

## Research Article

# Synthesis of Core-Shell SiO<sub>x</sub>/Carbon Nanofibers on Silicon Substrates by Ultrasonic Spray Pyrolysis

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We synthesized the core-shell SiO<sub>x</sub>/carbon nanofibers with diameters of 200–300 nm using ultrasonic spray pyrolysis with a phosphorus/ethanol mixture. High-resolution transmission electron microscopy (HRTEM) and energy-dispersive spectroscopy (EDS) investigations confirmed the core-shell structure, which consisted of a core of SiO<sub>x</sub> and a shell of amorphous carbon. The phosphorus atoms corroded the entire silicon substrate surface, and the Si-P liquid-catalyzed the solid-liquid-solid mechanism is proposed to explain the growth of the core-shell SiO<sub>x</sub>/carbon nanofibers.

## 1. Introduction

In recent years, the SiO<sub>x</sub>-based nanofibers have attracted interest worldwide because of their small sizes, which enable higher levels of functionality within a given space, and because of their peculiar and fascinating properties. The nanodevices and large-surface-area structures [1], which are a type of one-dimensional nanostructures, have many potential applications and have been used as versatile building blocks in the miniaturization of electronic and optoelectronic devices [2]. These devices also have a high strength-to-weight ratio and superior stiffness, as well as other excellent engineering properties such as good wear resistance, low expansion coefficients, and low relative flexibility. These properties allow them to be used as one-dimensional quantum transistors, composites, light-emitting diodes [3], and optical sensors [4]. For the realization of these excellent properties, the surface of the SiO<sub>x</sub> core needs to be passivated with highly thermally and chemically stable protective shells, for which carbon is an ideal candidate [5]. Several methods have been used to synthesize these SiO<sub>x</sub>-based nanofibers, including laser ablation [6], thermal stress [7], physical evaporation [8], and chemical vapor deposition (CVD) [9]. The growth of such SiO<sub>x</sub>-based nanofibers is attributed to the solid-liquid-solid (SLS) growth mechanism

[10], and different metal catalysts such as Ni [11], Co [12], and Au [13] are used.

In the present study, we report a simple method for the synthesis of core-shell SiO<sub>x</sub>/carbon nanofibers using ultrasonic spray pyrolysis. The silicon oxide shows stable and bright blue light emission [14] and is widely used for fabricating insulation layers in integrated circuits. The carbon is one of the most popular materials for the formation of protective shells because of its superior physical and chemical properties [15]. In particular, amorphous-carbon-coated nanofibers have been found to exhibit significantly enhanced field-emission properties [16]. A possible growth mechanism of such core-shell nanofibers is also discussed in the present study.

## 2. Experimental

Figure 1 shows a schematic diagram of the CVD apparatus. An ultrasonic nebulizer was connected to a quartz tube and N<sub>2</sub> gas cylinder. Si (100) substrates of size 10 × 10 mm were cleaned with acetone and methanol in an ultrasonicator, washed with deionized water, and finally dried using a nitrogen blower. The substrates were kept in a quartz boat, which was placed at the center of the quartz tube. One end of the quartz tube was attached to the ultrasonic

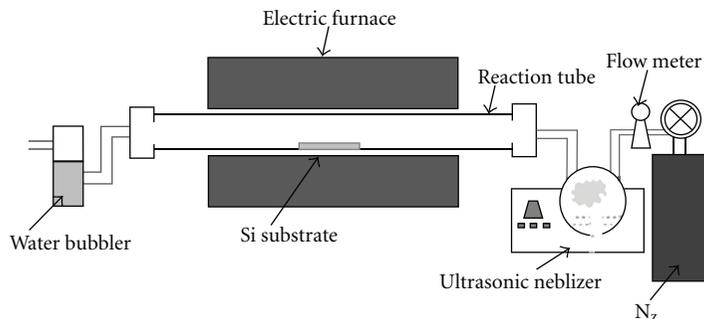


FIGURE 1: Schematic image of the apparatus of the ultrasonic spray pyrolysis CVD.

