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Collection
Generation of charged nanoparticles and their contribution to growth of silicon in the thermal chemical vapor deposition process
Abstract

Generation of charged nanoparticles and their contribution to growth of silicon in the thermal chemical vapor deposition process

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The growth mechanism of films and nanostructures has been commonly explained based on the terrace–ledge–kink (TLK) model by an atom. In the actually experimental observation, however, many puzzling phenomena, which could not be explained by an atomic growth, occur in the low-pressure synthesis of diamond by chemical vapor deposition (CVD). Hwang et al. suggested the possibility that charged nanoparticles generated in the gas phase during CVD can contribute to the growth of films and nanostructures. The generation of charged nanoparticles in the gas phase has been continually reported in many CVD processes. However, experimental confirmation on the generation of charged nanoparticles in the gas phase is not sufficient to say that the charged nanoparticles should become a building block of films and nanostructures.
In this thesis, first, the generation of charged nanoparticles in the gas phase was confirmed experimentally during the CVD of silicon using a differential mobility analyzer (DMA) connected to an atmospheric-pressure chemical vapor deposition (APCVD) reactor at various nitrogen gas flow rates as carrier gas, silane gas flow rates as precursor gas, and furnace temperatures. The processing parameters such as carrier, precursor gas flow rates and furnace temperatures affected not only the growth behavior of nanostructures but also the size distribution and number concentration of both positively and negatively charged nanoparticles. The size distribution and number concentration has a strong correlation with the microstructure evolution of films or nanostructures. Although there are numerous indirect evidences implying that charged nanoparticles should contribute to the growth of films and nanostructures, there has been no direct evidence, making it difficult to prove that charged nanoparticles are the building block of deposited films or nanostructures.

Second, we showed the experimental evidences that charged nanoparticles are the building block for films and nanowires. For this, the deposition behavior during silicon CVD was compared between only electrically floated and grounded substrates as fixing the other processing parameters such as temperature and gas flow rates. The microstructure evolution was drastically different between floated and grounded substrates. These results indicate that growth behavior was affected by the electrostatic interaction between charged nanoparticles and the growing surface.

Finally, considering that both positively and negatively charged nanoparticles exist abundantly in the gas phase, the charged nanoparticles would be affected by electric field. To exert the electric force on these
charged nanoparticles, the alternating current (AC) and direct current (DC) bias was applied to the stainless substrate holder during CVD. The bias frequency and voltage significantly affect the microstructure evolution and the growth rate. These results indicate that the bias such as AC and DC could be applied as a new process parameter in the thermal CVD process where charged nanoparticles are generated.

Keywords: charged nanoparticle; differential mobility analyzer (DMA); floated and grounded substrates; electrostatic interaction; alternating current bias; chemical vapour deposition

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1. Introduction

1.1. Theory of charged nanoparticles (TCN)

1.1.1 Formation of metastable diamond in the gas phase

The low-pressure synthesis of diamond was reported through many studies [1–4] but its underlying principle has not been clearly understood [3,5]. The fundamental question is that diamonds, which are metastable phase, can be synthesized at a low pressure.

Figure 1.1 schematically shows the general concept of the metastable phase formation in terms of thermodynamics and kinetics. In the thermodynamic term the formation of the stable phase from the unstable one is more favorable than that of the metastable phase because the Gibbs free energy of the stable phase is lower than that of the metastable phase. However, if the kinetic barrier of the formation of the metastable phase is lower than that of the formation of the stable phase, the formation of the metastable phase could be favorable. Usually, such a kinetic barrier corresponds to the nucleation barrier. Therefore, nucleation barrier should be compared between diamond and graphite.

The free energy of nucleation consists of the surface energy of the nucleus and the driving force for precipitation. For isotropic surface energies of graphite [6] and diamond [7], the surface energy of graphite is lower than that of diamond. The driving force for the precipitation of graphite from the gas phase is larger than that of diamond. If the comparison of the free energy between graphite and diamond with regard to the number of atoms as shown in Figure 1.2, the nucleation barrier of
diamond is slightly smaller than that of graphite in the range of a few hundred of carbon atoms. And diamond would be synthesized. If the surface energy of diamond is reduced by 10%, the nucleation barrier of diamond become lower than that of graphite as shown in Figure 1.2.

The number of atoms at which the free energies of diamond and graphite intersect as shown in Figure 1.2 can derived as [8]

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

Where $\Delta\mu_{\text{dia} \rightarrow \text{gra}}$ the free energy change per atom between diamond and graphite, $\sigma_{\text{dia}}$ and $\sigma_{\text{gra}}$ are the surface energies of diamond and graphite, $\Omega_{\text{dia}}$ and $\Omega_{\text{gra}}$ the atomic volumes of diamond and graphite, respectively. $n^*$ for equation (1-1) is 351 for the reported surface energies, $3.7 \text{ J/m}^2$ and $3.1 \text{ J/m}^2$ 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 [9].
Figure 1.1. Thermodynamic and kinetic explanation for the metastable phase formation from unstable state [10]

Figure 1.2. Gibbs free energy on the number of atoms for diamond and graphite [8]
1.1.2 Puzzling phenomenon: Diamond deposition with simultaneous graphite etching

Hwang and Yoon [11] suggested that the puzzling phenomena of simultaneous diamond deposition and graphite etching well known in the diamond CVD community would violate the second law of thermodynamics if diamond is deposited by individual atoms. They further suggested that in order not to violate the second law, the charged gas phase nuclei should be generated and they should deposit as diamond films whereas both diamond and graphite are etched into the gas phase by the atomic unit.

Figure 1.3 shows the chemical potential diagrams for three possible stabilities among graphite, diamond and gas under a low pressure. The direction of the carbon flux delivered by individual atoms is shown in Figures 1.3(a), (b) and (c). If diamond should deposit, graphite should also deposit as shown in Figure 1.3(a). Figure 1.3(b) shows that graphite deposition with simultaneous diamond etching is possible but experimental result is opposite. Figure 1.3(c) shows that if stable graphite should etch, less stable diamond should also etch. If gas phase nucleation does not occur, the chemical potential diagram would be Figure 1.3(a) but if gas phase nucleation occurs, the chemical potential diagram would be Figure 1.3(c). Therefore, from experimental result that diamond deposition with simultaneous graphite etching occurs, gas phase nucleation should take place in the diamond CVD process.

Figure 1.4 shows the paradox-free direction of carbon flux before and after gas phase nucleation. Figure 1.4(a) shows that the gas phase has the driving force for deposition of both graphite and diamond by atoms before
gas phase nucleation. Figure 1.4(b) shows that the gas phase has the
driving force for etching of both graphite and diamond by atoms after gas
phase nucleation and diamond gas phase nuclei could contribute to
deposition.

Figure 1.3. The direction of carbon atoms of thermodynamics when the
chemical potential of carbon in gas is highest (a), between diamond and
graphite (b) and lowest (c) [10]
Figure 1.4. The chemical potentials of carbon in diamond, graphite and the gas phase before (a) and after (b) gas phase nucleation [10].
1.1.3 Experimental confirmation of gas phase nucleation in the diamond CVD process

Hwang et al. suggested that gas phase nucleation could occur in the gas activated diamond CVD process [11–13]. And gas phase nucleation in the diamond plasma CVD process was also reported by many researchers [14–17].

To confirm experimentally the generation of gas phase nuclei, Jeon et al. [18] used a specially designed system, which is attached an energy analyzer combined with a Wien filter to the hot wire diamond CVD reactor. Figure 1.5 shows the size distribution of negatively charged carbon nanoparticles in the gas phase. The peak is at ~ 250 carbon atoms and the number density of negatively charged nuclei is ~ $10^6$ mm$^{-3}$.

![Figure 1.5. Mass distribution of negatively charged carbon nanoparticles in the HWCVD reactor under the processing condition of a gas mixture of 1.5%CH$_4$–98.5%H$_2$, a reactor pressure of 800Pa and a wire temperature of 2100°C [18].](image)
1.2. System for measurement of charged nanoparticles

1.2.1 Differential mobility analyzer (DMA)

Differential mobility analyzer (DMA) has been used to measure nanoparticles formed in chemical and physical processes and become the most common instrument widely used in the field of aerosol science for the determination of nanoparticles number and size distribution in the gas phase. DMA classifies nanoparticles according to their electrical mobility which are related to their size.

An electrical mobility aerosol measurement started to the first half of the 20th century. Ions in gases [19] and atmosphere [20] were measured by the electrical mobility determination method. This method to measure atmospheric airborne particles was investigated by Rohmann [21]. Knutson developed Rohmann’s concept to devise the differential mobility particle sizer [22]. A nano-DMA was reported and was improved by Chen and Pui [23,24].

Figure 1.6 shows operation schematic of a general DMA. The DMA consists of two concentric metal electrodes, which are inner and outer. Inner electrode can be applied voltage, ranging from 1V to 10kV while the outer electrode is electrically grounded. If voltage is applied to inner electrode, an electric field will be generated between inner and outer electrodes. The sheath gas flow rate \(Q_c\) come from the top of the DMA and flow down between the electrodes. If positive voltage is applied to inner electrode, negatively charged nanoparticles are attracted to inner electrode, which is collector rod, while positively nanoparticles are
attracted to outer electrode. If nanoparticles are a high electrical mobility, the nanoparticles are collected on the upper of collector rod. If nanoparticles are a low electrical mobility, the nanoparticles are collected on the lower of collector rod. If nanoparticles are a proper electrical mobility, the nanoparticles exit with monodisperse flow through a small slit located at the bottom of the collector rod. Therefore, the size distribution is measured by varying the applied voltage.

The location of the collecting nanoparticles depends on the electrical mobility \( (Z_p) \), the dimensions of the DMA, and fluid flow rate. The nanoparticles electrical mobility \( (Z_p) \) is described by the following equation [22]

\[
Z_p = \frac{Q_c \ln \left( \frac{R_2}{R_1} \right)}{2\pi LV}, \tag{1-2}
\]

In this equation, \( R_1 \) and \( R_2 \) are the radii of the inner and outer electrodes, respectively, \( L \) is the effective electrode length, and \( V \) is the applied voltage. \( Z_p \) is related to particle diameter, \( d_p \), is described by Stokes’ law

\[
d_p = \frac{peC_c}{3\pi \mu Z_p}, \tag{1-3}
\]

In this equation, \( \mu \) is the gas viscosity, \( p \) is the number of elementary charge units, \( e \) is the elementary unit of charge, and \( C_c \) is the Cunningham correction factor.
Figure 1.6. A schematic diagram of a general DMA [25]
1.2.2 Faraday cup electrometer (FCE)

A Faraday cup electrometer has widely used to measure the charged nanoparticles concentration. The Faraday cup electrometer consists of shield cup, filter element composed of stainless mesh with glass fiber, and an electrometer to measure a current of charged nanoparticles as shown in Figure 1.7.

An in-situ measurement of the number concentration (N) of charged nanoparticles is described by the following equation

\[ N = \frac{I}{q_e e} \]  \hspace{1cm} (1-4)

In this equation, \( I \) is the electrometer current [A], \( q_e \) is the aerosol flow rate [cc/s], and \( e \) is the elemental charge (=1.6 \times 10^{-19}) [C]. Therefore, the number concentration and size distribution of charged nanoparticles can be obtained by measuring current of electrometer and scanning the DMA applied voltage.
Figure 1.7. A schematic of the Faraday cup electrometer
1.3 Charging mechanism of nanoparticles in the gas phase in thermal reactor.

The generation of charged nanoparticles in the gas phase was experimentally confirmed during many CVD processes. Gas phase species by gas phase reaction are also generated in CVD processes. Figure 1.8 shows ionization potentials (IP) of silicon compounds generated in the gas phase. IP of silicon and silicon compounds is over 7.5 eV and EA of silicon bulk is 4.05 eV. Energy source in thermal CVD is thermal. Thermal energy at room temperature is 0.026 eV. The ionization of silicon or silicon compounds by thermal is extremely hard in silicon thermal CVD system.

<table>
<thead>
<tr>
<th>Species</th>
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<th>AP$_{SiH_4}$ (eV)</th>
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<td>Si$_6$</td>
<td>8.0–8.5</td>
<td></td>
<td></td>
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<tr>
<td>n-Si$<em>3$H$</em>{12}$</td>
<td>9.4</td>
<td></td>
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Figure 1.8 Ionization Potentials of silicon and silicon compounds [26]
The possible mechanism for the formation of charged nanoparticles is that nucleation takes place first in the gas phase and the neutral nuclei subsequently undergo surface ionization on any surface such as the quartz tube of the reactor. The positive and negative surface ionizations are described by Saha–Langmuir equations [27] as

\[
\frac{n^+}{n^0} = \frac{g^+}{g^0} \exp\left(-\frac{IP - WF}{kT}\right),
\]

and

\[
\frac{n^-}{n^0} = \frac{g^-}{g^0} \exp\left(-\frac{WF - EA}{kT}\right),
\]

where IP, EA, WF, and k are ionization potential, electron affinity of nanoparticles, work function of the quartz wall, and Boltzmann constant, respectively. \(n^0\), \(n^+\), and \(n^-\) are the numbers of neutral, positive, and negative species, respectively. \(g^0\), \(g^+\), and \(g^-\) indicate the statistical weight of neutral, positive, and negative species, respectively. Therefore, WF of the reactor wall and IP and EA of nanoparticles generated in the gas phase are the key factor in determining the polarity of charged nanoparticles. Since the nanoparticles generated in this experiment are sufficiently large, both IP and EA of nanoparticles approach the work function value of their bulk[28]. 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.
2. Generation of Charged Nanoparticles in the Gas Phase during Thermal Chemical Vapor Deposition Process of Silicon

2.1 Introduction

Silicon thin films and nanowires have been generally fabricated by in PECVD [29], HWCVD [30] and thermal CVD [31,32]. However, the nanostructure formation mechanism is not fully understood despite intensive studies over the past decade. In some PECVD and thermal CVD processes, the gas phase nucleation was reported to occur during processing [33–36]. The possibility that charged nanoparticles generated in the gas phase during CVD can contribute to the growth of films and nanostructures was studied extensively by Hwang et al. [10,18,37–42]. It was experimentally confirmed that charged nanoparticles are generated in the gas phase under the deposition condition of films and nanostructures in various CVD processes. For example, the generation of charged nanoparticles was confirmed during the syntheses of diamond films [18,37,43], zirconia films [44], copper films [45], silicon films [42,46–48], silicon nanowires [32], ZnO nanowires [49], carbon nanotubes [50,51], and GaN films or nanowires [52].

Motivated by these studies, we tried to confirm the effect of furnace temperature, the carrier and precursor gas flow rates on the generation of charged nanoparticles and the microstructure evolutions of silicon during the APCVD process.
2.2 Effect of the carrier and precursor gas flow rates on the generation of the charged nanoparticles and microstructure evolution

2.2.1 Experimental procedure

Silicon films and nanostructures were deposited on a quartz substrate for 2 hours by conventional APCVD using a quartz tube reactor at a deposition temperature of 900 °C with silane (SiH₄) diluted in helium (10%SiH₄−90%He), hydrogen (H₂) and nitrogen (N₂). The schematic of the experimental set-up is shown in Figure 2.1. In order to effect of nitrogen and silane gas flow rates on the microstructure evolution and generation of charged nanoparticles in the gas phase during silicon CVD process, first the flow rates of 10%SiH₄−90%He and H₂ (99.9999%) were fixed, respectively, at 5 standard cubic centimeters per minute (sccm) and 50 sccm whereas the flow rate of N₂ (99.9999%) as carrier gas was varied at 300, 500, 700 and 1000 sccm, second the flow rates of H₂ (99.9999%) and N₂ (99.9999%) were fixed, respectively, at 50 and 1000 sccm whereas the flow rate of 10%SiH₄−90%He as source gas was varied at 2.5, 5, 7.5 and 10 sccm. The quartz substrate of 10×10×1 mm³ was placed at the center zone of the quartz tube. The surface morphology of films and nanostructures was observed by the field-emission scanning electron microscopy (FESEM) (JSM−7500F).

