

Non-catalytic and template-free growth of aligned CdS nanowires exhibiting high field emission current densities†

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Various CdS nanostructures, including nanoparticle film, bundles of quasi-aligned and well-aligned nanowires, were fabricated with a non-catalytic and template-free MOCVD process. The well-aligned CdS nanowires exhibit unusually high field emission current densities of 225 mA cm⁻² at the applied electric field of 20 V μm⁻¹.

Semiconductor materials with one-dimensional (1-D) nanostructures have attracted much research attention in recent years because of the novel properties resulting from this special dimensionality.¹ It is generally accepted that 1-D nanostructures serve as a unique system to investigate the dependence of thermal, electrical, electronic, and optical properties on the dimensionality and structure size. Since CdS is one of the most important II–VI semiconductors with vital optoelectronic applications in non-linear optical devices and flat panel displays,² preparation of various 1-D CdS nanostructures such as wires, rods, and tubes has been intensively studied with a wide range of synthetic methods. For example, high-density CdS nanowires have been prepared by electrochemical deposition using anodic aluminium oxide as the sacrificial template.³ Production of CdS nanowires⁴ and nanotubes⁵ through gaseous routes was achieved with the vapour-liquid-solid (VLS) growth mechanism and the assistance of sacrificial template, respectively. These processes, however, involved usage of sacrificial templates or guiding catalysts, whose removal may complicate the application of the nanostructures. In this work, bundles of well aligned CdS nanowires were fabricated in a non-catalytic and template-free metal-organic chemical vapor deposition (MOCVD) process. In addition to nanowire bundles, films of nanoparticles were also obtained at lower deposition temperatures. Their field emission properties were investigated and compared. It is generally believed that the field emission property (efficiency) of a material is related to its shape. We found, in this work, well aligned CdS nanowires produced unusually high field emission current density, while no significant field emission was detected for the nanoparticle film sample. The unusually high field emission current density achieved makes the well-aligned CdS

nanowires a promising candidate for high current field emitter of flat panel displays and high brightness electron sources.⁶

CdS nanostructures were synthesized with a hot-wall MOCVD process operated in a three-zone horizontal tube furnace by using quartz plates as the substrates. The single-source precursor of CdS, Cd(S₂CNProp)₂, which had been proven capable of growing CdS nanowires with the VLS mechanism at low temperatures, was used and prepared according to our previous study.^{4b} The precursor was heated to a temperature of 160 °C to generate needed precursor vapours. The precursor vapours were introduced into the furnace by carrier gas N₂. The furnace temperature was set at 350, 450, and 550 °C for different runs of experiments. All reactions were run at a carrier gas flow rate of 50 sccm and a system pressure of 30 torr. At the furnace temperature of 450 °C, bundles of quasi-aligned CdS nanowires were found to grow on top of a 1 μm thick buffer layer laid on the substrate surface (Fig. 1a). The nanowires had a diameter of 30 nm and length of about 700 nm. On decreasing the furnace temperature to 350 °C, while keeping all other deposition conditions fixed, nanoparticle films of CdS with a particle diameter of 50 nm were found to grow uniformly over the substrate (Fig. 1b). If the furnace temperature was increased to 550 °C, bundles of CdS nanowires were again obtained but with much improved wire alignment (Fig. 1c). The well-aligned nanowires had a diameter of 30 nm and length of several micrometers. The furnace temperature certainly played an important role in determining the deposit morphology, which in turn led to dramatic differences in field emission performance, as discussed later.

