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Deposition behavior of Si on insulating and conducting substrates in the CVD process: approach by charged cluster model

Nong M. Hwang[a,b,*], Woo S. Cheong[c], Duk Y. Yoon[c]

[a] *Creative Research Initiative Center for Microstructure Science of Materials, School of Materials Science and Engineering, Seoul National University, Bldg. 37, Room 106, Seoul 151-742, South Korea*
[b] *Korea Research Institute of Standards and Science, P.O. Box 102, Daedok Science Town, Daejon 305-600, South Korea*
[c] *Korea Advanced Institute of Science and Technology, 373-1 Kusung-dong, Yusung-gu, Daejon 305-701, South Korea*

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Abstract

Deposition behaviors of silicon on dielectric and conducting substrates were studied focussing on the deposition mechanism in the Si–Cl–H system. On the dielectric substrate, silicon particles were deposited after some incubation time and then etched away at a later stage under the same processing conditions. On the conducting substrate, silicon particles were deposited without an incubation time with no observed etching during the experimental time period. In the early stages of etching on the dielectric substrate, the number of silicon particles decreased but the remaining unetched particles became larger, indicating that growth and etching took place simultaneously. This paradoxical phenomenon can be explained on a sound thermodynamic basis if we assume that charged clusters are formed in the gas phase and these clusters are the growth unit. The selective deposition on the conducting material as opposed to the dielectric material can also be explained by the electrostatic interaction between the charged cluster and the conducting or dielectric material.

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1. Introduction

Selective CVD is extensively utilized for the formation of patterned films in microelectronics [1]. In this process, a given material is made to deposit selectively on a specific pattern of the growth surface in the presence of a non-growth surface. The growth surface is typically a metal or a semiconductor and the non-growth surface is a dielectric material such as SiO_2. The process is based on the assumption that there can be a substantial difference in the nucleation rate on different substrates [2]. Frequently, the selective growth is

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* Corresponding author. Tel.: + 82-2-880-8922; fax: + 82-2-822-8164.
E-mail address: nmhwang@kriss.re.kr (N.M. Hwang)

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epitaxial on the pattern and is called selective epitaxial growth (SEG) [3] or selective nucleation-based epitaxy (SENTAXY) [4–6].

It is not clearly understood why the conducting or the semi-conducting material is more favourable to nucleation than the dielectric one. Quite often, the selectivity is lost before the desirable thickness of the selective growth is achieved. Selective growth can be changed to non-selective growth by introducing plasma CVD [1,7]. The reason for the loss of selectivity is not clearly understood.

Kumomi et al. [4–6] reported a peculiar phenomenon in the SENTAXY process of silicon, where silicon deposits selectively on periodic SiN_x patterns on SiO_2. In the initial stage (480 s) of their experiment, multiple fine particles were selectively formed on all SiN_x patterns. However, in the intermediate stage (720 s), one large cluster, which was apparently distinguishable, emerged among the pre-existing fine ones on some of the SiN_x portions while other particles disappeared due to etching. In the final stage (960 s), almost the whole area of each pattern was covered with one large particle while fine particles were being etched away. In addition, a few SiN_x patterns were vacant, where all particles on these patterns had etched away. The phenomenon seems paradoxical since two opposite irreversible processes of deposition and etching take place simultaneously.

In order to explain this phenomenon, Shi and Seinfeld [8] suggested a new nucleation process by considering the etching effect of HCl, which can be produced internally by the chemical reactions or supplied externally together with the reactant gases. The etching effect by HCl in the CVD of the Si–Cl–H system was mentioned quite frequently in the previous papers [9–11]. In these papers, it is implicitly assumed that two opposite processes of deposition and etching take place irreversibly and simultaneously. However, this assumption is against the thermodynamic concept when the material transfer takes place by the atomic unit.

The 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}). Furthermore, irreversible etching means that μ_{Si}^{gas} is lower than that of μ_{Si}^{solid}. Therefore, if we assume that two irreversible phenomena takes place simultaneously in opposite directions, the inequality in chemical potentials leads to violation of the 2nd law of thermodynamics. The thermodynamic driving force should be either for deposition or for etching. It cannot be for both.

The phenomenon should not be confused with microscopic simultaneous deposition and etching from the viewpoint of 'the principle of microscopic reversibility' [12]. From the principle, it can be deduced that when the state deviates slightly from the equilibrium and the driving force is for deposition, the etching process will take place simultaneously. In this case, the flux for etching should be smaller than that for deposition, accompanying a net flux for deposition. However, the phenomenon of simultaneous deposition and etching in the silicon CVD process is macroscopic in terms of a net flux. That is, the net flux of deposition is accompanied simultaneously with the net flux of etching.

