The zone-refine driven growth of jellyfish-like core–shell nanowires†

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Thermal evaporation of a Sn-silica mixture produces core–shell nanowires assembled into jellyfish-like structures. The growth mechanism involves zone-refine driven phase separation at the solid–liquid interface. The materials emit blue and red lights; the luminescence centers are discussed and verified.

1. Introduction

Owing to their excellent optical properties and quantum confinement induced blue-shift, silicon based nanowires have drawn much attention in recent years. For example, silica nanowires emit blue light1–12 and energy involved in optical transition decreases to infrared wavelength upon erbium ion implantation.3 Similar nanowires can also emit electrons at a low field and the current density is found to be comparable with that of carbon nanotubes.4 Materials can now be made of several microns in length and tens of nanometres across using catalytic carbothermal reduction and thermal evaporation.5–11 A new production technique using zeolite as template has been recently demonstrated and the grown oxide nanowires appear to be highly uniform with a single crystal Si-core along the wire axis.12 The nanowire growth is often interpreted according to the vapor–liquid–solid (VLS) model and unidirectional phase separation due to supersaturation-condensation at the liquid-solid interface has been verified with high-resolution transmission electron microscope (HRTEM) inspections.13 The existing theory, however, cannot explain well the radial growth of silica nanowires on large Co particles and inconsistencies include the oxide nucleation via sequential formations of SiC(s), C0(g), Si0(g) and SiO2(g) and the absence of phase separation induced droplet precipitation at the interface.14 A similar situation also occurs in the present study and core–shell nanowires obtained here possibly form through a zone-refining driven phase separation at the liquid-solid interface. The proposed mechanism is evidenced by the jellyfish-like morphology and light emission at the silica/Si interface.

2. Experimental

A mixture of powdered SiO and Sn (purity, 99.9%, 6 : 1 weight ratio) is ball-milled for two hours and is subsequently loaded into an alumina crucible placed in a two-section electrical furnace. An alumina substrate is placed 7 cm from the filled crucible to serve as sample collector. The furnace is purged with a Ar/H2 flow (9 : 1, 50 sccm). The ball-milled mixture and ceramic substrate are heated at 1350 °C and 850 °C (20 °C min⁻¹), respectively, for 30 min and the furnace is then allowed to cool to room temperature. The samples are examined by JEOL JSM-6500F field emission scanning electron microscope (FE-SEM) operating at 15 kV with a point-to-point resolution of 1.5 nm and JEOL-3000F field emission transmission electron microscope (FE-TEM). The chemical composition is analyzed by Link ISIS energy dispersive X-ray analyser (EDX) attached to the FE-TEM. Cathodoluminescence (CL) experiments are carried out using a Gatan Mono CL system equipped with FE-SEM and the optical signal is measured by a cooling PMT detector. Fourier transform infrared spectroscopy (FTIR) measurements are carried out using Bomem-DA8.3 at 75 °C and the operation is set in reflectance mode. Raman spectra are used for examining atomic bonding modes and the obtained spectra are calibrated with single crystalline silicon at 520.6 cm⁻¹/C0 and ceramic substrate are heated at 1350 °C and 850 °C (20 °C min⁻¹). The He–Ne laser (632.8 nm) equipped with notch filter is used to separate Rayleigh scattering light with an efficiency of 99.7%. For field emission experiments at room temperature, an indium tin oxide glass anode is spaced at a distance of 200 µm from nanowire emitters and the chamber vacuum is held at 10⁻⁷ torr. A Keithley 237 source-measure unit is used to monitor the current–voltage (Vmax = 1100 V) and related field emission characteristics.

