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Metal/semiconductor hybrids consisting of self-assembled CdS nanoparticles on Cd nanowires*

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We report on the synthesis and the characterisation of metal/semiconductor hybrids consisting of self-assembled CdS nanoparticles on Cd nanowires, which are grown by thermal evaporation of the mixture of CdS and Cr. The growth of the hybrids is attributed to the decomposition of CdS at high temperature and the strain relieving that arises mainly from the lattice mismatch between Cd and CdS. Temperature dependence of zero-field resistance of single nanohybrid indicates that the as-produced Cd/CdS nanohybrid undergoes a metal–semiconductor transition as a natural consequence of hybrid from metallic Cd and semiconducting CdS. The metal/semiconductor hybrid property provides a promising basis for the development of novel nanoelectronic devices.

Keywords: metal/semiconductor nanohybrids, electrical properties, thermal evaporation
PACC: 7280E, 6146, 7360

1. Introduction

Quasi-one-dimensional (1D) nanostructures have aroused increasing interest as a fascinating system for fundamental scientific research with the potential applications in different areas of nanotechnology.[1,2] They provide a good system for studying the dependence of electronic and thermal transport properties on the reduction in dimensionality, and play an important role as both interconnecting and functional units in fabricating electronic and optoelectronic nanodevices. Furthermore, the ultimate device miniaturisation would make individual nanostructures used as functional devices. To enhance the multi-functionality of nanostructures, a unique hybrid with 1D nanostructure, created by combining two materials with different atomic and electronic structures, has been proposed which should display a range of device applications. Until now, many researchers have reported on such a kind of 1D nanohybrid made from two or three types of materials including various metals, semiconductors, insulators, and carbon nanotubes.[3−9] Among these nanostructures, nanohybrids formed by metal and semiconductor are expected to possess "physically and mathematically interesting" properties when metallic inhomogeneities typically degrade the transport properties of a semiconductor, for example, extraordinary mangetoresistance[10] and piezoconductance.[11] In addition, metal/semiconductor nanohybrids may also possess a number of intriguing possibilities for novel electronic devices when their different quantum transport properties are combined.

Thermal evaporation is a common method used to synthesise 1D semiconductor nanostructures.[12−15] Recently, some groups also reported on 1D metal nanostructures synthesised by thermal evaporation.[16,17] In the present paper, we report on novel metal/semiconductor hybrids consisting of self-assembled CdS nanoparticles (NPs) on Cd nanowires (NWs) by thermal evaporation of the mixture of CdS and Cr. The details will be presented about their synthesis, structure and growth process. The electrical transport properties of single hybrid nanostructure are also included. Temperature dependence of zero-field resistance of single nanohybrid indicates that the as-produced Cd/CdS nanohybrids undergo a metal-semiconductor transition, which provides a promising basis for the development of novel nanoelectronic devices.

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2. Experiment

The synthesis was carried out by using an electrically heating furnace with a horizontal quartz tube. Mixture of Cr and CdS powders was selected as source material, which was loaded in a quartz boat and positioned in the centre of the furnace. A cleaned n-type Si wafer coated with an Au film of 20 nm in thickness was placed downstream in the tube (20 cm away from source material). Before evaporation, the reaction chamber was evacuated and flushed out several times using an argon flow to eliminate any residual oxygen. The carrier gas was conducted into the system through a mass flow controller. The evaporation temperature of the mixture powders was set to 1100 °C and maintained for 30 min with an Ar gas flow rate of about 500 sccm. After cooling to room temperature, it was found that the substrate was coated with sponge-like products. And the product was collected for further characterizations through scanning electron microscope (SEM, XL30 S-FEG), transmission electron microscope (TEM, Hitachi H-9000NAR, attached with an energy-dispersive x-ray spectra detector, EDS), and electrical measurement.

3. Results and discussion

Figures 1(a) and 1(b) show two typical low-magnification SEM images of the as-synthesized products with a line-like shape. The productive yield of each synthetical batch is reasonably high. The lengths of the wires range from several micrometers to tens of micrometers while their diameters are less than 100 nm with some nanoparticles on the nanowires (see Figs.1(a) and 1(b)). A highly magnified SEM image (see Fig.1(c)) shows that the morphology of the nanostructures looks like a chain, and a series of NPs are lined along an NW with a uniform spacing between two NPs. An interesting phenomenon is that the NPs are always self-assembled on one side of the NWs.

