Direct growth and photoluminescence of silicon nanowires without catalyst

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Abstract One-dimensional (1D) silicon nanowires (SiNWs) were fabricated on catalyst free Si (100) substrate using a thermal evaporation method. Based on SVLS growth mechanism, the obtained SiNWs were 30 to 265 nm in diameter and 1.7 μm to several tens of microns in length. It was found that the presence of graphite powder only is enough to accomplish growth. A systematic study of how the growth conditions, such as the Ar carrier gas flow rate, and the growth time was performed. There are five resultant PL peaks: two blue emission peaks 465 nm (2.67 eV) and 482 nm (2.57 eV) and two green bands centered at 502 nm (2.47 eV) and 526 nm (2.36 eV) and one ultraviolet emission peak at 350 nm (3.54 eV). The theory behind these emissions was discussed.

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1. Introduction
Recently one-dimensional materials such as silicon nanowires (SiNWs) have stimulated much interest because of their different electronic and optical characteristics compared with bulk materials (Duan et al., 2001; Xia et al., 2003; Sha et al., 2002; Niu et al., 2003). Many potential novel applications of SiNWs have been reported, including p–n junction (Cui and Lieber, 2001) and chemical sensors (Zhou et al., 2003). The electrical transport properties (Hu et al., 2003) and noise characteristics (Macucci et al., 2002) of SiNWs have also been reported. Various fabrication methods, including laser ablation (Kokai et al., 2013), chemical vapor deposition (Kong et al., 2011), and thermal evaporation (Ahmad and Hutagalung, 2011), have been used to produce Si nanowires via a vapor–liquid–solid (VLS) process requiring Si source materials. In most studies catalyst based growth is widely used (Liu et al., 2001; Wang et al., 2002, 2003; Chen et al., 2001; Wu et al., 2001; Takikawa et al., 1999; Suzuki et al., 2007; Zheng et al., 2002; Pan et al., 2002), while few reported the growth of SiNWs on the non-catalyst substrates (Peng et al., 2002; Dai et al., 2002, 2003; Hu et al., 2003). Hence, some studies reported that the growth of SiNWs can be explained by the solid–liquid–solid (SLS) mechanism Morales and Lieber, 1998; Liu et al., 2001; Wang et al., 1998; Yan et al., 2000; Yu et al., 2001; Paulose et al., 2003, were silicon atoms diffuse only...
from the substrate, but from thermodynamics point of view, Djamila and Perrot (2007) report that the SLS theory is not enough to explain the continued growth for too long wires, so they suggested the solid–vapor–liquid–solid (SVLS) growth mechanism. SVLS mechanism postulated the presence of SiO\(_2\) in the gaseous phase when the temperature \(\geq 900^\circ C\). Carter et al. (2001), found using carbon monoxide (CO) and carbon dioxide (CO\(_2\)) gases at 1130\(^\circ C\) led to rapid growth of crystalline SiO\(_2\) nanofibers (Carter et al., 2001; Zhu et al., 1998).

\[
\text{CO}_2(g) + \text{Si}(s) \rightarrow \text{CO}(g) + \text{SiO}(g)
\] (1)

Saulig-Wenger et al. (2003) grow silica nanowires by direct thermal treatment of a commercial silicon powder in the presence of graphite. From their point of view the mixture of carbon and silicon powder used as source of growth species feed stock. No observed SiO\(_x\) nanowires on any of the substrates when there is no carbon used to assist growth (Li et al., 2004). Also, increasing the carbo-thermal deposition time will increase the length of obtained silicon nanowires (Chiew and Kuan, 2010). Another group of people studied the SiO\(_x\) nanowires room-temperature photoluminescence (PL) measurements under excitation at 260 nm, which showed that the SiO\(_x\) nanowire arrays had a strong blue-green emission at 500 nm (about 2.5 eV) Tomozawa et al., 1994; Trukhin et al., 1992; Nishikawa et al., 1992; Meng et al., 2003; Lin et al., 1996. Therefore, we believe that the PL study of SiNWs gives information about electronic band gaps as reported previously in the study of luminescence bands of various silica glasses and NWs, which have different energy peaks ranging from 1.9 to 4.3 eV (Qing et al., 2006).

In this paper, the SiO\(_x\) nanowires have been fabricated by simple thermal evaporation. The effect of growth parameters, the Ar carrier gas flow rate and growth time in the formation of Si nanowires and their room temperature PL emissions were achieved. The detailed characterizations on the resulting nanostructures were carried out by field-emission scanning electron microscopy (FESEM), energy-dispersed X-ray spectroscopy (EDX), X-ray diffraction (XRD) and photoluminescence spectrometer (PLS).

