Side-by-side silicon carbide–silica biaxial nanowires: Synthesis, structure, and mechanical properties

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Elevated-temperature synthesis has been used to generate side-by-side biaxially structured silicon carbide–silica nanowires. The axial growth direction approaches [311] for nanowires with a high density of microtwins and is [211] for defect-free nanowires. The structure of these nanowires, their cross-sectional shape, and their structural transformation between a biaxial and coaxial configuration have been studied by transmission electron microscopy. The Young’s modulus of the biaxially structured nanowires was measured to be 50–70 GPa depending on the size of the nanowire. © 2000 American Institute of Physics.

One-dimensional quantum wires are of fundamental importance to the study of size-dependent chemical and physical phenomena. The properties of nanowires may sensitively depend on their geometrical shape/configurations, which can include tubular structures (multi/single-walled carbon nanotubes), solid cylindrical nanowires, or coaxial constructions. Devices made using nanowire heterojunctions can be critical for nanoelectronics. Silicon carbide is a wide band gap semiconducting material used for high-temperature, high-frequency, and high-power applications. The growth of β-SiC whiskers can be achieved using a variety of well-established techniques. Recently, Lieber, Lee, Yu, and co-workers have extrapolated on the ideas entailed in the vapor–liquid–solid technique to develop the laser ablation of metal containing silicon targets as a means of obtaining bulk quantities of silicon nanowires. Here, we report the synthesis of bulk quantities of biaxially structured silicon carbide–silica nanowires, composed of side-by-side subnanowires. We have applied the techniques of high-temperature synthesis to modify and generalize the approach of Lee et al. to synthesize dislocation-free Si nanowires, as reported in detail elsewhere. In the current letter, amorphous SiO is brought into intimate contact with carbon/graphite in an appropriate mix at elevated temperatures for an extended period. To produce the biaxial silicon carbide–silica nanowire configurations, the system was operated at temperatures close to 1500 °C for 12 h.

Figure 1(a) depicts a low-magnification transmission electron microscopy (TEM) image of the nanowires dispersed on a carbon film. The nanowires are uniform with diameter 50–80 nm, and a length which can be as long as 100 μm. The as-synthesized materials are grouped into three basic nanowire structures: pure SiO nanowires, coaxially sheathed β-SiC nanowires (Fig. 1(b)) (~50% of material), and biaxial β-SiC–SiO nanowires (Fig. 1(c)) (~30% of material). The coaxial SiC–SiO nanowires have a (111) growth direction with a high density of twins and stacking faults perpendicular to this growth direction. From the cross-sectional TEM images of the as-synthesized nanowires, the geometrical shapes of the coaxial SiC–SiO [Fig. 1(d)] and the biaxial SiC–SiO nanowires [Figs. 1(e) and 1(f)] are unambiguously revealed. The SiC nanowires have faceted shapes, and one type of the facet is {111}. The objective of this letter is to study the growth mechanism and the mechanical properties of the biaxial nanowires.

FIG. 1. (a) Low-magnification TEM image of the as-synthesized nanowires supported by a carbon film, showing their ultralong length and uniformity in diameter. Side views of a (b) coaxially and (c) biaxially structured SiC–SiO nanowire. (d), (e), and (f) Cross-sectional TEM images of coaxially structured SiC–SiO and biaxially structured SiC–SiO nanowires, respectively.

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The biaxial SiC–SiO\textsubscript{x} nanowires consist of two side-by-side subnanowires of silica and β-SiC [Fig. 2(a)], which can be simply referred to as a composite nanowire. If we image from the [011] direction perpendicular to the nanowire, the overlap between the amorphous SiO\textsubscript{x} side and the β-SiC is only ~4 nm. There is also a thin layer of silica passivated on the surface of the β-SiC. The β-SiC side has a high density of stacking faults and a few twins (so-called microtwins).

This can be seen more clearly in an enlargement of a local region [Fig. 2(b)], where the outermost surface of the β-SiC is composed of nanosize {111} facets. At the interface between SiC and SiO\textsubscript{x}, small segments of {111} faces are also identified [Fig. 2(c)]. The presence of a high density of planar defects results in a [311] axial direction for the biaxial nanowires, in contrast to [111] for the coaxial nanowires.\textsuperscript{3} Biaxial nanowires with a much lower density of stacking faults and a [211] growth direction have also been observed occasionally."

FIG. 2. High-resolution TEM image of a biaxially structured β–SiC–SiO\textsubscript{x} nanowire, showing the crystallographic and defect structures of the nanowire. The electron beam is along [011], perpendicular to the nanowire. A Fourier transform of the image from a defect-free area, given at the bottom, shows that the growth direction of the nanowire is [311]. (b) and (c) Enlargements of the areas between the interfaces of SiO\textsubscript{x}–SiC at the contact area and near the surface of SiC–SiO\textsubscript{x}, respectively, showing the {111} faceted nanoareas at the interface. S and T stand for stacking fault and twin, respectively.

FIG. 3. (a)–(d) TEM images from the SiC–SiO\textsubscript{x} biaxially structured nanowires, displaying structural evolutions and interface junctions in the nanowires. Bending appears wherever a defect free segment is created due to a change in growth direction from [311] or [211] to [111]. The electron beam is near [011]. (e) Structural transformation from a coaxial to biaxial nanowire, where a neck-shape junction is formed at the interfacial region. (f, g) Models for the structural transformation from a coaxial to a biaxial nanowire growing along the [211] and [311] directions.

