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Direct synthesis of aligned silicon carbide nanowires from the silicon substrates

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Aligned silicon carbide nanowires were synthesized directly from the silicon substrates *via* a novel catalytic reaction with a methane–hydrogen mixture at 1100 °C, with a mean diameter of 40 nm and length of 500 μm; they consist of a single-crystalline zinc blende structure crystal in the [111] growth direction; X-ray diffraction, Raman, and infrared spectroscopy confirm the synthesis of high-purity silicon carbide nanowires.

Silicon carbide (SiC) is a wide-band gap semiconductor material with extreme hardness and high thermal conductivity even at high temperature.[1,2] Lately, one-dimensional SiC nanostructure, SiC nanowire (SiC-NW), has attracted much attention because of its potential application for nanostructured composite materials and microelectronic devices. Recent work has shown that the elasticity and strength of zinc blende SiC-NWs (β-SiC-NW or 3C-SiC-NW) are substantially greater than those of the bulk.[3] Various methods, *e.g.*, carbon nanotube-confined reaction, arc discharge, laser ablation, carbothermal reduction, and chemical vapor deposition, have been developed to produce the SiC-NWs.[4–9] Here we report a notably simple and efficient method for the large-scale synthesis of highly aligned β-SiC-NWs directly from the silicon (Si) substrates. They were grown through a novel reaction of the Si substrate and a methane (CH_4)–hydrogen (H_2) mixture at 1100 °C, using gallium (Ga), gallium nitride (GaN), and iron (Fe) nanoparticles as catalysts.

The n-type Si (100) substrates with an area of 10–20 cm^2 were coated with 0.01 M $FeCl_2{\cdot}4H_2O$ (99%, Aldrich) ethanol solution. The thickness of $FeCl_2$ film was about 300 nm. The substrate was loaded on a quartz boat placed in a quartz tube reactor. About 0.01 g of Ga (99.999%, Aldrich) and GaN powder (99.99+%, Aldrich) with a 1 : 1 volume ratio was placed near to the substrates. Argon was flowed into the tube reactor while raising the temperature. A flow of the CH_4 (99.95%) and H_2 (99.999%) mixture was introduced through a mass-flow controller at a rate of 10–40 sccm and 300–500 sccm, respectively. The temperature of the substrates was set at 1100 °C and the growth time was 30 min–1 h. The morphology and structure of the nanowires have been examined by scanning electron microscopy (SEM, Hitachi S-4300), transmission electron microscopy (TEM, JEOL JEM-2010), electron diffraction (ED), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD, Philips X'PERT MPD), Raman spectroscopy (Renishaw RM1000) using a 514.5 nm argon ion laser, and infrared (IR) absorption spectroscopy (Bio-Rad FTS-6000).

After the reaction, a blue tinted gray colored film was deposited on the whole Si substrate. Fig. 1 shows SEM images of the film. The high-density SiC-NWs are grown homogeneously with a length of 500 μm on a large area of the Si substrate (Fig. 1(a)). The nanowires are vertically aligned on the substrate, similar to the multiwalled carbon nanotubes grown using chemical vapor deposition or pyrolysis (Fig. 1(b)). No catalytic nanoparticles were found at the tip. The EDS analysis demonstrated that the atomic ratio of Si and C is about 1 : 1 with a trace of Ga and O.

The TEM image shows the general morphology of the nanowires (Fig. 2(a)). The diameters are in the range 10–60 nm with an average value of 40 nm. The nanowires are straight and have a smooth surface (Fig. 2(b)). Fig. 2(c) shows a high-resolution TEM (HRTEM) image of one 40-nm-diameter SiC-NW, revealing a highly crystalline structure. The inset is the corresponding selected-area ED (SAED) pattern, which is consistent with that of the zinc blende structure. The wire axis is parallel to the [111] direction of a cubic unit cell. Its atomic-resolved image (Fig. 2(d)) shows that the (111) fringes perpendicular to the wire axis are on average separated by 2.53 Å, which is close to that of the bulk β-SiC, 2.5166 Å (JCPDS Card No. 29-1129). Most of the SiC-NWs exhibit stacking disorders. All SiC-NWs, we examined, are grown with an identical [111] growth direction. The yield of SiC-NWs is independent on the type of the Si substrates. The nanowires

