Template-free Growth of Vertically Aligned CdS Nanowire Array Exhibiting Good Field Emission Property

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A novel template-free solvothermal route was successfully designed to fabricate single-crystal vertically aligned CdS nanowire array, and its field emission property for the first time, was studied. The relatively high emission current density and low turn-on field make the CdS nanowire array one of the promising candidates for field-emission display.

In the past few years, one-dimensional (1-D) nanostructure semiconductors have received much attention because of their peculiar physical properties and potential applications in nanodevices. Many attempts have been made to fabricate 1-D nanostructure semiconductors utilizing a variety of nanofabrication technique and crystal growth methods. As we know, assembling these nanostructures into well-aligned arrays and patterning them conveniently is beneficial to make their way to nanodevice. As a regular procedure, the hard template (such as anodic aluminium oxide membranes) was used to induce the anisotropic growth of those condensing or depositing materials and form nanorod or nanowire array in the pore, and the diameter of the wire or rod can be controlled by the size of the pore. However, it is inevitable for those 1-D arrays to collapse when the template was dissolved. Even if those arrays can be kept by partly dissolved template, it is difficult to assemble this composite structure to nanodevice. Few reports was involved with template-free growth of 1-D nanostructure arrays.[1–3] In all, it is a great challenge to assemble those 1-D nanostructures into the arrays without assistance of hard template.

CdS, as one of the most important II–VI group semiconductors, exhibited vital optoelectronic applications for laser light-emitting diodes, optical devices, and solar cells, many procedures have been designed to obtain CdS single-crystal nanorods or wires including hard template methods (AAO membranes),[4] soft template methods (such as liquid crystal, micellar, polymer),[5] structure-directing coordinate solvent methods (such as solvothermal route),[6] thermolysing single-source precursor and vapor–liquid–solid (VLS) methods.[7] Furthermore, by constraining growth in AAO membranes, its array has also been successfully fabricated.[8] In our previous work, a novel organic amine-assisted solvothermal elemental route has been developed to obtain a series of II–VI group 1-D nanostructure including single-crystal CdS nanowire.[6] In our recent work ZnO nanorod arrays with high optical property have grown directly on zinc foil by a novel designed route,[9] which implied that the direct growth of the nanorod or wire array on metal basis might be a versatile method. In this communication well-oriented CdS nanowire array was synthesized on cadmium foil via the similar solvothermal elemental route reported in Ref. 6.

Well-aligned CdS nanowire array was grown directly on cadmium foil substrate. The experimental procedure was designed as follows: thiourea (A. R.) and cadmium foil (99.9975% Alfa Aesar) with a mol ratio of 1:5, were added to a Teflon-line stainless-steel autoclave with a capacity of 50 mL. Then the autoclave was filled with ethylenediamine up to 80% of the total volume. The autoclave

was maintained at 180 °C for 12 h and then allowed to cool to room temperature, The foil covered with yellow precipitation was then collected from solution, rinsed with deionized water and dried in air at 40 °C. The general morphology of the CdS nanowire array was observed by field emission scanning electron microscopy (FESEM), performed on a JEOL-JSM-6700F scanning electron microanalyzer. The crystallinity and the phase purity can also be analyzed by X-ray diffraction measurement (Rigaku X-ray diffractometer with Cu Kα radiation). The crystallinity and oriented growth direction were deduced by transmission electron microscope image combing with electron diffraction (Hitachi Model 800 at 200 kV), the sample was obtained by scraping the array on the metal surface and dispersed in absolute ethanol, then the solution was dropped onto Cu grids.