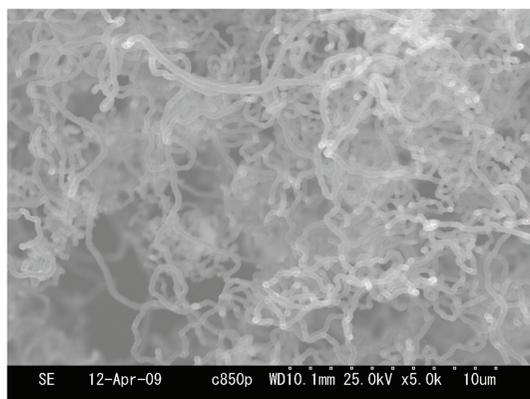


FIGURE 2: Typical SEM image of nanofibers synthesized at 950°C.

nebulizer, and the other to the gas bubbler. Phosphorus (phosphorus powder, Kojundo Chemical Laboratory, 99.5%) was mixed in the ethanol and placed inside the atomization chamber. A flow of  $N_2$  gas was introduced into the mixture of ethanol and phosphorus (100 mL, 10 wt%) to enter the quartz tube at a rate of 0.1 L/min. When the temperature of the electric furnace reached 950°C, the ultrasonic nebulizer was switched on, and the ethanol/phosphorus mixture was converted into a thin mist. The flow of  $N_2$  was maintained to pass this mist inside the electric furnace. The deposition was performed for one hour. After deposition, the furnace was switched off and allowed to cool down to below 100°C. In the ultrasonic spray pyrolysis, electric vibrators (1.65 MHz, Atom Medical Corp., Model 303) produced a mist of ethanol and phosphorus. Finally, the deposited samples were analyzed using scanning electron microscopy (SEM, Hitachi, S-3000H), scanning transmission electron microscopy (STEM), energy-dispersive spectrometry (EDS) (Hitachi, JEM-z2500), Raman spectroscopy (JASCO, NRS-1500), and X-ray photoelectron spectroscopy (XPS, Ulvac, PHI-5000). In the XPS measurements, a tablet of the deposition (peeled from the Si substrate and mixed with indium powder) was used in order to prevent any signal from the silicon substrate.

### 3. Results and Discussion

Figure 2 shows the typical SEM image of the product synthesized at 950°C. A high density of nanofibers of 200–300 nm in diameter is observed.

Figure 3 shows typical TEM images and the corresponding EDS spectra. The TEM images in Figure 3(a) show that the diameter of the fiber is about 300 nm. TEM observation also indicated that these nanofibers have a clear core (spot (i)); we also observed the amorphous carbon structure outside the core (spot (ii)). Figures 3(b)–3(d) show the elemental mapping of the nanofiber with an energy-filtered image, from which we found that the constituent parts of the fiber are composed primarily of carbon, oxygen, and silicon atoms. The Si and O atoms are mainly grouped in the core of the nanofiber, whereas the C atoms are primarily found in the shell. In addition, we found that Si, O, and C coexisted with each other. The EDS characterization revealed proportions of 95.54% carbon, 2.11% oxygen, and 1.40% silicon and showed that the fiber does not contain phosphorus. The EDS spectrum of this nanofiber (Figure 3(f)) shows three very distinct peaks of carbon, oxygen, and silicon, with the carbon peak possibly coming partially from the carbon supporting film on the TEM grid. We did not find any phosphorus in the nanofiber within the detection limits.

Figure 4 shows the Raman spectra of the sample, which were obtained using a green laser with an excitation wavelength of 532 nm. The carbon shared two common features in the Raman spectra: a G-peak at around 1580–1620  $cm^{-1}$  and a D-peak at around 1350  $cm^{-1}$ . We observed that the D-peak of the nanofibers was comparatively higher than the G-peak. The D-peak is induced by the disorder of the graphite structure, whereas the G-peak is caused by the stretching of the  $sp^2$  carbon atom in the graphite structure. The Raman spectra of the samples has strong D-peak, suggesting more disordered nanocrystalline structural defects such as distortion, vacancies, and straining of graphitic lattices; these features are all prevalent in the nanofibers [17].

Figure 5 shows the survey XPS spectra of the prepared nanofiber composite and the high-resolution XPS spectra of silicon and carbon. The survey XPS spectra (Figure 5(a)) clearly indicate that carbon, oxygen, and silicon exist in

