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Journal of Crystal Growth 218 (2000) 33–39

JOURNAL OF CRYSTAL GROWTH

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Growth of silicon nanowires by chemical vapor deposition: approach by charged cluster model

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Received 14 March 2000; accepted 1 June 2000

Communicated by D.T.J. Hurle

Abstract

Silicon nanowires can be grown by chemical vapor deposition. Using a $SiH_4 : HCl : H_2$ gas ratio of 3 : 1 : 96, a pressure of 1333 Pa, a substrate temperature of 1223 K and radiant heating by a halogen lamp, an appreciable quantity of silicon nanowires formed on Si, SiO_2 and Si_3N_4 substrates while on a Mo substrate, a silicon film deposited. An increase in the pressure to 13 332 Pa led to a deterioration in nanowire growth. Using a hot filament at 2073 K suppressed nanowire growth but resulted in deposition of a normal silicon film. The highly anisotropic growth of silicon nanowires was attributed to highly anisotropic landing of charged silicon clusters. © 2000 Elsevier Science B.V. All rights reserved.

PACS: 64.60.Qb; 78.66.Vs; 81.10.Aj; 81.15.Gh

Keywords: Chemical vapor deposition; Silicon; Nanowires; Charge; Clusters; Substrate

1. Introduction

Numerous studies have been made concerning the synthesis of nanotube [1,2] and nanorod [3] materials as they have many potential applications regarding quantum confinement effects as well as other unique properties. Understanding the growth mechanism of these materials is necessary for a systematic approach towards its fabrication and potential technology breakthrough.

Hwang et al. [4,5] suggested the charged cluster model (CCM) to explain the various observations in the diamond chemical vapor deposition (CVD) process, where charged diamond clusters are suspended in the gas phase during diamond deposition. Recently, these charged carbon clusters have been experimentally confirmed in a hot filament diamond CVD process [6]. However, if transition metal powders are present on the substrate surface, carbon nanotubes are observed to grow [7]. Since gas-phase nucleation of carbon clusters results in a driving force for etching at the temperature on the

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PII: S0022-0248(00)00543-1

substrate surface (at a given CH_4/H_2 gas mixture), the flux for any type of growth would thus be from the charged carbon clusters suspended in the gas phase. This being the case, it is therefore quite probable that the carbon nanotube structure might also result from growth by charged carbon clusters.

Recently, Si nanowires were fabricated by laser ablation [8–12]. The growth mechanism in this new process appears to be different from that of a previously well-known vapor–liquid–solid (VLS) mechanism for growth of silicon whiskers or nanowires [13,14]. In the mechanism suggested by Zhang et al. [12], silicon clusters which are formed in the gas phase are the growth unit of silicon nanowires.

While studying the applicability of the CCM to the silicon CVD process by comparing the deposition behavior between conducting, semi-conducting and insulating substrates [15], we found out that under certain conditions, silicon nanowires grew on Si, SiO_2 and Si_3N_4 substrates but never on Mo substrates. In this CVD process, not only was the growth rate high but large-scale synthesis is also possible.

In this paper, we report a new method of fabricating silicon nanowires by a typical CVD process using gas mixtures of SiH_4, HCl and H_2. Since CCM is already established in this processing condition [15–17], the growth mechanism of silicon nanowires is also approached by the CCM.

2. Experimental procedures

The CVD apparatus used in this study was modified slightly from a typical epitaxial reactor. The substrate was heated radiantly by a halogen lamp, which was placed below the substrate holder. Another halogen lamp heater was placed above the substrate. It should be noted that in a conventional epitaxial reactor, the halogen lamp is placed above a quartz plate, which separated a reactor from the lamp. In the new set-up, the halogen lamp is placed directly above the substrate without a quartz plate in-between as shown in Fig. 1. This set-up appears to have enhanced the growth of silicon nanowires. Heating by hot tungsten filament at 2073 K completely inhibited the nanowire growth. The substrate holder temperature, measured by a thermocouple, was maintained at 1223 K. Among the other processing conditions that were varied, nanowire formation was very sensitive to the gas ratio and reactor pressure. A gas mixture ratio of $SiH_4:HCl:H_2 = 3:1:96$ and a reactor pressure and 1333 Pa were found to be the optimum conditions for formation. 100 standard cubic centimeter (sccm) of the gas mixture was supplied to the chamber using a mass flow controller. The deposition times ranged from 3 to 6 min. After deposition, the substrate surface was observed by scanning electron microscopy (SEM).

