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Electronic and luminescent properties of Cr-doped cadmium sulfide nanowires*

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Cr-doped CdS nanowires were synthesized in large scale through thermal co-evaporation of CdS and metal Cr powders. General morphology, detailed microstructure and optical properties were characterized using various techniques. Devices consisting of individual Cr-doped CdS nanowire were fabricated and they exhibited remarkable rectifying characteristics. *I-V* curves of individual Cr-doped CdS nanowire devices demonstrate that the present nanowires are n-type doped and have high conductivity (10.96 Ω^{-1}cm^{-1}), indicating great potential applications in nanoscale electronic and optoelectronic devices.

Keywords: CdS nanowires, electrical properties, luminescent properties
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1. Introduction

During the very recent years scientists from different disciplines have demonstrated very keen interest in the large-scale synthesis and characterization of one-dimensional (1D) semiconductor nanostructures motivated by the need to understand their novel properties in fundamental research and their potential applications in building nano- and/or opto-electronic devices.[1,2] Considerable efforts have been focused on the synthesis of this class of materials. For instance, Yu *et al*[3,4] and Morales and Lieber[5] reported the synthesis of Si nanowires. Huang *et al*[6] and Park *et al*[7] presented the synthesis of well-aligned ZnO nanowires on sapphire substrate. Many unique and fascinating properties have also been proposed and demonstrated for these 1D semiconductor nanostructures, such as higher luminescence efficiency[8,9] and lowered lasing threshold.[10,11]

CdS, one of the most important II-VI group semiconductors, is the vital optoelectronic materials for field-effect transistor and optical devices due to its good photoconductive properties in visible regime. Optical or electrical devices based on CdS films have been realized.[12,13] With the size shrinking of devices, practical needs have initiated intensive research for CdS nanostructures. Recently, Lieber *et al*[14] have reported the electrically driven CdS nanowire lasers. Due to the promising applications of CdS nanowires in nanoscale optoelectronic devices, considerable efforts have been focused on the synthesis of CdS nanowires and/or nanorods using non-aqueous synthesis,[15] electrochemical deposition,[16] surfactant-assisted synthesis,[17] laser-assisted catalytic growth,[18] or a variety of other approaches.[19]

In order to design nanoscale electrical devices, it is important to be able to synthesize CdS nanowires with low resistivity for efficient operation. Impurity

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doping is an effective method for manipulating the physical properties of semiconductors, including optic- and electric- properties. In this paper, we report the fabrication of Cr-doped CdS nanowires via a simple thermal evaporation method. The optical and electrical characteristics of single Cr-doped CdS nanowire are also investigated in detail.

2. Experiment

Synthesis of Cr-doped CdS nanowires was carried out in a tube furnace. For this purpose, a compact powder mixture of CdS (70wt.%–90wt.%) and metal chromium powders was used as the evaporation source, and cleaned Si wafers coated with 10 nm gold film were used as substrates. The powder mixture was then placed in a quartz boat located inside a quartz tube reactor. Si substrate was placed next to the mixture along the downstream side of flowing Ar. After pumping of the air and venting with Ar (flow rate: 100 ml/min) the residual gas in the tube for several times to ensure that the oxygen in the tube was eliminated, an Ar flow at a constant rate of 20 ml/min and a total pressure of 6.7×10^4Pa were maintained throughout the whole process. Then the furnace was heated up to 1000°C and held for 30 min. White-coloured film-like products appeared on the entire substrate.

To characterize the electrical properties of single Cr-doped CdS nanowires, the as-synthesized nanowires were sonicated into a suspension in ethanol and then deposited onto a doped silicon wafer covered with 500 nm SiO_2. Then, four marks were made using focused ion beam system (FIB, model: DB235, FEI Co.) on the corners of the Si wafer in order to make the writing of the electrode pattern more precise. Afterwards a PMMA e-beam resist in a thickness of about 1μm was deposited on the silicon wafer by a spinning coater. Then the electrode patterns could be written directly by electron beam lithography (Raith 150, Raith Co.). The electrodes were formed after a bilayer evaporation of 10 nm Ti followed by 50 nm Au. Au wires were bonded to the contact pad for current–voltage (I–V) measurements using Keithley 4200 semiconductor parametric analyser.