The general morphology of the CdS nanowire array on the surface of the metal substrate was shown in Figrues 1a–1c. The nanowire array can be easily striped off, suggesting that the CdS nanowires stand freely on the substrate although the substrate also acts as one of reactant resources. As can be seen from the view of the cross-section SEM image, the densely packed arrays of CdS nanowires, with a uniform diameter of about 60 nm and length of 3.0 μm, are parallel to each other and perpendicular to the substrate, forming self-oriented regular array. They have smooth surface, and are straight along their axes. Furthermore, some rods were assembling into bundles, and TEM image also revealed these bundles shape (Figure 2a). This novel wire arrays resulted from the lamellar inorganic–organic intermediate, which will be discussed later. Figure 2b shows an individual CdS nanowire with the diameter about 60 nm. The corresponding SAED pattern (Figure 2c) taken from a single nanowire can be exactly indexed to a hexagonal CdS single crystal recorded from the [$\bar{1}10$] zone axis, and shows that the growth direction of CdS nanowires is [001]. Figure 3a showed the XRD pattern of the wire array. All of the reflection could be readily indexed to the mixed phase: the cadmium base and the hexagonal phase [space group: $P6_3/m$] CdS with [001] orientation. As expected, the highly enhanced (002) peak can be seen as a result of its vertical orientation. The result also shows consistency with the conclusion of the preferential orientation deduced from the SEAD pattern. From the XRD pattern the peaks from cadmium can be clearly identified, because it is reasonable that X-ray can penetrate the CdS nanowire array as its size just reaches several micrometer. The size and orientation of a single nanowire are similar to those obtained using Cd powder and ele-
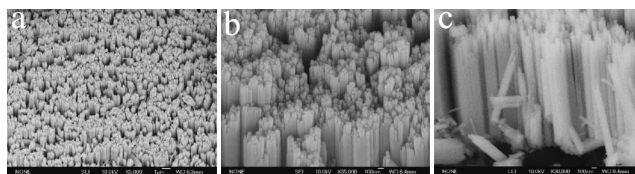

Figure 1. (a) FESEM image of CdS nanowire array grown onto cadmium foil. (b) An enlarged image of the nanowire array. (c) Cross-sectional FESEM image of the array.
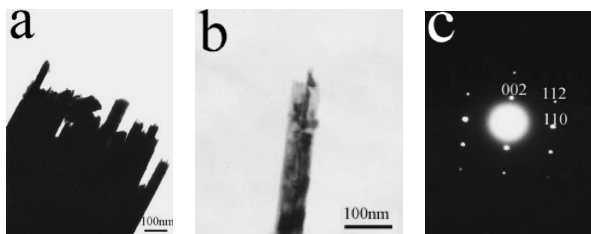
Figure 2. (a) TEM image of the wire array scraped from the metal surface. (b) Typical image of a single CdS nanowire. (c) Corresponding SEAD pattern recorded from the [110] zone axis implies its growth along *c* axis.

mental S as reactants, which also implies the similar growth mechanism.

XPS was carried out to derive composition information about the obtained arrays, Two strong peaks at 162.50 and 406 eV correspond to S(2p) and Cd(3d) binding energies, respectively, and the peak areas of the Cd and S cores were measured and used to calculate the Cd:S ratio for the nanowire. The quantification of the peaks gives a Cd:S ratio of 1.08:1 (not shown here). Elemental analysis indicates consistent result that the atomic ratio of Cd:S is 1.03:1 (not shown here).
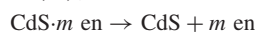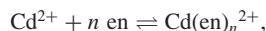
The field emission measurements were carried out by a two-parallel-plate configuration in a vacuum chamber with a pressure of 8.0×10^{-7} Pa. The sample was attached to a stainless-steel plate using conducting glue as cathode with the other stainless-steel plate as anode. The distance between the electrodes was $300 \mu m$. The emission current was measured by applying a voltage increasing from 1 to 4 kV with a sweep step of approximate 50 V, and was monitored using a Keithley 485 picoammeter. The curve of emission current densities versus electric field (J–E) for a typical CdS nanowire array with an emitting surface area of $5.4 \, mm^2$ is shown in Figure 3b. Electronic emission is observed at an electric field as low as $4.7 \, V/\mu m$. The electron emission turn-on field (E_{to}), defined as the macroscopic fields reqired to produce a current dencity of $10 \, \mu A/cm^2$, is only about $6.70 \, V/\mu m$, which is similar to carbon nanotubes.[10] Reproducibility tests from ten different samples indicate that the CdS nanowire array have E_{to} in the range of 5.1–7.3 $V/\mu m$. Field emission current density in excess $0.3 \, mA/cm^2$ has been observed at $12.8 \, V/\mu m$. The relatively high emission current density, high stability, and low turn-on field make the CdS nanowire array one of the promising candidates for field-emission display. However, the current-field characteristics deviate from Fowler–Nordheim theory, i.e., showing a nonliner Fowler–Nordeim plot, which might suggest a different field emission mechanism for our CdS nanowire array.

