

Silicon-based nanowires from silicon wafers catalyzed by cobalt nanoparticles in a hydrogen environment†

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We present here the synthesis of silicon-based nanowires directly from silicon wafers at high temperatures and in the presence of cobalt nanoparticles and hydrogen gas. All three ingredients were critical to the growth of Si-based nanowires, which were between 5–60 nm in diameter and μm –mm long. Both heavily coiled and straight Si-based nanowires were made. Experimental evidence suggested that the sources of silicon for the nanowires growth were in the gas phase.

Si-based nanowires, including crystalline and amorphous silicon and silicon oxide nanowires and doped silicon nanowires, can potentially be used in nanoscale electronics, sensors, and optoelectronics.^{1–3} They can also be used as templates for decorating other materials because Si surface can be easily functionalized. Other applications of these nanowires include photoluminescent materials.⁴

Si-based nanowires have been prepared in several different ways. Traditionally, they are made with chemical vapor deposition (CVD) methods. For instance, Westwater *et al.* and Yan *et al.* have shown that high quality Si nanowires can be made using externally provided silane gas.^{5,6} Among other methods, Sunkara *et al.* have made Si nanowires with the vapor-liquid-solution phase method.⁷ Tang *et al.* and Morales *et al.* have shown that laser vaporization can produce Si nanowires.^{8,9} In addition, hydrogen has been found to play an important role in making those nanowires.⁶ On the other hand, Zhang *et al.* have shown that Si nanowires can be made from Si powders without any nanoparticles, although the reaction temperature was higher than methods which used metal nanoparticles as catalysts.¹⁰ In addition, solution growth has been made possible by Holmes *et al.*¹¹ Recently, other semiconductor nanowires such as GaAs and InAs nanowires have been made by Persson *et al.*^{12,13}

In order to prepare uniformly structured Si-based nanowires with control over the location of their growth for patterning purposes, it is important to understand, control, improve and simplify the growth of those nanowires. In this communication, we present a method in which only Ar and hydrogen are used. The nanowires are directly grown from commercially available Si wafers. The results presented here also shed light on the growth mechanisms of those nanowires.

The preparation and deposition of Co nanoparticles on wafer substrates were described elsewhere.¹⁴ Briefly, nanoparticles (3 nm diameter) were deposited on doped or undoped Si (100) wafers

(Virginia Semiconductor) or Al_2O_3 substrates (Valley Design Corp.) that were cleaned with Piranha (4:1 H_2SO_4 (conc): H_2O_2 (30% aq)) and rinsed with DI water. All wafers or substrates were cut into 5 mm \times 5 mm pieces for growth tests, or 1 cm \times 4 cm for other measurements. The deposited wafers or substrates were placed in a quartz tube in a high temperature furnace (Lindburg/Blue) at 1100 °C for various reaction times. At a lower reaction temperature of 900 °C, crystalline CoSi_2 self-aligned nanostructures (SAN) were formed on Si wafers. Since the reaction time required for producing SAN is usually extremely short, on the order of a few seconds, all the Si wafers contained SAN when the reaction temperatures were raised to 1100 °C.¹⁴ The samples were then examined with scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyses available on SEM. High resolution transmission electron microscope (HRTEM) (CEM300 at the National Center for Electron Microscopy (NCEM)) and Raman microspectroscopy were used to characterize the nanowires.¹⁵ When both Al_2O_3 and Si(100) were used, Al_2O_3 shims (0.66 mm thick) were used to separate the two, with one wafer on top of the other. Ar (99.997%) and H_2 (99.95%) gases were used in the growth of Si nanowires. Fig. 1 shows the experimental setup of using both Al_2O_3 and Si wafers to investigate the source of Si for the nanowire growth.