A very similar phenomenon takes place in the diamond CVD process of the C–H system, where metastable diamond deposits and simultaneously stable graphite etches [13,14]. Yarbrough [15] pointed out that the phenomenon is 'a thermodynamic paradox' based on a detailed thermodynamic analysis. Hwang and Yoon [16] showed that this puzzling phenomenon could be solved by assuming that gas-phase nucleation occurs with these nuclei as the deposition unit. In the C–H system, carbon has the retrograde solubility in the gas phase and the solubility is minimal above the substrate temperature. Therefore, if gas-phase nucleation occurs, the driving force is for etching at the substrate temperature. However, if gas-phase nucleation does not occur, the driving force is for deposition at the substrate temperature. Hence, if gas-phase nucleation takes place, deposition takes place by these nuclei and the etching takes place by the atomic unit, which results in the observation of simultaneous deposition and etching in terms of a net flux.

Hwang [17] suggested that the Si–Cl–H system also has the retrograde solubility of silicon in the gas phase and the puzzling phenomenon observed by Kumomi et al. [4–6] can be explained by the charged cluster model in the same way as the phenomenon in the diamond CVD process. The charged cluster model [18,19] can also explain the selective deposition on the conducting material in the presence of a dielectric material. In the model, initiation of deposition is achieved by the landing of the clusters on the substrate. Since the clusters are charged, their landing depends on the electrical and electrochemical property of the substrate. Hence, the landing of charged silicon clusters on a dielectric substrate will be difficult whereas on the conducting substrate, it will be relatively easy. This landing behavior of charged clusters would make selective deposition possible. This effect would be pronounced if the gas phase is insulating, as in the thermal CVD process, where the charge density is relatively low. This situation is favourable to the selective growth. On the other hand, if the gas phase is conducting as in a plasma or hot-filament CVD process, the charged clusters can deposit on the insulating substrate relatively easily. This situation is favourable to the non-selective growth.

With this background on the possibility of the selective silicon growth by charged silicon clusters, we performed the deposition of the CVD silicon in the Si–Cl–H system. We compared the deposition behavior between five different substrates; two insulating ones of SiO_2 and Si_3N_4, one semi-conducting one of Si and two conducting ones of Mo and Pt. The evolution of the microstructure with time for each substrate was examined and the thermodynamic meaning of the time-dependent deposition behavior on the insulating substrate is analysed in detail in this report.

2. Experimental procedures

Normally, silicon deposition was done in a cold-wall CVD reactor. The substrate holder was stainless steel. The substrate was heated radiantly by the halogen lamp, which was placed below the substrate holder. The temperature of the substrate holder, measured by a thermocouple, was maintained at 950°C. However, the substrate temperature tends to be tens of degree lower than 950°C because the feeding gas was showered on the substrate through the gas inlet, which was placed just above the substrate. The gas ratio was $SiH_4 : HCl : H_2 = 1 : 2 : 97$ with the pressure of 100 Torr. Hundred standard cubic centimeter of the gas mixture was supplied to the chamber. Five different substrates, SiO_2, Si_3N_4, Si, Mo and Pt, were used for the comparison of the deposition behavior. These materials differ in electrical conduction; SiO_2 and Si_3N_4 are insulating, Si is semi-conducting and Mo and Pt are conducting. The deposition times were 3, 6, 12 and 24 min. The weight change of the substrates was measured before and after the deposition.

In order to check that the hot filament CVD should change the deposition behavior on the insulating substrate, the deposition was done in the hot tungsten filament at 1600°C. The gas ratio was $SiH_4 : HCl : H_2 = 1 : 1 : 98$ and the other deposition conditions were the same as before. After each deposition, the substrate surface was observed with SEM (scanning electron microscope).

3. Results

Figs. 1a–d show SEM photomicrographs of SiO_2 substrates after deposition of 3, 6, 12 and 24 min, respectively. After 3 min, silicon particles were hardly seen on the entire substrate as shown in Fig. 1a. After 6 min, an appreciable number density of silicon particles of sub-micron size was observed (Fig. 1b). The number density of silicon particles was $\sim 10^9/\mathrm{cm}^2$. However, after 12 min, most of the silicon particles had disappeared. The number density decreased drastically and the size of the remaining particles increased as shown in Fig. 1c. After 24 min, the silicon particles were hardly seen on the substrate. Fig. 1d shows one of the rare sites on the substrate where a remaining silicon particle was observed. Likewise in the case of the Si_3N_4 substrate, deposition was negligible for the first 3 min. In this report this 3 min time period will be referred to as the incubation time for deposition. Similar to the deposition behavior on the SiO_2 substrate, an appreciable number density of silicon particles was observed on the Si_3N_4 substrate after 6 min and then they were etched away almost completely after 24 min. The weight change was negligible for both SiO_2 and Si_3N_4 substrates during deposition.

