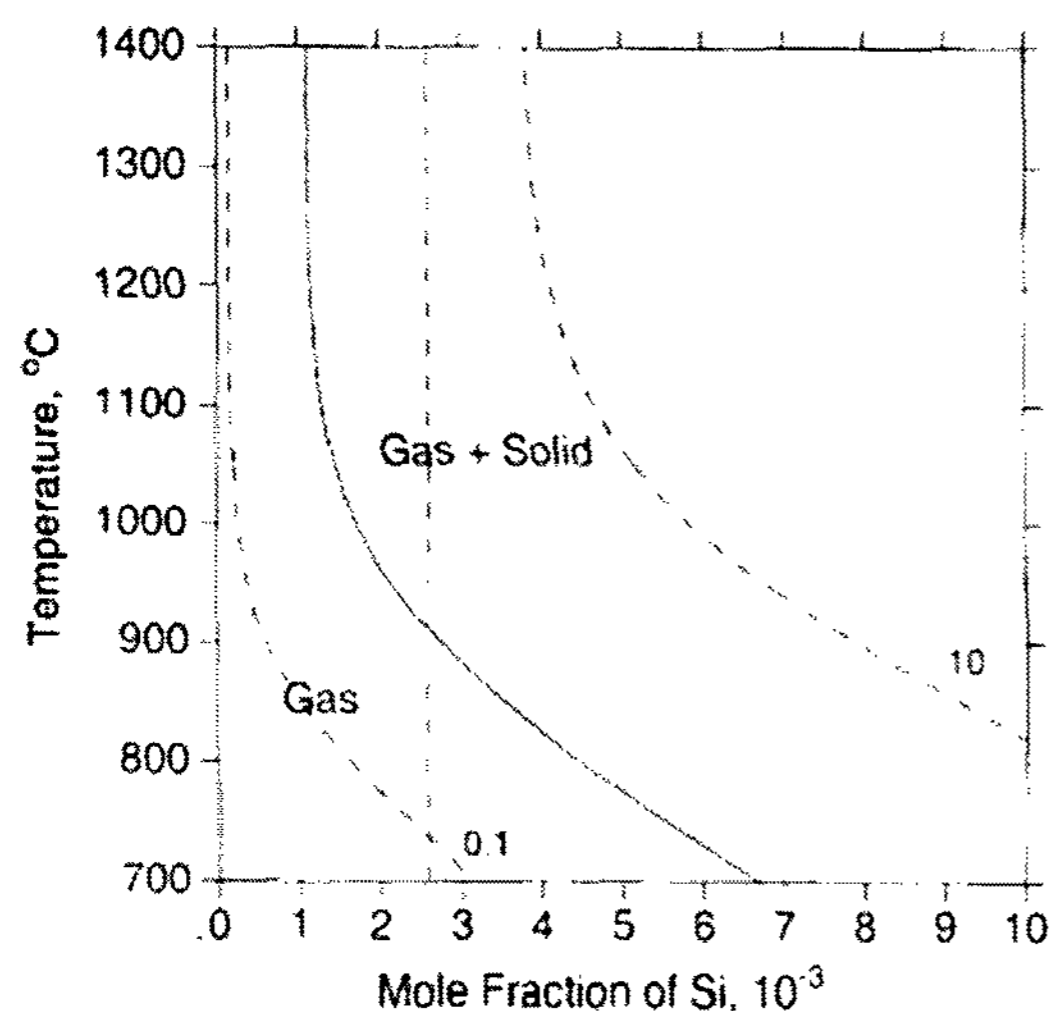

Fig. 2. Temperature dependence of solubility of silicon (solid line) in the gas phase in the Si-Cl-H system. The supersaturation ratios in the gas phase and

the gas + solid regions are, respectively, 0.1 and 10 along the dashed lines. The thermodynamic calculation was done under the conditions: pressure of 150 torr, 2.86 mol of Cl and 201.06 mol of H.

This composition falls into the gas + solid region at the substrate temperature of 950°C. For the composition used by Kumomi et al., the supersaturation ratio at 950°C is 1.39. For comparison, the supersaturation ratio at 1100°C is 2.93. However, this supersaturation can be maintained only when the gas phase nucleation is suppressed. If the gas phase nucleation takes place, most of the supersaturation is dissipated in the nucleation or the precipitation process. Precipitation of silicon in the gas phase above the substrate will shift the composition in the gas phase from that of the vertical dashed line to that of the solubility line in Fig. 2. In other words, the driving force is for deposition at the substrate temperature of 950°C if the gas phase nucleation is suppressed. However, the driving force changes for etching at 950°C if the gas phase nucleation takes place.