2. Experimental setup

An n-type Si (100) substrates with resistivity of 5.15\(\Omega\) cm\(^{-2}\) was used. These substrates were ultrasonically cleaned in acetone and methanol for 5 min. And then dried in air. Substrates were then, immersed in 48 wt% HF solution for 10 min to remove the SiO\(_2\) layer. After that, the substrate loaded into the middle of a 2.2 cm-inner diameter quartz tube placed at the center of an electric furnace. Graphite powder (2 g) on porcelain boat was mounted 2 cm before the silicon substrate. The argon (99.999%) gas was then flushed inside the quartz tube (to get rid of all other gases) and kept at 10 sccm. The temperature was then raised up to 1200\(^\circ C\) at a heating rate of 1.2 \(^\circ C\)/S and kept as required. After cooling down to room temperature, a thin layer of white-gray colored deposit was found on the substrate surface. These samples were taken to be examined by FESEM, (Quanta 200F), EDX, (Oxford Inst) and XRD (Siemens D5000 diffractometer, \(V = 40 kV\), \(I = 40 mA\) and \(\lambda (\text{Cu} K_{\alpha}) = 1.5418\) Å), HRTEM (JEOL JEM-2010, resolving lattice spacing of approximately 0.14 nm), Photoluminescence Spectrometer (PLS) with He-Cd laser (325 nm), source excitation power of 20 mW.

3. Result and discussions

The fabricated Si nanowires have 30 to 265 nm and 1.7 \(\mu m\) in length. FESEM in Fig. 1(a) shows the semi-organized growth of SiNWs fluffs, small wires, and the EDX spectrum, inset Fig. 1(a), reveals that most of the wires made of silicon with small percentage of oxygen. Here we can prove that these wires are not made from other element than silicon and oxygen compounds because the initial substrate is silicon. On the other hand, the oxidation percentage cannot be countered to be directly for SiNWs only because some areas in the substrate surface may get oxidized. The magnified image in Fig. 1(b) shows cracks or pits on the substrate surface. We believe the formation of these cracks is due to the evaporation of SiO gas through the carbo-thermal reaction in Eq. (1). The existence of cracks may be due to the high stress induced by silica thin film in the Si surface or out-diffusion.

![Figure 1](image.png)

**Figure 1**  FESEM and EDX of (a) SiO\(_x\) nanowires grown under 1200 \(^\circ C\), 30 min deposition time and 40 sccm Ar flowrate, (b) enlarged image of (a).
3.1. Effect of the argon flow rate

To study the argon gas flow rate, the temperature was kept at 1200 °C and the deposition time as 30 min. In Fig. 1(a–d), the FESEM images were taken at 60, 40, 20 and 10 sccm flow rates for three magnifications of 500×, 4 k and 30 k respectively. In Fig. 2(a) the SiNWs are sparse and short when the flow rate reaches 60 sccm. The wires become denser and longer as the flow rate reduced to 40 sccm, see Fig. 2(b). More reduction on Ar flow rate (20 sccm), the growth of SiNWs increased as in Fig. 2(c). The longest and highest yield has been found when the experiment ran at 10 sccm, see Fig. 2(d). This implies that there is silicon or silicon compound available in vapor form. It was found that the SiO vapor reaches the maximum amount when the argon flow rate has the lowest value (10 sccm).

Furthermore, when the argon flow rate reduces less than 10 sccm no growth observed. This can explain the high impact of argon flow rate on growth. Even small amount of Ar played an important role in the distribution of the growth species over the favorite growth sites or low energy places on silicon wafers.

Figure 2  FESEM of SiNWs grown under 1200 °C and 30 min (a–d) at 60, 40, 20 and 10 sccm flow rates for three magnifications of 500×, 4 k and 30 k respectively.
Also, Ar can assist the temperature variation on the Si substrate. Now let us consider one SiNW diameter in Fig. 2(a-3). The diameter is decreasing as we go far from the wires base or nano-ball. The diameter for the nano-ball is 250 nm, 150 nm on stem, 100 nm before end and 52 nm at the end of the sliding wire. Furthermore, the SiNWs density (counting the nanowires available per one cm$^2$) for each Ar flow rate has been plotted as in Fig. 3.

As expected the highest SiNWs density occurs when the Ar gas has the lowest rate at 10 sccm. This is also related to residence time of growth species to accomplish growth.

XRD results in Fig. 4 show no sharp peaks for all different samples under different flow rates and this maybe due to the oxidation process occurring on the surface of the SiNWs at high temperatures. Even there is small intensity broad peak at $2\theta = 58.92$ corresponding to Si (220) for 20 and 60 sccm flow rates, this peak may be due different spots taken by XRD which may related to the silicon substrate. And because most of the surface is either cover with oxide layer or amorphous SiNWs no discrete peaks were found. Therefore, to examine SiNWs morphology a high resolution TEM image for one nanowire side is shown Fig. 5. Here, we can see the oxide layer clearly covers the nanowire side, white part indicated by arrow inside the image.

