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2002 J. Phys.: Condens. Matter 14 L473

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LETTER TO THE EDITOR

Aligned silica nanofibres**L Dai, X L Chen¹, T Zhou and B Q Hu**Institute of Physics and Centre for Condensed Matter Physics, Chinese Academy of Sciences,
Beijing 100080, People's Republic of China

E-mail: xlchen@aphy.iphy.ac.cn

Received 5 April 2002

Published 14 June 2002

Online at stacks.iop.org/JPhysCM/14/L473**Abstract**

Large-scale highly aligned silica nanofibres were produced on silicon substrates. The diameters of these nanofibres vary from 50 to 100 nm and the lengths are up to several millimetres. Transmission electron microscopy and selected-area electron diffraction reveal that the fibres are in an amorphous state. The growth of silica nanofibres is probably controlled by a vapour–solid process. Gas-phase SiO seems to play the key role in the synthesis, serving as a transportation medium.

1. Introduction

The synthesis of one-dimensional nanostructures is of great interest in nanotechnology and nanoscience. Since the discovery of carbon nanotubes in 1991 [1], materials with one-dimensional nanostructures such as nanotubes, nanowires and nanorods have been extensively investigated in view of their interesting and novel properties and the opportunity that they provide for achieving a deep understanding of physics at the nanometre scale. Silicon and silica nanostructures have attracted a remarkable amount of attention because of their potential application in mesoscopic research, the promise of utility in new technologies and the potential applications of nanosized devices. Recently, many researchers have successfully synthesized various kinds of one-dimensional silica and silicon nanostructures by employing laser ablation [2], physical evaporation [3] and the sol–gel template method [4]. Zhu *et al* [5] have grown silica ‘nanoflowers’. Shi *et al* [6] have synthesized large-scale silicon nanowires with sheathed silica outer layers and shown that the oxides play an important role in the growth of these nanowires. Wang *et al* [7] have applied the techniques of high-temperature synthesis to modify the process of Lee *et al* and generate two interesting nanostructures: silica nanowire ‘bundles’ and ‘brush-like’ arrays. Very recently, the phenomenon of emission of stable visible blue light from both amorphous silica nanowires and crystalline silica nanotubes has been

¹ Author to whom any correspondence should be addressed.

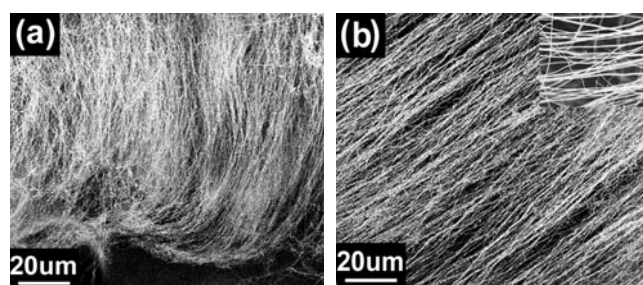


Figure 1. An SEM image of the curved silica nanofibres (a), appearing like hair; the aligned nanofibres in (b) are straight and uniform in diameter; the inset shows an enlarged image.

observed at room temperature [8, 9]. This new photoluminescence feature has stimulated extensive interest, as it means that silica nanostructures could be utilized in field-emission planar displays. However, it seems fairly difficult to produce large-scale aligned silica one-dimensional nanostructures under current experimental conditions. In fact, the fabrication of large-scale aligned silica nanowires is an important and challenging field. In the present work, we report the successful synthesis of aligned silica nanofibres, and their growth process is also discussed.