The morphology and crystallographic structures of the CdS nanostructures were further characterized with TEM and HRTEM. Fig. 2(a) shows a typical TEM image of the free-standing bundles of CdS nanowires. The dot pattern of the inset SAED image suggests single crystallinity for the bundle of CdS nanowires and was indexed to the hexagonal crystalline structure. The lattice-resolved HRTEM images taken at the marked regions of the bundle of quasi-aligned nanowires are shown in Figs. 2(b), (c), and (d) to further reveal their detailed crystallographic

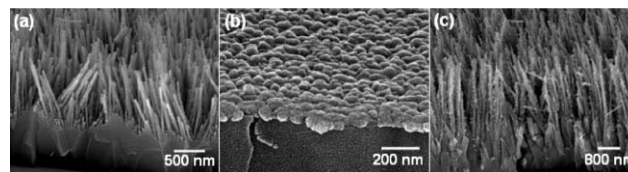


Fig. 1 Tilt-angled SEM images of CdS nanostructures grown on quartz substrates: (a) bundles of quasi-aligned nanowires, (b) nanoparticle film, (c) bundles of well-aligned nanowires.

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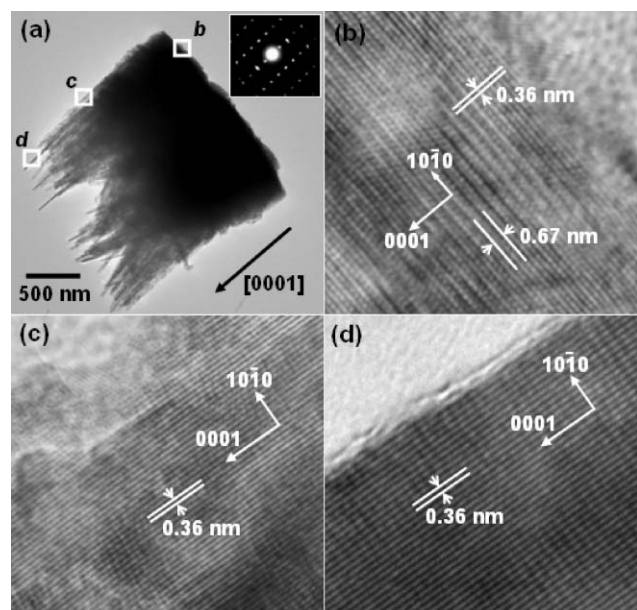


Fig. 2 (a) TEM image of the bundles of CdS nanowires prepared at furnace temperature of 450 °C. Inset SAED pattern was taken along the $[1\bar{2}10]$ zone axis. (b)–(d) Enlarged HRTEM images taken at the marked regions of (a).

structures. The images show interlayer spacings of 0.67 and 0.36 nm, in good agreement with the d spacings of the (0001) and (10–10) lattice planes of the hexagonal CdS crystal. The axis of the CdS nanowires was parallel to the [0001] direction, indicating the nanowires were grown along the [0001] direction. This [0001] direction was also found predominant in the buffer layer and buffer-wire interfaces. These results suggested that the bottom of the buffer layer of the bundle grew in a preferential direction of [0001], and this preferred growth direction remained predominant all the way through the buffer-wire interface to lead to the formation of 1-D nanowires on top of the buffer layer. For the well-aligned nanowire samples, their TEM and HRTEM images are shown in Figs. 3(a) and (b). From Fig. 3(a), the well-aligned CdS nanowires had a diameter of 30 nm and length of over two micrometers, in agreement with the SEM observation. The growth direction of [0001] was also found preferential in the well-aligned nanowire samples as shown in Fig. 3(b). For the nanoparticle film samples, they appeared polycrystalline with grains clearly visible from the HRTEM images (Figure S1†). The XRD patterns of the as-prepared CdS nanostructures are shown in Fig. 3(c). The diffraction peak of (002) is much more pronounced than it should be, as in the reference powder samples, which implies that the CdS nanostructures, both nanoparticle film and bundles of nanowires, were grown in the preferential direction of [0001] with large scale alignment present.