On the conducting Mo and Pt substrates, silicon deposition occurred without an incubation time. This was confirmed by both the mass increase of the substrates and SEM observation. After 3, 6, 12 and 24 min, the weight increases were 0.15, 0.19,

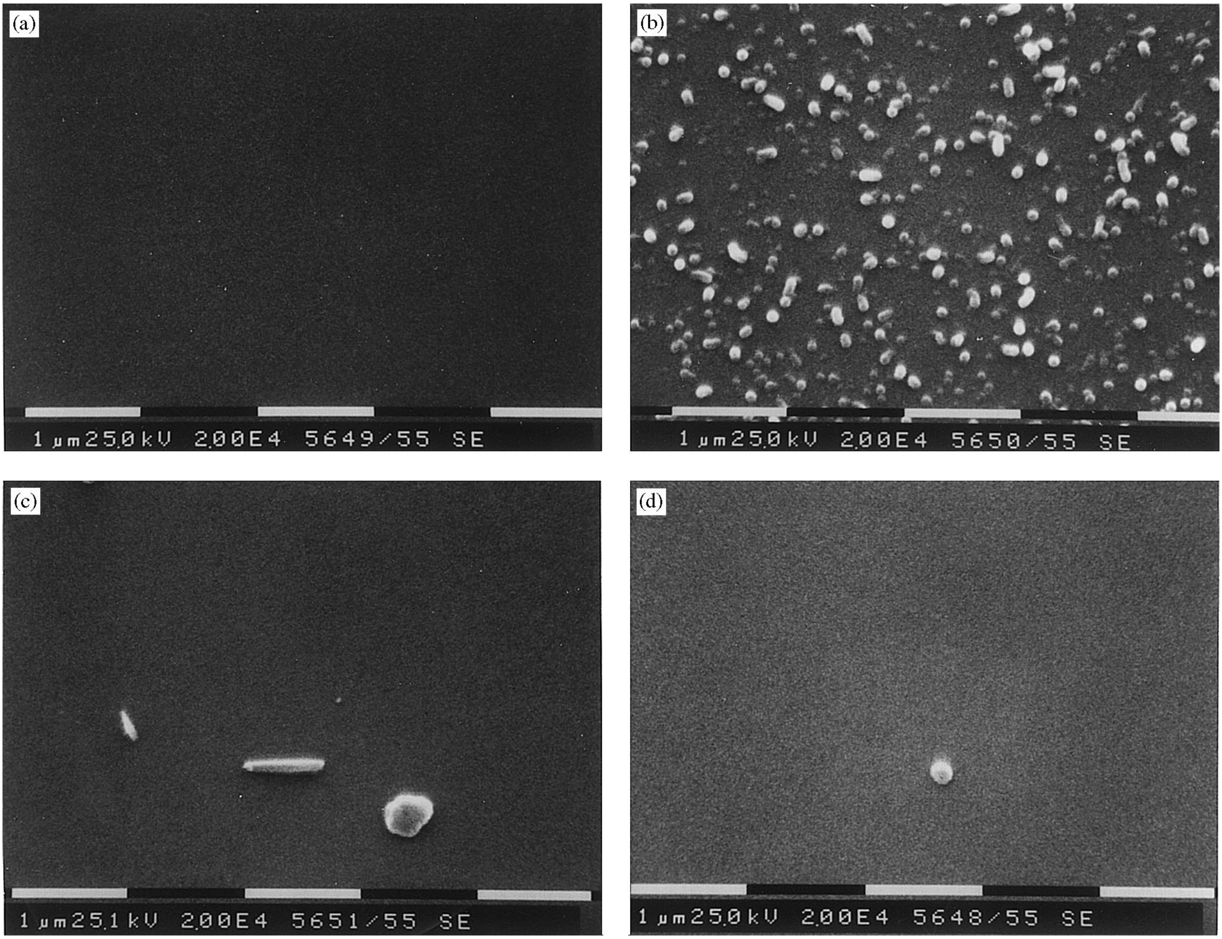

Fig. 1. Deposition behavior of silicon on the SiO_2 substrate with deposition time: after 3 min (a), 6 min (b), 12 min (c), and 24 min (d). The gas mixture of $SiH_4 : HCl : H_2 = 1 : 2 : 97$ was used under the pressure of 100 Torr, at the substrate temperature of 950°C and with the flow rate of 100 sccm. The scale bar in the photograph is 1 μm.