A solvent coordinating molecular template mechanism (SCMT) has been accounted for the growth of CdS nanowire array in our previous work. In a typical SCMT process, ethylenediamine(em) acts as a structure-directing molecule to be incorporated into the inorganic framework by forming unstable lamellar inorganic–organic intermediate, and then escapes from the framework to

form nanocrystals with desirable morphologies.[6] In the first step, thiourea decomposed into sulfur at low temperature in the basic environment, which combined with cadmium foil with and formed CdS under an ionization equilibrium.

$$Cd + S \rightarrow CdS \rightleftharpoons Cd^{2+} + S^{2-}$$

In en solution the equilibrium was destroyed, Cd^{2+} ion coordinated with en molecule to form $Cd(en)_n{}^{2+}$ as the complex of $[Cd(en)_n]^{2+}$ is quite stable (for example, as for$[Cd(en)_2]^{2+}$, the stability constants, $\log \beta_2 = 10.09$),

$$Cd^{2+} + n \text{ en} \rightleftharpoons Cd(en)_n{}^{2+},$$
$$Cd(en)_n{}^{2+} + S^{2-} \rightarrow CdS \cdot m \text{ en} + (n - m) \text{ en},$$
$$CdS \cdot m \text{ en} \rightarrow CdS + m \text{ en}$$

At relatively elevated temperature (180 °C) the reaction between $Cd(en)_2{}^{2+}$ and S^{2-} produced the CdS·*m* en, an inorganic–organic-layered structure, and the compound contain atomic sheets of inorganic CdS frameworks spaced by ethylenediamine molecules, which serve as bridged ligands between two Cd atoms in neighboring inorganic layers. As the layered structure is stabilized by the interlayer enthylenediamine molecules, it is considered that the layered structures would collapse upon the removal of the organic spacers, as this structure was unstable at a sufficiently high temperature, just bundles of CdS nanowires were left. In our designed experiment, two crucial factors were attributed to the formation of nanowire array; Firstly, as discussed above, the preformed lamellar precursors would crack into interlinked nanowires, and the products would exhibits bundle-like shape as shown in Figure 2a, these wires are parallel to each other and the distance between the neighboring nanowire is approximately as much as the size of the ethylenediamine molecule. Secondly, as Cd was acted as both cadmium resource and growth substrate, it is imaginable that the growth is prone to be perpendicular to the basis.

In summary, an organic amine-assisted solvothermal method was designed to fabricate CdS nanowire array directly on Cd foil for the first time. Field emission measurements showed that the oriented CdS nanowire array is a good field emitter with high emission current density and low turn-on field. The procedure is also converted on wafer just by evaporating cadmium on its surface and patterning it conventionally by covering Au or polymer. As solution-based approach holds intrinsic advantage of mild synthetic condition, simple manipulation and large scale-up production, the ability to grow high-quality CdS nanowire array is expected to greatly increase the versatility and power of these building block for "insitu bottom-up" designed nanoscale photo electronic device application based on CdS nanowire array.

Figure 3. (a) XRD pattern of the CdS well-aligned nanowire arrays on zinc foil. (b) Emission J–E curves from the oriented CdS nanowire emitter.

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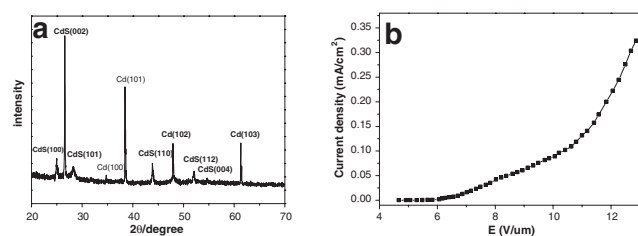10 X. P. Xu and G. R. Brandes, *Appl. Phys. Lett.*, **74**, 2549 (1999).