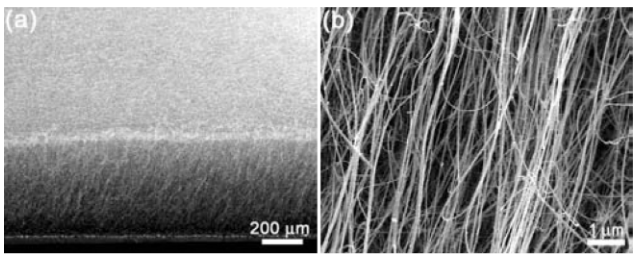

Fig. 1 (a) SEM image of the SiC-NWs homogeneously grown on a large area of the Si substrate. The length is 500 μm. (b) The SiC-NWs are highly aligned.

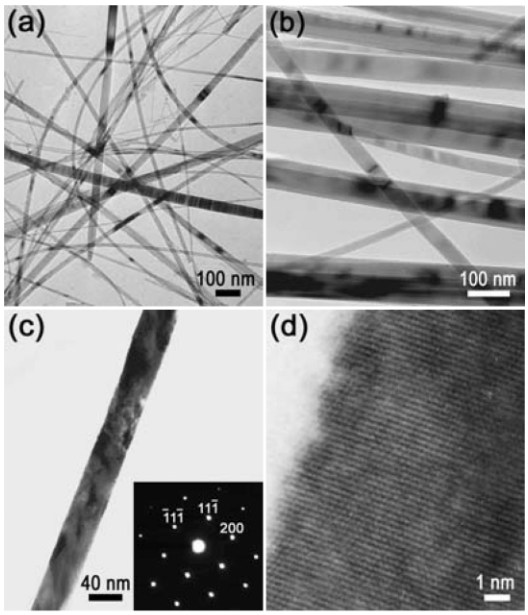

Fig. 2 A TEM image showing (a) the diameter in the range of 10-60 nm and no catalytic particles at the tip. (b) The nanowires are straight and have a smooth surface. (c) HRTEM image of a highly crystalline SiC-NW with a diameter of 40 nm. The inset shows the SAED pattern corresponding to the zinc blende structure. (d) Atomic-resolved image showing the (111) planes perpendicular to the wire axis.

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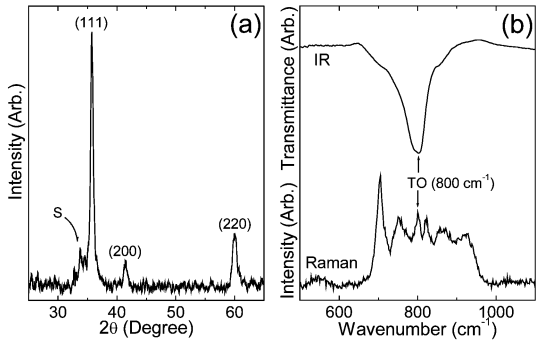

Fig. 3 (a) XRD pattern, (b) Raman scattering and infrared reflection spectra of the SiC-NWs.

always exhibit the zinc blende structure with a [111] growth direction.

The XRD pattern of the SiC-NWs detached from the substrate is shown in Fig. 3(a), and is typical of a β-SiC crystal. Miller indices are indicated on each peak. No other crystalline impurities are detected. There is a low-intensity peak (marked by S) at a lower diffraction angle than that of the strong (111) peak, which usually ascribes to the stacking faults in the (111) planes.[9] Fig. 2(b) shows the Raman and IR spectra measured in the reflection geometry. For the β-SiC bulk, it was reported that the first-order phonon frequencies of the transverse optical (TO) and longitudinal optical (LO) modes are at 796 and 972 cm^{-1}, respectively.[10] Both IR and Raman bands are present in the broad range 650–950 cm^{-1}. The IR peak at 800 cm^{-1} correspond to the TO mode.[11] The Raman peaks probably originate from the LO and TO modes. The peak broadening and down-shifting is related with the stacking faults of the nanowires.[12]

When only H_2 is used instead of the CH_4–H_2 mixture, less nanowires grow on the substrate, as shown in the SEM image (Fig. 4(a)). The nanowires are bundled with a length up to a few tenths of a μm. The TEM image reveals that the individual nanowire is made up of amorphous Si (Fig. 4(b)). The diameter is 5–8 nm. The corresponding ED reveals such an amorphous nature (inset). The EDS shows only Si component (Fig. 4(c)).