0.19 and 0.24 mg/cm^2 for the Mo substrate and 0.19, 0.20, 0.25 and 0.34 mg/cm^2 for the Pt substrate, respectively. Figs. 2a and b are SEM photomicrographs of the films on the Mo substrate after deposition of 3 and 24 min, respectively. The deposition behavior of Si on the semi-conducting silicon substrate was found to be in the midway between the insulating and the conducting substrates. The deposition continued on the Si substrate but the growth rate was much lower than that on Mo and Pt substrates.

When the hot tungsten filament was used, the deposition behavior changed completely. Figs. 3a and b show SEM microstructures after deposition on SiO_2 and Si_3N_4 substrates, respectively, for 6 min at the filament temperature of 1600°C. The entire surface of the substrate was covered by the deposits. In this case, the deposition started without any incubation time. Therefore, when the hot filament is used, there seems to be no selective nature in deposition between the conducting and insulating substrates.

4. Discussion

The results of Fig. 1 indicate that the silicon was deposited in the initial stage and then etched away

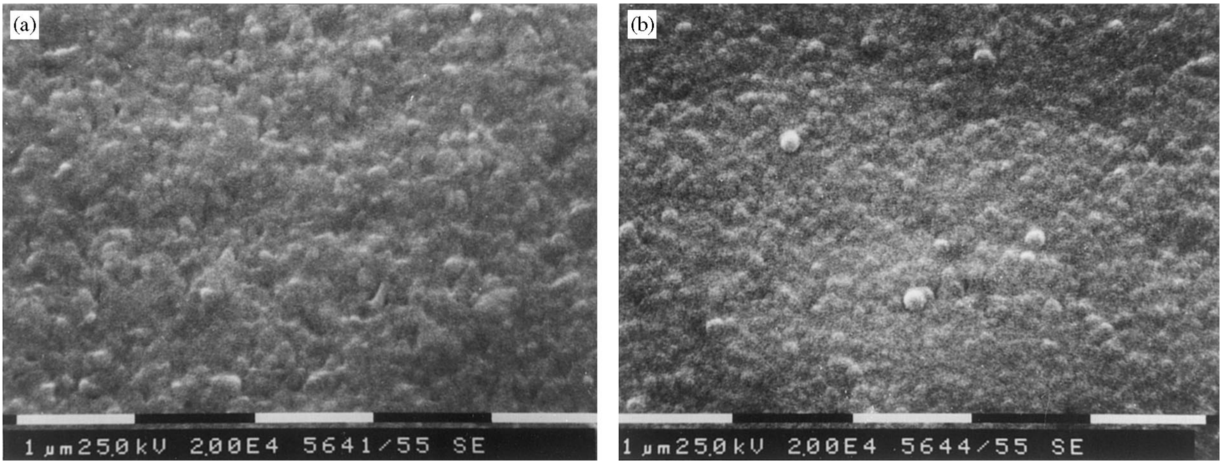

Fig. 2. Deposition behavior of silicon on the Mo substrate with deposition time: after 3 min (a) and 24 min (b). The processing conditions were the same as in Fig. 1.