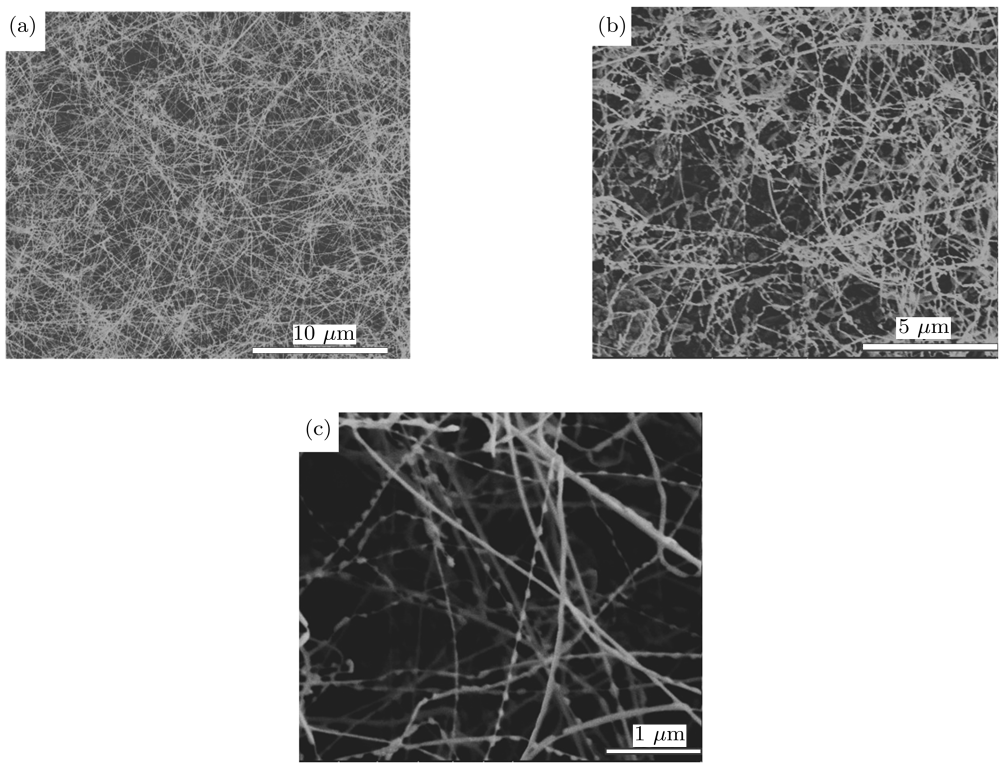


Fig.1. Typical SEM images of the as-synthesized products with a chain-like shape.

Figure 2(a) is a typical TEM image of the nanostructures. The axial NWs are as thin as approximately 20 nm, and their surfaces are fairly smooth. While the NPs have a cone-like shape, their average height is about 40 nm and their contact point onto the axial NW is about 60 nm in size. The spacing between two

adjacent NPs is in a range of 60–80 nm. The TEM image of a section of a typical nanostructure is displayed in Fig.2(b). EDS spectrum obtained by using a 2-nm electron probe from a few of selected areas as marked with the white solid circles in Fig.2(b) indicates that the NP is composed of CdS and the NW is dominantly Cd (Fig.2(c)), which results in a unique NW-NP nanohybrid composed of metallic Cd and semiconducting CdS. Because Cd and CdS have both a hexagonal crystal structure, an epitaxial growth between Cd and CdS could be expected. Figure 2(d) shows a high resolution TEM (HRTEM) image of an interface between CdS NP and Cd NW, which is recorded from the framed region in Fig.2(b). The lattice fringes and the epitaxial interface are clearly observable, which suggests that a well-developed interface is formed between CdS NPs and Cd NWs by our growth method. The HRTEM image also reveals that the axial Cd NW is structurally uniform and contains no defects (at least on the measured length scale), with a d-spacing of 0.234 nm corresponding to the [101] preferential growth direction. Structurally, the lattice parameters are $a = 0.2979$ nm and $c = 0.5617$ nm for a hexagonal Cd, and $a = 0.4135$ nm and $c = 0.6749$ nm for a Wurtzite CdS. There is a large lattice mismatch between Cd and CdS when forming an epitaxial layer. However, in the present work it has been relaxed by forming a set of misfit dislocations pointed out by white arrows in Fig.2(d).