3.2. Effect of deposition time

The temperature was kept at 1200 °C, the flow rate at 10 sccm and the deposition time varied by 5, 15, 30 and 60 min. The results appeared in Fig. 6(a-d) showing the increase in yield as the deposition time lengthened. As the deposition time increases the SiNWs becomes taller, thinner at the end. The length of SiNWs ranged from 2 to 10 μm. Therefore, the diameter of the SiNWs depends on deposition time. When the deposition time increases, the SiNWs diameters decrease when it is far away from the root see Fig. 7(a and b).

3.3. Growth mechanism

The initial stage starts when the silicon on the surface get oxidized as thin film and if the ratio of Si:O is about 1:1 then this film starts forming molten SiO balls. Then silicon starts to diffuse from Si substrate by SLS mechanism until the saturation stage occurs inside the nucleated ball. The growth should stop at this stage because of equilibrium between amount of silicon oxide inside the ball and the coming substrate silicon, but the growth continuous for long wires. As mentioned before, the silicon monoxide (SiO) gas is more likely to form at evaporation temperature $>950 \, ^\circ C$ through Eq. (1) with the help of carbon. Here, the SiO vapor is produced from the oxide layer as in equations inset in Fig. 8 (Gundiah et al., 2003). This gas is responsible in supplying the growth by Si feed stock, which then condenses at the cold zone and dissolves in the agglomerated balls of mixed Si and SiO$_x$ alloy. These alloys serve as droplets or nucleation sites. This raises a question about the favorite growth places. The SiNW nuclei could form on low energy places of silicon wafers such as defects. Defects, such as stacking faults in the nucleation sites, will enhance the...
one-dimensional growth. Therefore, when the pressure or concentration of the SiO vapor is enough and the temperature increases, Si and O start to condense into the nano-balls forming SiNWs, which start growing up from the ball or forming a root. Again both the SLS and VLS mechanisms could merge in the suggested SVLS growth mechanism. Then, the wire starts to slide on the surface of the substrate as it absorbed more growth precursors as in schematic diagram in Fig. 8.

The reduction of SiNWs diameters caused by the amount of growth species, Si and O available in vapor form, which decreased gradually until stopping at the tip of the wire. This is why the tip or the end of the wire has smallest diameter.

3.4. Si nanowires PL

Fig. 9 shows a broad emission band from 333 to 600 nm observed at room temperature. The broad band is composed of five bands, including a UV peak or band centered at 350 nm (3.54 eV), two blue bands centered at 465 nm (2.67 eV) and 482 nm (2.57 eV) and two green bands centered at 502 nm...
(2.47 eV) and 526 nm (2.36 eV) shown in the inset spectra in Fig. 9.

Unlike bulk silica, the Si nanowires have very large surface/volume ratio, which allow the molecules (oxygen, hydrogen, hydroxide and water) to be adsorbed and diffused into SiO nanowires during the growth process as well as when the sample exposed to air. There are two radicals may form intrinsic defects, the hydroxyl radicals (Si-O-H) and the peroxy linkage (≡Si-O-O-Si≡) Tomozawa et al., 1994. These intrinsic defects may change to be NBOHCs, (≡Si-O) by breaking the original bond as in Fig. 10.

It is possible for NBOHCs to be induced by the high-energy photon (3.8 eV) excitation in our PL measurement to form:

\[ \equiv Si - O - \rightarrow \equiv Si + O. \]

The emission of the blue light has been suggested due to oxygen deficient centers (ODCs) such as neutral oxygen vacancies (≡Si-≡) Meng et al., 2003, and some intrinsic diamagnetic defect centers, such as the twofold coordinated silicon lone pair centers (≡Si: i.e. ≡Si-O-Si-O-Si≡) and self-trapped excitons (STEs) Trukhin et al., 1992; Nishikawa et al., 1992. Our strong UV emission band is agreed with porous silicon excitons (STEs) Trukhin et al., 1992; Nishikawa et al., 1992.

The obtained amorphous silicon nanowires (SiNWs) have been synthesized with diameters between 30 to 265 nm and 1.7 μm to several tens of μm in length. Based on SVLS growth mechanism, the yield obtained decreased as the argon flow rate increased and the growth time decreased. A UV band centered at 350 nm (3.54 eV) and four bands, including two blue bands centered at 465 nm (2.67 eV) and 482 nm (2.57 eV) and two green bands centered at 502 nm (2.47 eV) and 526 nm (2.36 eV) were recorded.

**Figure 9** Room temperature PL spectrum of Si nanowires recorded with excitation at 325 nm.

**Figure 10** The formation of non-bridging oxygen centers.

### References


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