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Synthesis and photoluminescence of α -Al₂O₃ nanowires

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Abstract

α -Al₂O₃ nanowires have been synthesized in bulk quantity by using simple physical evaporation of mixture of pure Al powders and nanometre-sized TiO₂ powders at 1150 °C. Scanning electron microscopy and transmission electron microscopy observations show that α -Al₂O₃ nanowires have diameters ranging from 20 to 60 nm and lengths up to several tens of micrometres. The growth of α -Al₂O₃ nanowires is controlled by the vapour–liquid–solid (VLS) mechanism. Photoluminescence measurements revealed a blue luminescence band in the wavelength range of 400–500 nm with two peaks at 415 and 440 nm, which could be attributed to the F⁺ centres in the α -Al₂O₃ nanowires.

1. Introduction

Recent progress in the synthesis of nanowires has been driven by the need to understand the novel physical properties of one-dimensional nanoscale materials, and their potential applications in constructing nanoscale electric and optoelectronic devices [1]. Up to now, much attention has been paid to oxide one-dimensional nanostructures due to their interesting properties and applications in optics, magnetism, superconductivity and ferroelectricity. Several binary oxide nanobelts and nanowires such as Ga₂O₃, MgO, SiO₂, In₂O₃ and ZnO have been successfully synthesized [2–8].

Owing to their brittleness, ceramics have been regarded as materials of modest performance, especially under tension or bending conditions, in contrast to metals or polymers; however, the thermal stability of ceramics above 700 °C makes them suitable materials for many high-temperature applications. Microstructural design is critical in order to obtain reliable ceramic materials. Such materials are usually called ‘advanced ceramics’ [9].

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Recently, efforts have been made to obtain alumina and aluminosilicate fibres with a high Al_2O_3 content. Recently, one-dimensional Al_2O_3 nanostructures with various morphologies including nanowires or nanorods, nanofibres, nanobelts and nanotubes have been prepared by various methods [10–12]. Here, we report another method for synthesizing large-scale α - Al_2O_3 nanowires by heating a mixture of pure Al powders and nanometre-sized TiO_2 powders at 1150 °C. Photoluminescence measurements showed a strong blue luminescence band in the wavelength range of 400–500 nm with two peaks at 415 and 440 nm.

2. Experimental details

A mixture of pure Al and nanometre-sized TiO_2 (about 50 nm) powders (in molar ratio 4:3) were used as starting materials. The preparation of Al_2O_3 nanowires was carried out in a ceramic tube (i.d. = 4 cm), which was placed in a horizontal tube furnace heated by SiC rods. The system was rapidly heated to 1150 °C in 8 min, and kept at this temperature for 60 min in a flowing argon atmosphere in which high-purity Ar served as a carrier gas. During the heating process, the Ar flow rate was kept at 100 sccm (standard cubic centimetres per minute). After the system was cooled to room temperature, a thick layer of white, wool-like products was collected on the surface of the ceramic boat and the inner wall of the ceramic boat at the downstream end.

The as-synthesized products were characterized and analysed by scanning electron microscopy (SEM; JEOL JSM 6700F), x-ray diffraction (XRD; a PW1710 instrument with Cu $K\alpha$ radiation) and transmission electron microscopy (TEM; JEOL 2010, operated at 200 kV). For SEM observations, the product was pasted on an Al substrate using a conductive carbon paste. Specimens for TEM investigations were briefly ultrasonicated in ethanol, and then a drop of the suspension was placed on a carbon film coated holey copper grid. The photoluminescence (PL) spectrum was obtained using an Edinburgh FLS 920 fluorescence spectrophotometer (Xe 900 lamp) at room temperature. The excitation wavelength was 255 nm and the filter wavelength was 310 nm.

