

A TWO-STEP PROCESS GROWTH FOR SILICON NANOPARTICLES USING ATOMIC LAYER EPITAXY

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Introduction:

Over the last few years, there has been considerable interest in the growth of silicon nanoparticles (Si-NP) for applications in future electronic devices and systems. In particular, the small size of the nanoparticles gives rise to unique physical properties, because of strong carrier confinement, that enable the development of novel silicon (Si) functional devices such as single electron transistors,¹ resonant tunneling devices,² and quantum-dot floating gate memory devices.³ However, a major issue is engineering a strict control of the variability in size and distribution, morphology and location of the nanoparticle since the fundamental parameters ruling the electron transport, such as coulomb blockade effect and quantum confinement, are strong functions of size, shape and distribution. For example, single electron transistors and resonant tunneling devices require nanoparticles of lateral size ~2–5 nm for room-temperature operation, while quantum-dot floating gate memory devices require a density and mean diameter of 10^{11} - $10^{12}/\text{cm}^2$ and 5-10 nm ranges, respectively.

In this work, we report a novel two-step growth process for Si-NP using low pressure chemical vapor deposition (LPCVD) and atomic layer epitaxy (ALE). In the first step, we exploit the early stages of silane LPCVD process to form Si nucleation sites on silicon dioxide (SiO_2) substrates. Next, we use an ALE process, with Dichlorosilane (SiH_2Cl_2) and Silane (SiH_4) as precursor molecules, to selectively grow Si-NP from the nucleation sites.

Experimental

In order to investigate the Si-NP nucleation, three different Si substrates were used – hydrogen terminated Si (100) surface, 15 nm-thick SiO_2 substrate, and 15 nm-thick OH-terminated SiO_2 surface. All Si substrates were initially cleaned using piranha solution (1:3) followed by HF dip. The Si (100) substrates were oxidized at 1100 °C in dry O_2 to form 15 nm-thick SiO_2 layers. A few of these SiO_2 substrates were then etched in dilute HF solution (1:100) for 60 s to form Si-OH bonds on the surface. Subsequently the surfaces were exposed to SiH_4 gas at temperatures between 550-700 °C and deposition pressure of 250 mTorr.

In the next set of experiments, 15 nm-thick SiO_2 and OH-terminated SiO_2 surfaces were exposed to 2% SiH_4

diluted with N_2 at 625 °C and 250 mTorr for 1 min. Next, the temperature was lowered to 350 °C for ALE deposition. 2% SiH_2Cl_2 and SiH_4 diluted in N_2 were used as precursors for ALE growth at deposition pressures of 275 mTorr and 485 mTorr, respectively. The size and number density of the particles were analyzed with a Nanoscope III atomic force microscope (AFM) from Digital instruments. The Si-NP were identified using height images and the density and size was calculated from an image area of 500 nm X 500 nm.

Results and Discussion

Nucleation

To gain a fundamental understanding of nucleation and growth of Si-NPs, we have focused on evaluating the effects of substrate type and treatment and deposition time, temperature and pressure on the Si-NP density. The evolution of Si-NPs that have been deposited on three different substrates, H-terminated Si, 15 nm-thick SiO_2 and 15 nm-thick OH-terminated SiO_2 surfaces has been probed, at deposition time of 60 s and deposition temperature and pressure of 625 °C and 250 mTorr, respectively. It shows that surface nature and composition clearly plays a role in the size and density of the Si-NPs and provides an insight into the nucleation mechanism on different surfaces. In the case of H-terminated silicon substrate, the nucleation and growth rate of Si-NP is very small. Also, since the dominant product in SiH_4 decomposition is atomic silicon with small amounts of SiH , SiH_3 and Si_2H_6 , Leach et al.⁴ suggest that disilane cracking on tungsten produces similar highly active species, most likely atomic silicon. However, etching of a silicon substrate by HF results in H-terminates surface, which leads to low concentration on active silicon sites on the surface and hence a small rate of nucleation. We have found that density of Si-NP on SiO_2 surface ($n_{\text{SiO}_2} = 2 \times 10^{10} / \text{cm}^2$) is lower and the size larger than that of H-terminated SiO_2 surfaces ($n_{\text{OH-SiO}_2} = 6 \times 10^{10} / \text{cm}^2$). It has been speculated that the point dislocations, composed of Si bonds on surface, formed by the thermal dissociation of the Si-O bonds contribute to the creation of nucleation sites on a thermally grown SiO_2 surface,⁵ while the surface Si-OH bonds formed by dilute HF treatment act as nucleation sites for OH-terminated SiO_2 surface.

The morphology of the Si-NPs was investigated using a high resolution transmission electron microscope (TEM)

at an accelerating voltage of 200 kV. Figure 1 shows clear lattice images of Si-NP deposited at the following conditions - 625 °C, 250 mTorr and 90 s. The TEM plane view observations along with the selected area electron diffraction (SAED) pattern indicate that the core of the Si-NPs is crystalline. Furthermore, energy dispersive x-ray (EDX) analysis confirms that the core of the Si-NP comprises of Si while the surface has indeed oxidized to form a thin layer of amorphous SiO₂.