A possible growth mechanism for these CdS nanostructures was proposed as follows. Since no catalysts were used and no guiding heads were found at the tips of the as-grown CdS nanowires, the common 1-D growth mechanism of VLS can be ruled out. Initially, the CdS deposits grew in the 3-D island mode because of the large difference in surface free energy between CdS and the quartz substrate.⁷ With long enough deposition time, the islands grew larger and overlapped to form particle films as observed for

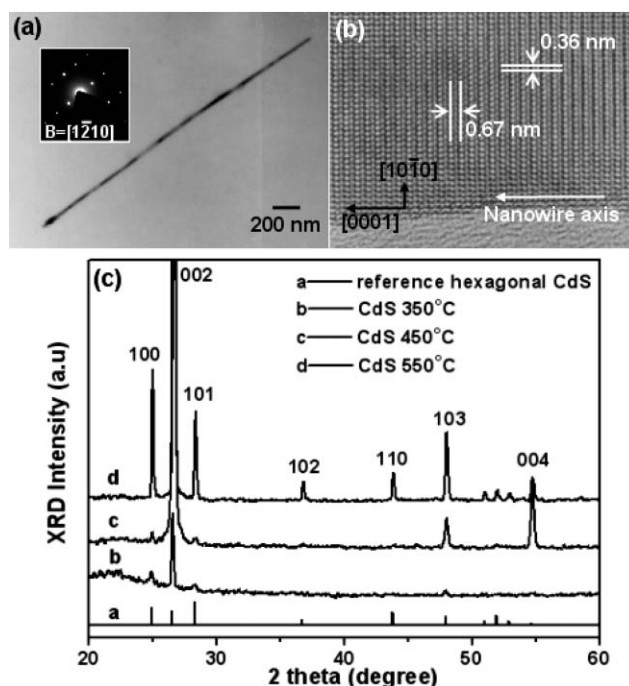


Fig. 3 (a) TEM image of a free-standing CdS nanowire, freed from the substrate with ultrasonic agitation, prepared at the furnace temperature of 550 °C. The inset of (a) is the corresponding SAED pattern. (b) Enlarged HRTEM image with the d -spacing, lattice planes, and growth direction indicated. (c) XRD patterns of the as-grown CdS nanostructures.

the case of 350 °C (Fig. 1b). When the furnace temperature was raised higher, the growth rate was increased and the particle film grew thicker, during which the preferential growth habit of CdS in [0001] became more and more dominant as evidenced from Fig. 2. Towards the end of the deposition, the consumption of precursor led to decrease in precursor vapour pressure although the total pressure was maintained constant. The decrease in precursor vapour pressure favours the growth mode of high surface-to-volume ratio,⁸ enabling a shift from film to wire growth. From another viewpoint, the amount of precursor vapour became insufficient to support film growth, thus favouring the island growth mode which together with the preferential growth habit of CdS resulted in nanowire formation. For typical hexagonal crystals, such as ZnS, ZnO, and CdS, growth of the nanocrystals with a preferential direction along the c -axis, the direction of the fastest growth rate, without the presence of guiding catalysts or templates was commonly observed in the literature.⁹ As has been pointed out in ref. 9(d), the growth of CdS may proceed as a stacking process of the $\{CdS_4\}$ tetrahedrals by sharing their common corners. Since at the interface of CdS each tetrahedral has a corner in the [0001] direction, this favors the growth of CdS along the [0001] axis (the c -axis).^{9(d)} In the present work, with suitable control of the deposition conditions, growth of 1-D CdS nanostructures along its c -axis direction was also achieved. Interestingly, even for the nanoparticle film, a more common deposit form of CdS,¹⁰ the c -axis was still the preferred growth direction as can be inferred from the XRD pattern shown in Fig. 3(c). The diffraction peak of (002) is much more pronounced than it should be as in the reference powder samples.

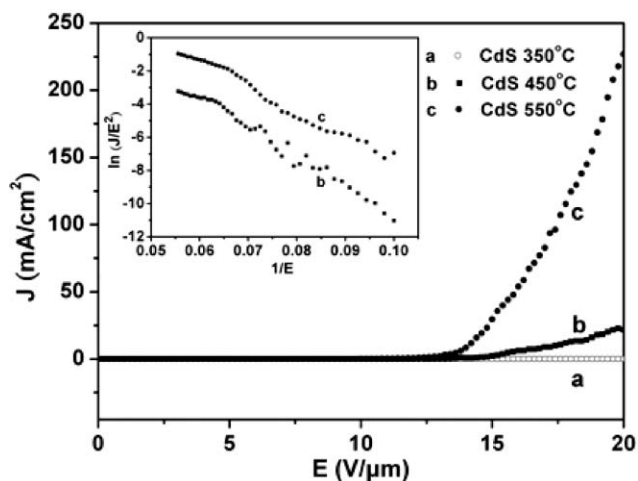


Fig. 4 Plot of field emission current density *versus* applied electric field for the as-grown CdS nanostructures. The inset shows the F-N plot for nanowires prepared at 450 and 550 °C.