A DMA (TSI model 3081 Long DMA) system [22] combined with a FCE, designed to measure sizes in the range of 10−1000 nm, was connected to the CVD reactor as shown in Figure 2.1 for measurements of the number
concentration and size distribution of charged gas phase nuclei generated during CVD. The amount of charged nanoparticles, which were size-classified by DMA, was measured as a current on a FCE. Our measuring system did not use the charging system because nanoparticles are self-charged in the quartz reactor of the CVD system [47]. The number concentration and size distribution of charged nanoparticles were measured in-situ during the synthesis of silicon with various carrier gas flow rates. A sampling position for nanoparticles was just above the substrate.

Figure 2.1. Schematic for the synthesis of silicon and the measurements of charged nanoparticles generated during the APCVD process
2.2.2 Results and discussion

Figure 2.2 shows the FESEM images of the surface microstructure of films or nanostructures synthesized on a quartz substrate without a catalyst at carrier gas flow rates of 300 sccm, 500 sccm, 700 sccm and 1000 sccm, respectively. At 300 sccm (Figure 2.2(a)), nanowires were formed with particles attached to nanowires. At 500 sccm (Figure 2.2(b)), nanowires grew extensively without particles attached. At 700 sccm (Figure 2.2(c)), a film was deposited in the early stage and then the porous structure is evolved on the initial film. At 1000 sccm (Figure 2.2(d)), the silicon film was deposited, being densest among Figures 2.2(a)–(d). It should be noted that silicon nanowires in Figures 2.2(a) and (b) were grown without catalytic metal particles. These results indicate that the carrier gas flow rate greatly affected the microstructure evolution of deposited silicon.

To examine the effect of the carrier gas flow rate on the generation of charged nanoparticles in the gas phase, in situ measurements of the charged nanoparticles were carried out using a DMA-FCE system under the same conditions as those of Figure 2.2. Figures 2.3(a) and (b) show the number concentration and size distribution of negatively and positively charged silicon nanoparticles, respectively, at various carrier flow rates. As the flow rate decreased, the number concentration of negatively and positively charged nanoparticles decreased but the peak of the size distribution increased. In the case of positively charged nanoparticles in Figure 2.3(b), the number concentration of ~40 nm nanoparticles at 1000 sccm of N₂ is roughly 100 times larger than that at 500 sccm. When the
carrier flow rate is lower than 500 sccm, the nanoparticles smaller than 20 nm were not detected.

Figure 2.2. FESEM images of silicon films and nanostructures. The various microstructures of deposited silicon evolved on a quartz substrate at N\textsubscript{2} gas flow rates of (a) 300, (b) 500, (c) 700, and (d) 1000 sccm.

Figure 2.4 shows the FESEM images of the surface microstructure of films synthesized on a quartz substrate at 10\%SiH\textsubscript{4}-90\%He gas flow rates of 2.5, 5.0, 7.5 and 10.0 sccm, respectively. At 2.5 sccm and 5.0 sccm as shown in Figures 2.4(a) and (b), films were deposited on the substrate and Figure 2.4(a) shows the surface of the films consisting of smaller
nanoparticles than that of the films in Figure 2.4(b). At 7.5 sccm in Figure 2.4(c), needle-like silicon nanowires start to be grown on the surface of films. At 10.0 sccm in Figure 2.4(d), needle-like silicon nanowires grown surface of films became more and bigger than that grown surface of films in Figure 2.4(c). These results indicate that 10%SiH$_4$−90%He gas flow rate also greatly affected the microstructure evolution of deposited silicon.

Figure 2.3. The number concentration and size distribution of (a) negatively and (b) positively charged nanoparticles at N$_2$ gas flow rate of 300, 500, 700, and 1000 sccm

Figure 2.5 shows the effect of 10%SiH$_4$−90%He gas flow rate on the generation of charged nanoparticles in the gas phase. In-situ measurements of the charged nanoparticles were carried out using a DMA–FCE system under the same conditions as those of Figure 2.4. Figures 2.5(a) and (b) show the number concentration and size
distribution of negatively and positively charged silicon nanoparticles, respectively, at various carrier flow rates. As the flow rate increased, the size distribution of negatively and positively charged nanoparticles increased and the peak of the size distribution also increased. When the 10%SiH$_4$–90%He gas flow rate was 10 sccm, negatively and positively charged nanoparticles cannot be measured in a certain range of size distribution because an amount of charged nanoparticles exceeded measuring range limit.

Figure 2.4. FESEM images of silicon films and nanostructures. The various microstructures of deposited silicon evolved on a quartz substrate at 10%SiH$_4$–90%He gas flow rates of (a) 2.5, (b) 5.0, (c) 7.5, and (d) 10.0 sccm
Figure 2.5. The number concentration and size distribution of (a) negatively and (b) positively charged nanoparticles at SiH4 gas flow rate of 2.5, 5.0, 7.5, and 10.0 sccm.

Figure 2.2 shows that the amount of the deposit on the substrate was decreased with decreasing flow rate of the carrier gas. This aspect would be related with Figure 2.3, which shows that the number concentration of charged nanoparticles generated in the gas phase is decreased with decreasing flow rate. Then why do the amount of the deposit and the number concentration of charged nanoparticles decrease with decreasing flow rate? According to our observation, the silicon tended to deposit on the tube wall near the inlet in the temperature zone of 600 ~ 800 °C, which is higher than the decomposition temperature of SiH4. It is further observed that the amount of silicon deposited on the tube wall increased with decreasing flow rate of the carrier gas. This means that the loss of silicon on the tube wall before the center is responsible for the decrease in the amount of the deposit on the substrate and the number concentration.
of charged gas phase nuclei with decreasing flow rate. With decreasing flow rate of the carrier gas, the mean residence time of the gas would be increased in the reactor although the total amount decreased due to the loss on the tube wall before center. The slight increase of the peak particle diameter with decreasing flow rate as shown in Figure 2.3 might come from the increased mean residence time.

Since the thermal decomposition of SiH$_4$ is known to start at ~400 °C [53], most SiH$_4$ would be decomposed before the gas reaches the hottest zone of 900 °C, where the substrate was placed. The hottest zone is ~13 cm away from the end of the refractory brick of the reactor, where the silicon loss on the tube wall takes place. This means that the additional decomposition of SiH$_4$ could be not expected at the deposition temperature of 900 °C. Therefore, the flux for the deposit shown in Figure 2.2 could not come from individual silicon atoms produced by the decomposition of SiH$_4$ on the substrate at 900 °C but come mainly from the nanoparticles generated in the gas phase, whose size distribution is shown in Figure 2.3.
2.3 Effect of the temperature on the generation of the charged nanoparticles and microstructure evolution

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2.3.1 Experimental procedure

Silicon films were deposited using a typical atmospheric CVD process at four reactor temperatures of 500, 600, 700, and 800 °C at 10 standard cubic centimeters per minute (sccm) of helium-diluted silane of 10% SiH$_4$–90% He for 30 min. High purity nitrogen gas (99.9999%) was supplied as a carrier gas at a flow rate of 1000 sccm. Nitrogen gas, which is commonly used as purge or carrier gas in silicon CVD, does not react with silane at a reactor temperature below 1000 °C. The quartz tube reactor was used for deposition. The length of the tube was 100 cm. In the preliminary experiment, the maximum deposition of silicon took place on the quartz tube wall 35 cm away from the entrance of the tube whereas the maximum reactor temperature was at the center zone, which was 50 cm away from the entrance. A quartz substrate of 10 mm × 10 mm × 1 mm was placed at 35 cm from the entrance of the tube to obtain the maximum deposition rate. The substrate temperatures were 439, 541, 641, and 750 °C, respectively, for the reactor temperatures of 500, 600, 700, and 800 °C.

Using nano DMA–FCE system, the size distribution of the charged nanoparticles was measured in situ during the synthesis of silicon films as a function of the reactor temperature. The sampling position was above the substrate, which was 35 cm away from the entrance and 65 cm away from
the exit of the tube.

The surface roughness and the morphology of films were observed by FESEM. The Raman spectra (Jobin Yvon, LabRam HR Raman spectrometer) were obtained with an Ar ion laser beam (514.5 nm) excitation and an incident power of 0.5 mW.
2.3.2 Results and discussion

Figures 2.6 (a), (b), (c) and (d) show the FESEM image of silicon films deposited, respectively, at reactor temperatures of 500, 600, 700 and 800 °C, which correspond, respectively, to the substrate temperatures of 439, 541, 641, and 750 °C. At a reactor temperature of 500 °C, silicon film was not deposited as shown in Figure 2.6 (a). As the reactor temperature was increased, the surface morphology of silicon films was changed as shown in Figure 2.6. The Raman spectra of Figure 2.7 show that the silicon films deposited at the reactor temperatures of 700 and 800 °C were amorphous and crystalline, respectively.

To confirm the generation of charged nanoparticles in the gas phase under the conditions of silicon film growth shown in Figure 2.6, in situ measurements of charged nanoparticles were carried out using the DMA–FCE system. Figure 2.8 shows the size distribution of charged nanoparticles measured at various reactor temperatures. Both positively (Figure 2.8 (a)) and negatively charged (Figure 2.8 (b)) nanoparticles were generated. The number concentration of positively charged nanoparticles was higher than that of the negatively charged ones at the reactor temperature of 500 °C. As the reactor temperature was increased, the number concentration of negatively charged nanoparticles increased, and became higher than that of positively charged ones at reactor temperatures above 600 °C. The particle diameter at the peak of the size distribution tended to decrease, passing through a minimum as the reactor temperature was increased.
Figure 2.6. FESEM images of silicon films at reactor temperatures of (a) 500 ℃, (b) 600 ℃, (C) 700 ℃ and (d) 800 ℃ with a SiH$_4$ flow rate of 10 sccm.

At the reactor temperature at or above 600 ℃, the particle number concentration increased drastically from that at 500 ℃. For example, the number density for the particle size of 100 nm at 600, 700, and 800 ℃ was more than an order of magnitude larger than that at 500℃. This result indicates that SiH$_4$ decomposed only partially at the reactor temperature of 500 ℃ but tended to decompose fully at or above 600℃. The partial decomposition of SiH$_4$ at 500 ℃ would be related with the fact that the
silicon film was not deposited in Figure 2.6(a). It should be noted that even under the condition that the film was not deposited, the charged nanoparticles were generated, which implies that under the condition of film deposition, the generation of charged nanoparticles in the gas phase is unavoidable.

![Raman spectra of silicon films deposited at reactor temperatures of 700 °C and 800 °C.](image)

Figure 2.7. Raman spectra of silicon films deposited at reactor temperatures of 700 °C and 800 °C.
Figure 2.8. The size distribution of (a) positively and (b) negatively charged nanoparticles at various reactor temperatures with a SiH₄ flow rate of 10 sccm.
2.4 Conclusions

This study demonstrates that the carrier, precursor gas flow rates and temperatures influenced the generation of charged nanoparticles as well as the deposition behavior under typical processing conditions of silicon deposition by APCVD. The microstructure evolution of films, nanowires and nanoparticles was closely related to the number concentration of charged nanoparticles and size distribution, which was affected by the carrier, precursor gas flow rates and temperatures.
3. Experimentally Evidences of Contribution of Charged Nanoparticles to Films and Nanostructures

3.1 Introduction

Although the possibility that crystals can grow by units much larger than individual atoms or molecules has been so frequency reported [10,54–56], it fails to convince the scientific community because of the lack of apparent evidences. It is very difficult to accept the idea that void–free crystals with perfectly smooth surfaces should grow by the building block of nanoparticles containing a few hundreds of or even hundreds of thousands of atoms. One possible reason that previous reports fail to convince the community is that the reported evidences were indirect. The other possible reason would be that the researchers themselves, who claimed the mechanism, did not clearly understand the detailed mechanism on the crystal growth by nanoparticles because the role of charge, which turns out to be critical in the crystal growth by nanoparticles, has been neglected.

Among the noticeable evidences that crystals can grow by nanoparticles, there is a well–known phenomenon in the diamond chemical vapor deposition (CVD) community that less stable diamond grows and simultaneously stable graphite etches away into the gas phase [57,58]. This experimental result violates the second law of thermodynamics because according to the second law, less stable diamond should etch also when stable graphite etches away. Some rigorous thermodynamic analyses showing that this phenomenon contracts with the second law were
reported by a few scientists [5,11,13], who called this phenomenon “thermodynamic paradox”. Hwang and Yoon [11] suggested that this paradox can be avoided if it is assumed that diamond nanoparticles are generated in the gas phase and deposit as diamond crystals. According to the C–H phase diagram, if the diamond nanoparticles nucleate in the gas phase, the driving force becomes for etching of both diamond and graphite at the substrate temperature. If those diamond nanoparticles deposit as diamond crystals on the substrate, what we observe macroscopically would be simultaneous diamond deposition and graphite etching. What actually happens is the diamond deposition by gas phase nuclei and simultaneous atomic etching of both diamond and graphite, which does not violate the second law. According to this suggestion, the diamond crystals grow 100% by the gas phase nuclei because the atomic contribution is negative since diamond etches away by the atomic unit.

Further, Hwang et al. [12] suggested that the diamond nanoparticles are electrically charged based on the observation that diamond crystals grow on the Si substrate and porous skeletal soot particles grow on the Fe substrate under the same experimental conditions. The charged diamond nanoparticles deposit like slow flocculation on the Si substrate, producing a highly regular array or self-assembly of nanoparticles, which is known as colloidal crystallization. In contrast, the charged diamond nanoparticles lose charge just before landing on the Fe substrate, transform to graphite and sediment like fast flocculation, producing a porous skeletal soot structure.

The possibility of the incorporation of the gas phase nuclei into the films or nanostructures was suggested by Ostrikov [59,60] and Cabarrocas
in the plasma enhanced CVD process. Cabarrocas [61] suggested that if these nanoparticles produced in the silane plasma are incorporated into films, it improves the electrical property of the films and called them “polymorphous films” . Yoshida and his colleagues [63–67] made extensive studies on the epitaxial growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films with a building block of nanoparticles by the method called thermal plasma flash evaporation.

On the other hand, the self-assembly of nanoparticles into various nanostructures has been more systematically studied in solution. [54–56,68,69] Penn and Banfield [54] reported an oriented attachment growth mechanism in the hydrolytic synthesis of TiO$_2$ nanocrystals. Tang et al. [56] showed clearly the non-classical crystal growth, where CdTe nanowires with a smooth surface can be grown by the building block of CdTe nanoparticles in solution. Zhang et al. [70] suggested that one-dimensional nanowires, two-dimensional nanosheets and three-dimensional films can be grown, depending on the balance between electrostatic energy and van der Waals interaction between charged nanoparticles. In these studies, the crystal growth by nanoparticles is clear because the starting materials are nanoparticles.

Hwang et al. suggested that such crystal growth by charged nanoparticles is very general in most CVD and some physical vapor deposition (PVD) processes. They confirmed the generation of charged nanoparticles and measured their size distribution in thermal CVD systems [49]. However, experimental confirmation on the generation of charged nanoparticles in the gas phase is not sufficient to say that the charged nanoparticles should become a building block of films and nanostructures.
Some direct evidence that the charged nanoparticles contribute to growth of films and nanostructures is lacking.