This analysis indicates that the puzzling phenomenon of simultaneous deposition and etching can be approached on a sound thermodynamic basis if the gas phase nuclei are formed in the reactor with their subsequent deposition. Therefore, simultaneous deposition and etching, more specifically, corresponds to simultaneous deposition of silicon clusters and etching of atomic silicon. From this analysis, charged gas phase nuclei are predicted in the silicon CVD process.

4.2 Experimental confirmation of silicon clusters

Charged silicon clusters have difficulty in landing on the carbon membrane for TEM observation in the conventional CVD process. In order to make their landing on the membrane easy, we used the hot filament CVD process, where the gas phase is relatively conducting. However, the sign of charge for the silicon clusters was changed from positive to negative with the change of the process from thermal to hot filament CVD. This aspect could be checked by measuring the electric current in the reactor during the process.

The existence of gas phase nuclei of silicon was experimentally confirmed by Cheong et al. [15], who observed individual silicon clusters of a few nanometers by TEM after capturing them on a carbon membrane in the hot filament CVD process. The clusters for the filament temperature of 1800 and 1600°C were ~ 2 nm and 5-7 nm, respectively.

4.3 Charging mechanism of silicon clusters

Negative currents of 0.2 – 5 $\mu A/cm^2$ were measured in the hot filament CVD reactor [15]. In the

thermal silicon CVD process, however, the current was positive with 1 ~ 5 nA/cm². Recently, charging mechanism of clusters could be understood more clearly by the analysis of the activation energy for charging during thermal evaporation of metals [24, 25].

Generally, there are two ways that the clusters can be charged. One is that ions are generated first in the reactor then these ions induce clustering, which is equivalent to ion-induced nucleation [9, 10]. Plasma and hot filament CVD fall into this category. In the case of plasma CVD, the generation of ions is well known and need not be mentioned here and thus the case of hot filament CVD will be mentioned. The hot filament is known as the efficient electron emitter when heated to a sufficiently high temperature. The activation energy for emitting electrons is the work function of the filament. This mechanism is valid in vacuum and the activation energy for negative charging can be made much lower under the condition of hot filament silicon CVD.

The silicon CVD is normally under the pressure higher than a few torr. In this condition, the tungsten filament changes to tungsten silicide at least on the surface. Therefore, the work function of tungsten silicide should be considered. When a gas molecule collides with the filament surface, its activation energy for negative charging becomes the work function of the filament surface subtracted by the electron affinity of the molecule, whose phenomenon is known as surface or contact ionization and is described by a Saha-Langmuir equation [4] for negative charging as

$$\frac{n^-}{n^o} = \frac{g^-}{g^o} exp\left[-\frac{WF-EA}{kT}\right],\qquad(1)$$

where n^0 and n^- are the number densities of a neutral atom and its negative ion, respectively, g^0 and g^- are the statistical weights of the neutral atom and its negative ion, respectively, WF is the work function of the ionization filament, EA is the electron affinity of the atom or the molecule to be ionized and T is the temperature of the ionization filament surface.

Therefore, the molecule or the atom with the high electron affinity tends to be negatively charged. Many kinds of molecules are generated in the silicon CVD process. In the gas mixture of SiH_4 + H_2, the species are Si, Si_2, SiH, SiH_2, and SiH_3, whose electron affinities are 1.385, 2.199, 1.277, 1.124 and 1.406 eV, respectively [26]. Among these, a silicon dimer has the highest electron affinity. In the gas mixture of SiH_4 + HCl + H_2, the species of high electron affinity such as Cl (3.61269 eV), Cl_2 (2.38 eV) and HCl_2 (4.896 eV) [26] are additionally generated.

In the hot filament silicon CVD process, the silicon is normally undersaturated at the filament temperature; otherwise, the filament will be deposited by silicon.

Away from the filament, the silicon becomes supersaturated and the driving force for clustering or nucleation is built up. Ions are known to provide the nucleation center because of their high electrostatic energy [12]. As a result, the silicon nuclei will be negatively charged.

While negative current is detected in the hot filament silicon CVD process, positive current is detected in the thermal silicon CVD, implying that the positive silicon clusters are generated in the latter process. In the thermal CVD process, the generation of the detected current of a few nA/cm² is difficult to understand because there exists no ionization source unlike the case of plasma or hot filament. The thermal CVD process falls into the second category of cluster charging, which was confirmed to be the charging mechanism of clusters during thermal evaporation of metals.