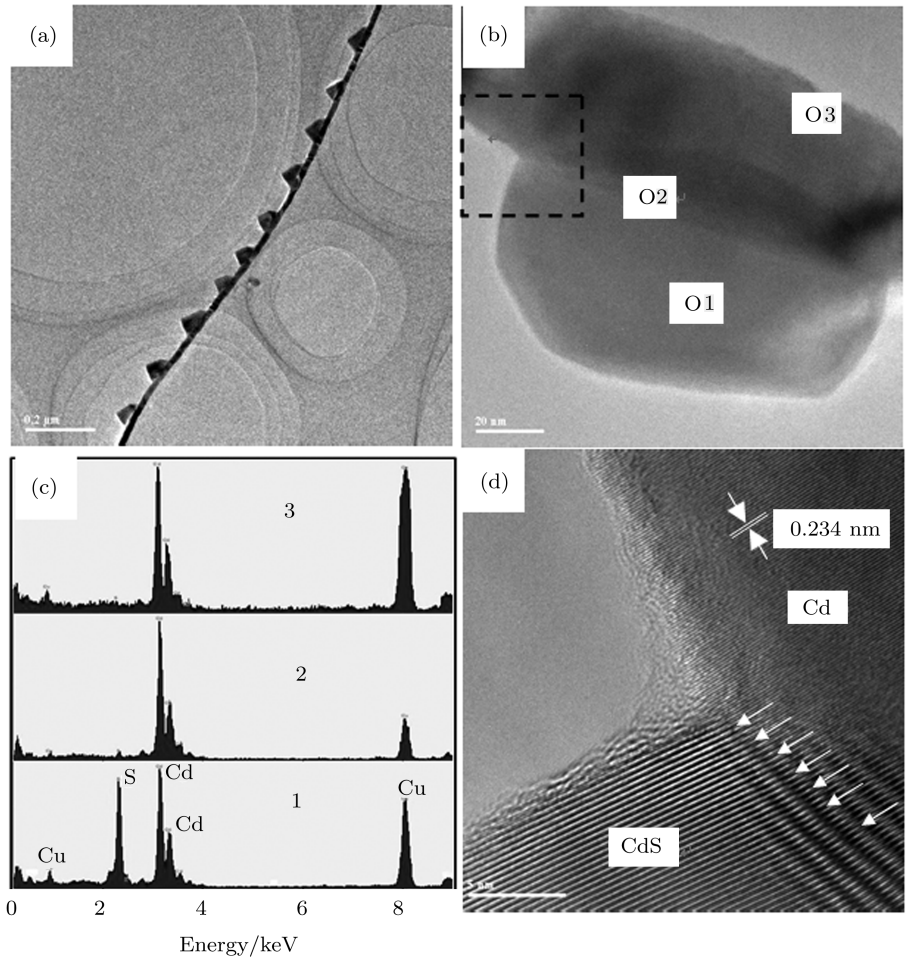


Fig.2. (a) TEM images of a typical nanostructure and (b) a section of a typical nanostructure, (c) EDS spectrum obtained from a few selected areas as marked by the white solid circles in Fig.2(b), which indicates a unique NW-NP nanohybrid composed of metallic Cd and semiconducting CdS, and (d) a typical high resolution TEM image of an interface between CdS NP and Cd NW, which is recorded from the framed region in Fig.2(b).

In the present study, although a mixture of Cr and CdS powders was used as the source material, the products were Cd/CdS NW/NP nanohybrids. It was reported that the decomposition of CdS occurred when it was heated to about 1000 °C,[17] so, we suggest here that the most reasonable source of metallic Cd nanowire comes from the decomposition reaction of CdS vapour because the applied temperature in this work was 1100 °C. Under the present conditions, while Cd atoms from the decomposition of CdS vapour were transported by Ar carrier gas to a low temperature region to form Cd nanowire with Au as catalyst, most of the resultant S atoms from this decomposition reaction reacted with Cr atoms in the powder mixture to form chromium sulphide, which occurs at about 1000 °C. Moreover, the resultant chromium sulphide was very stable even at temperatures higher than 1200 °C.[18] So, it is safely imagined that only less amount of the resultant S was transported to the low temperature region and reacted with Cd vapour to form CdS. Also, the small amount of CdS was absorbed by the chemically active Cd of liquid state at the growth temperature, leading to the formation of CdS NPs instead of thin films on the surface of Cd NW, driven by the large (∼38%) lattice mismatch between Cd and CdS. Strain-relieving three-dimensional island growth, or Volmer–Weber (V–W) growth was often observed in a highly lattice mismatched system.[19]