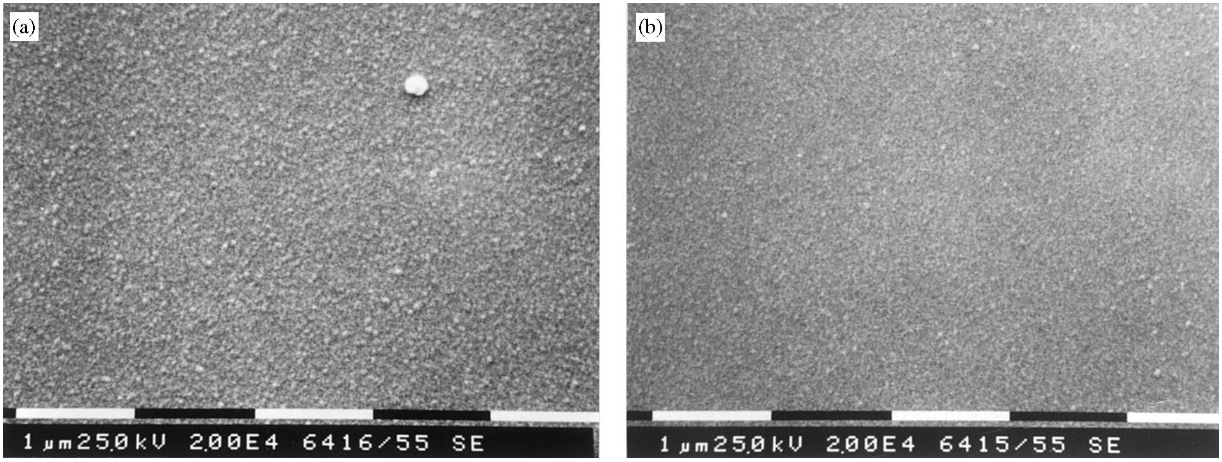

Fig. 3. Deposition behavior of silicon on SiO_2 (a) and Si_3N_4 (b) substrates after 6 min in the hot filament reactor with the filament temperature of 1600°C for the gas mixture of $SiH_4 : HCl : H_2 = 1 : 1 : 98$. The other processing conditions were the same as in Fig. 1.

in the later stage on the SiO_2 substrates. The same deposition behavior was also observed on the Si_3N_4 substrate. One possible explanation of these results would be that the thermodynamic condition changed between the initial and the later stages so that the driving force was for deposition in the initial stage and for etching in the later stage. In this explanation, it should be assumed that the driving force should be time-dependent for the given processing condition.

On the Mo and Pt substrates, however, the silicon deposition continued under the same processing condition, which indicates that the thermodynamic condition for deposition did not change to that for etching. The experimental results indicate that after about 6 min of the processing time, etching took place on the two insulating substrates while deposition continued on the two conducting substrates. These results suggest that the insulating or the conducting property of substrates affects the deposition behavior.

If Figs. 1b and c are compared, the number density of silicon particles decreased in Fig. 1c but the remaining particles grew much larger. This fact indicates that the remaining particles grew while the other particles, which had disappeared, must have undergone etching. Therefore, etching and deposition of silicon must have taken place simultaneously. Since this phenomenon seems to be critical to understanding a charged cluster model, which was suggested as a new growth mechanism of the thin film by Hwang et al. [18,19], it will be analyzed in detail. It will be shown that the experimental observations would lead to thermodynamic paradox under the assumption that the deposition unit is an atom.

4.1. *Thermodynamic analysis of the phenomenon of simultaneous deposition and etching*

The phenomenon of simultaneous deposition and etching revealed in Fig. 1 is basically the same as the reports by Kumomi and Yonehara [5]. In both cases, deposition and etching took place simultaneously in terms of a net flux. Since we intended to reproduce their result, our experimental condition is very close to that of Kumomi and Yonehara [5]. The thermodynamic analysis for this phenomenon will be made under the assumption that the deposition unit is the atom, in which case the deposition can be described by the inequality of the chemical potential of silicon between the gas and the solid phases.

In order for deposition of silicon to take place in terms of a net flux, the chemical potential of silicon ($\mu_{\mathrm{Si}}^{\mathrm{gas}}$) in the gas phase adjacent to the growing surface should be higher than that of the solid silicon ($\mu_{\mathrm{Si}}^{\mathrm{solid}}$). It should be noted that $\mu_{\mathrm{Si}}^{\mathrm{gas}}$ can also represent the chemical potential of silicon on the adsorbed state on the growing surface. In order that etching of silicon takes place, $\mu_{\mathrm{Si}}^{\mathrm{gas}}$ should be smaller than $\mu_{\mathrm{Si}}^{\mathrm{solid}}$. Therefore, simultaneous deposition and etching mean that $\mu_{\mathrm{Si}}^{\mathrm{gas}} > \mu_{\mathrm{Si}}^{\mathrm{solid}}$ and simultaneously $\mu_{\mathrm{Si}}^{\mathrm{gas}} < \mu_{\mathrm{Si}}^{\mathrm{solid}}$, which is apparently against the thermodynamic concept.

There are two possible explanations for this paradoxical phenomenon. One is that deposition and etching takes place under different thermodynamic conditions. The other is that the deposition unit is not an atom but a cluster having formed in the gas phase as suggested in the charged cluster model. First, the possibility of the different thermodynamic conditions will be considered.