2. Experimental details

The experimental apparatus used for the present study is a horizontal alumina tube that is inserted in a tube furnace. The silicon substrate, a $10 \times 10 \text{ mm}^2$ square 0.2 mm in thickness, was put on a silica boat located in the mid-part of the tube axially, where the heating system can provide a stable temperature zone. The polished silicon (100) substrate was cleaned carefully using ultrasonics in alcohol and distilled water, separately, for 10 min. Before starting the heating, the silica tube was pumped mechanically, and high-purity argon poured in to clean away the traces of impurity gas absorbed in the substrate, the silica boat and the tube wall. The entraining argon/oxygen (50:1) mixed gas flowed over the tube at a flow rate of 50 sccm (standard cubic centimetres per minute). The flow pressure in the alumina tube was kept at around 1 atm. The tube was heated to 1200°C at the rate of 5°C min^{-1} . Then the whole system was operated at 1200°C for 6 h. After cooling to room temperature, a thin layer of wire-like white product was found on the substrate.

The morphology and the chemical composition of the deposited products were characterized using a scanning electron microscope (SEM, Hitachi 3400) with an energy-dispersive x-ray fluorescence (EDX) spectroscopy attachment. The microstructure was studied by transmission electron microscopy (TEM, Philips CM12 at 100 kV) and high-resolution TEM (HRTEM, Jeol 2010 at 200 kV).

3. Results and discussion

Optically, a layer of white villiform substance can be observed on the silicon substrate. Under relatively low magnification, SEM images of the deposit (figures 1(a), (b)) show that the large-scale highly aligned fibre-like nanostructures are well spread on the surface of substrate. Figure 1(a) shows that these fibres grow in a form like human hair, with a slight curl at the end of each nanofibre. Through studying the whole substrate surface via SEM, we observe that the curly hair-like nanofibres mainly appear at the edge of the silicon substrate, where the growth is probably strongly influenced by the aerodynamics of the gas flow. However, the fibres

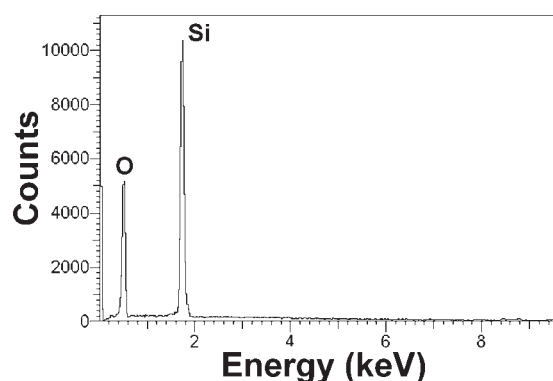


Figure 2. EDX measurement for silica nanofibres, showing Si and O only.

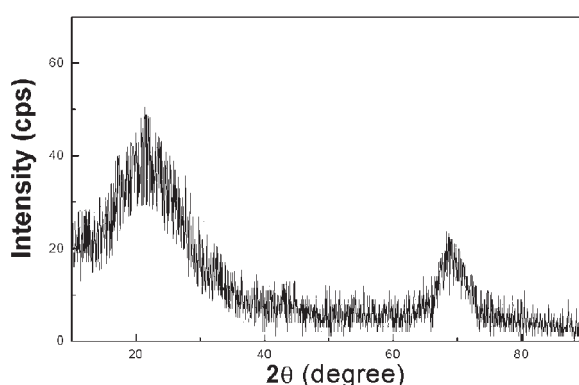


Figure 3. The XRD pattern for the silica nanofibres showing the characteristic form for an amorphous state.

located on the central part of the substrate are fairly straight (figure 1(b)). High-magnification SEM observation revealed that these nanofibres are very long (from tens and hundreds of micrometres to several millimetres) and their diameters vary from 50 to 100 nm. EDX data (figure 2) on the samples show that only silicon and oxygen are detected, with an approximate atomic ratio 1:2 (Si_mO_n , $m = 0.36$, $n = 0.64$), which is equal to the stoichiometric ratio of SiO_2 and unambiguously confirms that the prepared fibres are indeed silica nanofibres. In XRD measurement (figure 3), no reflection peak is observed. Instead, there is a broad hump at about $2\theta = 21.3^\circ$, indicating that the silica nanofibres are in an amorphous state. In addition, the peak ($2\theta = 69.3^\circ$) corresponding to the (400) plane of the silicon substrate is also observed.