The Saha-Langmuir equation for positive charging is

$$\frac{n^+}{n^o} = \frac{g^+}{g^o} exp\left[-\frac{IP-WF}{kT}\right],\qquad(2)$$

where n^0 and n^+ are the number densities of a neutral atom and its positive ion, respectively, g^0 and g^+ are the statistical weights of the neutral atom and its positive ion, respectively, IP is the ionization potential of the atom or the molecule to be ionized and WF is the work function of the ionization filament.

Comparison between Eqs. (1) and (2) indicates that the lower ionization potential of species to be ionized and the higher work function of the ionization surface are favorable for positive charging while the lower work function of the ionization surface and the higher electron affinity of species to be ionized are favorable for negative charging. Usually, the temperature typically used in the thermal CVD is too low for a single atom or molecule to undergo the positive or negative surface ionization because of relatively high ionization energy and relatively low electron affinity.

The cluster is an intermediate state between a single atom and the bulk. With increasing cluster size, the ionization potential of a cluster decreases from that of a single atom, approaching the work function of the bulk. The electron affinity of a cluster also increases from that of a single atom, approaching the work function of the bulk. Therefore, the activation energy for positive or negative charging is very low when clusters undergo the surface ionization. This mechanism was suggested for the generation of positive copper or gold clusters during thermal evaporation [24, 25]. This mechanism is also responsible for cluster charging in the thermal CVD process [16]. When a charged and a neutral cluster

collide each other, they coalesce into one large charged cluster. Under the typical pressure used in the CVD process, the mean free path is so small and the frequency of collisions between clusters is so high that all the clusters tend to be charged.

4.4 Deposition behavior of charged clusters

Because of charge, the cluster have difficulty in landing on the insulating surface while it has no difficulty in landing on the conducting surface, resulting in selective deposition [23]. The selective deposition in the thin film process is a strong indication for the thin film growth by charged clusters. It should be noted that no other theory can explain the selective deposition clearly.

Even for the conducting substrates, the deposition behavior of charged clusters is different. When the charged cluster approaches a substrate with a high charge transfer rate such as Pt, Fe and Ni, the cluster loses charge to the substrate just before the contact and the resultant neutral clusters undergo Brownian coagulation, resulting in a porous sooty structure [27]. When the Ni substrate is used in the silicon CVD, the porous sooty silicon deposits in the initial stage then the Ni surface is covered with silicon, which has a low charge transfer rate. Therefore, in the later stage, the crystalline silicon grows on the sooty silicon as shown in Fig. 3.
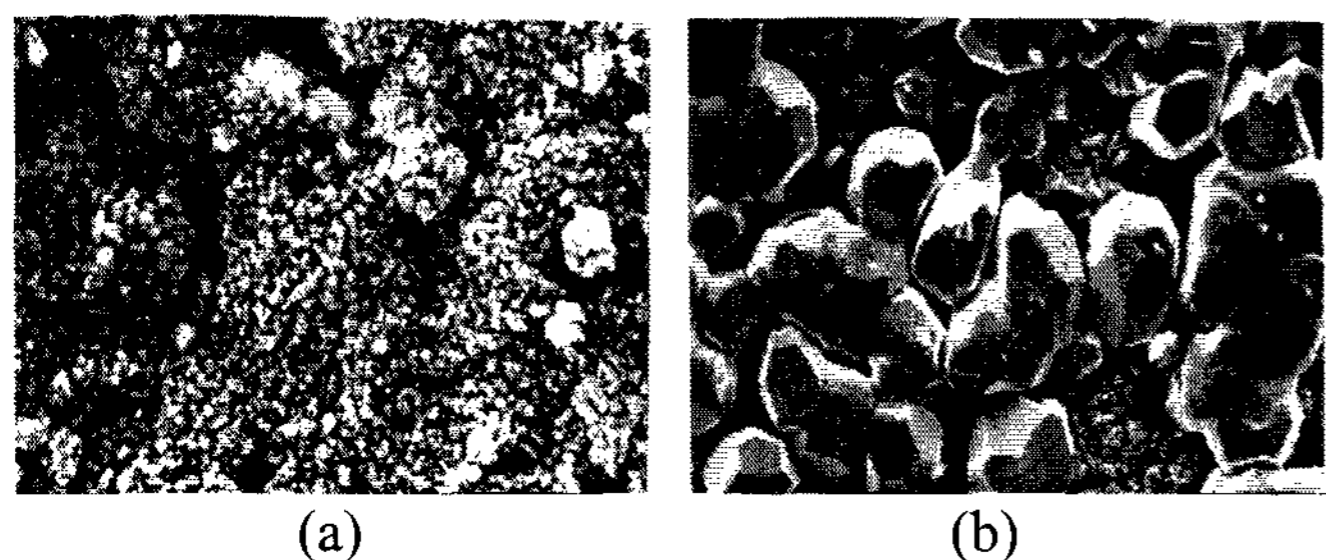

(a)   (b)

Fig. 3 SEM photographs of silicon deposits after 3 min (a) and 30 min (b) of deposition with the $SiH_4:HCl:H_2$ gas ratio of 1:1:98 under 10 torr at a substrate temperature of 850°C.