Fig. 2a shows a photo of two Si wafers (1 cm \times 4 cm), one without (left wafer, reaction temperature of 900 °C for 1 minute) and the other with Si nanowires (right wafer, reaction temperature of 1100 °C for 30 minutes). The white gray color of the right Si wafer was caused by the intense light scattered by the Si nanowires on the wafer. On the other hand, little scattering was seen from regular silicon wafers or SAN-covered Si wafers.

Fig. 2b–d, with increasing magnifications, show the effect of nanoparticles on the growth of nanowires. The sample was prepared differently from those shown in Fig. 2a. It was produced

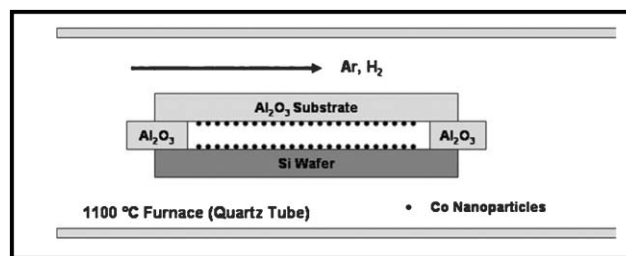


Fig. 1 Experimental setup for making Si nanowires on both Si and Al_2O_3 substrates. The spacing between the Si and Al_2O_3 substrates is \sim 0.66 mm. Growth conditions were the same as growing Si-based nanowires on only Si wafers.

† Electronic supplementary information (ESI) available: SEM images and EDX of Si-base nanowires. See <http://www.rsc.org/suppdata/cc/b4/b417740a/>

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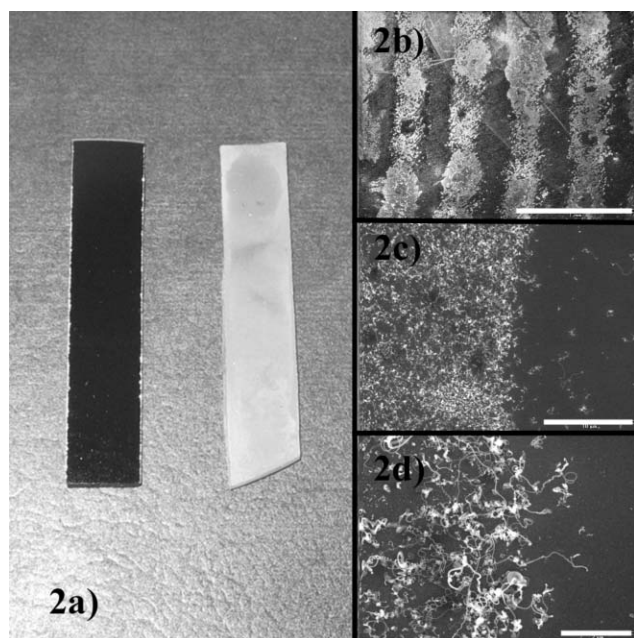


Fig. 2 Si nanowires on Si wafers. The left wafer in 2a) has no Si nanowires, whereas the one on the right is covered with nanowires. 2b)–2d) show the effect of nanoparticle catalysts. Neither nanowires nor nanoparticles were observed in the dark areas where no nanoparticles were deposited. The scale bar in 2b) is 1 mm, 10 μm in 2c), and 2 μm in 2d).

by first making a finger-print contact (similar to μ -printing) using a cleaned Si wafer. The finger-printed wafer was then directly immersed in the Co nanoparticle solution for 15 minutes. Because Co nanoparticles were covered with hydrophobic ligands, they were bound to the Si surface more tightly when the latter was coated with grease or oil from the finger tips. This process created a wafer with uneven nanoparticle-coated areas. After intense washing with σ -dichlorobenzene (DCB) to remove the nanoparticles from the clean Si surface, the nanoparticle-deposited Si wafer was placed in the quartz tube in the furnace for Si-based nanowire production, just as other nanowire samples were prepared. The results in Fig. 2b–d show that only those areas with nanoparticles have Si nanowires. In the SEM pictures, Co nanoparticles appeared to be bright spots. Therefore, the fact that there were only a few bright spots in the dark areas in Fig. 2b–d indicated that almost no Co species occupied those areas. These results also suggest that Co nanoparticles may not be able to migrate too far away from the original deposition sites on Si, or evaporate and redeposit onto different locations on Si.