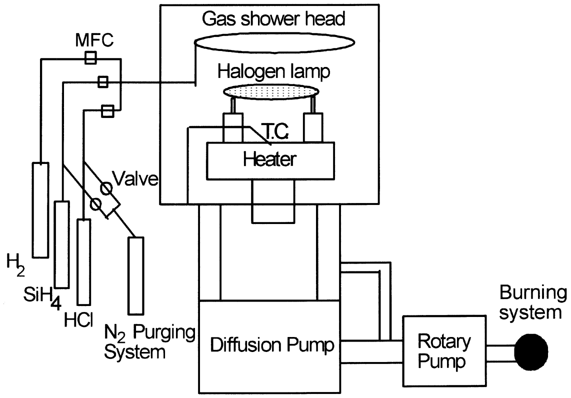

Fig. 1. Schematic diagram of the CVD reactor.

3. Results

Figs. 2(a)–(d) show the microstructure evolution, after 3 min deposition time and a pressure of 1333 Pa, on Mo, Si, SiO_2, and Si_3N_4 substrates. A normal silicon film was deposited on the Mo substrate (Fig. 2(a)). On the Si substrate, however, nanowires started to form (Fig. 2(b)). Moreover, an appreciable number of nanowires formed on SiO_2 and Si_3N_4 substrates (Figs. 2(c) and (d)). The diameter of nanowires was 20–70 nm. Considering the length of nanowires grown after 3 min, the growth rate is estimated to be higher than at least $\sim 50\,nm\,s^{-1}$.

The deposition behavior on the silicon substrate was less reproducible than with other substrates.

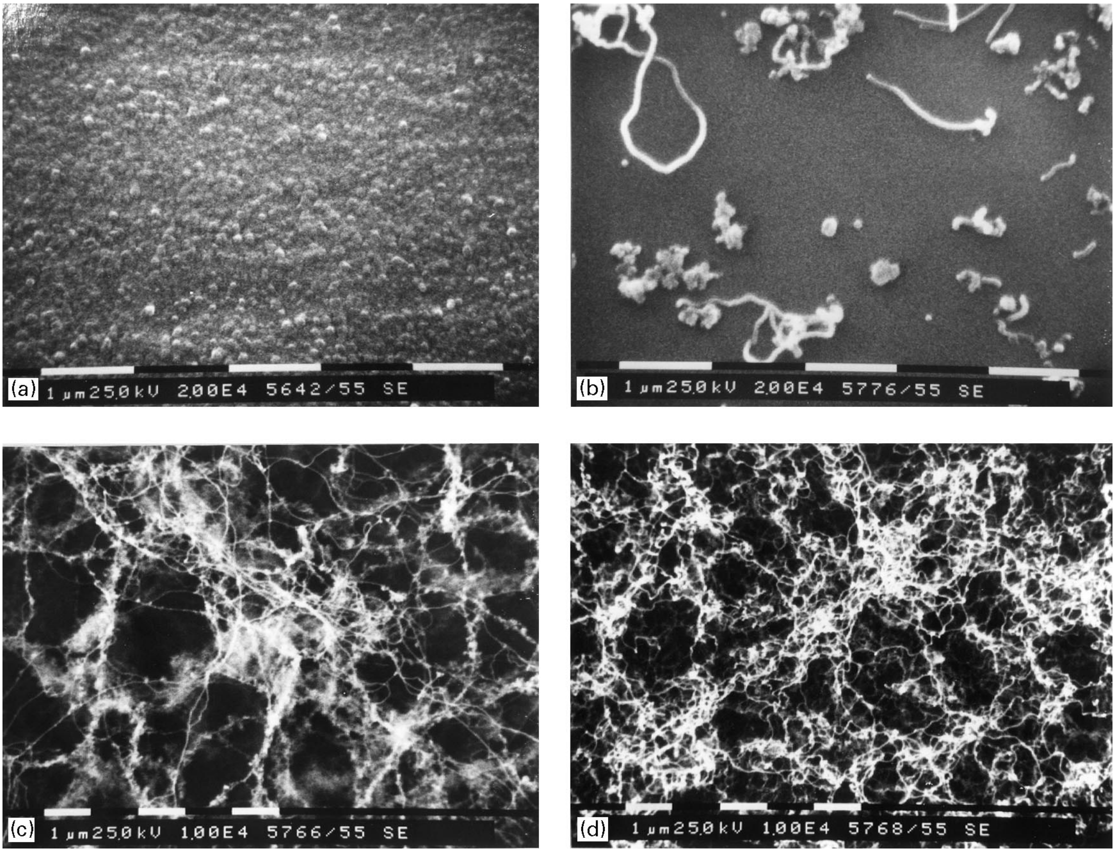

Fig. 2. SEM microstructure on (a) Mo, (b) Si, (c) SiO_2 and (d) Si_3N_4 substrates after deposition for 3 min under a pressure of 1333 Pa at a substrate temperature of 1223 K with a gas mixture ratio of $SiH_4:HCl:H_2 = 3:1:96$.

