Solid source growth of Si oxide nanowires promoted by carbon nanotubes

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Abstract

We report a method to promote solid source growth of Si oxide nanowires (SiONWs) by using an array of vertically aligned carbon nanotube (CNT). It starts with the fabrication of CNT array by plasma enhanced chemical vapor deposition (PECVD) on Si wafers, followed by growth of SiONWs. Herein, CNTs serve as a scaffold, which helps the dispersion of catalyst for SiONWs and also provides space for hydrogen which boosts the diffusion of Si atoms and hence formation of SiONWs. As the result, a three dimensional (3D) hybrid network of densely packed SiONWs and CNTs can be produced rapidly.

Keywords: silicon; nanowire; carbon nanotube; solid-liquid-solid mechanism.

1. Introduction

With confined dimensions, one-dimensional (1D) nanomaterials have exhibited unique properties. Recently intensive research has been carried out on 1D nanomaterials, including carbon nanotubes (CNTs) and Si oxide nanowires (SiONWs) [1-5]. For example, because of their exceptional mechanical robustness and structural stability, CNTs have been demonstrated as excellent templates for chemical reaction [6, 7]. As for SiONW, it is also considered as a promising material in a wide range of potential applications such as low-dimensional waveguides, blue light emitters, sacrificial templates and anode material in lithium ion batteries [8-11].

The controllable fabrication of 1D nanomaterials remains a topic of great importance and also challenges. For the growth of silicon-based nanowires, several methods have been developed and the representative mechanisms are understood as vapor-liquid-solid (VLS) [12, 13] and solid-liquid-solid (SLS) growth [11, 14-20]. In a VLS growth process, catalysts like Au nanoparticles are employed as active sites to absorb Si atoms from vapor phase source, typically gaseous sillane (SiH_4). On the other hand, in SLS mechanism, Si solids such as wafers and particles are utilized as the source for the nanowire growth. The SLS mechanism is of potential for low cost and abundant resources. More importantly, it completely excludes the need for SiH_4 which is extremely toxic [21]. Therefore, this method is more favorable for the fabrication of SiONWs and has caught a lot of research interest [11, 14-19, 22].

In this work, we develop a method to further promote the growth of SiONWs within the frame of SLS mechanism. With the introduction of vertical CNT arrays, rapid growth of SiONWs can be achieved using bulk substrate as the Si source.

2. Experimental Details

The growth process is shown in Figure 1, which mainly involves PECVD fabrication of CNTs and solid source growth of SiONWs.

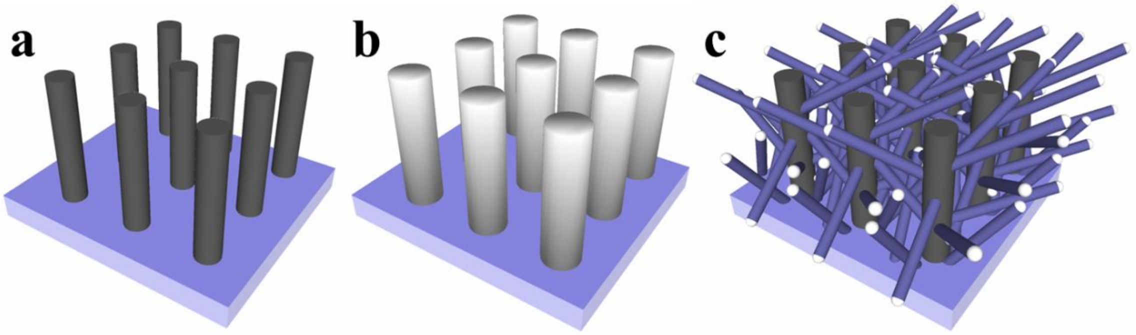

Figure 1. Schematics of the fabrication process. (a) PECVD growth of CNT array. (b) Magnetron sputtering of Ni. (c) Solid source growth of SiONWs.

2.1 PECVD fabrication of CNTs

Si wafers were used as the substrates. 15 nm Ni film was coated onto the substrates by electron beam evaporation as the catalyst. PECVD was performed by Aixtron BM system. In a typical process, 240 sccm NH_3 and 60 sccm C_2H_2 were introduced into the chamber and chamber pressure was kept at 9.0 mbar. The temperature was ramped up to 800 °C, after which plasma was generated and maintained at a power of 120W to initiate the formation of CNTs for 15 min.

2.2 Solid source growth of SiONWs

The samples with CNTs were coated by 100 nm nickel which served as the catalyst for

SiONW growth. Growth was carried out in a home-made tube furnace. 500 sccm Ar and 200 sccm H_2 were used as the process gases and the furnace pressure was maintained at atmospheric pressure during the entire growth process. Temperature is kept at 1000 °C for 15 min, followed by cooling down.