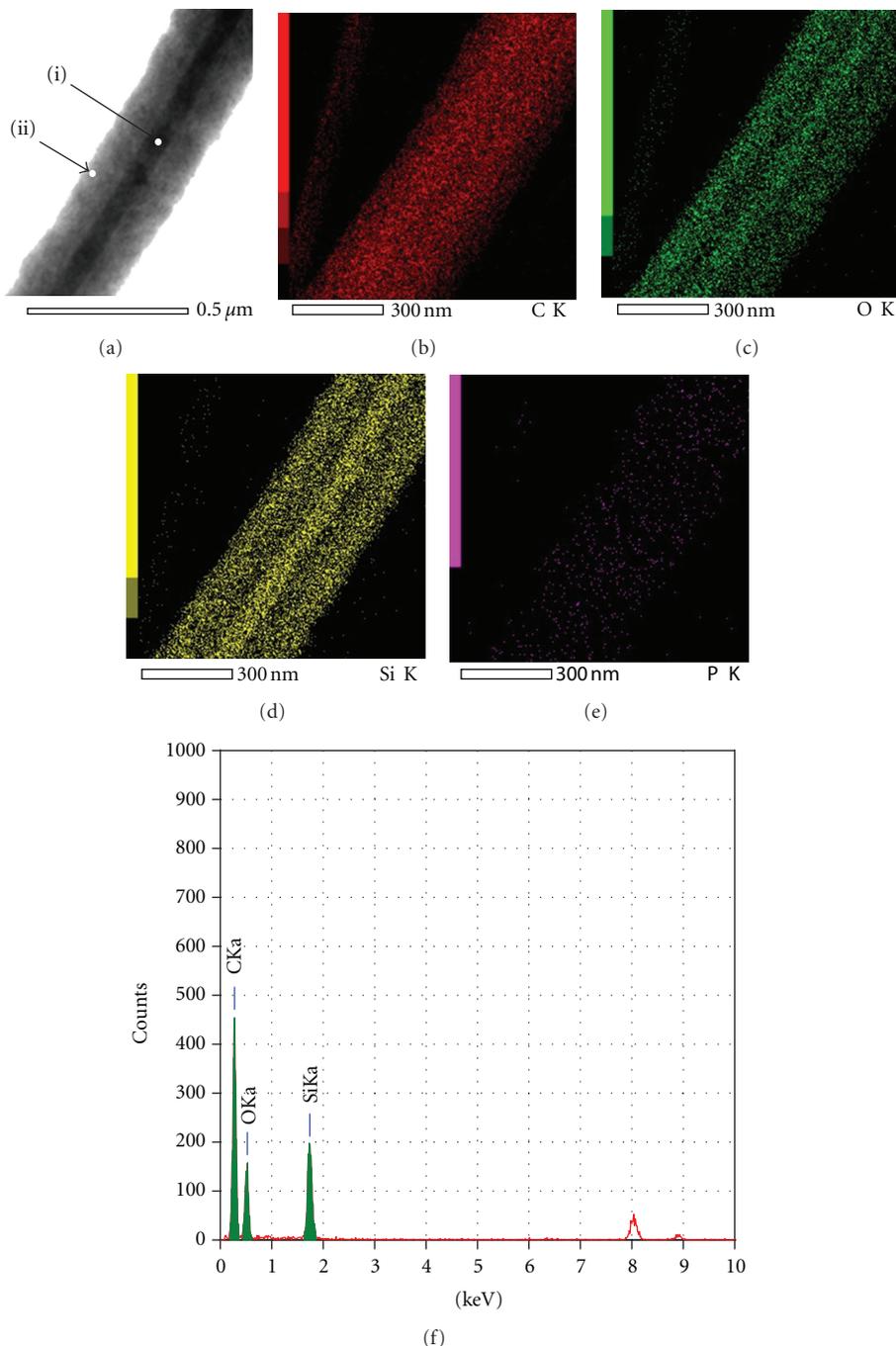


FIGURE 3: (a) TEM images of a core-shell nanofiber. EDS elemental mappings for (b) carbon, (c) oxygen, (d) silicon, and (e) phosphorus in the core-shell nanofiber; (f) EDS spectrum of a representative nanofiber fabricated using a mixture of phosphorus and ethanol.

the prepared nanofiber composite. In Figure 5(b), the two C 1s peaks are located at 284.4 and 285.6 eV, corresponding to the  $sp^2$  and  $sp^3$  atoms, respectively. The silicon-carbon composite peak is located at 282-283 eV, so it does not originate from SiC. The XPS peaks at 102.25 and 103.65 eV, corresponding to the lower oxide components of Si ( $Si^{3+}$ ), are clearly observed in Figure 5(c). These nanofibers show an XPS peak in the  $SiO_x/C$  composite that is related to  $x$ , as

shown in Figure 5(c) [18]. The peak suggests that the nanofibers have an  $SiO_x$  composition.