Motivated by these backgrounds, we compare the deposition behavior between the floated and grounded silicon substrates during the Si CVD process. Since the floated and grounded substrates differ only in the amount of built-up charges, the deposition behavior would be different if the charged nanoparticles contribute to deposition.
3.2 Comparison of deposition behavior of silicon between grounded and floated substrates during CVD

3.2.1 Experimental procedure

To detect charged nanoparticles generated in the gas phase during the CVD process, by which silicon nanowires and films were deposited, an in-situ DMA (TSI model 3081 Long DMA) system [22] combined with a FCE, designed to measure sizes in the range of 10–1000 nm, was connected to the CVD reactor. The amount of charged nanoparticles, which were size-classified by DMA, was measured as a current on a FCE. Our measuring system did not use the charging system because nanoparticles are self-charged in the quartz reactor of the CVD system [32,47,49,50,52]. The number concentration and size distribution of charged nanoparticles were measured during the synthesis of silicon nanowires and films at the N₂ gas flow rates of 500 and 1000 sccm. A sampling position for nanoparticles was just above the substrate.

Silicon nanowires and films were deposited on a silicon substrate without a catalyst for 2 h using a typical APCVD process at a deposition temperature of 900 °C. 10% silane (SiH₄) diluted in helium (He), hydrogen (H₂) and nitrogen (N₂) were used for the synthesis of silicon. The flow rates of helium-diluted silane and hydrogen (99.9999%) were fixed, respectively, at 5 standard cubic centimeters per minute (sccm) and 50 sccm whereas two kinds of the nitrogen flow rate (99.9999%) of 500 and 1000 sccm were used. The silicon substrate of 10×10×1 mm³ was placed at the center zone of the quartz tube.
The deposition behavior was compared between electrically floated and grounded substrates on a stainless substrate holder plate of $12 \times 12 \times 6 \text{ mm}^3$. For grounding of the silicon substrate, the stainless holder was connected by a stainless rod to the external ground. The surface morphology and cross section of nanowires and films were observed by the field-emission scanning electron microscopy (FESEM, JSM-7500F). The microstructure of nanowires was characterized by a high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) in a high-resolution mode (FEI, Tecnai-F20).
3.2.2 Results and discussion

Figure 3.1 shows the number concentration and size distribution of negatively and positively charged silicon nanoparticles, which were measured by a DMA-FCE system, at N$_2$ gas flow rates of 500 and 1000 sccm. The number concentration and size distribution of negative and positive nanoparticles at N$_2$ gas flow rate of 1000 sccm is larger and broader, respectively, than those at 500 sccm. At 1000 sccm of N$_2$, the number concentration of negative and positive nanoparticles is almost the same. At 500 sccm of N$_2$, however, the number concentration of negative nanoparticles is larger below 80 nm, and smaller above 80 nm than that of positive nanoparticles. When the N$_2$ gas flow rate is 500 sccm, charged nanoparticles start to be measured at ~20 nm. Considering the size and number density of charged nanoparticles, the surface area of the substrate is negligible compared with the total surface area of charged nanoparticles. This means that most precursors must have been decomposed in the gas phase or on the surface of charged nanoparticles rather than on the substrate surface. The precursors that remained undecomposed for decomposition and deposition on the substrate would be negligible.

After experimental confirmation of the generation of charged nanoparticles, we compared the deposition behavior between grounded and floated silicon substrates. Figures 3.2(a) and (b) show FESEM images of lower and higher magnifications, respectively, for the surface microstructure deposited for 2 h on the floated substrate without a catalyst at the substrate temperature of 900 $^\circ$C with gas flow rates of 5 sccm 10% SiH$_4$–90% He, 50 sccm H$_2$ and 500 sccm N$_2$. Figures 3.2(c) and (d) show
FESEM images of lower and higher magnifications, respectively, for the surface microstructure deposited on the grounded substrate with other deposition conditions being the same as those of Figures 3.2(a) and (b).

![Graph showing number concentration and size distribution of negatively (open) and positively (closed) charged nanoparticles at a reactor temperature of 900 °C with N₂ flow rates of 500 and 1000 sccm, respectively, at a SiH₄ flow rate of 5 sccm and H₂ flow rate of 50 sccm.

Figure 3.1. The number concentration and size distribution of negatively (open) and positively (closed) charged nanoparticles at a reactor temperature of 900 °C with N₂ flow rates of 500 and 1000 sccm, respectively, at a SiH₄ flow rate of 5 sccm and H₂ flow rate of 50 sccm.
Silicon nanowires grew extensively on the floated substrate as shown in Figures 3.2(a) and (b) whereas no silicon nanowire grew but only silicon nanoparticles were deposited on the grounded substrate as shown in Figures 3.2(c) and (d). The nanowires in Figure 3.2(b) had diameters of about 10~30 nm. Since neither catalytic metal nor seed of silicon oxide was used in our experiments, the growth of silicon nanowires in Figure 3.2(b) cannot be explained by the vapor-liquid-solid (VLS) [71] or oxide-assisted growth (OAG) [72] mechanism. Charge-building up would be maximized on the floating substrate and minimized on the grounded substrate. Since the only difference in the processing condition between Figures 3.2(b) and (d) is floating and grounding of the substrate, charge building up should be responsible for the growth of silicon nanowires in Figures 3.2(a) and (b), the result indicates that the electrostatic interaction between charged nanoparticles and the substrate is responsible for the growth of silicon nanowires.

To make the TEM observation of silicon nanowires in Figure 3.2(b), the sample of Figure 3.2(b) was immersed in ethanol with an ultrasonic treatment. The suspended nanowires, which had been captured on a TEM copper grid membrane of holey carbon, were observed by high-resolution transmission electron microscopy (HRTEM) and HAADF-STEM in a high-resolution mode. Figure 3.3(a) shows TEM images of silicon nanowires. Figure 3.3(b) shows an enlarged-image of the box marked in the lower part of Figure 3.3(a). The nanowire has a core-shell structure with the inner crystalline silicon core and the outer amorphous oxide (SiO_x) layer. The diameter of the silicon core is 15 nm and the thickness of the outer oxide layer is 4 nm. Figure 3.3(c) shows an enlarged-lattice
image of the box marked in Figure 3.3(b). The spacing between the parallel lattice fringes was measured to be 0.19 nm, which is close to the spacing of the (220) planes of silicon. The nanowire is a single crystal with the <220> growth direction. Figures 3.3(d) shows the dark-field Figure 3.2. The FESEM images: (a) a low-magnification and (b) a high-magnification images deposited on a floated silicon substrate and (c) a low-magnification and (d) a high-magnification images deposited on a grounded silicon substrate at a N₂ flow rate of 500 sccm
HAADF image and Figure 3.3(e) shows the energy-dispersive X-ray (EDX) analysis of the box marked in Figure 3.3(d). The EDX analysis shows that nanowires consist of Si and O. Figure 3.3(f) shows the line profile for the elemental analysis scanned along the line marked in Figure 3.3(d). The line profile shows that the Si peak is strong and the O peak is weak. The oxygen peak comes from the outer oxide layer.

Figures 3.4(a) and (b) show FESEM images of the surface and the cross section of a film, respectively, deposited on a floated silicon substrate whereas Figures 3.4(c) and (d) show those of a film deposited on a grounded substrate. The deposition condition was the same as that of Figure 3.2 except a N\textsubscript{2} gas flow rate, which is 1000 sccm in Figure 3.4. The film on the grounded substrate in Figures 3.4(c) and (d) was much more porous than that on the floated substrate in Figures 3.4(a) and (b). These results show that drastically different microstructures are evolved between floated and grounded substrates, indicating that the dense film in Figure 3.4(a) and (b) results from the electrostatic interaction between the charged nanoparticles and the growing surface. The film thicknesses of Figures 3.4(b) and (d) were ~220 nm and ~190 nm, respectively, indicating that the growth rate of the film on a floated substrate is higher than that on a grounded substrate. Besides, the film in Figure 3.4(b) is denser than that in Figure 3.4(d). The growth rate of the film in Figure 3.4(b) is much larger than that in Figure 3.4(d). Therefore, the deposition rate on the floated substrate is much higher than that on the grounded substrate.
Figure 3.3. TEM images of silicon nanowires deposited on a floated silicon substrate at a N$_2$ flow rate of 500 sccm: (a) a low-magnification TEM image, (b) a high-magnification TEM image, and (c) an enlarged HRTEM image from the square-enclosed area, (d) dark field HAADF image for elemental analysis, (e) EDX analysis of the square-enclosed area marked in (d), and (f) line elemental profiles of Si and O in (c).
Figure 3.4. The FESEM images: (a) plan view and (b) cross-section of films deposited on a floated silicon substrate and (c) plan view and (d) cross-section of films deposited on a grounded silicon substrate at a N$_2$ flow rate of 1000 sccm

The comparison of the deposition behavior between the grounded and the floated substrates reveals many important aspects. First, it indicates that the silicon nanowires in Figures 3.2(a) and (b) grow by an electrostatic self-assembly of charged nanoparticles. It indicates more
than that because just a self-assembly would produce a pearl-necklace aggregate. Instead, nanowires grow as a single crystal with a smooth surface. This means that each nanoparticle underwent epitaxial growth with the atomic diffusion enhanced so much as to produce the smooth surface of nanowires. These phenomena are difficult to explain without assuming that the charged nanoparticles act like a “quasi-solid”, whose atomic diffusion is enhanced almost like liquid. The origin of this enhanced diffusion seems to come from the charge carried by nanoparticles.

Second, it indicates that the dense film shown in Figures 3.4(a) and (b) grows also by an electrostatic self-assembly of charged nanoparticles. Again, it indicates more than that because just a self-assembly would produce a regular array of nanostructures with nanosized voids, considering that the densest packing of monodisperse hard spheres is 74%. Instead, a dense film without voids grows with grain sizes much larger than individual nanoparticles. This means that most nanoparticles underwent epitaxial growth with the atomic diffusion enhanced so much that no voids were left behind. These phenomena strongly imply that the charged nanoparticles act like a “quasi-solid”.

The particle-based crystallization, which is similar to the result observed in Figures 3.2 and 3.4, is relatively well-established in the colloidal solution. The so-called colloidal crystallization can yield various morphologies of nanostructures that cannot be grown via a classical atom and molecule based crystallization. Tang et al. [56] reported the self-assembly into nanowires by nanoparticles very similar to those of Figures 3.2(a) and (b). They observed that monodisperse CdTe nanoparticles in solution were spontaneously reorganized into crystalline nanowires upon
controlled removal of the protective shell of the organic stabilizer. Although they occasionally observed “pearl-necklace” aggregates, they observed the nanowires with a smooth surface in the standard dispersions of CdTe. Since then, various nanostructures in solution were reported to grow by the self-assembly of nanoparticles [69,73–75]. In most of these reports, the role of charge has been neglected. However, based on the observation that the behavior of the self-assembly was affected by the dielectric constant of the solution, Zhang and Wang [70] suggested that the electrostatic energy coming from the charged nanoparticles should be involved in the self-assembly.

Then, why the film growth rate on the floated substrate is higher than that on the grounded one? This result can be explained by the image force between the charged nanoparticles and the growing surface. When two charged conducting spherical particles approach each other, the Coulomb interaction is described by the following equation [76]

$$F = \frac{q_1 q_2}{4 \pi \varepsilon_o d^2} - \frac{q_2^2 r_1 d}{4 \pi \varepsilon_o (d^2 - r_1^2)^2} - \frac{q_1^2 r_2 d}{4 \pi \varepsilon_o (d^2 - r_2^2)^2} + \ldots,$$  \hspace{1cm} (3-1)

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. The first term is the well-known Coulomb equation, which can be attractive or repulsive depending on the sign of two interacting particles. The second and third terms come from the image force, which
are attractive regardless of the sign of charge. Let’s assume that an incoming particle has a radius of \( r_1 \) and a charge of \( q_1 \) and that the floated and ground substrates have charges of \( q_2 \) and \( q_2' \), respectively. By the definition of floating and grounding, \( q_2 \ll q_2' \approx 0 \). Since both floated and grounded substrate can be assumed to have an infinite radius of \( r_2 = \infty \), the third term in equation (3–1) vanishes.

Regardless of the sign of charge of the incoming nanoparticle, both the first and second terms would be zero for the grounded substrate because \( q_2' \approx 0 \). When a nanoparticle of the unlike charge approaches the growing surface of the floated substrate, however, both the first and second terms would be attractive. When a nanoparticle of the like charge approaches the growing surface, the first term is repulsive and the second term is attractive. Comparing the first and the second terms in equation (3–1), the denominator of the second term is smaller than that of the first term and the numerator of the second term would be larger than that of the first term because normally \( q_2 \gg q_1 \), considering that incoming nanoparticles would be singly charged. This means that even the nanoparticles of the like sign tend to be attracted to the growing surface on the floated substrate. This analysis explains the higher growth rate on the floated substrate than on the grounded one shown in Figures 3.4.

Then, why is the growth of nanowires favored on the floated substrate? Equation (3–1) shows that the interaction changes from repulsion to attraction as the size difference between two particles of the like sign increases. For example, if \( r_2 \gg r_1 \) and thus \( r_2 \approx d \), the interaction between the large and the small particles can be attractive. This analysis shows that the interaction between charged nanoparticles of similar size tends to
be repulsive while that between small and large ones can be less repulsive or even attractive.

The similar concept can be applied to the electrostatic interaction between an incoming nanoparticle and a rod, both of which are positively charged, as shown schematically in Figures 3.5(a) and (b). When the nanoparticle approaches the rod in the radial direction (Figure 3.5(a)), the positive charge in the rod will be repelled to the opposite side of the wall. Since the repelled distance is not much, the electrostatic interaction would be repulsive. When the nanoparticle approaches in the axial direction (Figure 3.5(b)), however, the positive charge in the rod will be repelled much further away to the opposite side and the electrostatic interaction would be attractive. Thereby, charged nanoparticles will be attached exclusively to the tip direction, leading to one-dimensional growth of nanowires.

If the spheres are dielectric, the magnitude of the force in equation (3-1) is decreased. This means that the image force of a metal substrate would be much stronger than that of an insulating substrate. Thus, charged nanoparticles would deposit more easily on the conducting area than on the insulating area. This explains the mechanism of the selective deposition widely used in the fabrication of microelectronics. It should be noted that the mechanism of the selective deposition has not been understood clearly until now.
Figure 3.5. A schematic diagram for coulomb interaction between an incoming positively charged nanoparticles and a rod: (a) repulsive force in radial direction (b) attractive force in axial direction
It is well known that metal nanoparticles on the insulating substrate enhance the nanowire growth. This phenomenon is explained by the VLS mechanism [71]. However, since the image force between charged nanoparticles and metal nanoparticles is much stronger than that between the charged nanoparticles than the insulating surface, the possibility for the strong image force between charged nanoparticles and metal nanoparticles to enhance the nanowire growth cannot be ruled out. The growth of silicon nanowires is enhanced under a slightly oxidizing atmosphere, which is called oxide-assisted growth (OAG) [72]. Although this phenomenon is well known, no satisfactory explanation has been made. However, if we consider that the image force of silicon will be much stronger than that of silicon oxide, the charged nanoparticles would land preferentially on the silicon core rather than on the oxidized surface, which would lead to one-dimensional growth of nanowires.

The image force between the charged nanoparticle and the cylindrical rod is much less repulsive or much strongly attractive in the axial direction than in the radial direction of the rod. In other words, the electrostatic interaction between the charged nanoparticle and the rod is highly anisotropic and this anisotropy increased with increasing length of the rod, which would promote one-dimensional or nanowire growth. Such anisotropic electrostatic interaction would not be induced on the grounded substrate, where charge building up is minimized.

