Synthesis of silicon nanowires and nanoparticles by arc-discharge in water

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Si nanowires of diameters 5–20 nm and nanoparticles of ~4 nm were synthesized by a simple arc-discharge method in water. The TEM analysis reveals that the growth direction of the observed Si nanowires is parallel to the {111} crystal planes.

One-dimensional nanostructures such as nanowires, nanobelts, nanorods and nanotubes have attracted much attention due to their physical properties as well as their potential application as nanosized optoelectronic devices.[1] The synthesis of semiconductor nanowires such as those of Si, makes them possible components in nanoelectronics. Several routes for the synthesis of Si nanowires have been reported, including the popular chemical vapor deposition (CVD) based on vapor–liquid–solid (VLS) or the oxide-assisted growth mechanism,[2–6] molecular-beam epitaxy (MBE)[7] and the supercritical solution-phase approach.[8] The MBE method needs high vacuum and expensive equipment. The CVD method relies on the decomposition of silane or evaporation of Si powders in a high pressure gas atmosphere over a catalyst to form wires, in which a laser is often used to produce the high temperature. Although the existing methods can prepare well-defined Si nanowires, they are still expensive. Finding new routes for facile synthesis of Si nanostructures remains a challenge which must be met in order to satisfy the demands of applications in the near future.

Here we report on an economical method for the synthesis of Si nanostructures, in which no metal catalysts are used, no explosive or corrosive gases are required, no vacuum equipment is needed, and the apparatus is easy to set up and modify. Si nanowires and nanoparticles have been produced by this method, using only arc-discharge between two Si electrodes submerged in water. Recently, Sano *et al.* synthesized carbon onions and carbon nanotubes (CNTs) by using carbon arc-discharge in water.[9–11] However, Si has a different chemistry to carbon, the formation and morphology of Si nanostructures by the arc-discharge method in liquid should be different from that of CNTs. Therefore the synthesis of Si nanostructures by this liquid arc was very attractive. We have synthesized several Si nanostructures by arc-discharge in water and studied their structures by transmission electron microscopy (TEM). To our knowledge, no synthesis of Si nanostructures by an arc-discharge method in liquid has been reported to date.

In a typical synthesis we used a Si electrode that is 5 mm in diameter as the anode and a Si rod with a diameter of 20 mm as the cathode. Both electrodes were submerged in de-ionized water and kept about 10 cm below the surface of the water. The anode could be shifted back and forth while the cathode was kept fixed. Ar was continuously supplied into the water to purge O_2 out. An arc was initiated by bringing the anode and the cathode in contact. Then they were separated to a distance of about 1 mm to sustain the discharge in water. The discharge voltage and current were 25 V and 10 A, respectively.

During the arc-discharge, a bluish light and bubbles were observed around the electrodes. The bubbles escaped from the vicinity of the arc spot and moved towards the surface of water. The transparency of the solution decreased with time during the synthesis, and the suspension became pale yellow after continuous discharge for 10 min. With the time extended to 1 h, the suspension became brown and powder was found at the bottom of the container. After the experiment, consumption of the anode was evident, while a little Si on the cathode surface also evaporated resulting in an uneven cathode surface.

The samples for study by TEM were collected directly from the water surface and bulk suspension onto carbon-coated Cu grids without any treatment. The TEM observation was conducted using a Hitachi H-8100 microscope operating at 200 kV. The sample collected from the water surface consisted mainly of nanoparticles. Fig. 1a shows a representative image of the particles floating on the water surface. The rings in the diffraction pattern

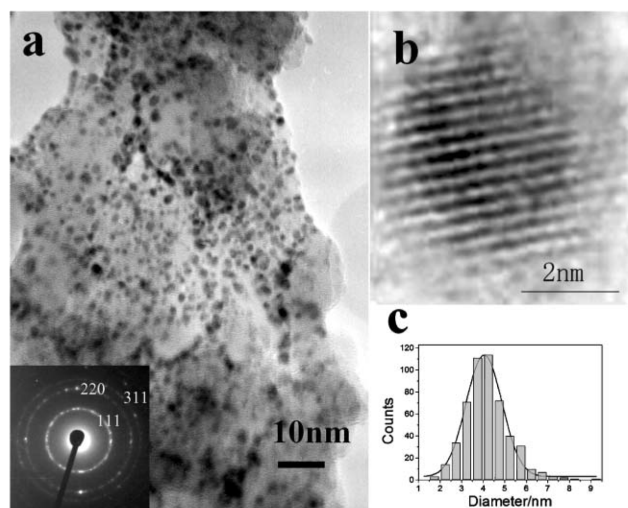

Fig. 1 (a) TEM image of Si nanoparticles collected from the water surface after arc-discharge with the electron diffraction pattern shown in the inset. (b) HRTEM image of a single particle. (c) Size distribution determined from approximately 600 particles.