In Fig. 1, deposition takes place in the initial stage but overall etching takes place in the later stage. This means that $\mu_{\mathrm{Si}}^{\mathrm{gas}}$ changes with time. In the initial stage such as in Fig. 1(b), $\mu_{\mathrm{Si}}^{\mathrm{gas}} > \mu_{\mathrm{Si}}^{\mathrm{solid}}$, but in the later stage such as in Figs. 1c and d, $\mu_{\mathrm{Si}}^{\mathrm{gas}} < \mu_{\mathrm{Si}}^{\mathrm{solid}}$. On the other hand, the remaining unetched silicon particles in Figs. 1c and d are larger than those of Fig. 1b. This indicates that those remaining particles continued to grow. Figs. 1c and d indicate that the condition of $\mu_{\mathrm{Si}}^{\mathrm{gas}} > \mu_{\mathrm{Si}}^{\mathrm{solid}}$ changes to the condition of $\mu_{\mathrm{Si}}^{\mathrm{gas}} < \mu_{\mathrm{Si}}^{\mathrm{solid}}$ within a distance of a few microns.

This aspect was much clearer in the results reported by Kumomi and Yonehara [5], where initially deposited silicon particles etched away while one silicon particle among them continued to grow. This simultaneous etching and deposition took place on numerous periodically patterned arrays of SiN_x, which are spaced a few microns away from each other. Therefore, the change of the thermodynamic condition from $\mu_{\mathrm{Si}}^{\mathrm{gas}} > \mu_{\mathrm{Si}}^{\mathrm{solid}}$ to $\mu_{\mathrm{Si}}^{\mathrm{gas}} < \mu_{\mathrm{Si}}^{\mathrm{solid}}$ should take place periodically within a distance of a few microns.

If such a change of the thermodynamic condition really takes place within a distance of a few microns, the difference between $\mu_{\mathrm{Si}}^{\mathrm{gas}}$ and $\mu_{\mathrm{Si}}^{\mathrm{solid}}$ should be negligible and as a result, the rate of deposition or etching should be negligible. However, Fig. 1 shows that the rate of deposition or etching is appreciable. Considering the rate of deposition and etching, as shown in Fig. 1, the thermodynamic condition must change abruptly within a distance of a few microns, which is unrealistic. The change of the thermodynamic condition with time is also unrealistic. It should be noted that all the processing variables are kept constant during the process and the steady state value of $\mu_{\mathrm{Si}}^{\mathrm{gas}}$ on the growing surface is expected.

On the conducting substrate under the same processing condition, however, the deposition continues as shown in Fig. 2, indicating that the condition of $\mu_{\mathrm{Si}}^{\mathrm{gas}} > \mu_{\mathrm{Si}}^{\mathrm{solid}}$ is maintained throughout the process. This difference between the dielectric and the conducting substrates is difficult to understand, too. This difference might be related to the mechanism of the selective deposition. Usually, selective deposition in the silicon CVD is explained by the difficulty of nucleation on the dielectric substrate. However, Fig. 1 shows that the nucleation did take place in the initial stage but the nuclei disappeared by being etched away in the later stage.

These phenomena can be approached by the charged cluster model [18,19], where the growth unit is a nanometer-size cluster containing hundreds to thousands of atoms. In the model, the gas-phase nucleation of solid silicon should take place, possibly induced by ions. Brownian coagulation among these charged nuclei is suppressed because of the Coulomb repulsion arising from the charge and the nanometer size cluster is maintained. The electrostatic interaction between the charged clusters and the substrate can account for the selective deposition on the conducting substrate. Once the gas-phase nucleation takes place, the driving force at the substrate is for silicon etching, due to the increasing solubility of silicon in the gas phase as a result of decreasing temperature in the Si–Cl–H system. Therefore, deposition takes place by a cluster unit and etching takes place by an atomic unit. What we observe macroscopically would be the paradoxical phenomenon of simultaneous deposition and etching. Details are explained in the following sections.

4.2. Possibility of gas-phase nucleation in the silicon CVD process

In the CVD process, the gas phase is supersaturated with respect to the precipitation of the solid phase, which deposits as a film. This supersaturation is the driving force for deposition but it also provides a driving force for nucleation in the gas phase. The gas-phase nucleation can be triggered by ions in the gas phase, as well established in the famous Wilson cloud chamber experiment [20,21]. It should be noted that even in clean room temperature air, ions are continuously generated by natural radio activity or by cosmic rays [22] and ion-induced nucleation always takes place at the supersaturation levels much lower than that required for the onset of the homogenous nucleation in the Wilson cloud and bubble chamber experiments [23,24].