Hwang et al. [38,77] and Ostrikov [60] suggested the possibility that the growth of silicon nanowires in the absence of a metallic catalyst can be explained by the electrostatic interaction of charged nanoparticles in thermal CVD and plasma CVD, respectively.
The floated substrate exert a more attractive force to charged nanoparticles in the gas phase than the grounded substrate, which is attributed to the difference in the amount of built-up charges. If the substrate is grounded, \( q_2 \) becomes zero and the first term in equation (3-1) becomes zero and only the second attractive term remains regardless of the sign of \( q_1 \). If the substrate is floated, however, \( q_2 \) has a finite value and the first term should be considered. If \( q_1 \) and \( q_2 \) have the same sign, the first term is repulsive. However, the second attractive term is more dominant than the first repulsive term, the net interaction would be attractive. If \( q_1 \) and \( q_2 \) have the opposite sign, both the first and the second terms are attractive.
3.3 Deposition behavior of silicon at low temperature

Figure 3.6 shows the silicon growth behavior deposited at a certain condition, which was deposited on the quartz substrate for 24 h without bias after silicon was deposited by applying bias with ±50V (1Hz) for 5 min at a deposition temperature of 500 °C (reactor temperature of 900 °C) at a SiH₄ flow rate of 10 sccm, H₂ flow rate of 50 sccm, and N₂ flow rate of 300 sccm as initiation step. Figure 3.6(a) and (b) show that a large particle, which was diameter of ~ 500 nm, places at the center and there is a part that almost never particles and a ring made by small nanoparticles exist away some distance from the large nanoparticle and small nanoparticles spread out. This growth behavior cannot be explained by an atom growth.

Considering the generation of charged nanoparticles in the gas phase, this growth behavior could be explained by the electrostatic interaction between charged nanoparticles. In general the other sign charged nanoparticles is always attraction by coulomb’s force but the electrostatic interaction between the same sign charged nanoparticles is always repulsion. Considering image force generated by the interaction between charged nanoparticles, the force may be expressed by equation (3–1). To investigate the interaction by image force between charged nanoparticles, Lee [78] calculated using the commercial software Maxell. The results indicate that the force between large and small nanoparticles is attraction but between same size of either large or small nanoparticles is repulsion when the sign is the same. These results can explain the instability phenomenon of Figure 3.6 because a larger particle grows faster and
Figure 3.6. The FESEM images: (a) a low-magnification and (b) a high-magnification images (c) enlarged image of (b) deposited on the quartz substrate for 24 h without bias after silicon was deposited by applying bias with ±50V (1Hz) for 5 min at a deposition temperature of 500 °C (reactor temperature of 900 °C) at a SiH$_4$ flow rate of 10 sccm, H$_2$ flow rate of 50 sccm, and N$_2$ flow rate of 300 sccm as initiation step.
3.4 Conclusions

This study demonstrates that the generation of charged nanoparticles in the gas phase occurs under typical processing conditions for the synthesis of silicon nanowires and films by APCVD. The drastic difference in the deposition behavior between floated and grounded substrates indicates that the electrostatic interaction between charged nanoparticles and substrates should be a critical parameter in the microstructure evolution. These results imply that charged nanoparticles are involved in the deposition of silicon nanowires and films as building blocks.
4. Effect of Electric Bias on the Deposition Behavior during Thermal Chemical Vapor Deposition

4.1 Introduction

In the chemical vapor deposition (CVD) process, it has been believed that the reactant gases decompose mainly on the surface and produce atoms or molecules, which contribute to the growth of films or nanostructures [79]. However, recently it has been shown that the reactant gases also decompose actively in the gas phase in many CVD systems, which is evidenced by the extensive generation of the gas phase nuclei [10,18,32–34,38,43,44,46,47,49–52,80]. Using a DMA or other particle detecting systems attached to a CVD reactor, Adachi et al. [34,81–83] made an extensive study that a huge amount of SiO\textsubscript{2} nanoparticles was generated in the gas phase almost unavoidably under the deposition condition of SiO\textsubscript{2} films. Considering these results, the generation of charged nanoparticles is so general that it appears to be the rule rather than the exception in the CVD process.

The fact that a significant amount of charged nanoparticles is formed during the CVD process has important implications since they could play a significant role in the microstructure evolution of films or nanostructures [10,38]. Considering that most of nanoparticles are charged, applying the electric bias to the substrate would exert an electric force on these charged nanoparticles and direct their motion according to the given electric field. Motivated by these considerations, first we tried to confirm the generation of charged nanoparticles by measuring their size.
distribution using a DMA combined with a FCE in the silicon CVD process. Second, we examined the alternating current (AC) bias effect on the microstructure evolution and the growth rate. Applying the AC bias turned out to be a new powerful processing parameter in the thermal CVD process where charged nanoparticles are generated.
4.2 Effect of alternating electric bias on the deposition behavior at high temperature

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4.2.1 Experimental procedure

Silicon films were deposited on a quartz substrate for 2 h by conventional atmospheric-pressure CVD using a quartz tube reactor at a deposition temperature of 900 °C with silane (SiH₄) diluted in helium (He), hydrogen (H₂), and nitrogen (N₂). Since quartz is insulating, the quartz substrate of 10x10x1 mm³ was on a stainless substrate holder plate of 12x12x6 mm³ to apply the bias. The substrate was placed at the center zone of the quartz tube. Another electrode of a stainless plate was placed above the substrate. In the experiments the distance between the substrate holder and the upper electrode was fixed at 1 cm. The bias by the AC power supply was applied between the two electrodes with the upper electrode being grounded. The schematic of the experimental setup is shown in Figure 4.1. The flow rates of 10% SiH₄–90% He, H₂ (99.9999%), and N₂ (99.9999%) were, respectively, 5 standard cubic centimeters per minute (sccm), 50 sccm, and 1000 sccm.

A DMA (TSI model 3081) [22] combined with a FCE, which was designed to measure particle sizes in the range of 10–1000 nm, was connected to the CVD reactor for measurements of the size distribution of charged nanoparticles generated during CVD. The amount of charged nanoparticles, which were size-classified by DMA, was measured as a
current on a FCE. Our measuring system did not use the charging system because nanoparticles are self-charged in the quartz reactor of the CVD system. The size distribution and number concentration of charged nanoparticles were measured in situ during the synthesis of silicon films. Details of the experimental set-up for the DMA-FCE system connected to the CVD reactor can be found elsewhere [49,50]. A sampling position for nanoparticles was just above the substrate.

Figure 4.1. Schematic of the experimental setup for the synthesis of silicon films with the AC bias applied to the substrate holder during the CVD process

After measuring the size distribution of the positively and negatively charged silicon nanoparticles in the gas phase during CVD, we applied the electric AC bias to the stainless substrate holder. To examine the effect of the bias frequency, four different frequencies of 0.2 Hz, 0.5 Hz, 1 Hz, and 5 Hz were applied to the holder at the bias voltage of ±100 V. The frequency of 1 Hz with the bias voltage of ±100 V means an alternating
bias of +100 and −100 V with an interval of 1 sec. For comparison, the film was also deposited without the bias (0 V). To examine the effect of a bias voltage, five different bias voltages of 0 V, ±50 V, ±100 V, ±150 V, and ±200 V with a frequency of 1 Hz were applied to the holder. 0 V corresponds to the floated substrate.

The microstructure was observed by the field-emission scanning electron microscopy (FESEM, JSM–7500F) and high-resolution transmission electron microscopy (HRTEM, JEM–3000F). To compare the growth rate, the mass change of films was measured by a microbalance (Denver Instrument TB–215D). To examine the crystallinity of films, the Raman spectra (JobinYvon, LabRam HR Raman spectrometer) were analyzed with an Ar ion laser beam (514.5nm) excitation and an incident power of 0.5 mW.
4.2.2 Results and discussion

Figure 4.2 shows the size distribution and the number concentration of both positively and negatively charged silicon nanoparticles generated during the CVD process, which was measured by the DMA–FCE system. Below the size of ~30 nm, the number concentration of positively charged nanoparticles is higher than that of negatively charged ones but from ~30 nm to ~75 nm, the number concentration of positively charged nanoparticles is lower than that of negatively charged ones. Above the size of ~75 nm, the number concentration of charged nanoparticles was reversed again. However, the total number concentration of positively and negatively charged nanoparticles is almost the same. As suggested by Hwang and Kim [38], the possible mechanism for the formation of charged nanoparticles is that nucleation takes place first in the gas phase and the neutral nuclei subsequently undergo surface ionization on any surface such as the quartz tube of the reactor.

To examine the frequency effect of the alternating bias on the deposition behavior, the AC bias voltage of ±100 V with frequencies of 0.2 Hz, 0.5 Hz, and 5 Hz was applied to the substrate holder. For comparison, the silicon was deposited on the substrate without the bias under the same processing conditions. Figure 4.3 shows the FESEM images of the surface morphology of silicon films deposited on the quartz substrates for 2 h at the reactor temperature of 900 °C with gas flow rates of 5 sccm 10% SiH$_4$–90% He, 50 sccm H$_2$, and 1000 sccm N$_2$. Figure 4.3(a) is for the zero bias and Figures 4.3(b)–(d) are for the bias voltage of ±100 V at frequencies of 0.2 Hz, 0.5 Hz, and 5 Hz, respectively. At the zero bias as
shown in Figure 4.3(a), the film shows appreciable roughness on the surface. At the frequency of 0.2 Hz, the surface is mainly covered with flake-like structures as shown in Figure 4.3(b). At 0.5 Hz, a flake-like structure disappeared and the surface became smoother than that of 0.2 Hz as shown in Figure 4.3(c). At 5 Hz, the surface had a very porous structure as shown in Figure 4.3(d). The surface morphology of the film deposited at the zero bias (Figure 4.3(a)) is similar to that of films deposited by PECVD [84] and HWCVD [85]. Care must be taken of when the AC bias is applied in PECVD and HWCVD processes, where the amount of negatively charged nanoparticles is much larger than that of positively charged ones. When the amount of positively and negatively charged nanoparticles is pronouncedly unbalanced, the unbalanced AC bias would be necessary to produce the result similar to Figure 4.3. These results indicate that the surface morphology of films can be changed considerably by changing the frequency of the alternating bias.

To examine the effect of the bias voltage, the bias was applied to the stainless substrate holder at the biases of ±50 V, ±100 V, ±150 V, and ±200 V with a frequency of 1Hz. Figure 4.4 shows the FESEM images of the surface morphology of silicon films deposited under the same processing condition of Figure 4.3. Under the bias of ±50 V as shown in Figure 4.4(a), the film microstructure tended to have a flake-like structure. When the bias was increased to ±100 V, the microstructure tended to have round nodules as shown in Figure 4.4(b). When the bias was increased to ±150 V, the microstructure became porous as shown in Figure 4.4(c). The nanoparticles of ~100 nm were aggregated as a chain-like structure with their surface covered with numerous nanorods. Finally,
as the bias was increased to ±200 V, the nanoparticles deposited on the surface were ~ 50 nm as shown in Figure 4.4(d), being smaller than those deposited at ±150 V. The microstructure deposited at ±200 V was much more porous than that deposited at ±150 V, whose aspect was shown more clearly in FESEM images of lower magnification.

Figure 4.2. The size distribution and the number concentration of negatively (open circle) and positively (closed circle) charged nanoparticles at a reactor temperature of 900 °C with gas flow rates of 5 sccm 10% SiH₄-90% He, 50 sccm H₂, and 1000 sccm N₂.

To have better understanding of the effect of the bias voltage on the microstructure evolution, the lower magnifications of Figure 4.4 are shown, respectively, in Figure 4.5. The microstructure became more porous as
the bias voltage increased. The film deposited at $\pm 50$ V is relatively dense as shown in Figure 4.5(a). Although the porosity difference between Figures 4.4(c) and (d) appeared not to be appreciable, the microstructure of lower magnification showed a drastically different porosity as shown in Figures 4.5(c) and (d). These results show that drastically different microstructures were evolved by changing the intensity of the alternating bias.

Figure 4.3. FESEM images of silicon films deposited on a quartz substrate at (a) the zero bias and the AC bias voltage of $\pm 100$ V with frequencies of (b) 0.2 Hz, (c) 0.5 Hz, and (d) 5 Hz applied to the substrate holder for 2 h at a reactor temperature of 900 °C at a SiH$_4$ flow rate of 5 sccm, H$_2$ flow rate of 50 sccm, and N$_2$ flow rate of 1000 sccm.
Figure 4.4. FESEM images of silicon films deposited on a quartz substrate at the AC bias voltages of (a) ±50 V, (b) ±100 V, (c) ±150 V, and (d) ±200 V with the frequency of 1Hz applied to the substrate holder under the same processing condition as Figure 4.3
Figure 4.5. Low-magnification FESEM images for silicon films deposited on a quartz substrate at the AC bias voltages of a) ±50 V, b) ±100 V, c) ±150 V, and d) ±200 V with the frequency of 1Hz applied to the substrate holder under the same processing condition as Figure 4.3.
To observe the magnified image of nanorods attached to nanoparticles in Figure 4.4(d), the sample of Figure 4.4(d) was immersed in ethanol with ultrasonic treatment. The suspended particles, which had been captured on a TEM grid membrane of holy carbon, were observed by HRTEM. Figure 4.6(a) shows the low-magnification TEM morphology of the silicon nanoparticles with their surface covered with numerous nanorods. Individual nanorods were single crystalline as revealed by the HRTEM image of Figure 4.6(b). Figure 4.6(c) shows an enlarged-lattice image of Figure 4.6(b). The spacing between the parallel fringes of the crystalline was measured to be 0.31 nm. It is equal to the spacing of the \{111\} planes of crystalline silicon.

These results imply that controlling the AC bias frequency or the magnitude of bias voltages may produce various microstructures. Besides, the AC bias technique can provide a promising method to produce highly porous microstructures. Charged nanoparticles are a kind of nano-sized colloidal particles, which undergo self-assembly and produce highly ordered three-dimensional arrays. This phenomenon is called “colloidal crystallization” [86]. In addition to the property of self-assembly, charged nanoparticles have the property of charge-enhanced diffusion, resulting in the epitaxial colloidal crystallization without voids. Therefore, the self-assembly of charged nanoparticles tends to produce a dense structure. The AC bias would prevent charged nanoparticles from undergoing the self-assembly and produce a porous structures. The structure grown by charged nanoparticles without the AC bias would resemble the dense deflocculation of colloidal particles whereas that with the AC bias would resemble the porous flocculation of them. The highly
porous structure has a high surface area, which is favorable for a low
dielectric constant [87], catalytic effect [88], and electrode materials [89].
The bias frequency and the magnitude of bias voltages can be changed
during deposition, producing more diverse microstructure. This technique
could also produce films of a layered structure with each layer of different
microstructures. For example, the first layer is dense, the second layer is
porous and the third layer is dense again. These results provide a
significantly implication in the CVD process, showing clearly that the
electric bias, which can be either AC or DC, can be a new processing
parameter in the deposition process, where the charged nanoparticles are
generated.
Figure 4.6. TEM images of silicon nanoparticles with numerous nanorods deposited on a quartz substrate at the AC bias voltages of ±200 V: a) a low-magnification TEM image, b) a high-magnification TEM image, and c) an enlarged HRTEM image from the square-enclosed area.
To examine the bias effect on the film growth rate, the mass increase in the substrate after deposition was measured using a microbalance with a scale in $10^{-5}$g. Figure 4.7(a) shows the effect of the bias frequency on the mass change of silicon films grown on the substrate. As the frequency was increased, the mass continued to increase. As the frequency was increased from 0.2 Hz to 0.5 Hz, 1 Hz, and 5 Hz, the mass of the film was increased by 1.1, 2.0, 3.0, and 3.5 times, respectively, compared with that of the film deposited under the zero bias. The slope of the mass increase with respect to bias frequency in Figure 4.7(a) tended to decrease with increasing frequency. Figure 4.7(b) shows the effect of the bias voltage on the mass change of silicon films. The effect of the mass increase by bias voltage is more pronounced than that by bias frequency. As the bias voltage was increased from 0 V to ±50 V, ±100 V, ±150 V, and ±200 V, the mass was increased, respectively, by 1.8, 3, 4.5, and 8.5 times.
Increasing the bias voltage applied to the substrate holder means the increase of the electric field between the two electrodes, which would increase the electric force to attract the charged nanoparticles toward the electrodes. Considering that both positively and negatively charged nanoparticles exist abundantly in the gas phase as shown in Figure 4.2 and that the charge would not build up on the quartz substrate because the AC bias is applied, it is expected that the deposition rate continued to increase with increasing bias voltage as shown in Figure 4.7(b).