Ga has been recently used as a catalyst to synthesize the Si or silicon oxide (SiO_x) nanowires by a number of research groups.[13,14] The dissolved Si substrate in molten Ga is the Si source for those Si or SiO_x nanowires and also for the present nanowires. At the growth temperature 1100 °C, the solubility of Si in molten Ga is ~28 atomic %.[15] The use of GaN significantly increases the yield of SiC and Si nanowires. The

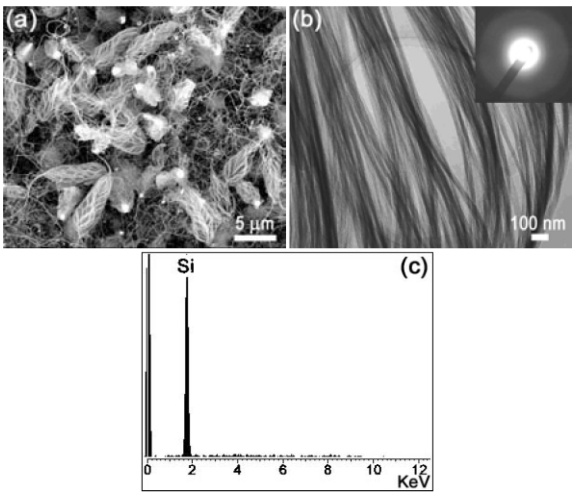

Fig. 4 (a) SEM image of the Si-NWs bundles grown on the Si substrate. (b) TEM image and SAED pattern (inset) showing that the Si bundles consist of amorphous Si-NWs with a diameter of 5–8 nm. (c) EDS reveals only a Si component.

mixing of Ga and GaN apparently produces a suitable vapor pressure of Ga for the growth of nanowires, following the deposit on the Si substrate. The SEM and XRD analyses were conducted for the Fe-deposited Si substrate before the reaction, revealing that the coated $FeCl_2$ film undergoes the reduction into the Fe nanoparticles by the H_2 flow. The size of nanoparticles was 20–100 nm and the density was ~10^{10} cm^{-2}. The Si nanowires were grown out from the catalytic nanoparicles that presumably consist of Ga-Fe-Si alloy. Under the flow of CH_4–H_2 mixture, the SiC-NWs grow by the continuous dissolution of the C source into the alloy nanoparticles. Since the Si and C sources are supplied separately from the solid and the gas phase, the growth mechanism of SiC-NWs can be uniquely categorized as a combination of solid–liquid–solid and vapor–liquid–solid mechanisms. It is noteworthy that the SiC-NWs lack any catalytic particles at the tip, suggesting a base growth mechanism where the nanowires grow from the catalytic nanoparticles attached to the substrate.

In summary, we have successfully synthesized highly aligned β-SiC-NWs on a large-area Si substrate using a novel catalytic reaction at 1100 °C. The Si substrate and CH_4 were used as the Si and C sources, respectively. The catalysts were Ga metal, GaN powder, and Fe nanoparticles deposited on the Si substrate. The diameter is 10–60 nm with an average value of 40 nm and the length is 500 μm. The HRTEM images and SAED patterns reveal the single-crystalline zinc blende structure and the [111] growth direction. If no CH_4 flows, the amorphous Si-NW bundles are grown from the Si substrates under the same growth conditions. The dissolution of the Si substrate in molten Ga is crucial for the growth of the SiC and Si nanowires. The XRD, Raman, and IR spectroscopy show the high purity and the stacking faults of the SiC-NWs. We expect that the present method would be a promising way for a mass-production of high purity SiC-NWs.

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