2.3 Structural characterization

Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS), Raman spectroscopy, transmission electron microscopy (TEM), high-solution TEM (HRTEM) and X-ray photoelectron spectroscopy (XPS) were used in the characterization. SEM characterization was carried out in a field-emission SEM (LEO 1550 Gemini). TEM and Fast Fourier Transform (FFT) pattern were performed in JEOL JEM-2100F (HR) equipped with an EDS detector. Raman spectrum was obtained using a WITec Raman system with a laser with λ=532 nm as the excitation source. XPS was carried out using a Thermo Scientific Theta Probe XPS. Monochromatic Al Kα X-ray (hν=1486.6eV) was employed for analysis with an incident angle of 30° with respect to surface normal. Photoelectrons were collected at a take-off angle of 50° with respect to surface normal.

3. Results and discussion

The SEM image of the CNTs fabricated is shown as Figure 2(a). Owing to the electrical field applied in the chamber during PECVD growth, the CNTs are well aligned vertically, forming an array. The plasma helps the dissociation of the carbon precursor and therefore facilitates the formation of CNTs. The CNTs exhibit a length in the range of 7 to 10 μm, and a rather large and uniform diameter around 100 nm. It may be noteworthy that the density of CNTs is not very high, around ca. 3.45×10^{8} cm^{-2}, leaving plenty of space between neighboring CNTs. This is beneficial for the complete coating of CNTs by materials in PVD processes, for example, magnetron sputtering, as evidenced by previous reports [23, 24]. The relatively large diameter brings in more surface areas which also help the accommodation of coating material.