The increased deposition rate by the AC bias indicates the increased production yield. Therefore, in the process where the production yield is important, the AC bias can be highly effective. For example, in the Siemens process, which produces polysilicon by decomposing trichlorosilane using CVD, the gas phase nuclei would have an adversary effect on the production yield. The AC bias would efficiently collect the charged nanoparticles, increasing the production yield.

Figures 4.8(a) and (b) show the Raman spectra of the films deposited with different bias frequency and different bias voltage, respectively. To determine the volume fraction of crystalline silicon in the films, $X_c$, the Raman spectra in Figure 4.8(a) were deconvoluted into three parts of crystalline $I_c$ at about 520cm$^{-1}$, intermediate $I_m$ at around 505–517cm$^{-1}$, and amorphous component $I_a$ at around 480 cm$^{-1}$ [90]. The volume fraction of the crystalline phase is determined by $X_c = (I_c+I_m)/(I_c+I_m+I_a)$. $X_c$ was evaluated to be 0.50, 0.56, 0.60, 0.67, and 0.58, respectively, at the zero bias, 0.2 Hz, 0.5 Hz, 1 Hz, and 5 Hz. As the frequency increased, the crystalline fraction was increased up to 1 Hz but was decreased when the frequency was 5 Hz. Figure 4.8(b) shows the Raman spectra for the
films deposited at the bias voltages of 0 V, ±50 V, ±100 V, ±150 V, and ±200 V. From the Raman spectra, $X_c$ was evaluated to be 0.50, 0.60, 0.67, 0.74, and 0.61, respectively, at the biases of 0 V, ±50 V, ±100 V, ±150 V, and ±200 V. The crystalline fraction was increased with increasing bias voltage up to ±150 V but was decreased at ±200 V.

The reason why the crystalline fraction increased with increasing bias frequency and voltage would be that the amount of deposition increased with increasing bias frequency and voltage. It was reported that the crystalline fraction evaluated from the Raman spectra tended to increase with increasing film thickness when the film thickness is below the penetration depth of Raman [85]. The reason for crystallinity to decrease at the bias frequency of 5 Hz and the bias voltage of ±200 V seems to come from the fact that the films were more porous. It is known that Raman spectra of porous silicon films became broader than those of dense silicon films [91].

The fact that charged nanoparticles tend to be generated in the gas phase and contribute to film growth during many CVD implies many potential applications. One example is the low temperature deposition of a crystalline phase, which turned out to be quite successful in the deposition of silicon nitride [92] and silicon [42] using HWCVD. In this case, crystalline nanoparticles are formed in the high temperature region near the hot wires, carried to the low temperature region, and deposited on the substrate at low temperature. Another example would be the acceleration of charged nanoparticles by electric field toward the substrate. This situation would be very similar to the ionized cluster beam deposition (ICBD) [93], which is known to be very powerful in low temperature
epitaxy. In addition to these examples, many applications would be possible based on the crystal growth by charged nanoparticles.

Figure 4.8. Raman spectra of silicon films deposited on a quartz substrate for (a) the AC bias frequencies and (b) the voltages
4.3 Effect of alternating electric bias on the deposition behavior at low temperature

4.3.1 Experimental procedure

Silicon were deposited on a quartz substrate for 2 h by conventional atmospheric-pressure CVD using a quartz tube reactor at a deposition temperature of 500 °C with silane (SiH₄) diluted in helium (He), hydrogen (H₂), and nitrogen (N₂). Since quartz is insulating, the quartz substrate of 10×10×1 mm³ was on a stainless substrate holder plate of 12×12×6 mm³ to apply the bias. The substrate was placed as shown in Figure 4.9. In the experiments the distance between the substrate holder and the upper electrode was fixed at 1 cm. The bias by the AC power supply was applied between the two electrodes with the upper electrode being grounded. The flow rates of 10% SiH₄—90% He, H₂ (99.9999%), and N₂ (99.9999%) were, respectively, 5 sccm, 50 sccm, and 1000 sccm. Charged nanoparticles were measured using DMA–FCE system. A sampling position for nanoparticles was just above the substrate. We applied the electric AC bias to the stainless substrate holder. For comparison, silicon was deposited without the bias (0 V). To examine the effect of a bias voltage, five different bias voltages of 0 V, ±50 V, ±100 V, ±150 V, and ±200 V with a frequency of 1 Hz were applied to the holder. The microstructure was observed by the field–emission scanning electron microscopy (FESEM, JSM–7500F).
Figure 4.9. Schematic of the experimental setup for the synthesis of silicon films with the AC bias applied to the substrate holder during the CVD process.
4.3.2 Results and discussion

Figure 4.10 shows the size distribution and the number concentration of both positively and negatively charged silicon nanoparticles generated during the CVD process, which was measured by the DMA–FCE system. Below the size of ~10 nm, the number concentration of negatively charged nanoparticles is higher than that of positively charged ones but from ~10 nm to ~50 nm, the number concentration of positively charged nanoparticles is higher than that of negatively charged ones. Above the size of ~50 nm, the number concentration of negatively charged nanoparticles was more than that of positively charged nanoparticles whereas the number concentration of positively and negatively charged nanoparticles is almost the same at the size of ~200 nm.

To examine the effect of the bias voltage, the bias was applied to the stainless substrate holder at the biases of ±50 V, ±100 V, ±150 V, and ±200 V with a frequency of 1 Hz. Figure 4.11 shows the FESEM images of the surface morphology of silicon deposited under the same processing condition of Figure 4.10. Figure 4.11(a) shows the surface of substrate after deposited. Silicon was not deposited on the substrate at the condition without bias but under the bias of ±50 V as shown in Figure 4.11(b) silicon nanoparticles started to be deposited by applying alternating bias. As the bias intensity was increased from ±100 V to ±200 V as shown in Figures 4.11(c)–(e), the amount of deposited silicon was largely increased.

The levitation force imposed on the nanoparticles by flow would act as a barrier for their deposition on the substrate as shown in the Figure 4.11(a).
If the nanoparticles are electrically charged as shown in Figure 4.10, the electric field generated by applying bias plays an important role in overcoming the barrier. Therefore, as the bias was increased, silicon was deposited more and more as Figures 4.11(b)–(e). Considering that both positively and negatively charged nanoparticles exist abundantly in the gas phase during many CVD process, we can deposit materials at the condition, which is not deposited, using bias system.

![Graph of size distribution and number concentration of nanoparticles](image)

**Figure 4.10.** The size distribution and the number concentration of negatively (open circle) and positively (closed circle) charged nanoparticles at a deposition temperature of 500 °C at with gas flow rates of 5 sccm 10% SiH₄–90% He, 50 sccm H₂, and 1000 sccm N₂ when a reactor temperature was at 900 °C
Figure 4.11. FESEM images of silicon films deposited on a quartz substrate at the AC bias voltages of (a) ±50 V, (b) ±100 V, (c) ±150 V, and (d) ±200 V with the frequency of 1Hz applied to the substrate holder under the same processing condition as Figure 4.10.
4.4 Effect of directing and alternating electric bias on the deposition behavior of silicon films

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4.4.1 Experimental procedure

The electric bias was applied to the stainless substrate holder plate of $2 \times 2 \text{ cm}^2$ to check whether these charged nanoparticles should contribute to film growth or not. Another electrode stainless plate was placed above the substrate. The bias by the DC power supply was applied between the substrate holder and the upper electrode, which was grounded. Four different biases of $0 \text{ V}$, $+50 \text{ V}$, $-50 \text{ V}$ and $\pm 50 \text{ V}$ were applied to the stainless substrate holder beneath the quartz substrate of $1 \times 1 \text{ cm}^2$ during silicon film deposition. Here, $\pm 50 \text{ V}$ means an alternating bias of $+50 \text{ V}$ and $-50 \text{ V}$ with an interval of 5 sec. In the bias experiments, silicon films were deposited for 30 min at the substrate temperature of 750 °C, where the reactor temperature was 800 °C, at the gas flow rates of 10 sccm 10% $\text{SiH}_4$–90% He and of 1000 sccm $\text{N}_2$.

The films growth rate was evaluated from the thickness measurements of cross-sectional microstructures using field-emission scanning electron microscopy (FESEM, JEOL JSM–6330F). The surface roughness and the morphology of films were observed by both FESEM and AFM (Surface Imaging Systems, NANOStation II). The Raman spectra (Jobin Yvon, LabRam HR Raman spectrometer) were obtained with an Ar ion laser beam (514.5 nm) excitation and an incident power of 0.5 mW. The crystalline
phase was indentified by means of X-ray diffractometer (XRD, MAC Science Co, M18XHF-SRA) using Cu Kα radiation.
4.4.2 Results and discussion

Figure 4.12 shows the FESEM images of the cross-sections of silicon films deposited at the biases of 0, +50, −50 and ±50 V on the stainless substrate holder, respectively, for 30 min at the substrate temperature of 750 °C, which corresponds to the reactor temperature of 800 °C, with gas flow rates of 10 sccm 10% SiH$_4$−90% He and 1000 sccm N$_2$. The average film thicknesses at the biases of 0, +50, −50 and ±50 V were, respectively, 2.1, 2.4, 2.6 and 2.9 μm. The mass increase of the substrate after deposition was measured using a balance with a scale in $10^{-5}$ g (Denver Instrument TB-215D). The mass increases at the biases 0, +50, −50 and ±50 V were 0.61, 0.86, 0.95 and 1.04 mg, respectively. This result was consistent with the change of film thicknesses from the cross-sectional views of silicon films in Figure 4.12. These results show that the deposition flux of silicon films was affected by applying an electric bias, indicating that the charged nanoparticles are involved in the film growth.

When the positive bias was applied, the negatively charged nanoparticles will be attracted to the substrate. When the substrate surface is covered with negatively charged nanoparticles, some negative charge will be built up on the surface since the conductivity of intrinsic silicon would be low. Then further attraction of negatively charged nanoparticles will be suppressed due to the repelling electric force. The similar logic would be applied to the case of the negative bias, to which the positive nanoparticles are attracted. Then, positive charges will build up, repelling the incoming
positive nanoparticles and attracting the negative nanoparticles. This results in the higher growth rate for the negative bias when the amount of negative nanoparticles is larger than that of positive ones as shown in Figure 2.8.

Figure 4.12. Cross-sectional FESEM images of silicon films deposited at electric biases of (a) 0, (b) +50, (c) −50 and (d) ±50 V at a reactor temperature of 800 °C
Surface morphologies of the films were investigated by AFM as shown in Figure 4.13. The root-mean-square (RMS) surface roughness was 27.66, 51.89, 119.8 and 277.8 nm at the biases of 0, +50, −50 and ±50 V, respectively. Although the electric bias increased the deposition rate, it also increased the surface roughness. When the electric bias was applied to the stainless substrate holder beneath the substrate, which has a growing surface consisting of convex and concave areas, the electric field would be higher in the convex area than in the concave area. Therefore, the convex area would grow faster than the concave area, which will increase the roughness of the growing surface, producing microscopically the hill-and-valley structure as shown in Figure 4.12(d).

Figure 4.14 shows the Raman spectra of silicon films deposited at the biases of 0, +50, −50 and ±50 V. In order to determine the volume fraction of crystalline silicon, $X_c$ was evaluated to be 0.66, 0.81, 0.91 and 0.84 at the biases of 0, +50, −50 and ±50 V, respectively. Therefore, the electric bias also increased the volume fraction of crystalline silicon, which is also supported by the X-ray diffraction in Fig 4.15.

The deposited films were examined by X-ray diffraction, as shown in Figure 4.15. At bias of 0 V, the peak of (220) appeared with a weak peak of (111). When the electric bias was applied, the peak of (111) became more distinct and the peak of (311) newly appeared. And the intensity of (111) plane significantly increased at ±50 V, which indicates that the preferred orientation was changing from (220) to (111) planes. The preferred orientation, which is determined by the growth rate of each plane of silicon, is also changed. This result indicates that the bias, which attracted the charged nanoparticles to the growth surface, affected the
growth rate of each plane of silicon.

Figure 4.13. Three-dimensional AFM images of silicon films deposited at electric biases of (a) 0, (b) +50, (c) -50 and (d) ±50 V at a reactor temperature of 800 °C
Figure 4.14. Raman spectra of silicon films deposited at electric biases of 0, +50, -50 and ±50 V at a reactor temperature of 800 ℃

Figure 4.15. X-ray diffraction patterns of silicon films deposited at
electric biases of 0, +50, −50 and ±50 V at a reactor temperature of 800 ℃

4.5 Conclusions

Both positively and negatively charged nanoparticles were shown to be naturally generated in the gas phase during deposition of silicon by thermal CVD. The bias frequency as well as the bias voltage affected the microstructure and the growth rate of the deposited films. As increasing voltage and frequency, the microstructure evolution tends to be grown as the porous structure and growth rate also increased. We can deposit the silicon at the condition, which could not be deposited, by applying the bias. The bias applied on the substrate or the substrate holder can be a new processing parameter in the thermal CVD process where charged nanoparticles are generated.
5. Conclusion

In this study, first the generation of charged nanoparticles in the gas phase was experimentally confirmed using DMA–FCE system under changing the processing parameters for silicon deposition by APCVD. The processing parameters such as carrier and precursor gas flow rates and furnace temperature influenced the size distribution and number concentration of charged nanoparticles as well as the deposition behavior. The microstructure evolution of films and nanostructures such as nanowires and nanoparticles was closely related to the number concentration of charged nanoparticles and size distribution. As the carrier gas flow rate decreased, the number concentration of both positively and negatively charged nanoparticles was decreased the growth mode underwent the transition from films to nanowires.

Second, this study shows the experimental evidence that charged nanoparticles are the building block of deposited films and nanowires as comparing the deposition behavior between electrically floated and grounded substrates during silicon CVD. On the floated substrate, silicon nanowires grew whereas on the grounded substrate, silicon nanoparticles were deposited. In the other processing conditions, a dense silicon film grew on the floated substrate whereas a porous silicon film grew on the grounded substrate. These results indicate that silicon nanowires and dense films grow by the electrostatic interaction between charged nanoparticles and the growing surface. This study demonstrates that
silicon nanowires and films grew by electrostatic self-assembly and enhanced atomic diffusion of charged nanoparticles generated in the gas phase during CVD, posing a possibility that the growth of nanowires and films by electrostatic self-assembly and enhanced diffusion of charged nanoparticles might be a general mechanism in many CVD processes.

Finally, considering that both positively and negatively charged nanoparticles exist abundantly in the gas phase, the bias frequency as well as the bias voltage affected the microstructure and the growth rate of the deposited films. Therefore, the intentional control of bias such as AC or DC on the substrate or the substrate holder in the film reactor would be important in controlling the deposition behavior such as the various microstructures shape, growth rate and quality. The bias can be a new processing parameter in the thermal CVD process where charged nanoparticles are generated.
6. Low-Temperature Deposition of Crystalline Silicon Nitride Nanoparticles by Hot Wire Chemical Vapor Deposition

6.1 Introduction

Since silicon nitride has excellent oxidation resistance [94] and a high dielectric constant, which is 7.5 as compared with 3.9 of silicon dioxide [95]; further, it has been applied to a microelectronic device, used as a barrier layer or a gate insulating layer. With shrinking dimensions in semiconductor devices, higher capacitance is needed and has been pursued by reducing the thickness of dielectric layers.