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shown in the inset respectively correspond to the {111}, {220} and {311} plane of diamond-like silicon. Fig. 1b shows a high resolution TEM (HRTEM) image of a single particle with clearly visible lattice fringes (0.32 nm) consistent with the {111} plane of diamond-like crystalline silicon. The average size and size distribution was determined by measuring 600 particles as shown in Fig. 1c. The mean size of the particles was $\sim 4 \pm 1.2$ nm.

Furthermore, the sample from the bulk suspension produced in this work exhibited interesting 1-dimensional nanostructures as represented by Fig. 2. Fig. 2a shows a TEM image of curved Si nanowires (or nanobelts). The diameter of the nanowires was found to be in the range of 5–20 nm. The length of the nanowires could hardly be determined since it was difficult to find their ends from the TEM image. Besides the normal randomly curved shape, bamboo-like assemblies of Si nanowires were also found on the same TEM grid as shown in Fig. 2b. The assemblies were composed of Si wires with diameter distribution 5–20 nm. Fig. 2c shows a high magnification TEM image of several bundles of curved nanowires with the selected area electron diffraction (SAED) shown in the inset. The diffraction rings obviously exhibit the crystalline structure of cubic Si as indexed in the pattern. It is also noticeable that the intensity of the cubic Si {111} diffraction ring exhibits bright diffuse streaks. This indicates that the crystals in the nanowires should have several particular orientations in their {111} planes due to their one-dimensional structures. Besides the nanowires described above, we also found some Si particles of 30–50 nm. Fig. 2d shows the X-ray diffraction (XRD) pattern of the sample collected from the Si aqueous suspension. The data was obtained on a Rigaku Rint 2000 diffractometer with Cu Kα radiation (λ = 1.5418Å) operated at 40 kV and 20 mA. The diffraction peaks are respectively indexed to {111}, {220} and {311} lattice planes of cubic diamond-like silicon crystal (JCPDS card No. 27-1402) as indicated in the figure.

Further studies on the structures of Si nanowires have been carried out with the HRTEM images. After examining many nanowires, we found that the observed {111} planes of the Si crystal were usually parallel to the axis of the nanowires. The Si nanowires grown by the VLS mechanism usually exhibit the {111} planes normal to the growth direction,[2–4] but this morphology was not found in our case. Fig. 3a shows the HRTEM image of a typical thin straight Si wire having a diameter of ~ 8 nm. The measured spacing of the crystallographic planes is 0.32 nm, which corresponds to the {111} lattice fringes of the cubic diamond silicon structure, confirming that the nanowire consists of crystalline Si. The wire growth direction is perpendicular to the {111} axis. This growth direction has also been reported for the Si nanowire prepared by the CVD method.[12–14]

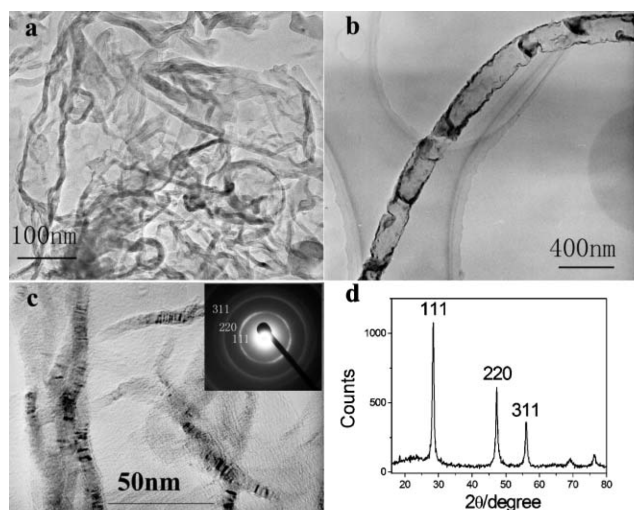

Fig. 2 TEM images of Si nanowires suspended in the bulk solution with random curled nanowires (a), a bamboo-like assembly (b), high magnification image of curled nanowires with the SAED in the inset (c), and XRD pattern of the sample (d).