Fig. 3a shows an SEM image of Si-based nanowires that are relatively straight; their radii of curvature are much larger than 10–100 microns. A single wire with a catalyst nanoparticle on the tip is shown in the insert of Fig. 3a. On the other hand, Fig. 3b shows another kind of Si-based nanowires which are heavily coiled, with their radii as small as 100 nm. An insert shows a coiled nanowire with a nanoparticle at its tip. These nanowires resembled the ZnO nanowires made by Yang *et al.*,¹⁶ but were quite different from the SiO₂ nanosprings made by Zhang *et al.*¹⁷

The morphology of the Si-based nanowires made here was studied with HRTEM and Raman microspectroscopy. The sample for those measurements were prepared by using Co nanoparticle

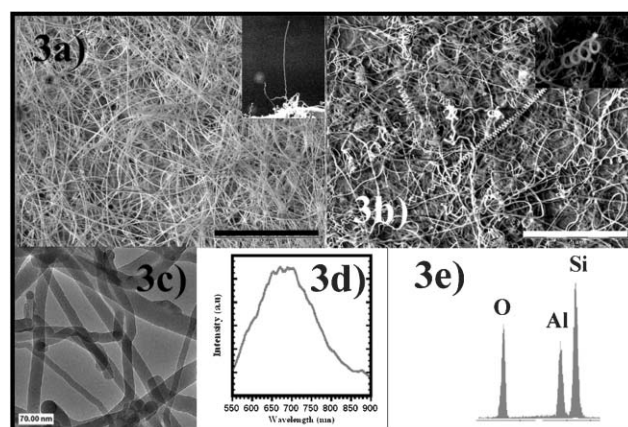


Fig. 3 Examinations of Si-based nanowires. 3a) shows the straight nanowires with an insert of a single nanowire with a nanoparticle at its tip. 3b) shows the coiled nanowires with an insert of a single nanowire with a nanoparticle at its tip. 3c) shows the HRTEM image of the amorphous nanowires. 3d) shows the Raman/photoluminescence result. 3e) shows the EDX result in which Si signal is the biggest, higher than Al and O. The scale bars in 3a) and 3b) are 5 μm and 70 nm in 3c).

deposited wafers without washing. Thick films of Si-base nanowires were made, and the thin films were peeled off from the Si wafers for measurements. This process avoided the contamination of Raman signals from the Si substrate. An SEM image of the film is given in the Electronic Supplementary Information† (Fig. 1s). EDX was performed on the thin film placed on graphite substrate, and the ration of Si to O was between 1:5 to 2:0 (Fig. 2s in the Electronic Supplementary Information).

The structure of the nanowires was amorphous at the time of examinations, as shown in Fig. 3c (TEM) and 3d. Electron diffraction also revealed a diffused ring without spots from polycrystalline Si. Fig. 3d shows that intense photoluminescence was detected, and almost no Raman signals at 530 cm^{-1} (crystalline Si) and 480 cm^{-1} (amorphous Si) were present.^{18,19} However, we do believe that at least some of the nanowires adopted crystalline or crystalline core structures, as indicated by many heavily coiled nanowires.

We found that H₂ was essential to producing Si-based nanowires: no Si-based nanowires were made without the presence of hydrogen, at any temperatures and with any substrates, including Al₂O₃ substrates shown below.

Since nanowires did not grow when no cobalt nanoparticles were present, and many nanowires were clearly seen with nanoparticles at the tip, we consider it strong evidence for Co or Co silicide nanoparticles catalyzing the growth of Si nanowires. However, the source of Si to facilitate the growth were unclear. Two possibilities exist. The first is the diffusion of Si through Co or Co silicide nanoparticles to form Si nanowires. The second is that Si actually leaves the surface and becomes gasified, and is then deposited on Co or Co silicide nanoparticle catalysts to form Si nanowires.