3. Results and discussion

Fig. 1a shows the SEM image of materials grown at the alumina substrate and the zoomed-in image reveals oriented nanowires covered with large crystallized particles, similar to jellyfishes (Fig. 1b–c). The number of supporting nanowires varies from particle to particle and more than 50 tentacles have been observed in a large jellyfish with particle diameter exceeding 10 µm (Fig. 1d). Estimations of over 50 individual structures indicate that particle size distributes around 0.3–5 µm and nanowires are 15–30 µm in length and 10–35 nm in diameter. The crystallized particles revealed by selective area EDX mainly consists of Sn, along with a trace of Si and O. The Si and O adsorptions become strong when the Si and O adsorptions become strong when the...
at nanowires is due to the core–shell structure. First, an interfacial structure is present along the c-axis. Second, the microscope analyses clearly show the amorphous silica at the outer rim and crystallized Si at inner core region (top, Fig. 2a). Third, selective area electron diffraction confirms the Si (111) domain along wire axis (lower, Fig. 2a). Fourth, the elemental mapping profile obtained at an energy count of 20 000 displays Si : O = 3–4 : 1 at the inner core and 0.6–0.8 : 1 at the coating layer (Fig. 2b), the coating thickness being 20–30 nm for nanowires and 5–15 nm for Sn particles. The latter accounts for the low profile of Si and O in EDX spectra. We find that alumina crucible heated at 1250 \(^\circ\)C and 1350 \(^\circ\)C yielded a similar jellyfish-like structure (Fig. 3a–b), whereas the nanowire length appears to scale with gas flow in the 10–50 sccm range (Fig. 3c–d). Between 50–100 sccm, the lengthening becomes insignificant and abundant particles coated with thin oxides begin to emerge above 100 sccm, attributable to cooling induced rapid precipitation of Si.\(^{15}\)

Electrical heating of MoSi\(_2\) in the presence of NH\(_4\)F:HF also yields core–shell nanowires, whereas oxide formation due to incomplete oxidation between thermally precipitated Si and residual O\(_2\) at disilicide surfaces does not lead to nanowire aggregation into a radial morphology.\(^{16}\) In the current study, the nanowires aggregated at catalytic particles, however, suggest a different growth mechanism: first, the substrate where nanowires are formed is 7 cm away from the precursor loaded crucible, indicative of non-in situ growth. Second, the solubility (\(d_x\)) of Sn in Si is very low at the eutectic point (0.6 at%) according to the binary phase equation \(d_x = 40z/\left[R^T\ln(C/C_{eq})\right]\) where \(\Omega\) is molar volume, \(z\) is surface free energy and \(C\) and \(C_{eq}\) are Si concentration in a liquid alloy and at an equilibrium.\(^{17}\) In other words, the phase separation due to supersaturation upon Si–vapor adsorption is unlikely. Third, the particle size exceeds nanowire diameter, implying the absence of the Gibbs-Thompson effect, known as an indication of epitaxial growth.\(^{13}\) Fourth, silica is insoluble in Sn so nanowire seeding through oxide particles previously detected in Sun et al.’s experiment is unlikely.\(^{18,19}\) Fifth, the Al signal is absent in our EDX profile, ruling out the rooting growth via ceramic substrate. The fact that SO is used as precursor in the current study means that Si nanowires must grow through three consecutive reactions as follows,