A silicon nitride film has been synthesized by plasma enhanced chemical vapor deposition (PECVD) or low pressure CVD (LPCVD). However, the silicon nitride film prepared by PECVD or LPCVD is generally amorphous [95–99] with some exception in the case of PECVD [100]. Although a thick amorphous silicon nitride film may have an acceptably low leakage current, the amorphous film with a thickness less than 5 nm may have an appreciable leakage current [95,101]. This problem can be solved if a crystalline silicon nitride film is used as a gate insulating layer [95].

Jehanathan et al. [96] reported that initially amorphous PECVD SiN$_x$ thin films crystallize when heated to temperatures $\geq 875^\circ$C in air. Similar
crystallization was also observed for amorphous Si$_3$N$_4$ powders [102–106]. These results indicate that crystallization of amorphous SiN$_x$ occurs at relatively high temperatures, typically $>1200^\circ$C. The direct deposition of crystalline films of silicon nitride has been reported only in a few cases. Hirai et al. [107] reported the production of $\beta$-Si$_3$N$_4$ using SiCl$_4$–NH$_3$–H$_2$ in the temperature range of 1350 $-$ 1450$^\circ$C. Lee et al. [108] prepared the crystalline films by LPCVD using SiF$_4$ and NH$_3$ at temperatures above $\sim1410^\circ$C. Endler et al. [109] reported the deposition of $\alpha$-Si$_3$N$_4$ by PECVD using SiCl$_4$–N$_2$–H$_2$ at a substrate temperature of 900$^\circ$C. Recently, silicon nitride thin films deposited by hot wire chemical vapor deposition (HWCVD) have attracted an interest owing to a low hydrogen content [97,101,110,111]. However, silicon nitride films deposited by HWCVD were amorphous under deposition conditions of wire temperatures of 1500–2000$^\circ$C, substrate temperatures of 200–500$^\circ$C, reactor pressures of 0.001–0.5Torr [97,98,101,112–114]. It is well established that nano or microcrystalline silicon can be deposited on a glass substrate at temperatures less than 500$^\circ$C by HWCVD and PECVD [97,115]. One explanation for the low temperature deposition of crystalline silicon is the two-step growth mechanism, where the crystalline silicon nanoparticles are formed in the high temperature region of the gas phase, near the hot wire and then incorporated into a film, in the low temperature region [38,59,61,116]. If this concept of two-step growth is applied to the HWCVD of silicon nitride, nano or crystalline silicon nitride might be deposited at the relatively low temperature.

The purpose of this paper is to study the possibility of crystalline silicon nitride deposition at the substrate temperature of 700$^\circ$C using HWCVD. In
depositing the crystalline $\alpha$-$\text{Si}_3\text{N}_4$ by HWCVD, the reactor pressure turned out to be critical. Thus, we used much higher reactor pressures of 4 and 40Torr than previously-used ones of 0.001–0.5Torr [97,98,101,112–114].

6.2. Experimental procedure

The HWCVD system used in this study is similar to those described elsewhere [30,117]. Four helical tungsten wires (99.99%) were used, each wire being 8 cm long with a diameter of 0.3 mm. The size of a silicon wafer substrate was 2.5 x 2.5 cm$^2$ and the substrate holder made of stainless steel had a diameter of 10 cm. The substrate temperature was controlled by the radiation of hot wires combined with a feedback-programmed substrate heater with a diameter of 15 cm. The temperatures of the hot wire ($T_w$) and the substrate ($T_s$) were measured, respectively, by an infrared optical pyrometer and a thermocouple in direct contact with the substrate. The reactor wall and the substrate-heater holder were water cooled.

The gas mixture of 20% SiH$_4$ and 80% H$_2$ was supplied at a flow rate of 5 standard cubic centimeters per minute (sccm) and NH$_3$ was supplied at 200 sccm. Therefore, the concentration ratio in the flow, $R=[\text{NH}_3]/[\text{SiH}_4]$, was 200. The distance between the hot wires and the substrate was 6.5 cm and $T_s$ was maintained at 700$^\circ$C. The deposited products were compared between two levels of the following parameters: reactor pressures of 4 and 40Torr, $T_w$ of 1430 and 1730$^\circ$C and deposition times of 30 and 120 minutes.

A high resolution transmission electron microscope (HRTEM, JEM–
4010) was used for imaging and electron diffraction analysis. Cross-sectional samples for TEM analysis were obtained by means of focused ion beam (FIB) milling (SMI 3050TB). The composition of deposited silicon nitride was determined using X-ray photoelectron spectroscopy (XPS, KRATOS AXIS). The crystalline phase was identified by means of high resolution X-ray diffractometer for thin films (XRD, Rigaku ATX–G) using CuKα radiation in the range of 2θ = 2–160°.

6.3. Results and discussion

Figure 6.1 shows the TEM images of nanocrystalline silicon nitride films deposited on the Si (100) wafer with a natural silicon oxide surface layer under 4 Torr for 30 min at T_w of 1430°C (Figure 6.1(a)) and 1730°C (Figures 6.1(b) and (c)). The diffraction pattern is shown in the inset at the lower bottom of the image in Figure 6.1(c). In the cross sectional views of Figures 6.1(a) and (b), silicon nitride appears, respectively, as dark layers 1.0 ~ 1.4 nm thick at T_w of 1430°C and 2.5 ~ 4.0 nm thick at 1730°C. The dark layer is on the natural silicon oxide layer ~1.5 nm thick, which is formed on the silicon wafer. Although the silicon nitride dark layer appears to be a continuous film in the cross sectional images of Figures 6.1(a) and (b), the plan view of Figure 6.1(c) shows that silicon nitride exists as isolated nanoparticles. At T_w of 1430°C, the silicon nitride nanoparticles were mostly amorphous although some of them have the crystalline lattice as shown by the magnified TEM image in Figure 6.1(a). At the wire temperature of 1730°C, the silicon nitride nanoparticles were mostly crystalline as shown in Figures 6.1(b) and (c). The mean diameter of nanoparticles was ~ 4.2 nm at T_w 1730°C as shown in the plan view
image (Figure 6.1(c)). These results indicate that $T_w$ affects the size and the crystallinity of silicon nitride nanoparticles.

Figure 6.1. High-resolution TME images of nanocrystalline silicon nitride deposited on a Si (100) wafer with a natural silicon oxide layer at the wire
temperatures of (a) 1430°C and (b) and (c) 1730°C, under the reactor pressure of 4 Torr.

Figures 6.2(a) and (b) show the TEM images of the cross-section and plan view of nanocrystalline silicon nitride deposited under 40 Torr at $T_w$ of 1730°C for 120 min. All nanoparticles that we observed by TEM showed the crystalline lattice. From the cross-section image of Figure 6.2(a), the film thickness was determined to 3.2 ~ 4.6 nm. From the plan view image of Figure 6.2(b), the mean diameter of nanoparticles was determined to be ~ 4.4 nm. Considering the silicon nitride thickness of ~ 7.1 nm after deposition for 120 min at 4 Torr at 1730°C, whose image is not shown here, the growth rate is lower at 40 Torr than that at 4 Torr. In some part of the silicon nitride dark layer, the crystalline lattice of silicon nitride coincided with that of the silicon wafer as shown in the magnified inset of Figure 6.2(a). We are not sure whether this coincidence is meaningful or not because the physical contact between the $\alpha$-$\text{Si}_3\text{N}_4$ layer and Si substrate is mediated by the natural thin SiO$_2$ layer. If we assume that the lattice matching between the $\alpha$-$\text{Si}_3\text{N}_4$ layer and Si substrate is meaningful, the following analysis can be made. The observed lattice spacing of the (220) plane of $\alpha$-$\text{Si}_3\text{N}_4$ is 0.194 nm, and that of the (002) plane of Si is 0.271 nm. Interplanar spacing of (110) $\alpha$-$\text{Si}_3\text{N}_4$ in the [110] direction is 1.3426 nm and that of (100) Si in the [001] direction is 0.54307 nm. The percentage difference of \{5$\times$[001] (Si) - 2$\times$ [110] ($\text{Si}_3\text{N}_4$)\} is only +1.09 %. Therefore, the orientation relationship between
the Si₃N₄ layer and Si substrate appears to be preserved as (110) Si₃N₄/(100) Si. This tendency of epitaxy was higher at 40 Torr than at 4 Torr.

Figure 6.2. Cross-section (a) and plan (b) views of high-resolution TEM images of nanocrystalline silicon nitride deposited on a Si (100) wafer with a natural silicon oxide layer, under the reactor pressure of 40 Torr at the wire temperature of 1730℃.

The atomic concentration of the deposited layer was measured by XPS. For the samples prepared under experimental conditions of Figures 6.1 and 6.2, the Si/N ratio was in the range of 0.77 ~ 0.87 being close to the
stoichiometry of Si/N = 0.75. Figure 6.3 shows the X-ray diffraction patterns of the surface deposited under the reactor pressures of 4 and 40 Torr at $T_w$ of 1730°C. The XRD peak positions identified by the database of JCPDS 97 [118] indicated that the main peaks represented by an open circle correspond to $\alpha$-Si$_3$N$_4$. Some silicon peaks represented by an open square were from the silicon wafer.

Figure 6.3. High-resolution X-ray diffraction patterns of nanocrystalline silicon nitride deposited on the Si substrate, under the reactor pressures of 4 and 40 Torr at the wire temperature of 1730°C.

These results clearly indicate that crystalline silicon nitride
nanoparticles can be deposited at the substrate temperature of 700°C by HWCVD. Diffusion of silicon nitride at 700°C would be so negligible that the crystalline silicon nitride is not expected to have formed on the substrate surface by atomic or molecular diffusion. One possible explanation would be the two-step growth, where the crystalline silicon nitride nanoparticles are formed in the gas phase in the high temperature region near the hot wire and land on the substrate at 700°C. This two-step growth mechanism was also suggested to explain nano or microcrystalline silicon depositions at the substrate temperature below 500°C by HWCVD [30,39,42,119,120].

An analogous mechanism was suggested by Cabarrocas [61] and Ostrikov [116] for the silane plasma CVD process. It is well known that charged nanoparticles are formed in the gas phase and suspended during plasma CVD, which is called ‘dusty plasma’. Cabarrocas [61] suggested that these nanoparticles produced in the silane plasma can be incorporated into films and produce the so-called ‘polymorphous structure’. Ostrikov [59] 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.

According to the two-step growth model suggested for silicon HWCVD [30,39,42,119,120], the nanoparticles formed in the gas phase are electrically charged. Because of charges carried by nanoparticles, the deposition behavior was affected by the bias applied to the substrate [39,119,120]. In some case, these nanoparticles have dominantly one sign of charge and the charge removal becomes a rate-determining step in the film growth, resulting in a non-uniformed deposition of silicon on a glass
substrate [30]. As the reactor pressure increased, the collision between charged and neutral species would be increased, leading to a very high degree of ionization [29]. This means that the charged flux would be increased with increasing the reactor pressure. Besides, by considering collisions between positively-charged and negatively-charged ions or nanoparticles that travel from the hot filament to the substrate, the carrier of the minor charge disappears and the dominantly unipolar-charged flux approaches the substrate, which would retard the growth rate due to the electrostatic repulsion on the native oxide of the substrate surface. The relatively low growth rate of silicon nitride in Figures 6.1 and 6.2 may be attributed to such a charge effect. In order to check this possibility of two-step growth by charged silicon nitride nanoparticles, more systematic study should be made.

There are two sources of supersaturation: one from the decomposition of reactant gases near the hot filament and the other from the temperature gradient. According to our previous studies [30,38,39,42,119,120], the gas phase nucleation is triggered very easily by the supersaturation built up by the decomposition of the reactant gases rather than by the temperature gradient. In the case of hot wire CVD, ions are formed by surface ionization of the gas molecules on the filament and act as a nucleation center, producing charged nanoparticles in the gas phase; ion-induced nucleation is well-known in the famous Wilson cloud chamber experiment. Since the surface area of the numerous gas phase nuclei is much larger than the substrate area, the additional supersaturation that might come from the temperature gradient is expected to be consumed by the growth of the gas phase nuclei.
Based on the two-step growth mechanism, the effect of $T_w$ on the size and the crystallinity of silicon nitride nanoparticles can be explained. With increasing $T_w$, the amount of ions would increase. Since each ion would act as a center for nucleation, the size of nuclei would decrease with increasing $T_w$. Whether the gas phase nuclei have a crystalline or an amorphous structure would depend largely on the temperature where the gas phase nuclei are exposed. If the temperature is high, the nuclei would have a crystalline structure; otherwise, they would have an amorphous structure. The temperature where the gas phase nuclei are exposed would increase with increasing $T_w$. Since the major deposition flux comes from the gas phase nuclei in the two-step growth mechanism, the high $T_w$ would favor the deposition of crystalline silicon nitride.
Figure 6.4. Effect of a reactor pressure on the equilibrium mole fraction of silicon nitride precipitation. The thermodynamic calculation was done under the condition of the gas ratio of SiH$_4$/NH$_3$ = 1:200.

Then, a question arises as to why the previous deposition of silicon nitride by HWCVD produced amorphous films under the processing conditions of $T_w$ of 1500–2000°C, $T_s$ of 200–500°C, and the reactor pressure of 0.001–0.5 Torr [97,98,101,112–114]. The important parameter that made the difference between crystalline and amorphous silicon nitride deposition seems to be the reactor pressure. In order to understand the role of the reactor pressure in the deposition by HWCVD, the temperature dependence of the equilibrium amount of precipitation of solid silicon nitride was calculated for various reactor pressures using ThermoCalc [121], which is shown in Figure 6.4.

The pressure was varied at 0.004, 0.04, 0.4, 4, and 40 Torr at a fixed amount of SiH$_4$, H$_2$ and NH$_3$ as 1, 4 and 200 sccm, respectively. In the calculation, the decomposition rate of NH$_3$ was set at 10% of the input flow rate [113,122]. Since the equilibrium amount of precipitation increased with increasing pressure, it was normalized by the total moles of the system. Therefore, the axis of ordinates in Figure 6.4 represents the mole fraction of silicon nitride. As pressure increased, the temperature at which silicon nitride can precipitate increased. For example, at the pressure of 0.004, 0.04, 0.4, 4 and 40 Torr, the precipitation of silicon nitride is possible below 1036, 1130, 1247, 1383 and 1519°C, respectively. This means that at 0.4 Torr, silicon nitride can precipitate below ~1247°C.
where the formation of crystalline silicon nitride nanoparticles is expected to be difficult. At 40 Torr, however, silicon nitride can precipitate below 1519°C, which is high enough to produce crystalline silicon nitride nanoparticles. Therefore, the thermodynamic calculation of Figure 6.4 indicates that the high reactor pressure is favorable for the formation of the crystalline silicon nitride nanoparticles in the gas phase.

Since silicon nitride would precipitate below 1519°C under 40 Torr according to Figure 6.4, the hot wire itself would be deposited by silicon nitride at the wire temperature below 1519°C during HWCVD. Deposition of silicon nitride on the hot wire may have an advantage to reduce the evaporation of tungsten or its compound such as tungsten silicide. Once silicon nitride is deposited on the hot wire, the work function of the hot wire surface would be changed and the surface ionization behavior on the hot wire would also be changed. The change of surface ionization behavior would affect the deposition behavior because molecular ions, which are produced by surface ionization in HWCVD [38], induce ion-induced nucleation, producing eventually charged nanoparticles.