In the plasma CVD process, abundant ions would exist in the gas phase. In the plasma process of microelectronics, the formation of the charged particles in the gas phase is a general feature, which is called the dusty plasma [25–27]. In addition, the formation of such particles is known to be almost unavoidable. This can be beneficial or harmful to the properties of the thin film. The sources of particles can be the reactor walls, the substrate used, and the gas reactants. The particulates are charged and act like a colloid suspension. The size of these particulates ranges from nanometer to submicron. Recently, Jang and Hwang formulated the ion-induced nucleation in the presence of abundant charges, focusing on the diamond CVD process [28].

In the thermal CVD process, it is generally believed that the amount of ions would be negligible. But in the thermal silicon CVD chamber, we measured the nano-ampere current, which is attributed to the chemionization process during the decomposition of the reactant gases. One ampere corresponds to $\sim 10^{19}$ flux of ions or electrons per second. One nano-ampere corresponds to $\sim 10^{10}$ flux of ions or electrons per second, which is an enormous amount of ions. It should be noted again that even in the clean room temperature air, where the amount of ions was negligible, the ion-induced nucleation was almost unavoidable in the early Wilson cloud chamber experiment.

Recently, we confirmed such hypothetical nanometer silicon clusters in the gas phase by capturing them on the grid for transmission electron microscopy (TEM) observation during the hot-filament CVD of silicon of the Si–Cl–H system [29]. The clusters tend to have a monosize distribution with the size of ~ 2 nm at the filament temperature of 1800°C, while at 1600°C, they were larger and deviated a little from the monosize distribution with the size of 5–10 nm.

4.3. Effect of the gas-phase nucleation on the supersaturation at the substrate

If the gas-phase nucleation takes place in the supersaturated gas phase, most of the supersaturation is dissipated in the nucleation process and the remaining supersaturation is relatively small. The remaining supersaturation would arise from the capillary effect of the nuclei, which is the driving force for Ostwald ripening, coagulation or coalescence among the nuclei clusters. In some cases, the gas-phase nucleation reverses the supersaturation into the undersaturation. This situation arises from the temperature dependence of the amount of the gas-phase precipitation. Let us assume that the equilibrium amount of precipitates at the temperature of T_1 is larger than that at T_2. If the precipitates formed in the region of T_1 are supercooled to the region of T_2, the precipitates will be etched at T_2. If T_1 is the gas-phase temperature and T_2 is the substrate temperature, the driving force at the substrate is for etching. It should be noted that unless gas-phase nucleation took place, the driving force at the substrate would be for deposition.

Even though the driving force is for etching at the substrate, the particles or clusters above the substrate can deposit. In this case, simultaneous deposition and etching can take place: deposition by the cluster unit and etching by the atomic unit. This picture is free from the thermodynamic paradox and can explain the experimental observation of simultaneous deposition and etching. In the C–H system of the diamond CVD process [16] and in the Si–Cl–H system of the silicon CVD process [17], the gas phase has the retrograde solubility in the temperature range used for a substrate. This means that if the gas-phase nucleation took place, the amount would decrease toward the substrate temperature and the driving force at the substrate would be for etching. The details are described in the respective reference.

The additional suggestion of the charged cluster model is that the clusters are charged. Without charge, the clusters would be neutral and will undergo Brownian coagulation, which would result in the fractal-like porous skeleton of particles. This kind of deposition takes place on the substrate with the high charge transfer rate such as Fe, Ni and Pt [30,31]. On the other hand, because of the electrostatic interaction, charged clusters can undergo self-assembly packing like the deflocculation in the colloid chemistry. This aspect is combined with the unusually high rate of diffusion of the nanocluster smaller than the Fujita's magic size [32–34], making a perfect epitaxial sticking on the growing surface [19]. In the next section, we will explain the different deposition behavior between the insulating and conducting substrates of Figs. 1 and 2 based on the charged cluster model. It should be noted that in the selective epitaxial growth (SEG), this different behavior is utilized.

4.4. Difference in deposition behavior between insulating and conducting substrates

When the growth unit is a charged cluster, the charge will build up on the insulating substrate. Building-up of charge will be time-dependent. Initially, the insulating surface has no charge; as the processing time goes on, the charge will continue to build up and eventually becomes saturated. When the charge is saturated, the further deposition of the charged clusters will be unlikely because of the Coulomb repulsion. Owing to the gas-phase nucleation, however, the driving force at the substrate is for etching and etching by the atomic unit will continue.

This picture can explain the evolution of microstructure in Fig. 1. Fig. 1a shows that for the first 3 min, the deposition hardly starts. Fig. 1b shows that at 6 min, the relatively high density of silicon particles is formed on the insulating substrate. Such a high density of the silicon particles is possible because there was no charge build-up in the initial stage. In this stage, the deposition flux by the cluster unit is dominant over the etching flux by the atomic unit.