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\begin{align*}
2\text{SiO}(s) + 2\text{Sn}(s) & \rightarrow \text{O}_2(g) + 2\text{SiSn}(l) \\
\text{SiSn}(l) & \rightarrow \text{Si}(s) + \text{Sn}(l) \\
2\text{Si}(s) + 3/2\text{O}_2(g) & \rightarrow \text{SiO}_2 + \text{SiO}_2(s)
\end{align*}
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Apparently, the oxide shell is produced in the 3rd reaction and is evident by EDX mapping profile at the outer rim (Fig. 2a–b). A question, however, remains as to how Si segregates from the alloy phase to form nanowires in the 2nd reaction. For an alloy, the metal with the higher m.p. tends to precipitate upon solidification and phase separation.
preferentially occurs at grain boundaries. This process is known as the zone-refining and has been detected in the anisotropic growth of nonequilibrium alloyed nanowires.\textsuperscript{20} A similar precipitation is expected here: first, the Si\textsubscript{mp} \(\gg\) Sn\textsubscript{mp} implies Si segregation from metal at elevated temperature, and second, the oxide coating confines phase separation in a narrow channel, thus facilitating zone-refining.\textsuperscript{14} Based on the descriptions above, we propose a growth model and mechanism that includes thermal decomposition of SiO\textsubscript{2} precursor into Si\textsubscript{g} and O\textsubscript{2} upon heating (I, Fig. 4), Si vapor adsorption and Si–Sn alloy formation (II, Fig. 4), the zone-refine driven Si precipitation (III, Fig. 4), surface oxidation (IV, Fig. 4), and coalescence of Sn droplets (V–VI, Fig. 4). Steps I and II have been verified by Sun \textit{et al.}\textsuperscript{18} and step III is supported by an indistinct boundary between wire and particle known as a result of a coexisting liquid–solid phase upon zone refining (Fig. 2a).\textsuperscript{20} For step IV, the luminescence spectra provide useful information regarding surface oxidation. Fig. 5a displays cathodoluminescence (CL) profiles obtained from 30–40 jellyfishes (blue) within a 50 \(\times\) 50 \textmu m measuring window. Two distinct bands are detected at 448 and 620 nm and can be assigned as blue and red light emissions, respectively, consistent with bulk silica. Compared with reported data on oxide nanowires, the emission intensity here is a factor of 2–4 lower, attributable to the fact that optical transition only takes place at surface oxides. We find that the blue band cannot be well fitted by a single Gaussian function and an additional component is found at 460 nm, indicative of two luminescence centers. A similar side feature also appears at the red band and the peak spacing appears to be larger (30 nm). The blue emission has been well documented and is owing to excitonic transition between ground and triplet states of oxygen deficient centers (ODCs), including twofold coordinated defects (\(\equiv\text{Si-O-Si-O-Si}\equiv\)) and neutral oxygen vacancies (\(\equiv\text{Si-Si}\equiv\)).\textsuperscript{21} Light emission from surface silica can be further verified by NH\textsubscript{4}F:HF etching (BOE) and coating removal results in vanishing of peaks at 448, 460 and 650 nm (red, Fig. 5a). Emission at 620 nm, however, remains after BOE and the luminescence possibly involves the oxygen deficiencies at the silica/Si interface. Fig. 5b shows infrared spectra (IR); a pristine sample displays a broad adsorption centered at 760 cm\textsuperscript{-1} and distinguishable shoulder at 1030 cm\textsuperscript{-1} (dark), corresponding to bending and stretching modes of Si–O. The etched sample, however, displays an up-shift by 110 cm\textsuperscript{-1} and the profile becomes well fitted by two Gaussian functions at 790 cm\textsuperscript{-1} (green) and 910 cm\textsuperscript{-1} (pink); the former comes from the same origin as in the pristine sample and the latter appears to match with the scissor mode of Si–H.\textsuperscript{21} Prolonged BOE enhances the Si–H band intensity and the band center is further shifted by 80 cm\textsuperscript{-1} (blue), attributable to Si–H:O–Si coupling.\textsuperscript{21} The Si–O vibration in the pristine sample and BOE induced hydrogenated Si
suggests that emissions at 460 and 650 nm probably arise from the peroxy linkage (Si–O–O–Si) and the blue band at 448 nm is related to neutral oxygen vacancies. First, the peroxy is a precursor of non-bridging oxygen hole centers (NBOHCs, \( \equiv \text{Si}–\text{O}^\bullet \)) and can therefore emit blue and red lights simultaneously, consistent with CL spectra shown in Fig. 5a. Second, both characters can be reduced via \( E^0 \) center acting as intermediate state and is evident by enhanced Si–H adsorption (blue, Fig. 5b). Quantum confinement induced luminescence is unlikely because the average diameter of nanowires exceeds the excitonic radius of hole-electron pairs (<3 nm) and the smallest nanowire in the current study is found to be 25 nm. Accordingly, the remaining CL peak at 620 nm must arise from a different origin, most likely the oxygen deficient defects at the core–shell interface. First, the luminescence center at the interface remains upon electron irradiation and acid treatment, and the CL intensity is only reduced by 2–4%.\(^{16,21,23}\) Second, the residual oxides remain at nanowire surfaces after BOE (Fig. 2c–d). Third, the band shape and intensity only slightly change, indicative of undamaged luminescence centers. Fig. 5c shows a panchromatic CL image obtained from etched sample and an experiment was carried out on a cold stage using low energy beam (5 keV) to avoid irradiation induced heating. Compared with nanowires the luminescence intensity detected at metal particles is very low (i.e. dark area) and a similar result is also detected at different particles, indicative of ODC population mostly at Si nanowire surfaces. In other words, oxidation takes place mainly at Si nanowires and interfacial ODCs form upon reaction termination, consistent with the 3rd reaction and step IV. Additional evidence in support of interfacial ODCs comes from field emission before and after BOE (Fig. 6a–b) and corresponding Fowler-Nordheim (F–N) plots are displayed in Fig. 6c. For the pristine sample the current density is 1.59 \( \mu \text{A cm}^{-2} \) and the turn-on field \( (F_{TO}) \) has been estimated to be 5.2 \( \text{V \mu m}^{-1} \), similar to the value seen in bulk silica.\(^{13,17,19}\) Etching results in \( F_{TO} \) being reduced by only