3. Results and discussion

The morphology of the products was examined using SEM. A typical SEM image for Al_2O_3 nanowires is shown in figure 1(a). The image shows that large-scale Al_2O_3 nanowires were formed in high yield and the nanowires have diameters ranging from 20 to 60 nm and lengths up to several tens of micrometres. A bulk quantity of the products was analysed by means of XRD. As shown in figure 1(b), all the diffraction peaks can be indexed to those of the bulk α - Al_2O_3 (JCPDS: 10-173). The general TEM morphology for the as-synthesized product and a single nanowire is shown in figures 2(a), (b) and (c). It can be seen from figures 2(a) and (b) that the diameter of these Al_2O_3 nanowires is about 30 nm, and it should be noted that particles were observed at the top of the nanowires. Figure 2(c) shows Al_2O_3 nanowires (about 20 nm) ended with a very thin sheet (width of about 120 nm and thickness of about 10 nm). Energy-dispersed x-ray spectrometry (EDX) analysis shows that the nanoparticles mainly contain Ti and Al and a minor amount of O (figure 2(e)) and the stem only contains Al and O (figure 2(f)), where Cu peaks were generated from the supporting Cu grids and the C peak was mainly a result of the carbon film on the Cu grid. Figure 2(d) shows a typical high-resolution TEM (HRTEM) image and SAED pattern (inset) recorded perpendicular to the long axis and reveals that the Al_2O_3 nanowire is single crystalline with an inter-planar spacing of 0.65 nm, in agreement with the d value of the (002) planes ($d = 0.6498$ nm) of the α - Al_2O_3 crystal. The result also indicates that the nanowires grew along the $\langle 001 \rangle$ direction.

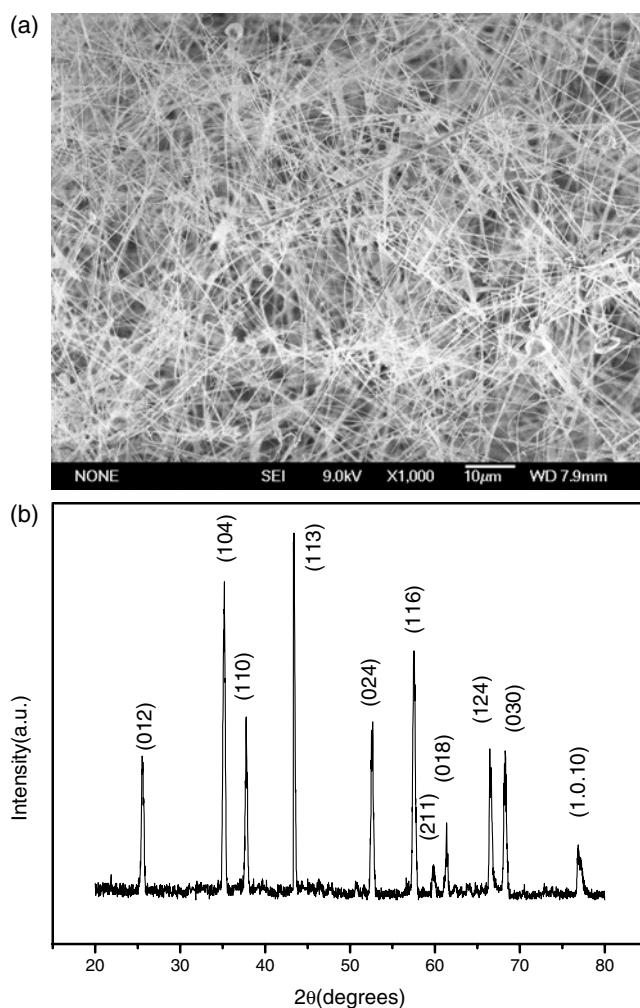


Figure 1. The structure of α -Al₂O₃ nanowires: (a) an SEM image of the as-synthesized large-scale Al₂O₃ nanowires; (b) an XRD pattern from the Al₂O₃ nanowires.