The reason might be that silicon, which is a semiconductor, can have a thin surface layer of silicon oxide, which is insulating. Under all conditions varied in this study, no silicon nanowires were observed on Mo substrates, which are conductors. The deposition behaviors of the two insulating substrates, SiO_2 and Si_3N_4, were similar to each other. Therefore, the results of Mo and Si_3N_4 substrates will not be included hereafter.

Figs. 3(a) and (b) show the microstructural evolution on Si and SiO_2 substrates, respectively, after deposition for 6 min. In both cases, well-developed nanowires formed.

In order to determine the effect of pressure, the pressure was increased to 13 332 Pa. The results for the Si and SiO_2 substrates are shown in Figs. 4(a) and (b), respectively. In this case, the surface of the nanowires is not smooth. Some nanowires increased in diameter to ~500 nm. Appreciable growth took place in the radial direction of the nanowires. This suggests that an increase in pressure is unfavorable for nanowire growth.

Heating by a hot filament at 2073 K completely altered the deposition behavior and silicon films were deposited on both the Si and SiO_2 substrates as shown in Figs. 5(a) and (b). In this case, the morphology of the deposits between metal and insulating substrates was identical.

4. Discussion

Zhang et al. [12] suggested a cluster-solid mechanism for the one-dimensional growth of silicon

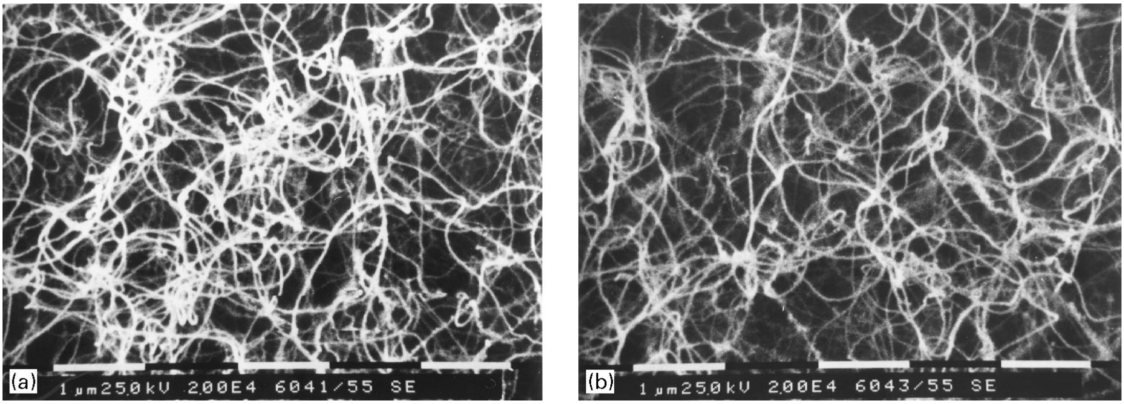

Fig. 3. SEM microstructures on (a) Si and (b) SiO_2 substrates after deposition for 6 min with the other conditions being the same as those for Fig. 2.

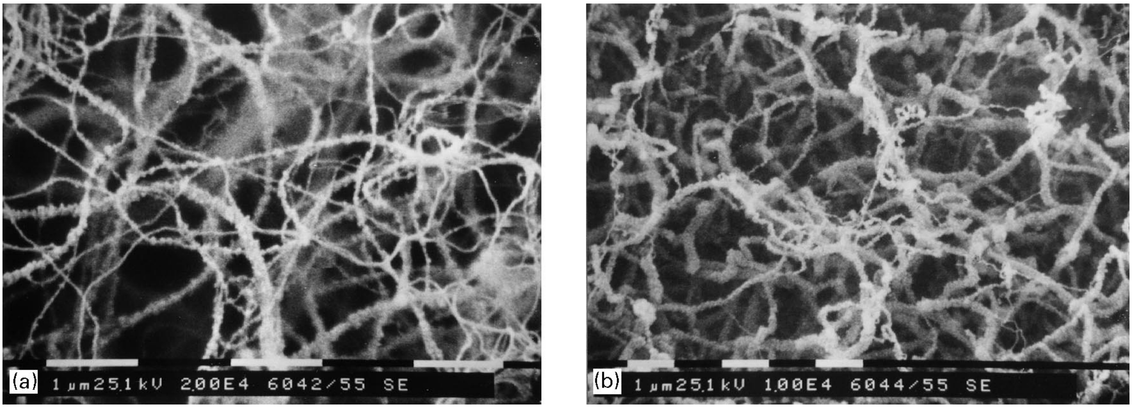

Fig. 4. SEM microstructures on (a) Si and (b) SiO_2 substrates after deposition for 6 min under a pressure of 13 332 Pa with the other conditions being the same as those for Fig. 2.