Figure 6(a) is a schematic illustration of the growth mechanism. It involved in the formation of the amorphous-carbon-coated  $SiO_x$  core are proposed as follows. Initially, the phosphorus coating on the silicon substrate forms a P film, as illustrated in Figure 6(a)-(i). When the temperature increases, the silicon substrate is oxidized by  $O_2$  in

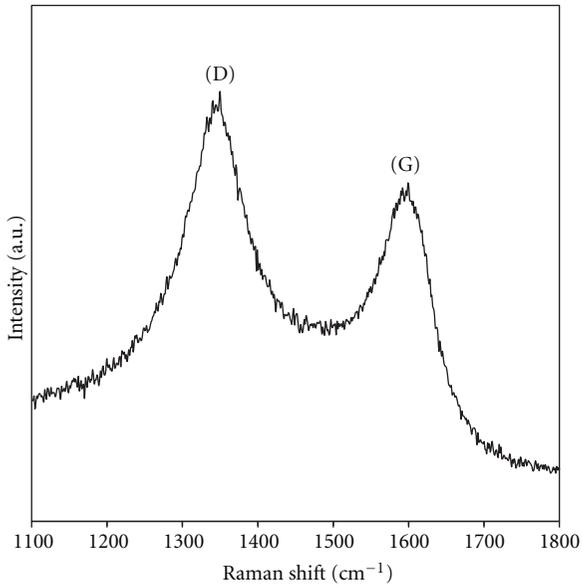


FIGURE 4: Raman spectrum of nanofibers synthesized at 950°C.

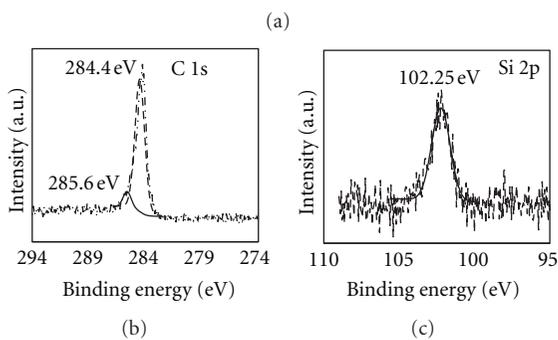
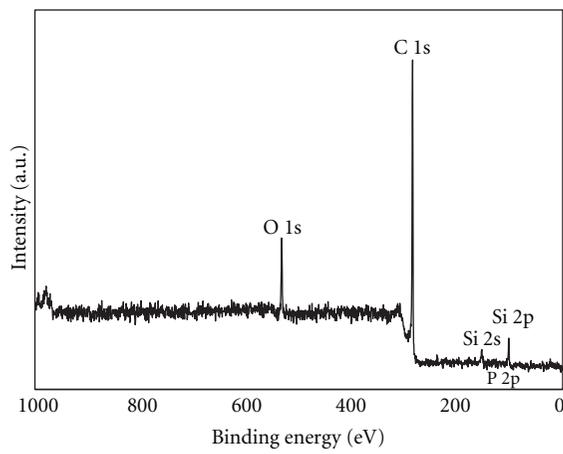


FIGURE 5: XPS spectra of the nanofiber film fabricated using a mixture of phosphorus and ethanol: (a) survey spectrum; (b) C 1s spectrum; (c) Si 2p spectrum. The solid curves in (b) and (c) are the best Gaussian fits for the two peaks.

the carrier  $N_2$  and by water from the decomposition of ethanol. An eutectic reaction between the oxidized Si and P occurs to form an Si-P eutectic liquid [19], as illustrated in Figure 6(a)-(ii). Because the melting point of silicon is 1414°C, a temperature at which the Si vapor phase is