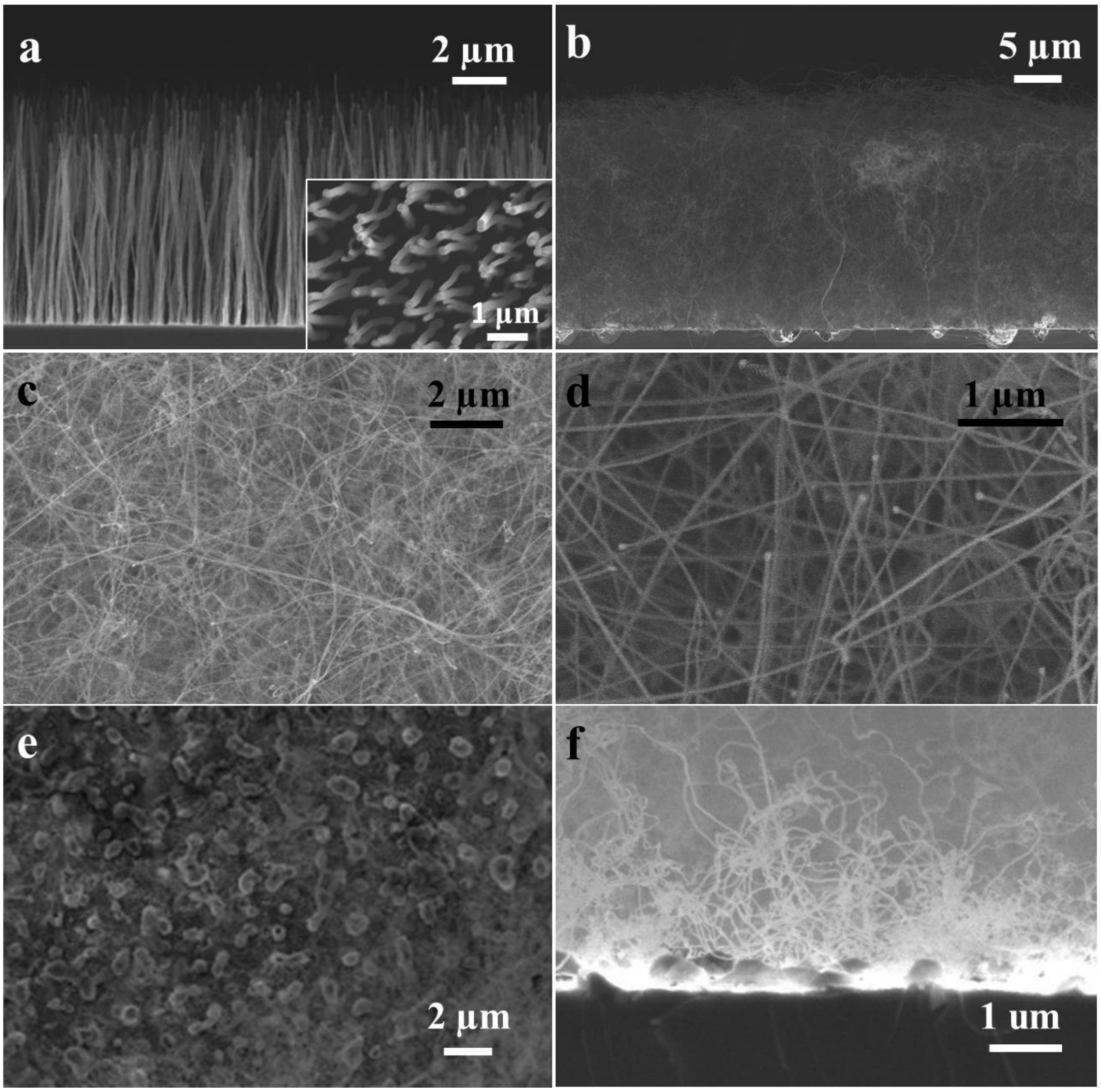

Figure 2. (a) Cross-section view SEM image of the vertical CNT array, inset is the top view SEM. (b) (c) (d) Cross-section, top and higher magnification top views SEM

images of the SiONWs and CNTs hybrid film, respectively. (e) (f) Top and cross-section view SEM images of the growth results without CNTs.

Figure 2 (b), (c) and (d) display the SiONWs after growth in the tube furnace. Clearly, SiONWs completely fill the space among the CNT array. The density of the SiONWs is so high that the SiONWs and CNTs hybrid networks become a densely packed layer on the substrate. It is also consistent with top angle view SEM shown in Figure 2(c), in which on entire surface of the sample is the dense network of SiONWs. Distinctly different from CNTs, SiONWs display diameters below 40 nm, as shown in Figure 2(d), which are much smaller than those of the CNTs. Besides, there are some particles on tip parts of the SiONWs, which are possibly the Ni catalysts. The growth is likely to follow a tip growth mode, which typically happened in solid source growth of SiONWs [25, 26]. Here, the lengths of the SiONWs could reach several tens of micrometers, forming a densely packed layer with thickness of over 30 μm. Given the 15 minutes' growth time, the growth rate can be considered as very fast as compared to previous reports on solid source growth of SiONWs catalyzed by Ni [11, 14, 16-18]. On the contrary, without the CNTs, growth of SiONWs is dramatically impeded as shown in the Figure 2(e) and (f). SiONWs are merely formed in limited area on the surface. The difference probably comes from the enhancement role of the CNT array, which will be analyzed in details later.