6.4. Conclusion

The crystalline α-Si₃N₄ nanoparticles could be deposited on a Si substrate at a relatively low substrate temperature of 700°C by HWCVD under a reactor pressure of 4 and 40 Torr. The size and crystallinity of α-Si₃N₄ nanoparticles increased with increasing wire temperature. As the reactor pressure increased, the crystallinity of α-Si₃N₄ nanoparticles increased. The thermodynamic calculation shows that a high reactor pressure is needed to precipitate silicon nitride at temperatures high
enough to make them crystalline nanoparticles.

7. Generation of Charged Nanoparticles during the Synthesis of Carbon Nanotubes by Chemical Vapor Deposition

7.1 Introduction

Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have attracted much attention recently for their high chemical stability and current density [123,124]. However, their growth mechanisms have not been fully understood in spite of intense research on the growth and characteristics of CNTs over the last decade. Recently, it has been reported that the application of electromagnetic fields improves uniformity, alignment and growth rates in various CNT syntheses, such as chemical vapor deposition (CVD) [125–127], flame [128–130], hot-filament CVD [51,131] and plasma CVD [132–138]. Judging from the fact that the electromagnetic field has an effect on the growth behavior of CNTs, there is a possibility that the moving charged carriers might be involved in CNT growth.

Chiang and Sankaran [139] observed the generation of carbon nanoparticles in the gas-phase synthesis of CNTs using C$_2$H$_2$ at reactor temperatures above 700 °C without a catalyst. Lee and Hwang [51] confirmed the generation of charged nanoparticles during the
synthesis of CNTs by hot-filament CVD and suggested that the negatively charged nanoparticles were the major growth flux for CNTs. Moreover, in the plasma-enhanced CVD process, Yoo et al. [140] observed a strong correlation between CNF growth and the charge transfer rate of the base layers of the substrates. They reported that amorphous carbon was deposited on the base layers with a high charge transfer rate, such as Pt, Ni and W, whereas CNFs were grown on the base layers with a low charge transfer rate, such as Ag, Mo and Ti. These results were obtained based on the previous study of Hwang et al. [12,30,38,77,141], who suggested that the charged nanoparticles could be the main flux for the growth of films, nanowires and nanotubes. This two-step growth mechanism has been studied in relative detail in the hot-filament diamond CVD process [12,18,142], wherein the generation of charged carbon nanoparticles in the gas phase has been experimentally confirmed [18,43,142,143]. Furthermore, the generation of charged nanoparticles in the gas phase was also experimentally confirmed in other CVD processes [39,42,46,49,119,120,144]. A concept similar to the two-step growth process was suggested to explain the growth of silicon nanowires and other nanostructures by Ostrikov [59] in the silane plasma CVD process. It is well known that charged nanoparticles are formed and suspended in the gas phase during plasma CVD, which is called ‘dusty plasma’ [29,59]. Ostrikov [59] conducted an extensive review on the incorporation of gas phase nuclei into nanostructures during a reactive plasma-assisted nanoassembly process and noted that cations were supplied as precursors for the carbon nanostructures.

To explain the one-dimensional growth of silicon nanowires prepared
via CVD in the absence of catalytic metal particles, Hwang et al. [38,77] suggested that the electrostatic energy arising from the charged clusters or nanoparticles generated in the CVD processes acts as the main driving force. Recently, Kim et al. [49] showed that charged nanoparticles were generated during the synthesis of ZnO nanowires via thermal CVD by measuring the size distribution using a DMA. All of these results suggest that charged carbon nanoparticles might also be generated during the synthesis of CNTs via thermal CVD. Motivated by these findings, in this study, the authors tried to confirm, using a DMA connected to the reactor, whether charged nanoparticles are generated in the gas phase during the synthesis of CNTs via atmospheric-pressure thermal CVD.

7.2. Experimental procedure

The experimental apparatus used in this study is shown in Figure 7.1. CNTs were synthesized using a typical atmospheric-pressure CVD process at reactor temperatures of 950, 990, 1000 and 1010 °C at CH$_4$ (99.995%) flow rates of 30, 50 and 100 standard cubic centimeters per minute (sccm) for 120 min. High purity nitrogen gas (99.9999%) was supplied as a carrier gas. Hydrogen gas (99.9999%) was additionally supplied at flow rates of 0, 50 and 100 sccm. Although the flow rates of CH$_4$ and hydrogen varied, the total gas flow rate was fixed at 1000 sccm. A Ni-coated silicon substrate was placed at the center of the quartz-tube furnace.

For in-situ measurements of the size distribution of charged nanoparticles, a DMA (TSI model 3085 Nano DMA, USA) system [22,145] designed to measure sizes in the range of 1 ~ 100 nm was set up. The
size-classified charged particles were detected as a current on a Faraday cup electrometer (FCE). In general, the particles were electrically charged by an artificial charging system before DMA measurements because DMA can measure only charged particles. However, the measuring system in this study did not use an artificial charger because nanoparticles in the reactor are self-charged. Using this DMA–FCE system, the size distribution of the charged nanoparticles was measured in-situ during the synthesis of carbon nanostructures as a function of the reactor temperature, CH$_4$ flow rate and hydrogen flow rate. The nanostructures deposited were examined via field-emission scanning electron microscopy (FESEM, JEOL JSM–7401F) and transmission electron microscopy (TEM, JEOL JEM–3000F).

Figure 7.1. Schematic of experimental set-up for measurements of charged nanoparticles generated during the thermal CVD process.
7.3. Results and discussion

In the pyrolysis reaction, the decomposition of pure CH₄ begins at 950 ℃, whereas the decomposition rate in the presence of a catalyst slightly increases at the same temperature [146]. Thus, to investigate the effect of the reactor temperature on the formation of nanoparticles in the gas phase and on the deposited CNTs, the reactor temperature was varied from 950 to 1010 ℃ at a total gas flow rate of 1000 sccm, with a CH₄ flow rate of 100 sccm. In this case, hydrogen was not supplied.

Figure 7.2 shows the FESEM images of materials formed at different reactor temperatures. At a furnace temperature of 950 ℃ (Figure 7.2(a)), no CNTs were produced; however, solid carbon was formed on the Ni particles. When the reactor temperature increased to 990 ℃ (Figure 7.2(b)), CNTs with a diameter of ~20 nm began to form. As the reactor temperature was further increased to 1000 ℃ (Figure 7.2(c)), CNTs with a diameter of ~300 nm were produced. At a reactor temperature of 1010 ℃, CNTs became longer, concurrent with a smaller diameter of ~130 nm. These results indicate that the CNT growth is enhanced with increasing reactor temperatures within the examined temperature range.

The reactor temperature affects both the decomposition of CH₄ and the diameter of the catalytic Ni particles. In general, a higher reaction temperature leads to a higher reaction rate and enhances CNT growth [147]. Veríssimo et al. [148] also reported that a higher temperature produced longer CNTs. As the reactor temperature increases, the catalytic
Ni particles may rearrange, and the size of the Ni particles may decrease. Ermakova et al. [149] reported that the yield of carbon produced by CH$_4$ decomposition was possibly related to the average size of the Ni particles on the substrate, and that the maximum yield was obtained in the size range of 20–60 nm.

Figure 7.2. FESEM images of CNTs. The CNTs synthesized at a reactor temperatures of (a) 950 ℃, (b) 990 ℃, (c) 1000 ℃ and (d) 1010 ℃ with a CH$_4$ flow rate of 100 sccm.

To confirm the generation of charged nanoparticles in the gas phase
during the synthesis of CNTs by atmospheric-pressure CVD, *in-situ* measurements of charged nanoparticles were carried out using the DMA–FCE system. Figure 7.3 shows the size distribution of charged nanoparticles generated in the gas phase at various reactor temperatures. Both positively and negatively charged nanoparticles are generated under the typical processing conditions of CNTs. At reactor temperatures below 990 °C, charged nanoparticles were not detected. This result indicates that charged nanoparticles were not formed or that their number was small enough not to be detected by the DMA–FCE system. It appears that the decomposition of CH$_4$ occurred mainly on the surface of the Ni catalyst at reactor temperatures below 990 °C [146]. Figure 7.3 shows that both positively and negatively charged nanoparticles were generated at a reactor temperature of 990 °C and peaked at 2–4 nm. The number concentration and the peak diameter of both positively and negatively charged nanoparticles increased drastically with increasing reactor temperatures. This indicates that nucleation and charging of nanoparticles in the gas phase are enhanced with increasing reactor temperature due to enhancement of the decomposition of CH$_4$.

To examine the effect of the CH$_4$ flow rate on both the CNT growth and size distribution of charged nanoparticles, the experiment was repeated under various CH$_4$ flow rates without a hydrogen supply at a reactor temperature of 1010 °C. Figure 7.4 shows the FESEM images of CNTs formed at different CH$_4$ flow rates. As the CH$_4$ flow rate was increased from 30 to 50 sccm, both the diameter and length of CNTs increased, with the diameter being 210 and 290 nm at CH$_4$ flow rates of 30 and 50 sccm. As the CH$_4$ flow rate further increased to 100 sccm, the diameter tended
to decrease, though the length drastically increased. The high resolution TEM (HRTEM) image of a sample deposited at a CH$_4$ flow rate of 100 sccm showed multiwalled CNTs with a diameter of ~ 60 nm, as shown in Figure 7.4(d). This result indicates that the CH$_4$ concentration is an important parameter controlling the diameter and length of CNTs.

Figure 7.3. The size distribution of (a) positively and (b) negatively charged carbon nanoparticles at various reactor temperatures with a CH$_4$ flow rate of 100 sccm.

Therefore, the size of the catalyst nanoparticles does not appear to be the only parameter that determines the diameter of the CNTs grown on them. This is in contrast with the previous report by Choi et al. [150], who
reported the dependence of CNT diameter on the size of the catalyst. In agreement with the current results, Garg et al. [151] reported that the CNT diameters tended to decrease with increasing CH₄ flow rates. They also reported that the quality of the growth product was generally improved with increasing CH₄ flow rate. Chen et al. [152] reported that the diameter of CNTs was not always controlled by the metal particle size because the metal particles might undergo reconstruction, sintering and fragmentation. De Jong and Geus [153] also found that the diameter of CNTs changed with the operating conditions and the composition of the reactant mixture.
Figure 7.4. FESEM (a–c) and TEM (d) images of CNTs at CH₄ flow rates of (a) 30 sccm, (b) 50 sccm and (c, d) 100 sccm at a reactor temperature of 1010 ℃.

Figure 7.5 shows the particle size distribution of positively (Figure 7.5(a)) and negatively (Figure 7.5(b)) charged carbon nanoparticles generated at various CH₄ flow rates. In both cases, the particle number concentration and the peak of the size distribution increased with increasing CH₄ concentrations. For the positively charged nanoparticles, the peak diameters corresponded to 6.13, 35.04 and 67.13 nm at CH₄ flow rates of 30, 50 and 100 sccm, respectively. For the negatively charged nanoparticles, the respective peak diameters corresponded to 5.54, 48.34 and 75.03 nm. At a CH₄ flow rate of 100 sccm, the number concentration of charged nanoparticles increased abruptly. This behavior shows that the generation of charged nanoparticles is sensitive to the amount of CH₄ present.

Hydrogen has often been used as a dilution gas for CH₄ during CNT growth, and is known to both lower the rate of carbon formation and prevent the catalyst particles from being encapsulated by carbon [123,154–157]. The role of hydrogen may be understood better if the effect of hydrogen on the generation of charged nanoparticles is examined. With this objective, the flow rate of hydrogen was changed from 0 to 100 sccm at a fixed CH₄ flow rate of 100 sccm and a reactor temperature of 1010 ℃. Figure 7.6 shows the FESEM images of CNTs at two different hydrogen concentrations of 0 and 100 sccm. When the flow rate was increased from 0 to 100 sccm, the length of the CNTs was decreased; however, the diameter was increased and the morphology changed from a
curved to straight structure, as shown in Figures 7.6(a) and (b). Thus, it must be acknowledged that the straight nanofibers in Figure 7.6(b) might not be Nanotubes, but rather nanorods, a possibility that is not examined in this study.

Figure 7.5. The size distribution of (a) positively and (b) negatively charged carbon nanoparticles as a function of CH$_4$ flow rates at a reactor temperature of 1010 °C.

Figure 7.7 shows the particle size distribution of positively (Figure 7.7(a)) and negatively (Figure 7.7(b)) charged carbon nanoparticles generated at various hydrogen flow rates. In both cases, the particle
number concentration and the peak of the size distribution decreased with increasing hydrogen concentration. This result indicates that the generation of charged nanoparticles was suppressed as the hydrogen content increased. This result might be related to a previous report that CH$_4$ decomposition is decreased by hydrogen addition via hydrogenation of carbon species [154,155,158]. Although hydrogen might affect the particle size and activity of the catalyst by preventing the oxidation of catalyst particles, an appreciable amount of amorphous carbon sediment may also be deposited on the CNTs when H$_2$ is supplied in sufficient amounts [123,154,156], as shown in Figure 7.6(b).

Figure 7.6. 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 ℃.

Figures 7.3, 7.5 and 7.7 clearly show that charged nanoparticles are
generated under typical processing conditions for CNT synthesis. There are two possible mechanisms for the formation of charged nanoparticles as measured in Figures 7.3, 7.5 and 7.7. One is that ions are formed first in the reactor and nanoparticles are formed in the gas phase by ion-induced nucleation, which is the case for the formation of charged nanoparticles in hot filament CVD [12, 38, 39, 77] or plasma CVD [59, 159, 160]. In this experiment with thermal CVD, however, the temperature of the reactor is so low that the formation of ions would be negligible. The other possible mechanism is that nucleation takes place first in the gas phase, and the nuclei subsequently undergo surface ionization on any surface such as the quartz tube of the reactor [38]. Magnusson et al. [161] reported similar unusual charging behavior of gold nanoparticles during reshaping at high temperature.
Figure 7.7. The size distribution of (a) positively and (b) negatively charged carbon nanoparticles at H\textsubscript{2} flow rates of 0 and 100 sccm at a CH\textsubscript{4} flow rate of 100 sccm and a reactor temperature of 1010 °C.

Although this study shows that charged carbon nanoparticles are generated under typical conditions for CNT synthesis, their role in the growth of CNTs is not known. It is not yet certain whether the charged nanoparticles are mainly involved, partly involved or hardly involved in the growth of CNTs. However, the experiments herein show that under conditions where charged nanoparticles were not generated, CNTs did not grow, implying that charged nanoparticles might play a major role in the growth of CNTs as was suggested by Lee and Hwang [51] based on the bias effect on the CNT growth during hot-filament CVD.

Under conditions that generate charged nanoparticles, the expected deposition behavior of charged nanoparticles in the CVD reactor during CNT synthesis is as follows. Charged nanoparticles should land preferentially on the conducting Ni rather than on the insulating natural oxide layer on the silicon substrate. Hwang et al. [38,77] suggested that this preferential landing on a conducting area might be related to the selective deposition in the CVD process widely used in the fabrication of microelectronics [162–165]. Even after CNTs start to grow when mediated by Ni nanoparticles, the charged nanoparticles would land preferentially at the tip where the Ni nanoparticle is positioned, rather than on the sides of the CNTs. Such preferential landing of the charged nanoparticles at the tip and the diffusion of carbon through the Ni nanoparticle may produce the one-dimensional growth of CNTs. The charged nanoparticles seem to interact with catalytic metals, in which
nanoparticles are dissolved, supplying individual carbon atoms for the growth of CNTs. As was analyzed previously in detail [166–168], the CNTs grow dominantly via surface diffusion of carbon atoms at low substrate temperatures whereas both surface and bulk diffusions may contribute to the CNT growth at relatively high substrate temperatures. Because the CNTs are smooth on the surface, the charged nanoparticles do not appear to have been attached to the sides of the CNTs. Otherwise, the sides of the CNTs should be very rough, with irregular attachments of the charged nanoparticles, especially when the size of charged nanoparticles is so large that they are not disintegrated after landing on the side. This non-attachment to the side might be attributed to the electrostatic interaction energy between charged nanoparticles and charged CNTs. This electrostatic interaction energy might be related to the fact that the catalytic metal particles should be laid on an insulating substrate such as quartz and alumina.