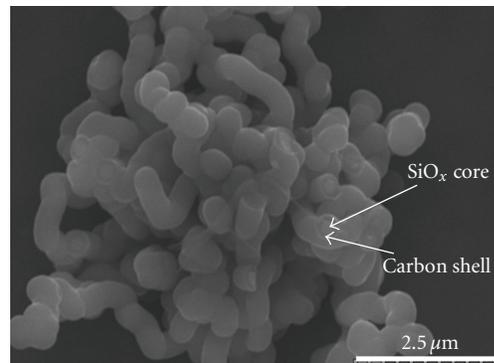
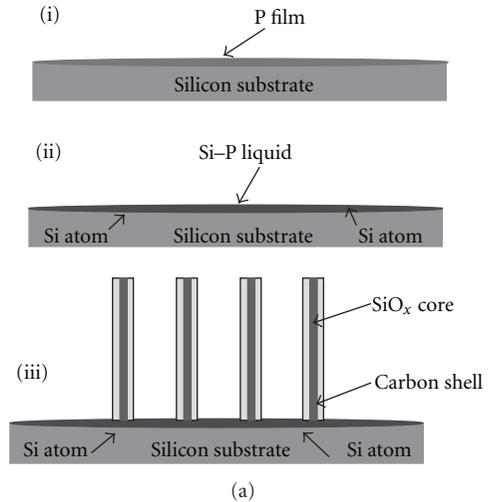


FIGURE 6: (a) Schematic illustration of the growth processes; (b) SEM image revealing that core-shell  $SiO_x$ /carbon nanofibers were grown from the surface of the silicon substrate.

negligible, and the silicon substrate itself serves as an Si source without any additional external source, the nanofibers should be formed via a solid-liquid-solid (SLS) mechanism [20]. Finally, the surface of the Si-P eutectic liquid soon becomes supersaturated, and then,  $SiO_x$ /carbon nanofibers precipitate out and continue to grow from this supersaturated surface, possibly through the oxidation reactions of  $Si + O_2 \rightarrow SiO_x$ . At the same time, the amorphous carbon shell is also deposited from the carbon of the ethanol dissolved on the outside of the  $SiO_x$  core, as illustrated in Figure 6(a)-(iii). These growth processes occurred in the presence of all the four elements (silicon, oxygen, carbon, and phosphorus) and affected each other to varying degrees. Figure 6(b) shows an SEM image of the core-shell  $SiO_x$ /carbon nanofibers in a low-density area, which allows us to see clearly that the core-shell  $SiO_x$ /carbon nanofibers are grown from the Si substrate at the critical temperature of 930°C [21].

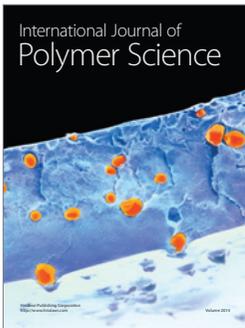
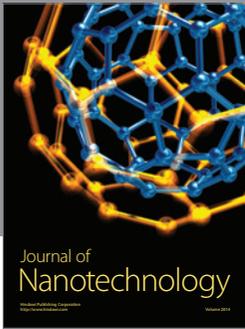
#### 4. Conclusion

In the present study, we successfully synthesized the nanofibers with a mixture of phosphorus/ethanol on a silicon

substrate using ultrasonic spray pyrolysis method. The Core-shell  $\text{SiO}_x$ /carbon nanofibers were produced on the surface of the silicon substrate, and the molten phosphorus played an important role in their synthesis. A possible mechanism for this process is the formation of the  $\text{SiO}_x$  core of the nanofibers from the surface of the Si-P liquid and the formation of the carbon shell from the ethanol. We believe that this approach to the synthesis of core-shell  $\text{SiO}_x$ /carbon nanofibers may be further used in the fabrication of building blocks for device miniaturization and optoelectronic devices.