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**Fig. 5** Cathodoluminescence (CL) spectra obtained from pristine (blue) and BOE treated nanowires (red) (a), FTIR spectra obtained from the pristine sample (dark) and nanowires treated by BOE for 10 s (red) and 180 s (blue); green and pink curves are Gaussian fits to the red profile (b), and panchromatic CL images of BOE treated sample (left) in comparison with bright-field image (right): arrows indicate particle diameter (= 600 nm) (c).

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**Fig. 6** Field emission profile of nanowires before (a) and after BOE treatment (b) and corresponding F–N plots (c).
growing nanowires often coalesce to form a branching structure from interfacial characters. It is noteworthy in Fig. 6c that the F–N curve shows a consistent with Fig. 6a–b and supports the BOE improved field function (\(E_0\)) reduction by hydrogenation and is supported by the Fowler-Nordheim equation gives \(J \propto E^{3/2}\). The band, however, tends to shift when stress is present and the study indicates the blue- and red-shifts for compressive and tensile stress, respectively.21 Here we find the primary Raman band at 514 cm\(^{-1}\), supporting zone-refine created thermal stress along the wire axis. Again, the BOE removal of surface oxide is evident by the disappearance of the amorphous Si induced strain tensor component at 495 cm\(^{-1}\).27 We find that the 514 cm\(^{-1}\) band does not shift with BOE etching time and is verified by repeat experiments on several selected samples, excluding surface oxide induced compressive stress around nanowire circumference. In other words, the Raman shift truly originates from the zone-refining induced tensile stress. The small feature at 300 cm\(^{-1}\) also comes from amorphous Si27 and its existence after BOE is consistent with oxygen deficient lattices at the oxide-nanowire interface mentioned above.

4. Conclusions

The core–shell nanowires aggregated into jellyfish structures are produced and electron diffraction and elemental mapping confirm the Si nanowires coated with thin oxides. Nanowires grow via zone-refine induced recrystallization at the solid–liquid interface and is supported by microscope analyses. The blue and red light emissions are detected and luminescence centers come from oxygen deficient characters. The 620 nm emission remains unchanged after BOE and its origin possibly involves oxygen deficient lattices at the oxide–Si interface.

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Notes and references