To identify the microstructure of these nanofibres, we peeled off a small piece of deposited product from the substrate randomly to perform TEM observations. Figure 4 shows a typical TEM image of an individual silica nanofibre with a uniform diameter of about 80 nm. This fibre is clean, smooth and straight; no tapered or beaded morphology such as is often observed for other nanowires is found [10, 11]. The selected-area electron diffraction (SAED) pattern (inset of figure 4), taken from this nanofibre, shows an amorphous halo ring; no diffraction spots were recordable. This further confirms that the silica nanofibres are in a non-crystalline state. Meanwhile, the TEM analysis shows that the growth of silica nanofibres may not be dominated by the conventional vapour–liquid–solid (VLS) mechanism proposed for nanofibres

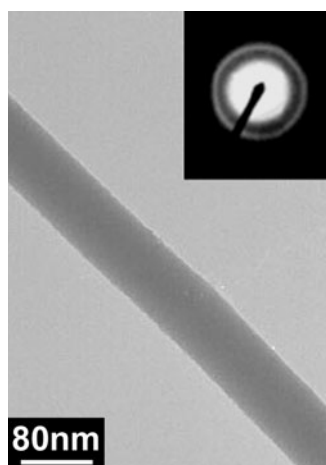


Figure 4. A TEM image of a typical silica nanofibre. The inset showing the SAED pattern reveals that the nanofibre is amorphous.

grown by a catalyst-assisted process, in which a transition metal particle is capped at the tip of the fibre and serves as the active catalytic site [12]. We have not observed any metal particles in nanowires (which would be evidence supporting the VLS growth mechanism) in extensive TEM observations. Here, we believe that the growth process might be as follows: first, at a relatively low temperature, a thin layer of SiO_2 is produced on the silicon substrate surface through the oxidization of silicon; second, with the increasing of the heating temperature (1200°C), the silica reacts with silicon taking the following route: $\text{Si}(\text{s}) + \text{SiO}_2(\text{s}) \rightarrow 2\text{SiO}(\text{g})$ (where s and g represent solid and gas, respectively); then the gas-state SiO undergoes further reaction with the O_2 contained in the mixed flowing gas following the route $2\text{SiO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SiO}_2(\text{s})$, and solid-state one-dimensional SiO_2 fibres are generated because of the low SiO gas concentration; finally, the silica fibres are highly oriented along the flow direction, which can be attributed to the directing effect of the carrier gas. At the same time, overcrowding of these fibres restricts the possibility of nanofibres growing in other directions.

Therefore, we think that the growth of silica nanofibres is probably controlled by the VS (vapour–solid) process. Furthermore, we point out that the synthesis process was carried out with no starting powder material. This means that the silica nanofibres are directly grown from the silicon substrate. It seems that the growth is a kind of *in situ* process. To verify this, we carried out the synthesis process repeatedly and in all cases we obtained silica nanofibres. In addition, the vapour-phase SiO seems to play a key role in the synthesis by acting as a necessary intermediate substance.

4. Conclusions

In summary, large-scale highly aligned silica nanofibres were produced on silicon substrates. The diameters of the nanofibres ranged from 50 to 100 nm and the lengths were up to millimetres. The nanofibres are structurally uniform along their whole lengths. TEM and SAED indicate that the fibres are in an amorphous state. Their growth is probably controlled by the vapour–solid process. The gas-phase SiO seems to play a key role in the synthesis by serving as an intermediate substance. The approach provided here for producing silica

nanofibres is very simple; also, it offers an opportunity to study silica nanostructures and has the potentiality for use in fabrication of nanodevices.

We thank Professor Z Zhang and Dr A Z Jin for the electron microscopy analysis. This work is supported by the National Nature Science Foundation of China (NSFC, Grant Nos 59972040, 59925206).

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