## References

- [1] Y. L. Chiew and K. Y. Cheong, "Formation and characterization of  $\text{SiO}_x$  nanowires and Si/ $\text{SiO}_x$  core-shell nanowires via carbon-assisted growth," *Physica E*, vol. 42, no. 5, pp. 1338–1342, 2010.
- [2] T. X. Nie, Z. G. Chen, Y. Q. Wu et al., "Amorphous  $\text{SiO}_x$  nanowires catalyzed by metallic Ge for optoelectronic applications," *Journal of Alloys and Compounds*, vol. 509, no. 9, pp. 3978–3984, 2011.
- [3] C. L. Tsai, Y. L. Chou, R. M. Lin, F. M. Lee, M. C. Wu, and S. C. Ko, "An alternative method to fabricate the planar-type resonant-cavity light-emitting diodes by using silicon oxide for short-reach communications," *Materials Science in Semiconductor Processing*, vol. 10, no. 6, pp. 235–240, 2007.
- [4] X. L. Liu, Y. H. He, S. L. Wang, and M. Song, "In situ growth of  $\text{SiO}_x$  nanowires catalyzed by Bi on Si substrate," *Physica E*, vol. 43, no. 9, pp. 1679–1688, 2011.
- [5] J. Zhu, F. Kwong, M. Lei, and D. H. L. Ng, "Synthesis of carbon coated silica nanowires," *Materials Chemistry and Physics*, vol. 124, no. 1, pp. 88–91, 2010.
- [6] D. P. Yu, Q. L. Hang, Y. Ding et al., "Amorphous silica nanowires: intensive blue light emitters," *Applied Physics Letters*, vol. 73, no. 21, pp. 3076–3078, 1998.
- [7] X. N. Zhang, C. R. Li, and Z. Zhang, "One-dimensional growth induced by thermal stress," *Materials Letters*, vol. 58, no. 12-13, pp. 1917–1919, 2004.
- [8] X. S. Fang, C. H. Ye, T. Xie, G. He, Y. H. Wang, and L. D. Zhang, "Synthesis and characterization of ultra-long silica nanowires," *Applied Physics A*, vol. 80, no. 2, pp. 423–430, 2005.
- [9] J. Zhang, B. L. Xu, Y. D. Yang et al., "Catalyzed-assisted growth of well-aligned silicon oxide nanowires," *Journal of Non-Crystalline Solids*, vol. 352, no. 26-27, pp. 2859–2862, 2006.
- [10] H. F. Yan, Y. J. Xing, Q. L. Hang et al., "Growth of amorphous silicon nanowires via a solid-liquid-solid mechanism," *Chemical Physics Letters*, vol. 323, no. 3-4, pp. 224–228, 2000.
- [11] B. R. Huang, J. F. Hsu, and C. S. Huang, "The effects on the field emission properties of silicon nanowires by different pre-treatment techniques of Ni catalysts layers," *Diamond and Related Materials*, vol. 14, no. 11-12, pp. 2105–2108, 2005.
- [12] H. W. Kim and S. H. Shim, "Helical nanostructures of  $\text{SiO}_x$  synthesized through the heating of Co-coated substrates," *Applied Surface Science*, vol. 253, no. 7, pp. 3664–3668, 2007.
- [13] H. K. Park, B. Yang, S. W. Kim et al., "Formation of silicon oxide nanowires directly from Au/Si and Pd–Au/Si substrates," *Physica E*, vol. 37, no. 1-2, pp. 158–162, 2007.
- [14] X. C. Wu, W. H. Song, K. Y. Wang et al., "Preparation and photoluminescence properties of amorphous silica nanowires," *Chemical Physics Letters*, vol. 82, no. 1-2, pp. 53–56, 2003.
- [15] A. H. Lu, W. C. Li, N. Matoussevitch, B. Spliethoff, H. Bonnemant, and F. Schuth, "Highly stable carbon-protected cobalt nanoparticles and graphite shells," *Chemical Communications*, vol. 98, no. 1, pp. 98–100, 2005.
- [16] L. Liao, J. C. Li, D. F. Wang et al., "Field emission property improvement of ZnO nanowires coated with amorphous carbon and carbon nitride films," *Nanotechnology*, vol. 16, no. 6, pp. 985–989, 2005.
- [17] M. S. Dresselhaus, G. Dresselhaus, A. Jorio, A. G. S. Filho, and R. Saito, "Raman spectroscopy on isolated single wall carbon nanotubes," *Carbon*, vol. 40, no. 12, pp. 2043–2061, 2002.
- [18] W. B. Ying, Y. Mizokawa, Y. Kamiura, K. Kawamoto, and W. Y. Yang, "The chemical composition changes of silicon and phosphorus in the process of native oxide formation of heavily phosphorus doped silicon," *Applied Surface Science*, vol. 181, no. 1-2, pp. 1–14, 2001.
- [19] F. Hirose and H. Sakamoto, "Thermal desorption of surface phosphorus on Si(100) surfaces," *Surface Science Letters*, vol. 430, no. 1–3, pp. L540–L545, 1999.
- [20] R. S. Wagner and W. C. Ellis, "Vapor-liquid-solid mechanism of single crystal growth," *Applied Physics Letters*, vol. 4, no. 5, pp. 89–90, 1964.
- [21] Z. W. Pan, Z. R. Dai, L. Xu, S. T. Lee, and Z. L. Wang, "Temperature-controlled growth of silicon-based nanostructures by thermal evaporation of  $\text{SiO}$  powders," *Journal of Physical Chemistry B*, vol. 105, no. 13, pp. 2507–2514, 2001.



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