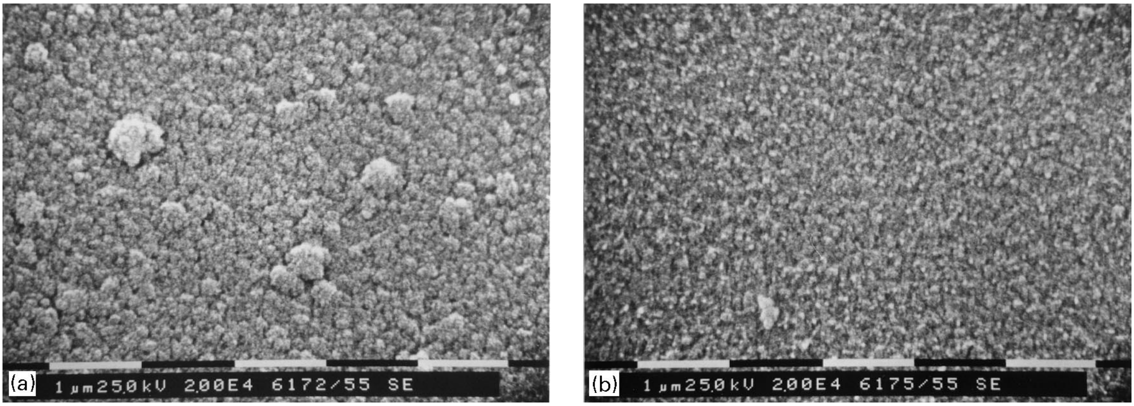

Fig. 5. SEM microstructure on (a) Si and (b) SiO_2 substrates after deposition for 6 min using a hot filament at 2073 K with the other conditions being the same as those for Fig. 2.

nanowires based on their observation that Si nanoclusters had deposited on the cool finger during the growth of Si nanowires by laser ablation [10,12]. In this mechanism, silicon clusters, which are formed in the gas phase, are building block of silicon nanowires. We also experimentally confirmed the existence of silicon clusters in the gas phase of the silicon CVD process [17]. Therefore, a similar mechanism might apply in the growth of silicon nanowires.

However, if these clusters are neutral, i.e., not electrically charged, they will undergo rapid Brownian coagulation in the gas phase, leading to porous fractal and skeletal structures. Thus, the highly anisotropic growth of nanowires is not expected from neutral clusters. The additional effect of charge will be considered in order to explain the highly anisotropic growth behavior of silicon nanowires.

Recently, it was suggested that silicon films in the CVD process grow by charged clusters [15–17]. The microstructure evolution in this paper can be best explained by considering the deposition behavior of charged silicon clusters suspended in the gas phase. Since the processing conditions in this paper are the same as reported previously, except the gas ratio and the heating method, the deposition behavior may be closely related. In our previous report [15], a gas mixture ratio $SiH_4:HCl:H_2 = 1:2:97$ was used, where appreciable deposition took place only on conducting substrates. This deposition behavior was explained based on the electrostatic interaction of charged silicon clusters with the substrates. Charged silicon clusters can land relatively easily on conducting surfaces but have difficulty in landing on insulating surfaces, leading to selective deposition.

By changing the gas mixture ratio to $SiH_4:HCl:H_2 = 3:1:96$, the cluster size is expected to increase. This increase in cluster size might be related to growth of silicon nanowires. The deposition behavior on a Mo substrate was not affected by changes in the gas ratio. However, the deposition behavior on Si, SiO_2 and Si_3N_4 substrates was affected. It should be stressed that charged silicon clusters have difficulty in landing on the insulating surfaces. They will deposit on a site where their charge can be removed. If the silicon nanowire wall is repulsive to a charged silicon cluster and its tip is less so or even attractive, preferential growth at the tip will occur. This will lead to the axial growth of nanowires. In this respect, there should be preferential growth on the tips over on the walls of nanowires.

