Crystalline Core/Shell Si/SiO₂ Nanotubes Formed via Interfacial Stress Imbalance

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Crystalline core/shell Si/SiO₂ nanotubes (NTs) with outer diameters of 130–220 nm and lengths of ~1 μm have been synthesized using thermal evaporation. High resolution scanning electron microscopy reveals that the NT formation stems from the intrinsic interfacial stress imbalance in the strained Si/SiO₂ bilayered film, consequently leading to NTs with different orifice levels. The NT diameters depend strongly on the bilayer film thicknesses and crystal orientations of the Si and SiO₂ layers. A modified Timoshenko formula is derived to calculate the dependence of the tube diameter on the bilayer film thickness. The obtained results are consistent well with experimental data.

Keywords: Si/SiO₂ Nanotubes, Formation Mechanism.

1. INTRODUCTION

Crystalline nanotube (NT) structures have attracted much attention in recent years because of their interesting optical and electrical properties as well as potential applications in micro- and opto-electronics.¹⁻⁵ However, research on Si NTs (SiNTs) has been difficult due to the sp³ configuration. Many methods have been adopted to prepare SiNTs,⁶⁻⁷ but they tend to have many disadvantages. For example, SiNTs fabricated by the template method cannot be easily separated from the embedded templates.⁶⁻⁷ More importantly, it is difficult to obtain crystalline SiNT structures.⁶⁻⁷ Although the supercritical hydrothermal method has been demonstrated to produce crystalline SiNTs, the formation efficiency is low.⁸⁻⁹ Furthermore, the existence of SiNTs has been confirmed theoretically, but more experimental explorations are still required. In this letter, we report the fabrication of core/shell crystalline Si/SiO₂ NTs (S/SONTs) with outer diameters ranging from 130 to 220 nm using simple thermal evaporation. The production efficiency can reach 95%. Our experiments and theoretical calculation reveal that the Si and SiO₂ bilayer can bend into a S/SONT with the Si layer as the inner wall and silicon dioxide layer as the outer wall due to the intrinsic interfacial stress imbalance between the Si and SiO₂ layers. The NT formation depends strongly on the bilayer film thickness and the crystal orientation of the Si and SiO₂ layers. This work provides a possible way to fabricate crystalline SiNTs efficiently and conveniently.

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2. EXPERIMENTAL DETAILS

The S/SONT samples were produced by thermal evaporation. Si powders (99.99% purity) placed in an alumina crucible on one side of an alumina boat were evaporated onto a series of cleaned Si(100) substrates located 13–15 cm away on the other side of the alumina boat. The alumina boat was inserted into an alumina tube with the alumina crucible at the center of electric heater. The alumina tube was evacuated to 1 × 10⁻³ Pa and the 99.99% Ar was introduced as the carrier gas at 10 sccm throughout the experiment during which the alumina tube was heated to 1400 °C for 5 h. Finally, the alumina tube temperature was slowly reduced to room temperature and a chocolate brown product was produced on the Si substrate.

3. RESULTS AND DISCUSSION

Figures 1(a–d) depict the scanning electron microscopy (SEM) images of the product. Bulk quantities of NTs with outer diameters of 130–220 nm and lengths of ~1 μm can be found on the substrate. The wall thicknesses of the NTs are in the range of 30–50 nm. These NTs have similar morphologies (Fig. 1(a)). The production efficiency reaches 95%. The high-magnification SEM images in Figures 1(b–d) illustrate that these NTs are not closed and have various types of openings (Fig. 1(b)). A half-open NT is shown in Figure 1(c) (indicated by the arrow). An almost closed NT is depicted in Figure 1(d). These results strongly suggest that the NTs are formed via film curving. In addition, the tube walls are not smooth and consist...
of many curved sheets. These sheets overlap together and bend into a NT.

The X-ray diffraction (XRD) spectrum of the NTs is shown in Figure 2(a). All the diffraction peaks can be indexed to the reflections related to crystalline Si and SiO$_2$ except for the (100) peak from the Si substrate, indicating that the tube walls consist of crystalline Si and SiO$_2$ sheets with the main growth orientations along (111) and (220) for Si and (010) for SiO$_2$. This is an interesting feature of these NTs.$^{12-15}$ The high resolution transmission electron microscopy (HRTEM) image of a typical tube orifice is displayed in Figure 2(b). Clear SiO$_2$ lattice fringes along the (010) direction indicate that the tube orifice is covered by crystalline SiO$_2$. Another HRTEM image of the tube wall with two kinds of lattice fringes is presented in Figure 2(c). The lattice fringes with small spacings belong to the Si(111) sheet local to the inner wall of the NT. Thus, it can be inferred that these NTs are core/shell crystalline Si/SiO$_2$ NTs. They are formed via overlapping and bending of the Si and SiO$_2$ sheets. For confirmation, an energy dispersive X-ray (EDS) line scan is acquired by simultaneously monitoring silicon and oxygen. The corresponding result is shown in Figure 2(d) and the inset shows the measurement direction along the marked white line. Along the scan from 25 to 135 nm, the Si content firstly decreases (across the outer SiO$_2$ layer) and then gradually increases (across the inner Si layer) to a maximum, whereas the oxygen content changes oppositely. This indicates that the NT has an outer diameter of 220 nm. The crystalline SiO$_2$ layer is located at the outer wall, whereas the crystalline Si layer is at the inner wall.