The first possible model is unlikely for two reasons. If Co or Co silicide nanoparticles can catalyze the growth of Si nanowires, then no H₂ would be needed. The second reason is that Co or Co silicide nanoparticle catalysts may be easily lifted off the surface by Si nanowires, as shown in Fig. 3. Once that happens, the growth

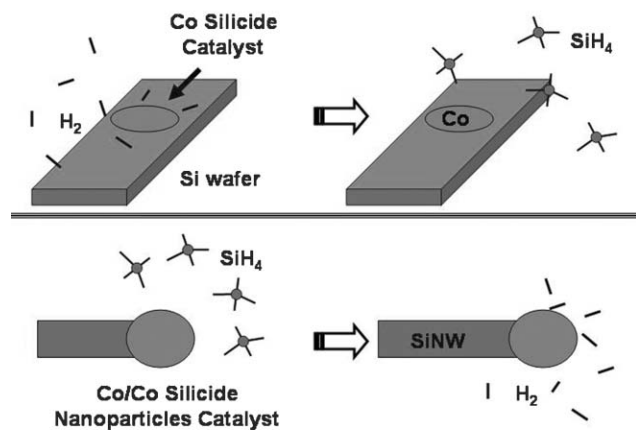


Fig. 4 Proposed growth model based on the results presented in this work. The top panel shows the production of SiH_4 in the presence of H_2 and Co silicides. The lower panel shows the catalysis of Si-based nanowires from silane and Co or Co silicide nanoparticle catalysts.

may cease immediately because the supply of Si from the substrate loses its contact with the catalyst.

The second possibility is more plausible. In this case Si or SiO_2 reacts with H_2 to form gaseous silanes to act as Si feedstock. An even more plausible scenario is that Co nanoparticles may react with Si to form cobalt silicides, which are then reduced by H_2 to form silanes and Co. These two steps form a catalytic cycle, which provides the Si for the growth of Si nanowires.

We therefore investigated whether Si was airborne at $1100\text{ }^\circ\text{C}$. The experiment setup is shown in Fig. 1. Fig. 3b and 3e show the SEM and EDX results of the nanowires on the Al_2O_3 substrate. High yields of Si-based nanowires were observed, and only Al, Si, and O signals were observed in EDX, proving that nanowires were made of Si. No carbon was detected, suggesting these were not SiC nanowires as observed by Kim *et al.*²⁰ The amount of Co (10^{-8} to 10^{-9} g mm^{-2}) was too little to be detected. This amount was calculated based on comparing the results of EDX and X-ray measurements on SAN and Si-based nanowires.

These results clearly suggest not only that the nanowires were made of Si, but also that the source of Si for such growth migrated from the Si(100) wafer on the bottom to cross the 0.66 mm gap onto the Al_2O_3 substrate on the top. Since the vapor pressure of Si at $1100\text{ }^\circ\text{C}$ is $\sim 10^{-3}$ torr, and far fewer Si nanowires were made on the top Al_2O_3 substrate when no nanoparticles were deposited on the lower Si wafer, it was apparent that Si must be transported in the gas phase in other forms such as silanes to reach the top Al_2O_3 substrate. Again, no H_2 , no Si-based nanowires.

Based on the results shown here, we propose a growth mechanism that is illustrated in Fig. 4. In this model, Co plays a

dual-catalytic role by both catalyzing the production of gaseous silane and the Si-based nanowires.

In conclusion, we have produced Si-based nanowires directly from Si wafer using Co or Co silicide nanoparticle catalysts and hydrogen. These nanoparticles may possess a dual-catalytic role by catalyzing both the growth of Si nanowires from silane gas and the production of silane gas from Si wafers.

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