To measure the electrical properties of individual Cd/CdS nanohybrid, the products were first removed from the substrate by sonicating the Si wafer in ethanol. The resulting nanostructure suspension was then deposited onto another doped silicon substrate covered with 500 nm SiO_2. Electron beam lithography (Raith 150, Germany) and successive Ti/Au deposition were used to pattern two electrodes to contact individual nanohybrid. Figure 3(a) displays the I–V curves of single Cd/CdS nanohybrid measured at 300, 200, and 2 K, separately. All the I–V curves are nonlinear and asymmetrical about zero bias. This characteristic is analogous to Schottky junction between a metal and a degenerate n-type semiconductor.[20] However, a gap around zero bias can be clearly seen from all the I–V curves, no matter whether it is measured at room temperature or low temperature, indicating that the electron transport here was dominated by quantum-tunneling effect; on the other hand, the contribution from the contact with metal electrodes and nanostructure tunnelling, which can also give rise to the observed behaviour, cannot be excluded explicitly. It needs further investigating.

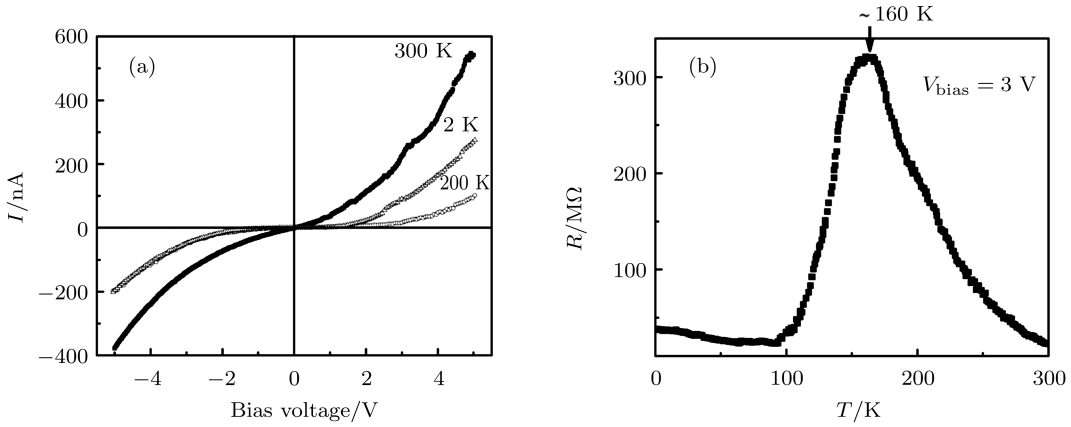


Fig.3. I–V curves of single Cd/CdS nanohybrid at 300, 200, 2 K (a) and temperature-dependent zero-field resistance $R(T)$ of the nanohybrid (b).

More interestingly, the conductance of the Cd/CdS nanohybrid first decreases and then increases when the temperature changes from 300 K to 2 K (see Fig.3(a)). To further explore the electrical properties of the nanohybrids, we measured the temperature-dependent zero-field resistance $R(T)$ of the nanohybrid at $V_{bias} = 3$ V. The result is presented in Fig.3(b). It can be seen from this figure that the resistance of the nanohybrids increases with temperature increasing from about 90 K to 160 K, which is consistent with

a metallic behaviour; when the temperature increases to over 160 K, the resistance begins to decrease, which is an indication of a semiconductor. The metal–semiconductor transition of the as-produced nanohybrids is an intrinsic consequence of the different temperature coefficients of resistance between metallic Cd and semiconducting CdS. It is noticeable that the resistance changes very little with temperature increasing from 2 K to about 90 K (see Fig.3(b)). The reason is that for a conventional metal with a large overlap between valence and conduction bands (normally on the order of eV), the temperature dependence of the carrier density can be observed only at relatively high temperatures.[21] We also note that the resistance decreases slightly with temperature increasing from 2 K to about 90 K. This phenomenon was suggested to be dominated by diffusive 1D electron–electron interactions which result in a decrease in resistance with temperature increasing for an NW with a small diameter at low temperature.[22] And a similar phenomenon has been demonstrated in early studies of Bi nanowires.[21]

4. Conclusions

By the thermal evaporation of a mixture of CdS and Cr, a novel metal/semiconductor hybrid consisting of self-assembled nanometer-sized CdS particles on Cd nanowire is synthesised. The growth of the nanohybrid is attributed to the decomposition of CdS at high temperature and the strain relieving that arises mainly from the lattice mismatch between Cd and CdS. Temperature-dependent conductivity of a single nanohybrid reveals a metal–semiconductor transition that occurs at about 160 K as a result of the difference in resistivity between metallic Cd and semiconducting CdS. This method can be used to fabricate, through further adjustment of the source composition, a great variety of nanohybrids with conductivities of both metal and semiconductor, which have potential applications in various nanodevices.

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