Si-NP Growth using ALE

In order to realize the growth of Si-NPs with narrow density distribution and controlled size, the nucleation and growth reactions need to be isolated. Therefore we use a two step process to separate the nucleation and growth process. After nucleation, the deposition temperature is lowered to 350 °C and the ALE growth is used. The precursors used for ALE growth are SiH₂Cl₂ and SiH₄ with nitrogen as purge gas.

Figure 2 shows the AFM images and corresponding size distributions of similar size Si-NPs grown by the one step process, using only SiH₄ precursor, and by the two step process, using Si ALE. The size distribution in the case of Si ALE process (Fig. 2a) is significantly narrower than that of the one step process (Fig. 2b). This clearly suggests that no new “nuclei” were formed during the ALE growth. Only the Si nuclei formed during the first step of SiH₄ deposition were grown during the ALE growth step. The remaining size distribution is probably due to the inhomogeneity in the size of the initial nucleation sites. Moreover, the consistency of these estimates indicates that the growth rates and the selectivity have been controlled precisely during the localized ALE growth, and that quantum nanostructures can be fabricated according to design. The initial nucleation density can be controlled by changing the SiH₄ or by changing the chemical nature of the surface.

Conclusion

In this study we describe a two step growth process of Si-NPs using Si ALE. Using this method we have been successful in isolating the nucleation and growth steps of SI-NP. In the first step we use the early stages of thermal decomposition of SiH₄ to form the nucleating sites. Next, Si ALE is used to selectively grow the nucleating sites and precisely control the size of the Si-NPs. Selective Si ALE is accomplished using SiH₄ and SiH₂Cl₂ as precursor gases. The self-limiting effect of Si ALE can be a significant advantage for atomic level control of the Si-NP structure. We also show that using this process allows for better control of the Si-NP density and results in a narrow size distribution.

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References

1. T. Yasuo, F. Akira, Y. Kenji, et al., Applied Physics Letters **76**, 637 (2000).
2. M. Fukuda, K. Nakagawa, S. Miyazaki, et al., Applied Physics Letters **70**, 2291 (1997).
3. S. Tiwari and F. Rana, Applied Physics Letters **68**, 1377 (1996).
4. W. T. Leach, J. Zhu, and J. G. Ekerdt, Journal of Crystal Growth **240**, 415 (2002).
5. A. A. Saranin, A. V. Zotov, V. G. Kotlyar, et al., Applied Surface Science **243**, 199 (2005).

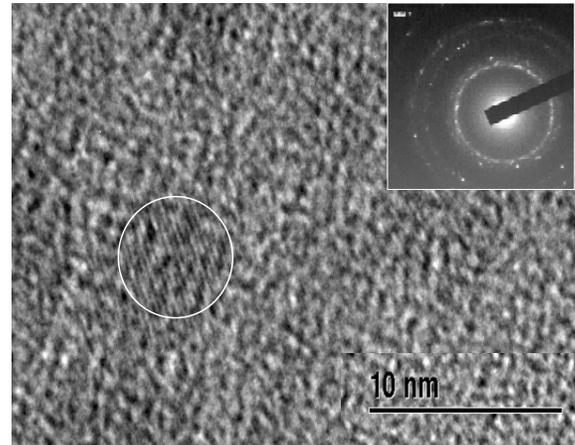


Fig. 1. Plane view TEM observations of Si-NP deposited using silane at deposition Temperature = 625 °C; Pressure = 250 mTorr; Deposition time = 60 s. The inset picture shows the SAED pattern of the Si-NPs which shows that the particles have a crystalline core.

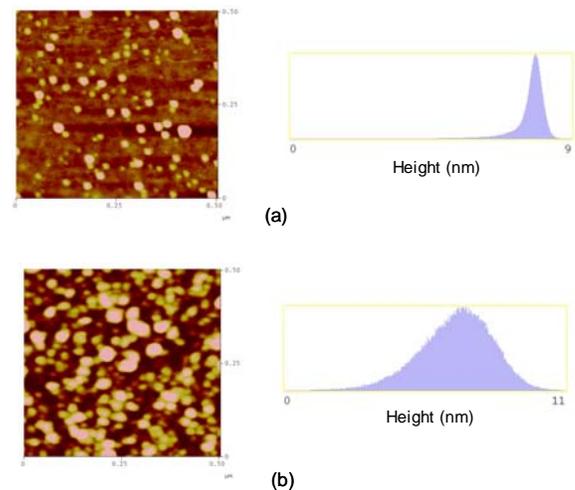


Fig. 2. AFM images and comparison of size distribution of Si-NP obtained by (a) one step process and (b) two step process. The Si-NP densities are 3.5×10^{10} particles/cm² and 4.0×10^{10} particles/cm², respectively. The mean sizes are ~ 7.0 and 8 nm, respectively.