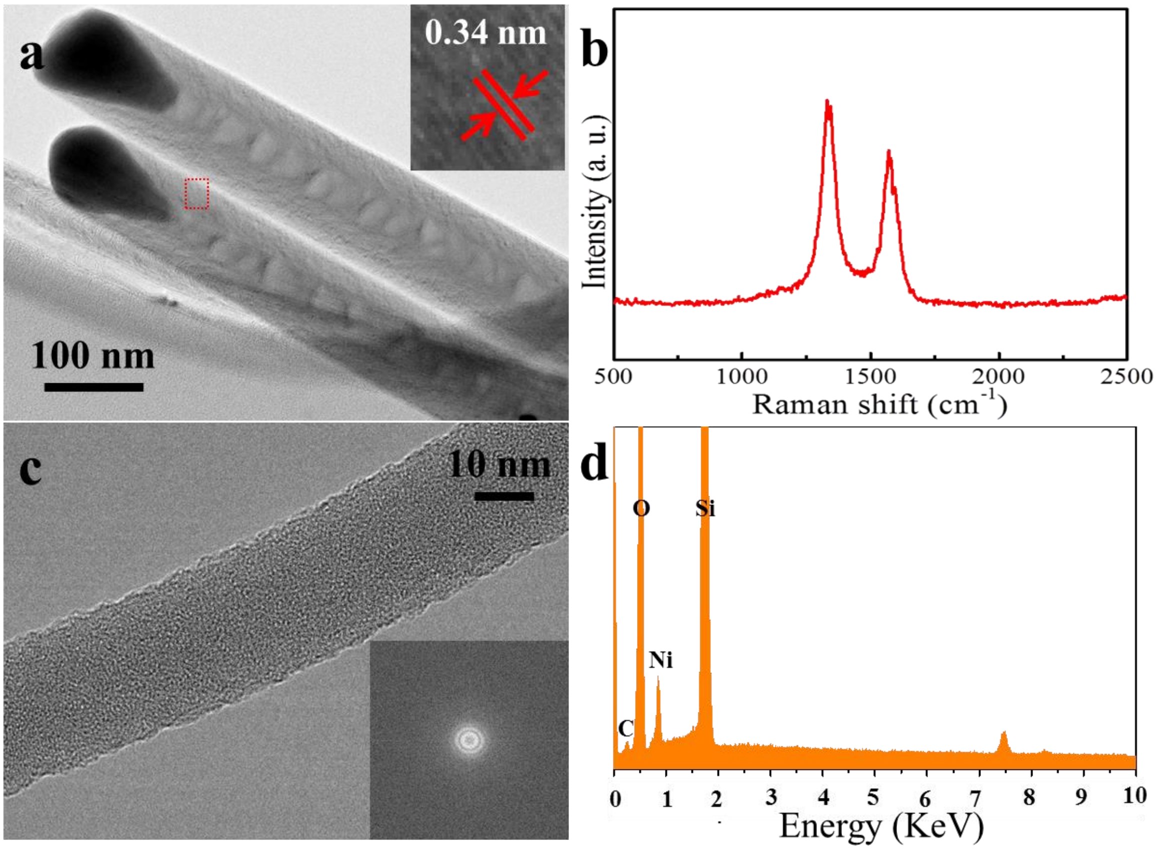

Figure 3. (a) TEM image of the CNTs; Inset is the HRTEM, representing the constructing structure. (b) Raman spectrum of the CNT array. (c) HRTEM image of a randomly selected SiONW; Inset is the corresponding FFT diffraction pattern. (d) EDS spectrum of the hybrid film fabricated.

TEM image of the CNTs is shown in Figure 3(a), clearly manifesting their multi-walled CNT (MWCNT) characteristics. Walls of the MWCNTs are constructed by several tens of carbon layers which surround cavities around 30 nm in diameter in the axis, therefore giving them much larger diameters than single walled CNTs (SWCNTs). The diameters of the MWCNTs are around 100 nm, in line with the SEM observations in Figure 2(a). The constructing carbon layers in the wall are separated by ca. 0.34 nm, consistent with the theoretical value [27]. In the Raman spectrum, Figure 3(c), there are two characteristic peaks of CNTs at around 1582 cm^{-1} and 1350 cm^{-1}, which belongs to the G and D bands, respectively. The G peak is the signature for the graphenic lattice of the CNT walls while D band represents the defects and imperfections in the structure [28]. The relatively high I_D/I_G ratio could come from the MWCNT nature and also the plasma utilized during growth which may increase the possibility of vacancy and disordering of the constructing carbon atoms in the structure. Figure 3(c) gives the TEM image of a randomly selected SiONW. The diameter is around 25 nm. There is not any obvious crystalline lattice that can be observed in wide range. Hence, FFT pattern in the inset ascertains that the SiONWs obtained are amorphous. EDS spectrum in Figure 3(d) reveals the film is mainly composed by Si, O and C elements, in accordance with its composition of SiONWs and CNTs.

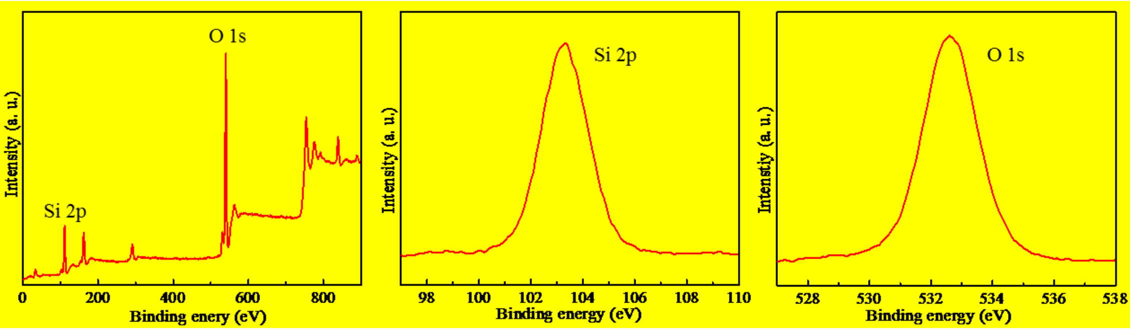

Figure 4. XPS spectra of SiONWs: (a) Survey scan; High resolution scan of the Si 2p (b) and O 1s (c), respectively.

The properties of the SiONWs are further characterized by XPS, by which the stoichiometric ratio of O to Si is determined to be 1.66. Moreover, as shown in Figure 4, Si 2p peak located at 103.3 eV clearly evidences the Si^{4+} state in the Si oxide while signal from the unoxidized state of Si^0 at 99.4 eV could hardly be detected in the binding energy. Meanwhile, O 1s peak can be observed at 532.6 eV. Therefore, the XPS data confirms the successful synthesis of the Si oxide compound in the nanowires [29-32].