Shown in Fig. 3 are a group of TEM images that indicate the structural transformation in the SiC–SiO\textsubscript{x} nanowire systems. The segment containing a high density of planar defects grows straight along the axis, while the presence of a defect free region results in bending [Figs. 3(a)–3(c)] and sharp turns [Fig. 3(d)] along the nanowires. This is the result of switching the growth direction from [311] or [211] for the biaxial structure to [111] for the coaxial structure, while a common (111) plane is preserved. It is important to note that the SiC and SiO\textsubscript{x} sides also switch across a bending area.\textsuperscript{4}
TABLE I. Measured Young’s modulus of coaxial cable structured SiC–SiO$_2$ nanowires (SiC is the core, and silica is the sheath). ($\rho_{\text{SiC}} = 2.2 \times 10^3$ kg/m$^3$, $\rho_{\text{SiO}_2} = 3.2 \times 10^3$ kg/m$^3$).

<table>
<thead>
<tr>
<th>$D_i$ (nm)</th>
<th>$D_o$ (nm)</th>
<th>$L$ (nm)</th>
<th>$f$ (MHz)</th>
<th>$E_{\text{eff}}$ (GPa)</th>
<th>Expt</th>
<th>Theor</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>12.5</td>
<td>6.8</td>
<td>0.693</td>
<td>46.9 ± 9.0</td>
<td>87</td>
<td></td>
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<tr>
<td>74</td>
<td>26</td>
<td>7.3</td>
<td>0.953</td>
<td>56.9 ± 9.2</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>83</td>
<td>33</td>
<td>7.2</td>
<td>1.044</td>
<td>52.8 ± 8.2</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>132</td>
<td>48</td>
<td>13.5</td>
<td>0.588</td>
<td>78.7 ± 7.0</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>105</td>
<td>19.0</td>
<td>0.419</td>
<td>81.5 ± 5.1</td>
<td>109</td>
<td></td>
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</tbody>
</table>

TABLE II. Measured Young’s modulus of biaxially structured SiC–SiO$_2$ nanowires. $D_{\text{wire}}$ and $D_{\text{SiC}}$ are the widths across the entire nanowire and across the SiC subnanowire, respectively.

<table>
<thead>
<tr>
<th>$D_{\text{wire}}$ (±2 nm)</th>
<th>$D_{\text{SiC}}$ (±1 nm)</th>
<th>$L$ (±0.2 µm)</th>
<th>$f$ (MHz)</th>
<th>$E_{\text{eff}}$ (GPa)</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>58</td>
<td>24</td>
<td>4.3</td>
<td>1.833</td>
<td>54 ± 24.1</td>
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<tr>
<td>70</td>
<td>36</td>
<td>7.9</td>
<td>0.629</td>
<td>53 ± 8.4</td>
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<tr>
<td>83</td>
<td>41</td>
<td>4.3</td>
<td>2.707</td>
<td>61 ± 13.8</td>
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<tr>
<td>92</td>
<td>47</td>
<td>5.7</td>
<td>1.750</td>
<td>64 ± 14.3</td>
<td></td>
</tr>
</tbody>
</table>

For a beam with one end hinged and the other free, the resonance frequency is given by

$$f_0 = (\beta^2/2\pi)(EI/m)^{1/2}/L^2,$$

where $f_0$ is the fundamental resonance frequency, $\beta = 1.875$, $EI$ is the flexural rigidity (or bending stiffness), $E$ is the Young’s modulus, $I$ is the moment of inertia about a particular axis of the rod, $L$ is the length of the beam, and $m$ is its mass per unit length. For a coaxial cable structured nanowire whose core material density is $\rho_i$ and diameter is $D_i$, a biaxial nanowire whose core material density is $\rho_i$ and diameter is $D_i$, and sheath material density which is $\rho_s$ with outer diameter $D_s$, the average density of the nanowire is given by $\rho_\text{avg} = \rho_i(D_i^2/D_s^2) + \rho_s(1 - D_i^2/D_s^2)$. The effective Young’s modulus of the composite nanowire, $E_{\text{eff}}$, is $\rho_\text{avg} = \rho_i(D_i^2/D_s^2)^3$. The bending modulus for the coaxial cable structured SiC–SiO$_2$ nanowires results in combination from SiC and SiO$_2$. The bending modulus increases as the diameter of the nanowire increases (Table I), consistent with the theoretically expected values of $E_{\text{eff}} = \alpha E_{\text{SiC}} + (1 - \alpha) E_{\text{SiO}_2}$, where $\alpha = (D_i/D_s)^3$. The data match well to the calculated values for larger diameter nanowires.

From the cross-sectional TEM image of a biaxially structured nanowire displayed in Fig. 1(e), the outermost contour of the cross-section of the nanowire can be approximated to be elliptical. Thus, the effective Young’s modulus of the nanowire can be calculated using the formula for a uniform beam with the introduction of an effective moment of inertia and density. The experimentally measured Young’s modulus is given in Table II.

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