The field emission property of the various CdS nanostructures was measured with a 100 μm gap between the anode and the cathode in a vacuum chamber maintained at a pressure of 1.5×10^{-5} torr. To conduct the measurements, CdS nanostructures were grown on Si(100) substrates. The CdS nanostructures grown on Si(100) substrates were with similar morphologies to those grown on fused silica substrates (Figs. S3–S5†). The plot of the field emission current density (J) *versus* the applied electric field (E) for nanoparticle films, bundles of quasi-aligned and well-aligned nanowires is shown in Fig. 4. No apparent field emission was observed for the nanoparticle film sample. As for the bundles of quasi-aligned and well-aligned nanowires, turn-on electric fields of 8.9 and 7.8 $\text{V } \mu\text{m}^{-1}$ (at the current density of $0.1 \mu\text{A cm}^{-2}$) were observed, with corresponding threshold current density (1 mA cm^{-2}) achieved at about 14.4 and 12.2 $\text{V } \mu\text{m}^{-1}$, respectively. The turn-on electric fields of the present work are higher than that for the array of CdS nanowires prepared with a solvothermal process reported in ref. 11. This may be due to the existence of the thick buffer layer grown between the roots of the nanowires and the substrate surface. Stronger electric fields are needed to push electrons through this buffer layer which lacks the strong electron guiding capability that 1-D nanostructures have. Nevertheless, an unusually high emission current density of about 225 mA cm^{-2} was achieved at the applied electric field of $20 \text{ V } \mu\text{m}^{-1}$ for the well-aligned nanowire samples. This value is much higher than those commonly reported for semiconductor materials.^{6b,11,12} The field emission characteristics were further analyzed with the Fowler–Nordheim (F-N) theory.¹³ The typical F-N plot for the bundles of quasi-aligned and well-aligned nanowire samples is shown as the inset of Fig. 4. Straight lines resulted at high applied electric fields. This linearity indicates that the field emission from the CdS nanostructures prepared in our work followed the F-N theory. From the line slopes, the field enhancement factor β was estimated to be about 324 and 397 for the bundles of quasi-aligned and well-aligned nanowires, respectively, by using the work function of 4.2 eV for CdS.¹⁴ The value of β relates to the geometry, structure, and density of the nanostructures grown.^{6b} In

this work, CdS nanowires prepared at 550 °C were with a higher aspect ratio ($L/r = 2.5 \mu\text{m}/30 \text{ nm}$) and better alignment (see Fig. 1) than those of nanowires prepared at 450 °C ($L/r = 0.7 \mu\text{m}/30 \text{ nm}$). This accounted for the higher field enhancement factor obtained for nanowire samples prepared at 550 °C.^{12b,15} Consequently, the as-grown bundles of well-aligned CdS nanowires showed much better field emission property with high emission current densities.

In conclusion, by carefully controlling the deposition conditions, we successfully synthesized various CdS nanostructures in a non-catalytic and template-free MOCVD process. The as-grown nanoparticle films (350 °C), bundles of quasi-aligned (450 °C), and well-aligned nanowires (550 °C) were fabricated at increasing furnace temperatures. The furnace temperature certainly played an important role in determining the deposit morphology, which in turn led to dramatic differences in field emission performance. The as-grown bundles of well-aligned CdS nanowires can achieve high emission current densities. This high current density would enable bundles of well-aligned CdS nanowires to produce sufficient brightness for the application of flat panel displays and to serve as high brightness electron sources.⁶

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