Wagner and Morales suggested a vapour–liquid–solid (VLS) growth process [13, 14] based on the observation of Au–Si particles and FeSi₂ nanoparticles at the ends of Si whiskers and nanowires. For Al₂O₃ nanowires, there exists a nanoparticle at the end of the nanowire (figures 2(a) and (b)). The different compositions of the stem (figure 2(f)) and the nanoparticle (figure 2(e)) reveal that the presence of Ti and Al and a minor amount of O in the nanoparticle at the end of the nanowire presents strong evidence for a growth process dominated by a VLS mechanism. In the case of inorganic particles, it is experimentally and theoretically well established that, in the nanometre range, the melting temperature, T_m , decreases with decreasing radius, R [15, 16]. While the lowest liquid eutectic shown on the published binary phase diagram for Ti and Si is above 1300 °C, Kamins *et al* [17] reported that Ti-catalysed Si nanowires were grown in the mid-600 °C temperature range by the CVD method. Korgel *et al* [18] used size-monodisperse Au nanocrystals to direct Si nanowire growth with narrow wire diameter distributions with a supercritical fluid solution-phase approach at a temperature of 500 °C. In our experiment, while the melting temperature and transition temperature of

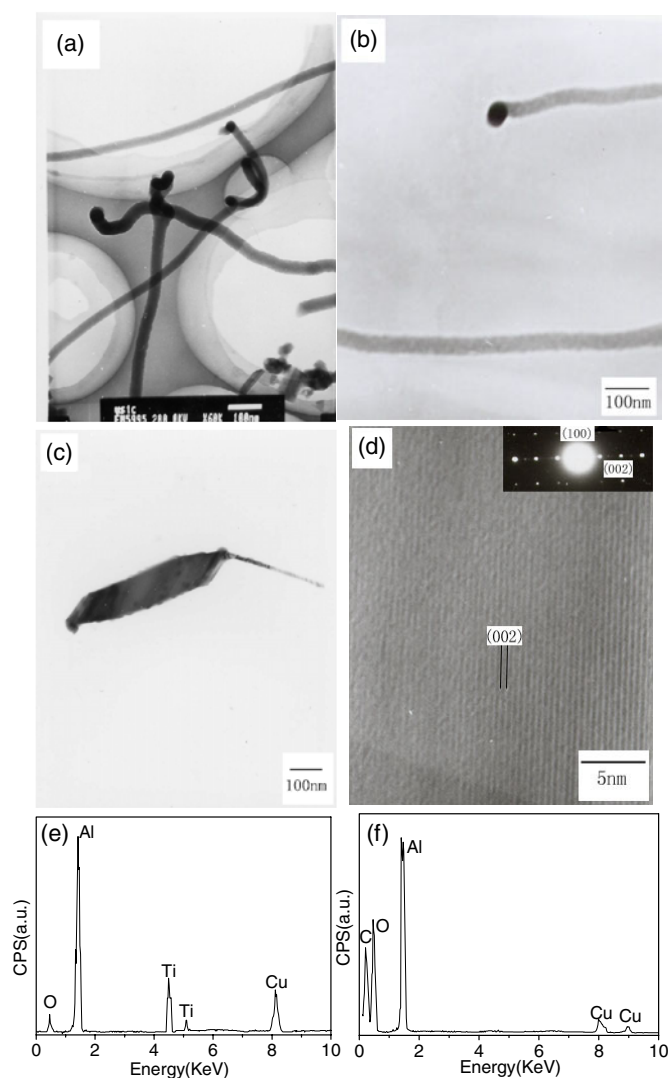


Figure 2. Typical TEM images showing the general morphology of Al_2O_3 nanowires: (a) a TEM image of Al_2O_3 nanowires; (b) a TEM image of an Al_2O_3 nanowire with an Al/Ti alloy tip; (c) a TEM image of an Al_2O_3 nanowire ended with a very thin sheet; (d) an HRTEM image of an Al_2O_3 nanowire and a corresponding SAED pattern (the inset) of the nanowire; (e), (f) EDX spectra of the nanoparticle and nanowire: (e) corresponds to the nanoparticle at the end of the nanowire and (f) to the nanowire.