In our experiments, the evaporated Si atoms first deposit on the substrate to interact with neighboring Si atoms to form an unsteady sheet-like structure. They are gradually oxidized to form the SiO$_2$ cover layer finally becoming a stable Si/SiO$_2$ bilayered film. At a high temperature, the bilayer film begins to curl due to the interfacial stress caused by the lattice mismatch giving rise to a long coiled S/SiO$_2$ NT by overlapping with neighboring curled bilayer films. Here, the tensile/compressive strain gradients play a key role in the NT formation. The intrinsic tensile strain may be increased with increasing bilayer film thickness. Its magnitude increases from the substrate to the covering SiO$_2$ film layer and thus the deposited Si film layer has large contraction compared to the SiO$_2$ layer (the inset of Fig. 3). A net bending force is thus formed toward the Si film layer. Consequently, the Si film layer is slowly enwrapped by the SiO$_2$ layer to form the S/SiO$_2$. Evidently, both the bilayered film thickness and crystal orientation determine the S/SiO$_2$ diameter.

A modified Timoshenko formula is utilized to illustrate schematically how a Si/SiO$_2$ bilayered film bends into a S/SiO$_2$. We assume $K$ and $z_0$ to be the average bending curvature and position of the neutral plane,
respectively. Considering the temperature effect, the bending levels induced in the SiO$_2$ and Si layers can be expressed as $\varepsilon_f = K(z - z_0) + \varepsilon_0 + \varepsilon^* + \mu \Delta T$ and $\varepsilon_i = K(z - z_0)$, and the strain energy per area of the Si/SiO$_2$ bilayer as $U = (C_f/2) \int \varepsilon_f^2 dz + (C_i/2) \int \varepsilon_i^2 dz$, where $C_f = E_f/(1 - \nu_f)$ and $C_i = E_i/(1 - \nu_i)$ are the elastic constants, $E_i(E_f)$ and $\nu_i(\nu_f)$ are Young’s modulus and Poisson’s ratio for Si (SiO$_2$), respectively.$^{18}$ Minimization of the strain energy with respect to $K$ and $z_0$ can be obtained by $K = -H_f/2H_1$, where “-” signifies opposite curvature direction associated with the description in the inset of Figure 3. Here $H_1 = C + 3BD + 3HB^2$, $H_2 = 3/2AD + 6ABH - F/2$, $A = \alpha \beta \varepsilon_0/(1 + \alpha \beta)$, $B = (\alpha \beta t_f - t_i)/2(1 + \alpha \beta)$, $F = 3\alpha \beta \varepsilon_0(2B - t_i)$, $C = \alpha \beta t_f^2 + t_i^2$, $D = t_i - \alpha \beta t_f$, $H = \alpha \beta + 1, \alpha = C_f/C_i$, and $\beta = t_i/t_f$, where $t_f$ and $t_i$ are the film thicknesses of SiO$_2$ and Si. In our calculation, $\varepsilon_0 = 0.0021$ and $\mu = 2.6 \times 10^{-16} \text{Nm}^2$ are the average misfit strain between the two crystalline regions of the bilayered film and average thermal expansion coefficient.$^{20,21}$ The reasonable experiential parameter $\varepsilon^* = 0.338$ is introduced into our calculation. It is determined by imperfections induced by the twisted convex concave tube wall and overlapping crystal sheets.

Using the above calculation, we can derive the diameter of the S/SONT as a function of bilayer film thickness, in which the SiO$_2$ film thicknesses are set at 15, 18 and 20 nm, respectively. The inset shows the geometrical configuration used in our calculation. $t_i$ and $t_f$ are the thicknesses of Si and SiO$_2$ film layers.

**Fig. 2.** (a) XRD spectrum of the S/SONTs; (b) and (c) HRTEM images of two tube orifice parts; (d) EDX spectrum (line scanning mode) along the marked white line in the inset.

**Fig. 3.** Diameter of the S/SONT as a function of bilayer film thickness, in which the SiO$_2$ film thicknesses are set at 15, 18 and 20 nm, respectively. The inset shows the geometrical configuration used in our calculation. $t_i$ and $t_f$ are the thicknesses of Si and SiO$_2$ film layers.

**Fig. 4.** Dependence of the temperature variation ($\Delta T$) on the tube diameter. The diameter is seen to increase with the observed ones. This confirms that the bilayer thickness determines directly the bending level of the S/SONT. The inset in Figure 4 depicts the dependence of the temperature variation ($\Delta T$) on the tube diameter. The diameter is seen to increase with
to be reduced linearly from 172.9 to 172.5 nm when $T$ increases from 1350 to 1650 °C. The temperature effect on tube diameter is very weak. We also plot the NT diameter as a function of the bilayer film thickness in Figure 4, in which the Si layers grow along the (100), (220) and (111) directions. Compared to the experimental data, we can see that the inner wall grows easily along the (111) direction because the elastic strain constant of the (111) Si film is larger than those along (100) and (220) directions for a given thickness. Under the same conditions, the (111)-oriented Si film is relatively easy to detach from the (100) substrate to form the S/SONT. According to the lowest energy principle, the enwrapped crystalline SiO$_2$ layer can even exist stably along the (010) direction and so it often appears as the tube outer wall, as in the case of our S/SONTs.

4. CONCLUSION

We have synthesized crystalline core/shell Si/SiO$_2$ NTs with outer diameters of 130–220 nm and lengths of ~1 μm using thermal evaporation. High resolution scanning electron microscopy reveals that the NT formation stems from the intrinsic interfacial stress imbalance in the strained Si/SiO$_2$ bilayered film, consequently leading to NTs with different orifice levels. The NT diameters depend strongly on the bilayer film thicknesses and crystal orientations of the Si and SiO$_2$ layers. We have presented a modified Timoshenko formula to calculate the dependence of the tube diameter on the bilayer film thickness. The obtained results are consistent well with experimental data.

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References and Notes


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