The growth of SiONWs using solid source in our method follows a typical solid-liquid-solid mechanism. In this mechanism, Ni catalyst react with the Si at the solid interfaces between them and form liquid droplets of Ni-Si alloys at a relatively low temperature [14]. With further increase of the temperature, vast amount of the Si atoms start to transfer from the Si substrate and diffuse into the Ni-Si droplets through the solid and liquid interfaces. When these droplets are saturated, Si atoms precipitate into the solid form [11, 14, 16-18, 20, 22]. It should be mentioned that O_2 absorbed on the surface of samples as well as residual O_2 in the growth atmosphere also take part in the reaction [11]. As the consequence, amorphous SiOx clusters are formed as precursors. Eventually, continuous diffusion of the Si atoms to the Ni-Si/SiOx interfaces results in the formation of amorphous nanowires of SiOx.

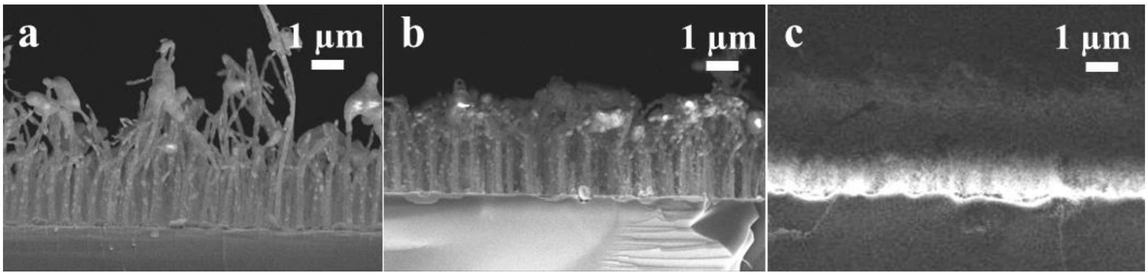

Figure 5. (a) (b) (c) Cross-section view SEM images of samples obtained after growth at 800°C, 900°C and 950°C respectively.

Aforementioned, with introduction of the CNT array, the growth of SiONWs is promoted significantly, but the underlying mechanism is yet to be known. To investigate the role of the CNTs, we carried out verification experiments, in which CNTs on Si substrate samples were heated to lower temperatures with other experimental conditions unchanged. The growth results at temperature of 800 °C, 900 °C and 950 °C are shown in Figure 5. As evidenced by the SEM images, SiONW formation started at around 950 °C. Despite of some slight bending, the structures of the CNTs are well maintained in the entire ramping-up process and they are still organized in vertical aligned array. More importantly, the Ni catalysts are well dispersed on the CNTs. It is widely known that CNTs are able to serve excellent support for metal catalysts, because of their stubborn mechanical strength and structural stability [6]. The CNTs fabricated by our PECVD method come with large diameters which further benefit accommodation of the catalysts. Hence, the distribution of the SiONWs obtained can be improved, resulting in a densely packed film. On the contrary, if not for the CNTs, Ni catalysts are agglomerated into large particles, as shown in Figure 2 (e) (f). Large particles come with greatly reduced surface-volume ratio, which is not favorable for diffusion, saturation and precipitation of the Si atoms. This probably accounts for the greatly deteriorated growth results. Nevertheless, with the introduction of the CNT array, the catalysts are prevented from agglomeration and they can be kept at small dimensions which enhance their reactivity. In this manner, the growth of SiONWs can be accelerated with the existence of CNTs. In addition, it is noteworthy that the CNT array is also a good scaffold with a lot of space left inside for the process gases. As one of process gases, H_2 is able to enhance surface diffusion kinetics [20]. With H_2 filled in the space provided by the CNT scaffold, Si transport from the substrate can be promoted dramatically. Hence, enhanced supply of the Si atoms will boost the formation of SiONWs. In summary, CNT array provides excellent support for the catalysts and also enhances Si supply, therefore promoting the growth of SiONWs.

4. Conclusion

In conclusion, a method is developed to produce SiONWs rapidly with Si substrate as solid sources. In this approach, vertical CNT array is grown on Si substrate by PECVD method. The CNT array helps dispersion of the catalysts and also enhances Si diffusion by providing space for H_2. As a result, a densely packed layer of SiONWs and CNTs can be obtained. This method sheds light on a possible application of CNTs and it may not be limited for SiONW growth but also applicable for rapid production of other nanowires.

5. Acknowledgement

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