7.4 Conclusions

This is the first report showing that a significant amount of charged nanoparticles is generated under typical conditions of CNT growth during the thermal CVD process. No CNTs were produced when these charged nanoparticles were not detected in the gas phase. The size distributions of charged nanoparticles were affected by reactor temperature, CH₄ flow rate and hydrogen flow rate.
8. Generation of Charged Nanoparticles during Synthesis of ZnO Nanowires by Carbothermal Reduction

8.1 Introduction

ZnO nanostructures have stimulated great interest for its catalytic, electrical, optoelectronic and photochemical properties [169]. Various mechanisms such as vapor–liquid–solid (VLS) growth, vapor–solid (VS) growth and redox growth were proposed to understand their growth [170]. However, the mechanisms have not been fully understood in spite of intense research over the past decade. Recently, a new growth mechanism of ZnO nanostructures based on the electrostatic energy was suggested. [171] reported the charging model for the ZnO nanobelts and nanorings. They suggested that the electrostatic energy plays a critical role in the growth of ZnO nanorings by a spontaneous self-coiling process of polar nanobelts [172]. Parkansky et al. [173] reported a novel method for the growth of ZnO nanorods by applying an electric field to the ZnO film at low temperature.

On the other hand, by photon correlation spectroscopy, Michael et al.
confirmed the existence of the crystalline zinc particles that were produced from a heater in a vacuum chamber containing argon. And in the plasma-enhanced CVD process Liu et al. [175] observed that ZnO rods grew only when the nanoparticles existed on the sapphire substrate, which served as seeds for the growth. Recently, Kim et al. [49,50] showed that the charged nanoparticles were generated during the syntheses of silicon films, ZnO nanowires and carbon nanotubes (CNTs) by thermal CVD by measuring the size distribution using a DMA. These measurements were done based on the previous study of Hwang et al. [12,30,38,77,141], who suggested that these charged nanoparticles should be a main flux for the growth of films, nanowires and nanotubes. The generation of charged nanoparticles in the gas phase was experimentally confirmed in various CVD processes [18,39,43,46,142,144]. A concept similar to the two-step growth was suggested by Ostrikov [59] in the silane plasma CVD process. It is well known that charged nanoparticles are formed in the gas phase and suspended during plasma CVD, which is called “dusty plasma” [29,59]. Ostrikov [59] made an extensive review in 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 order to explain the one-dimensional growth of nanowires and nanotubes prepared by CVD in the absence of catalytic metal particles, Hwang et al. [38,77] suggested the electrostatic energy arising from the charged clusters or nanoparticles generated in the CVD processes as a main driving force. Considering these results, the electrostatic energy that was suggested to play a critical role in the growth of ZnO nanostructures
such as nanobelts and nanorings [171] might be originated from the charge carried by the nanoparticles. The first step of this possibility would be to confirm the generation of charged ZnO nanoparticles during the synthesis of ZnO nanowires. Motivated by this background, here we tried to confirm experimentally the generation of charged nanoparticles in the gas phase during the synthesis of ZnO nanowires by the carbothermal reduction process using a DMA connected to the reactor.

8.2. Experimental procedure

ZnO nanowires were synthesized using a typical carbothermal reduction process. 2 g of ZnO (99.9%) powder and 2 g of graphite powder (99.99%) were mixed. 4 g of the resultant mixture in an alumina boat was placed at the center of a quartz-tube furnace. Above the alumina boat, a silicon substrate coated with 50Å-thick gold was loaded. High purity nitrogen gas (99.9999%) was supplied as a carrier gas together with four different oxygen flow rates of 0, 2, 10 and 90 standard cubic centimeter per minute (sccm). The total flow rate was fixed as 1000 sccm. For in-situ measurements of the size distribution of charged nanoparticles, we set up a DMA (TSI model 3085) system [22,145] designed to measure the size range of 1 ~ 100 nm. The size-classified charged particles are detected as a current on a Faraday cup electrometer (FCE). Normally, particles are made to be electrically charged by the artificial charging system before DMA measurements because a DMA can measure only charged particles. However, our measuring system did not use an artificial charger. Using this DMA–FCE system, the size distribution of the charged nanoparticles was measured in-situ during the synthesis of ZnO nanowires as a function
of reaction temperature and oxygen flow rate at atmospheric pressure. In the experiment, the aerosol flow rate of the DMA was 900 sccm and the excess aerosol flow was purged, while the sheath air flow rate of the DMA was maintained at 15000 sccm. The schematic diagram of DMA–FCE system connected to the CVD reactor is shown in Figure 8.1. The deposited nanostructures were examined by scanning electron microscopy (SEM, JEOL JSM–7401F).

Figure 8.1. Schematic diagram of experimental set-up for measurements of charged nanoparticles generated during carbothermal reduction process.

8.3. Results and discussion

In a carbothermal reduction process, it has been reported that ZnO nanowires can be fabricated at a furnace temperature above 900°C [176,177]. Thus, to investigate the effect of furnace temperature on the
formation of ZnO nanoparticles in the gas phase and on the deposited ZnO nanostructures, the furnace temperature was varied from 800 to 1000°C at a total gas flow rate of 1000 sccm with an oxygen flow rate of 10 sccm. Figure 8.2 shows the FESEM images of ZnO nanostructures formed at different furnace temperatures. At a furnace temperature of 800°C, no nanowire was produced as shown in Figure 8.2(a), which shows the formation of gold nanoparticles from the film deposited by sputtering. When the furnace temperature increased to 900°C (Figure 8.2(b)), nanowires were produced with a diameter of ~100 nm. As the furnace temperature increased to 1000°C (Figure 8.2(c)), nanosheets began to form along the basal nanowires but the diameter of nanowires was almost the same as that formed at 900°C.

During the synthesis of ZnO nanostructures, in-situ measurements of charged nanoparticles were made by the DMA-FCE system. Figure 8.3 shows the size distribution for ZnO charged nanoparticles generated in the gas phase at various furnace temperatures. Both positively and negatively charged nanoparticles are generated under the typical processing conditions of ZnO nanostructures such as nanowires. At the furnace temperature below 850°C, charged nanoparticles were not detected. The detection limitation of our measuring system could be one reason for no detection of charged nanoparticles at furnace temperature of 800°C. Figure 8.3 shows that both positively and negatively charged nanoparticles were generated at the furnace temperature of 850°C and had a single peak at 4 ~ 5 nm. With increasing furnace temperature above 900°C, both positively and negatively charged nanoparticles tend to have a bimodal size distribution. Most nanoparticles are smaller than 10 nm. At all
temperatures, the number concentration of negatively charged nanoparticles was higher than that of the positively charged ones. The particle number concentration of the negatively charged nanoparticles increased with increasing furnace temperature, while that of the positively charged ones tended to decrease, passing through a minimum as the furnace temperature increased. However, the particle diameter at the peak did not change sensitively with the furnace temperature.

Figure 8.2. FESEM images of ZnO nanowires at furnace temperatures of (a) 800℃, (b) 900℃, and (c) 1000℃ and at an oxygen flow rate of 10 sccm.
In the synthesis of ZnO nanowires, the morphology of ZnO nanowires is known strongly to depend on the oxygen flow rate [170] and various fascinating ZnO nanostructures [178] were produced by controlling the oxygen flow rate. In order to examine the effect of oxygen flow rate on the evolution of ZnO nanostructures and on the size distribution of charged nanoparticles, depositions were done on the silicon substrate with *in-situ* measurements of charged nanoparticles by DMA–FCE under oxygen flow rates of 0, 2, 10, and 90 sccm at a furnace temperature of 1000°C. When the oxygen gas was not additionally supplied into a reactor, only nanowires were formed as shown in Figure 8.4(a). When the oxygen gas was supplied at 2 and 10 sccm, nanosheets started to form as shown in Figures 8.4(b) and (c). When the flow rate was increased to 90 sccm, very rugged structure was formed as shown in Figure 8.4(d).

Figure 8.5 shows the size distribution of charged ZnO nanoparticles for different oxygen flow rates at a furnace temperature of 1000°C. As the oxygen content increased, the size and the number concentration of charged nanoparticles decreased appreciably. It is possible that the increase in size and number concentration of charged nanoparticles in the absence of additional supply of oxygen comes from the enhanced evaporation rate for Zn in the gas phase. This aspect is in agreement with the expectation that the rate of the reduction reaction, ZnO + C → Zn + CO, should be increased at low oxygen partial pressure. Considering these, the nanowires and the charged nanoparticles formed without the additional oxygen supply would be oxygen-deficient compared to those formed with the additional oxygen supply.
The change of ZnO nanostructures with varying oxygen flow rate might be related with two factors. One is the change of electrical properties of ZnO with the stoichiometry change by oxygen content. The other is the change in the size and the number concentration of charged nanoparticles. Further systematic studies are needed to understand the effect of the oxygen flow rate on the evolution of ZnO nanostructures.

Figure 8.3. The size distribution of (a) positively and (b) negatively charged ZnO nanoparticles at various furnace temperatures and at an oxygen flow rate of 10 sccm.
There are two possible mechanisms for the formation of charged nanoparticles measured in Figures 8.3 and 8.5. One is that ions are formed first by surface ionization in the reactor and nanoparticles are formed in the gas phase by ion–induced nucleation, which is the case of formation of charged nanoparticles in hot filament CVD [12,38,39,77] or plasma CVD [159,179,180]. The temperature of the reactor is so low that the
formation of ions would be negligible. The other possible mechanism is that nucleation takes place first and then the nuclei undergo surface ionization on any surface such as the quartz tube of the reactor [38]. Magnusson et al. [161] reported similar unusual charging of gold nanoparticles during reshaping at high temperature. However, further theoretical and experimental studies are needed to understand the charging mechanism in the syntheses of ZnO nanowires.

Figure 8.5. The size distribution of (a) positively and (b) negatively charged ZnO nanoparticles at oxygen flow rates of 0, 2, 10, and 90 sccm and at the furnace temperature of 1000℃.
It should be noted that the actual number concentrations in the reactor are higher than the number concentrations shown in Figures 8.3 and 8.5, considering the loss of charged nanoparticles on the way up to the particle detection point. Considering the surface area of such numerous charged nanoparticles formed in the gas phase, most supersaturation for precipitation of ZnO would be consumed on the formation of charged nanoparticles and the remaining supersaturation on the substrate would be given by the Gibbs–Thompson effect of charged nanoparticles. This means that the flux for the formation of nanostructure on the substrate is mainly from the charged nanoparticles formed in the gas phase.

Charged ZnO nanoparticles should land preferentially on the conducting gold rather than on the insulating natural oxide layer on the silicon substrate. This preferential landing on a conducting area might be related to the selective deposition in CVD widely used in the fabrication of microelectronics [162,163]. Even after ZnO nanowires start to grow mediated by gold nanoparticles, the charged nanoparticles would land preferentially at the tip, where the gold nanoparticle is placed, over the side of ZnO nanowires. Such selective landing seems to result in extensive one-dimensional growth of nanowires [164,165]. Without such selective landing arising from electrostatic energy, ZnO nanoparticles would land on the side of the nanowires, making the side very rough.

It is not clear whether the growth of nanosheets shown in Figures 8.4(b) and (c) is mediated by gold or not. Barnard et al. [181] reported the relationship between size, structure and orientation in ZnO nanobelts. They suggested that the growth in the width of nanostructures is a decisive factor in determining the orientation. It indicates that the
processing conditions are important in the formation of the initial nanostructure morphology. The two-dimensional growth of nanosheets is also expected to come from the electrostatic energy originated from the charge carried by ZnO nanoparticles. Besides, the electrostatic energy previously suggested to explain the growth mechanism of the self-coiling process of ZnO nanorings and nanobelts [171,172] and silicon nanowires [38,77] should come from the charge carried by nanoparticles such as those shown in Figures 8.3 and 8.5. And the charged nanoparticles seem to be also involved in the one-dimensional growth of oxides such as Nb$_2$O$_5$ [182] and V$_2$O$_5$ [183]. Rutkevych et al. [184] reported further details of this phenomenon.

8.4 Conclusions

The generation of charged nanoparticles was experimentally confirmed under the typical growth condition of ZnO nanowires. No nanowires were produced in the absence of these charged nanoparticles in the gas phase. The size distributions of charged nanoparticles are affected by reactor temperature and oxygen flow rate. The results suggest that the electrostatic energy originated from charged nanoparticles would be an important factor for the growth of ZnO nanowires.
Bibliography


국문 초록

박막 및 나노구조체의 성장 메커니즘은 원자에 의한 테라스-리지-킹크 (TLK) 모델을 기초로 설명 되어 왔다. 그러나 실질적인 실험적 관찰에서는 원자에 의한 성장으로 설명할 수 없는 풀리지 않는 많은 현상이 화학기상증착을 이용한 저압 다이아몬드 합성 시 나타났다. 이에 황 그룹은 화학기상증착 중 기상에 생성된 하전된 나노입자가 박막 그리고 나노구조체의 성장에 기여할 가능성이 있다고 제안하였고 많은 화학기상증착 공정 중 기상에 하전된 나노입자가 생성되는 것이 계속적으로 보고되어 왔다.

이 학위 논문에서 첫번째로 실리콘 화학기상증착 공정 중 기상에 하전된 나노입자 생성을 상업 화학기상증착장비에 연결된 DMA-FCE (Differential Mobility Analyzer - Faraday Cup Electrometer) 시스템을 이용하여 다양한 캐리어 및 전구체 가스 속도와 온도 조건에서 확인하였다. 이러한 공정변수는 나노구조체의 증착 거동뿐만 아니라 기상에 생성된 양과 음의 하전된 나노입자의 사이즈 분포 및 농도에 영향을 주었다. 그 크기 분포 및 농도는 바막 및 나노구조체의 미세구조 형성에 크게 관여한다. 그러나 이러한 결과들은 하전된 나노입자가 박막 혹은 나노구조체 성장에 기여한다는 간접적인 증거로 박막 및 나노구조체의 증착 단위가 하전된 나노입자가 된다는 직접적인 증거는 없다.

두번째로 우리는 모든 공정조건을 고정한 후 기판을 전기적으로 플로트 그리고 그라운드 함으로써 두 조건에서 증착 거동이 매우 차이가 낼을 확인함으로 증착거동이 기판표면과 하전된 나노입자 사이의 정전기적 상호작용에 의해 영향을 받으며 그것이 하전된 나노입자가 박막 및 나노구조체의 직접적인 증착 단위로 작용됨을 실험적으로 보여주었다.
마지막으로 양과 음으로 하전된 나노입자가 기상에 많이 존재하는 것을 고려하면 그 하전된 나노입자들은 전기장에 의해 영향을 받을 것이다. 전기장을 인가하기 위해 화학기상증착 공정 중 교류 (AC) 및 직류 (DC) 바이어스를 스테인리스 기판 홀더에 가하였다. 바이어스의 주파수와 전압은 미세구조 형성 및 성장 속도에 상당하게 영향을 주었다. 이러한 결과는 하전된 나노입자가 생성되는 열 화학기상증착 공정에서 교류 및 직류 바이어스가 새로운 공정 변수로 적용될 수 있음을 보여준다.

주요어: 하전된 나노입자; DMA; 플로트 그리고 그라운드 기판; 정전기적 에너지; 교류 바이어스; 화학기상증착

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