The Coulomb interaction of two approaching charged particles with identical sign is expressed as

$$F = \frac{q_1 q_2 e^2}{4\pi\varepsilon_o d^2} - \frac{q_1^2 e^2 r_2 d}{4\pi\varepsilon_o \left(d^2 - r_1^2\right)^2} - \frac{q_2^2 e^2 r_1 d}{4\pi\varepsilon_o \left(d^2 - r_2^2\right)^2} + \ldots, (3)$$

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. The equation shows that the interaction changes from repulsion to attraction as the size difference between two clusters increases. For example, if $r_2 \gg r_1$ and thus $r_2 \approx d$, the interaction between the large and the small charged particles of the same sign can be attractive.

According to Eq. (3), when the spherical charged cluster approaches the ellipsoidal charged particle, the Coulomb interaction varies with the direction of the approach. When the direction is along the long axis, the interaction tends to be attractive while the direction is along the short axis, the interaction tends to be repulsive. Because of such anisotropic Coulomb interaction of charged clusters, the charged clusters can deposit one-dimensionally, leading to the formation of silicon nanowires as shown in Fig. 4.
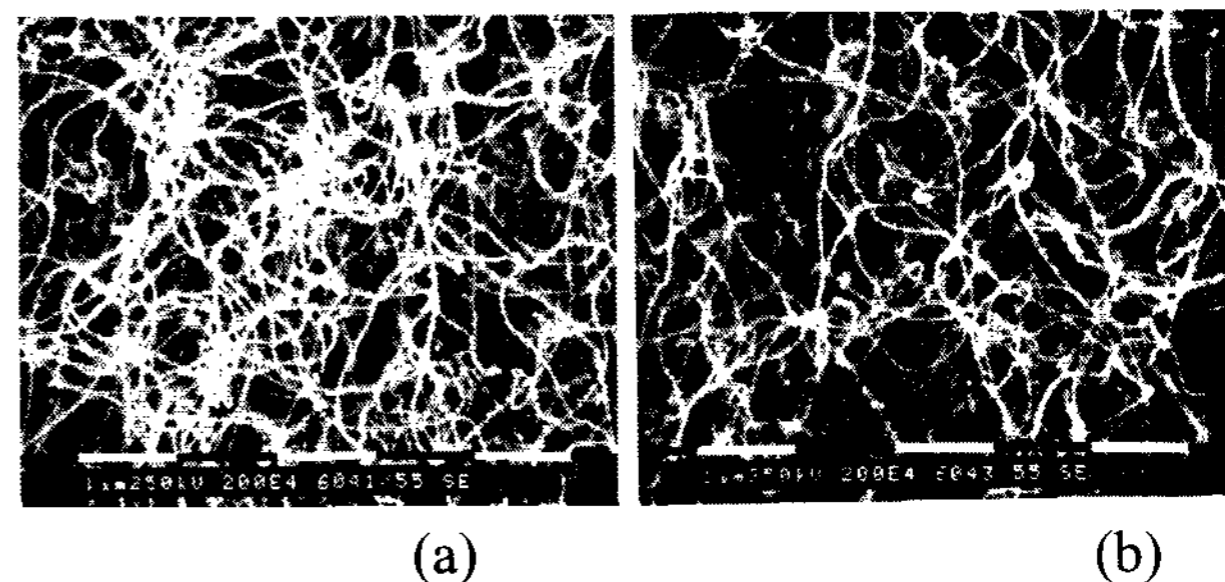

(a)   (b)

Fig. 4   SEM microstructures on (a) Si and SiO_2 substrates after deposition for 6 min under 10 torr at 950°C with a gas ratio of $SiH_4:HCl:H_2 = 3:1:96$

5. Conclusions

Charged clusters are suggested to form spontaneously in many thin film processes without our notice. With this new theory of film growth, the process optimization can be approached more systematically. The charged clusters deposit not only as dense films but also as quantum dots or nanowires. This theory can provide a systematic way for the low temperature deposition of crystalline and amorphous silicon films.

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