As the experimental time increases, charge builds up and incoming charged clusters tend to be repelled. Fig. 1c shows that for the time interval between 6 and 12 min, some particles grew and others etched. In this stage, simultaneous deposition and etching are observed. Fig. 1d shows that in the time interval between 12 and 24 min, most of the silicon particles etched away. In this stage, the charge is saturated and most of the incoming charged clusters are repelled. The etching flux by the atomic unit is dominant over the deposition flux by the cluster unit.

However, few particles undergo coarsening for the time interval between 6 and 12 min. This coarsening behavior can be approached by considering the interaction between the two charged conducting spheres [17]. Dove [35] reported that net attraction could exist between a small and a nearby large particle even if two conducting particles carry charges of the same sign, based on the following equation:

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

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 $\frac{1}{4}\pi\varepsilon_o$ the permittivity. If singly charged two particles of $r_1 = 1$ μm and $r_2 = 2$ nm approach each other, the integration of Eq. (1) from $2\,r_1$ to $r_1 + r_2$ will produce the attractive energy of $\sim 2.85 \times 10^{-20}$ J, which is higher than the thermal energy of $\sim 1.73 \times 10^{-20}$ J at 1250 K. As r_1 decreases, the attractive energy decreases, which means that larger the particle size, the more favorable the growth. Therefore, even if the thermodynamic condition is for etching by the atomic unit, some large particles can grow by the attachment of the charged clusters.

Conversely, conducting substrates, shown in Fig. 2, do not build up charge and charged clusters continue to deposit. The deposition flux by the cluster unit is always dominant over the etching flux by the atomic unit. On the semi-conducting silicon substrate, the deposition behavior would be between the behaviors of the insulating and the conducting substrate, as was confirmed in the experiment. In this interpretation by the charged cluster model, two assumptions were made: one is the gas-phase nucleation of the silicon particles and the other is that the temperature at the substrate should be lower than the surrounding gas phase. In relation to the first assumption, we already confirmed the nanometer silicon clusters formed in the gas phase during the silicon CVD process [29]. In relation to the second assumption, the substrate was placed just below the outlet of the gas mixture in our experiment. Therefore, the substrate temperature can be lower than the other location of the substrate holder because of the feeding of the cold reactant gas. In the direction vertical to the substrate, the temperature gradient may not be for etching at the substrate. However, in the direction not vertical to the substrate, the temperature gradient can be for etching at the substrate.

On the other hand, generally a stoichiometry compound is more difficult to deposit than a non-stoichiometry compound. Sato and Yonehara [36] reported that the selective deposition on Si-rich SiN_x over SiO_2 is easier to control than on stoichiometric Si_3N_4 over SiO_2. Also the deposition is easier on Si-rich SiO_x than on SiO_2. This difference seems to come from the resistivity or the conductivity difference between stoichiometric and nonstoichiometric compounds. If Si is in excess in the compounds of Si_3N_4 and SiO_2, the anionic vacancies should form to maintain the charge neutrality. Since the ionic conductivity would be proportional to the concentration of the anionic vacancies, the nonstoichiometric compound would have higher conductivity than the stoichiometric one. The Coulomb repulsion between the incoming charged clusters and the substrate surface will be higher for the stoichiometric compound substrate, which has the higher resistivity.

In the above analysis of the deposition behavior on the insulating substrate, it is also assumed that the gas phase is insulating. When hot filament or plasma is used in the silicon CVD process, the gas phase is conducting because of the high concentrations of ions. In this case, the charge building-up on the insulating substrate will be diminished. We confirmed in Fig. 3 that in the hot filament CVD process, deposition continued on the insulating SiO_2 and Si_3N_4 substrates without any incubation time. As a rough measure of the conductivity in the gas phase, we can use the electric current in the gas phase. In this hot filament CVD reactor, we could measure the current of ~ 1 μA, which is three orders of magnitude higher than the current that we could measure in the cold-wall CVD reactor.

In relation to this problem, in selective deposition of many systems [1], deposition tends to take place selectively on the conducting substrate. However, when plasma CVD is used, the deposition becomes non-selective and the deposition also takes place on insulating substrates [1]. Plasma CVD will make the gas phase conducting and diminish the charging effect on the insulating substrate, which make the deposition of the in-coming charged clusters possible.

5. Conclusions

The phenomenon of simultaneous deposition and etching of silicon on a dielectric substrate could be approached by the charged cluster model. The selective deposition in the silicon CVD process was also approached by the electrostatic interaction between the charged clusters and the substrate.

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