Al_3Ti are about 1350°C , the liquid nanoparticles can be formed because the size of Al_3Ti is in the nanometre range. The growth of these Al_2O_3 nanowires may involve the following reactions [19]:



A Ti-rich region can be formed according to reaction (1) at 600°C and then reacted with Al to form Al_3Ti nanoparticles according to reaction (2) [19]. The Al_3Ti alloys may form a liquid phase that can initiate nanowire growth by absorbing gaseous Al and O through the VLS step

where O comes mainly from the residue oxygen in the reaction chamber and from leaking into the reaction chamber [20, 21]; when Al and O supersaturate in the liquid droplets, Al₂O₃ precipitates continuously to form nanowires.

The influence of reaction temperature, the pressure in the furnace and reaction time on the morphology of Al₂O₃ nanowires was investigated. If the temperature was lower than 1050 °C (other parameters being essentially the same) the reaction was very incomplete, and little of the Al and TiO₂ powders still existed in the final product. If the temperature was increased beyond 1300 °C, a product with α -Al₂O₃ crystals was detected. Therefore, the essential temperature range for the synthesis of Al₂O₃ nanowires is 1050–1300 °C. The content of oxygen in the reaction chamber is also important for the morphology of as-synthesized product. Overabundance of O in the reaction chamber is unsuitable for growing α -Al₂O₃ nanowires. The tube furnace was purged with high-purity Ar for 2 h prior to heating to remove some oxygen from the furnace and the pressure of the reaction chamber is about 250 Torr. Because if there is sufficient oxygen in the system a thin Al₂O₃ layer will be produced on the surface of the starting material to prevent the reaction from continuing. For example, we introduced a mixture gas (90% Ar and 10% O₂) into the reaction chamber on purpose, and the other reaction parameters are kept the same as before; we did not find any wire-like nanostructures and a thin layer of Al₂O₃ was found to form on the surface of the starting material of the reaction materials. In our experiment, it was also found that the reaction time had a great influence on the product morphology. When the reaction time was shorter than 30 min the reaction was incomplete. If the reaction time was longer than 100 min, a product with α -Al₂O₃ whiskers was detected. In addition, we find that the as-synthesized product only contains α -Al₂O₃ crystals (no α -Al₂O₃ nanowires were found) when we used commercial TiO₂ powders (about 1 μ m) instead of nanometre-sized TiO₂ powders (about 50 nm). The growth mechanism of Al₂O₃ nanowires is similar to previous reports [22–24]. The morphologies of the Al₂O₃ nanowires are determined by means of a combination of growth kinetics and thermodynamics. Thermodynamics requires the formation of crystals with well-faceted surface planes with low surface energy that is strengthened by kinetics where the growth rate is higher for high-energy surfaces and lower for low-energy ones, and only surfaces with low energy could survive in the final crystals. However, as for the growth of low-dimensional nanostructures such as Al₂O₃ nanowires, the difference in growth rate between varied planes could be enhanced and a real thermodynamic equilibrium crystal shape would not be reached. The low-energy surface defines the planes that can be present in the final product from the thermodynamic point of view, while the growth kinetics determines the growth direction and the morphology of the product.

In previous work, it was proposed that the growth of nanostructures with different morphologies—sizes, compositions and microstructures—was mainly controlled by the distance between substrates [25], the total reaction time [26] and the substrate temperature [27, 28]; however, the gas flow rate and the pressure in the furnace also have an influence on the product size and property distributions. Both these parameters are correlated in such a manner that higher flow rate increases the Al partial pressure. The Al vapour pressure at equilibrium is a function of the temperature which can be altered by varying the position of the source materials containing Al in the temperature field of the furnace. Therefore, the Al partial pressure could also be varied at the constant Ar gas flow rate. For example, a too high temperature leads to large crystals, while a too low temperature generally favours the formation of amorphous particles [29]. More work is under way in an effort to provide a better understanding of the growth mechanism and to prepare nanostructures with different structures or different materials.