As mentioned above, the nanowires synthesized in this work have many bent parts as seen from the TEM images. Fig. 3b shows a thick Si wire with a core diameter of 14 nm covered by an amorphous layer of ~ 5 nm. The core has the {111} planes parallel to the wire axis. The ripple-like contrasts are due to the strain resulting from the bending. At present the origin for those bent parts is not clear since they might form during nanowire growth or during the preparation of the TEM samples. Our sample also contained many kinks as shown in Fig. 3c. At the kink point, the growth direction of the wire switches to an equivalent direction also perpendicular to the (111) direction. At the position the Si nanowire changes its growth direction, a twinning defect shows up. Besides the Si nanowires or nanobelts, a few tubular nanostructures have also been found as shown in Fig. 3d. Even though CNTs are generally produced from the carbon arc-discharge method in liquids,[9,10] the tubular morphology as shown in Fig. 3d is rare in the present work. This is reasonable since silicon has a cubic diamond structure, different from the layer-structured graphite. The detailed analysis of this interesting tubular structure cannot be presented at the moment due to the small amounts available, but this is under investigation. Very recently, an Italian group reported their Si nanotubes synthesized by a dc-arc plasma in inert gases,[15] but their Si nanotubes shown by a TEM image look different from the tubular structure here. The difference might come from the different environments of the dc-arc.

The variety of Si nanostructures as observed by the TEM analysis suggests a complex formation process during the arc-discharge process. As described above, the two electrodes contact

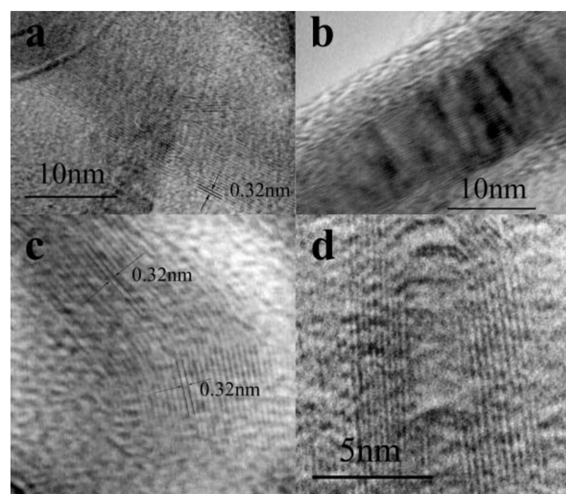

Fig. 3 HRTEM image of a thin straight Si nanowire (a), a curved nanowire covered by an amorphous layer (b), the kink part of a nanowire (c) and a tubular nanostructure with hollow center (d).

to initiate arc-discharge. Since the electrode surfaces are not perfectly smooth, the roughness leads to many visible small contact spots. A high current density is thus expected around these contact spots during discharge. At the vicinity of the arc spot, the temperature is expected to be higher than the melting point (1685 K) and near the boiling point (2953 K) of silicon, which results in vaporization of the electrodes and formation of a gaseous bubble. In the bubble there should exist Si species with different morphologies dependent on the local discharge conditions in different discharge spots. During discharge, the charged species are expected to have directional motion parallel to the electric field. Formation of wire structures is expected to occur at this time. On the other hand, Si particles are likely to be formed in the region where the effect of the electric field on vaporized species is not significant.

According to the morphology of the Si nanowires observed by TEM in this work, we suggest that the {111} surfaces may play an important role during the growth of these wires. It is known that the {111} surfaces have the lowest surface energy among the other surfaces in Si. It has been reported that thin Si nanowires produced by the CVD method also show the {111} planes parallel to the direction of wire growth,[12–14] while those in thick wires are perpendicular to the growth direction based on the VLS mechanism.[2] In this work, as no catalyst was used, the wire growth cannot be explained by the VLS mechanism. On the other hand, the diameter of Si wires produced in this work lies in the range $5 \sim 20$ nm. In this range with a small diameter, the surface energy is rather important, thus the formation of {111} surfaces with low energy in the form parallel to the axes of the nanowires can minimize the system energy. Furthermore, it is known that there are several possible growth directions parallel to the {111} planes, but due to the limited TEM resolution we cannot obtain TEM images of the lattice planes other than {111}, while diffraction spots in our SAED patterns are rather diffuse due to the small diameter and bent parts in the wires. So we cannot determine exactly which direction among those parallel to {111} planes is the growth direction for the observed Si wires at present.

In summary, this paper represents a simple, economic way of producing Si nanowires and nanoparticles by arc-discharge in water for the first time. In contrast to the popular CVD method, this method dose not use any metal catalyst. The synthesized samples with different sizes and morphologies can auto-separate, *i.e.* very small nanoparticles may move to the surface of the water, nanowires with some middle-sized particles stay in the bulk suspension, while very large particles sink to the bottom. TEM analysis indicates the growth direction of most observed nanowires in this work is parallel to the {111} crystal planes. Future work will focus on optimization of the experimental apparatus to control the discharge more accurately and on the investigation of products at different stages of discharge to elucidate the growth mechanism. The optical and electronic properties of these Si nanowires will also be investigated to further clarify the effect of morphology.

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