This preferential attachment of charged silicon clusters can be achieved by several possible ways. One would be the existence of metallic impurities at the growth tip. The metallic impurities will make the tip more conducting than the wall of the nanowires. This mechanism might be related to the VLS mechanism, where a gold impurity is typically used [13,14]. However, in our case metal impurities were not intentionally added.

The second possible way is in the growth of silicon nanowires by laser ablation [8,9]. In this case, two factors were suggested to be important in nanowire growth. Hu et al. [18] suggested the catalytic synthesis of nanowires; a metallic nanocluster catalyst at the end of the nanowire causes nanowire growth. Zhang et al. [12] added silicon dioxide to silicon target. As it turned out, silicon dioxide played an important role in the growth of silicon nanowires where the outer wall of the silicon nanowires consists of silicon dioxide. The preferential attachment of charged clusters to the tip over the wall is thus expected. In our case, however, neither a metallic catalyst nor silicon dioxide was added. Beside, the formation of silicon dioxide during processing is improbable, considering the fact that the Si–Cl–H atmosphere is highly reducing.

The third possibility is related to electrostatic interactions between charged clusters and growing silicon particles. These interactions were represented by a previous observation that larger silicon particles grew while smaller particles etched away [15,19,20]. For example, when the gas mixture ratio of $SiH_4:HCl:H_2 = 1:2:97$ was used, this phenomenon took place on the insulating substrate [15]. This can happen if large silicon particles attract charged silicon clusters while small ones repell them. This phenomenon can be understood by the Coulomb interaction for two conducting particles carrying charges of the same sign, which is given by the following equation [21]:

$$F = \frac{q_1 q_2 e^2}{4\pi\varepsilon_0 d^2} - \frac{q_1^2 e^2 r_2 d}{4\pi\varepsilon_0 (d^2 - r_2^2)^2} - \frac{q_2^2 e^2 r_1 d}{4\pi\varepsilon_0 (d^2 - r_1^2)^2} + \dots, \tag{1}$$

where the sphere of radius r_1 has a net charge q_1 and the other of radius r_2 has charge q_2, d is the distance between their centers and $1/4\pi\varepsilon_0$ the permittivity. Eq. (1) tells us that if the size difference between two conducting charged particles is small, they are repulsive. However, if the size difference is large, both clusters can be attractive. The elongated particle of a cylindrical shape or a nanowire has a small dimension in a radial direction but a large dimension in an axial direction Therefore, Eq. (1) implies that the small clusters might be attractive to the axial direction while it might be repulsive to the radial direction of nanowires. If a negatively charged conducting particle approaches in the axial direction of the nanowire, the electrons in the nanowire will move along the axial direction away from the approaching particle. However, if the same particle approaches in the radial direction, electrons in the nanowire cannot move a long distance away from the approaching particle because the dimension in the radial direction is small. Once an elongated shape is initiated, anisotropic growth will accelerate, leading to the growth of nanowires.

A pressure increase will increase the amount of precipitation in the gas phase, which will increase cluster size. As the cluster size becomes larger, the selective tendency of charged clusters will diminish according to Eq. (1). Then the selectivity in cluster deposition between the wall and the tip of the nanowires will decrease, resulting in the microstructures observed in Figs. 4(a) and (b).

Previously, we showed that the selective deposition between conducting and insulating surfaces was lost when the hot filament was used [15]. The reason for the loss of selectivity comes from the fact that the gas phase becomes conducting. Then, even an insulating substrate can exchange charge through the gas phase. This might be why the hot filament suppressed nanowire growth and resulted in deposition of normal silicon films as shown in Figs. 5(a) and (b).

It can be argued that the gas mixture ratio of $SiH_4:HCl:H_2 = 1:2:97$ at 1333 Pa should give the smallest cluster size, the best selectivity, and hence, the most appreciable nanowire growth, which does not agree with the experimental results. In this case, however, the clusters have difficulty in landing on the insulating substrate and the appreciable deposition does not initiate. Instead, etching is dominant, whose aspect was shown in our previous report [15].

5. Conclusions

By the silicon CVD process using the gas ratio of $SiH_4:HCl:H_2 = 3:1:97$, we were able to grow the silicon nanowires on Si, SiO_2 and Si_3N_4 substrates but not on Mo substrates. The growth mechanism of silicon nanowires was approached by the CCM. The highly anisotropic growth of nanowires could be explained by Coulomb interactions between nanowires and charged clusters, which tends to be attractive in the axial direction but repulsive in the radial direction.

Acknowledgements

This work was supported by Creative Research Initiative Program of Korea Ministry of Science and Technology.

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