The room temperature photoluminescence of the Al₂O₃ nanowires was examined and is shown in figure 3 (curve (b)). PL measurements showed a strong blue luminescence band in

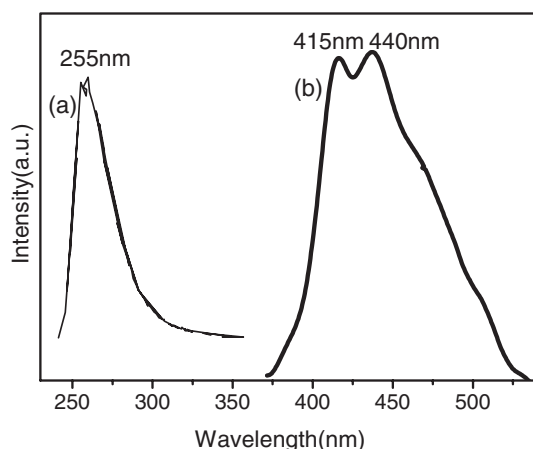


Figure 3. A PLE (curve (a)) spectrum and a PL spectrum (curve (b)) of the Al_2O_3 nanowires.

the wavelength range of 400–500 nm with two peaks at 415 and 440 nm. It is reported that Ti doped Al_2O_3 showed a broad blue emission band near 420 nm besides the red one. As regards the origin of the 420 nm blue emission in Ti doped Al_2O_3 , Lacovara *et al* [30] interpreted this as being possibly F colour centres, while Chen *et al* [31] proved that the blue emission is due to a centre other than a trivalent Ti^{3+} ion or a tetravalent Ti^{4+} ion and most probably an F^+ -type colour centre formed in the crystal by using synchrotron radiation. They supported the suggestion that an F^+ -type colour centre is responsible for the blue emission band near 420 nm rather than a trivalent Ti^{3+} ion or a tetravalent Ti^{4+} ion. Ti has some solubility in Al_2O_3 and there is a minor amount of Ti in the as-synthesized $\alpha\text{-Al}_2\text{O}_3$ nanowires. If the stem of the nanowires contains Ti, EDX analysis would have detected Ti along the length of the nanowire rather than only at the top end. To clarify the origin of the PL band with two peaks at 415 and 440 nm, we examined the PLE spectrum of the as-synthesized $\alpha\text{-Al}_2\text{O}_3$ nanowires and the corresponding result is displayed in figure 3 (curve (a)). This spectrum clearly shows a PLE peak at about 255 nm. For F centres, it should have a strong PLE band at 207 nm (6.05 eV) [32], but we have not observed the 207 nm PLE band. Previously, Wu and Zhang *et al* have assigned the PLE bands at 258 and 255 nm as corresponding to a certain transition of the F^+ centre [11, 33]. It has been reported that F^+ centres (oxygen vacancies with one electron) in $\alpha\text{-Al}_2\text{O}_3$ cause ultraviolet or violet PL bands and blue PL bands in nanostructured alumina [11, 33–35]. For example, PL bands at 394 and 392 nm were observed from $\alpha\text{-Al}_2\text{O}_3$ nanowires and nanobelts [11], two peaks in the wavelength region of 400–550 nm were seen in the emission from Al_2O_3 films [34] and a PL band occurs in the wavelength range of 400–600 nm in porous alumina membranes [35] which has been reported to originate from singly ionized oxygen F^+ centres. We believe that the PL peaks observed in our experiment are associated with such F^+ centres.

4. Conclusions

In summary, we have described a method for the synthesis of $\alpha\text{-Al}_2\text{O}_3$ nanowires in bulk quantities by simple physical evaporation. SEM and TEM observations show that $\alpha\text{-Al}_2\text{O}_3$ nanowires have diameters ranging from 20 to 60 nm and lengths up to several tens of micrometres. PL measurements showed a strong blue luminescence band in the wavelength

range of 400–500 nm with two peaks at 415 and 440 nm, and the origin of these PL bands was attributed as F⁺ centres in the nanowires. These α -Al₂O₃ nanowires may possibly be useful as reinforcements in composites. In addition, considering their high aspect ratio, good optical properties and low cost, the α -Al₂O₃ nanowires are also suitable building blocks for use in protective films in composites.

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