3. Results and discussion

The general morphology and detailed microstructure of the as-synthesized products were examined by FIB and high-resolution transmission electron microscope (TEM, H-9000NAR). SEM images show that this approach can in products in good yield and with uniform wire-like morphology (Fig1(a)). The length of the wires is up to several tens of micrometres. Figure 1(b) is a representative TEM image of several wires. It reveals that the wires are straight, and their diameter is uniformly 20 nm. High-resolution TEM image is shown in Fig.1(c), indicating that the nanowire

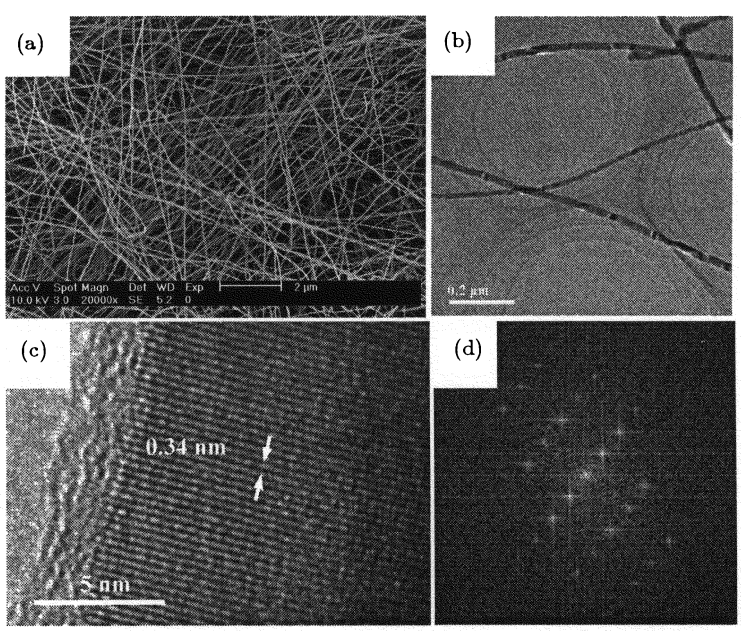


Fig.1. (a) SEM images of the prepared products, suggesting a wire-like morphology; (b) Typical low magnification TEM image of several nanowires; (c) High-resolution TEM image of part of individual Cr-doped CdS nanowire, revealing a hexagonal crystalline structure of CdS; (d) Fourier transform of the high-resolution image shown in (c).

has a hexagonal structure. The (002) fringes perpendicular to the growth direction are separated by 0.34 nm, which is consistent with that of bulk wurtzite CdS crystals (a=4.136 Å, c=6.713 Å; JCPDS Card No. 77–2306). Figure 1(d) is the corresponding Fourier transform of the high-resolution image, demonstrating that the nanowires prefer to grow along direction [002]. The similarity of crystalline structures of the nanowires to pure CdS crystals does not mean there is no chromium in the wires, because CdS crystals can keep its original hexagonal structure with low doping level of chromium.[20] In our experiment, both of the commonly-used EDX and wet chemical analysis cannot detect chromium of such low doping level.

Figure 2 gives the room-temperature photoluminescence (PL) spectrum of the prepared nanowires. It shows a broad doublet centred at ~2.408 eV and ~2.357 eV separately, which is different from the pure CdS nanowires.[21] Because the sizes of the as-synthesized CdS nanowires (~20 nm) are significantly larger than the Bohr radius of exciton in bulk CdS (~2.8 nm), the shallow impurity states in our nanowires should be similar to those in bulk CdS. So, the two peaks located at 2.402 eV and 2.415 eV would be assigned to the radiative recombination of free excitons or excitons bound to neutral donors and acceptors.[22] On the other hand, the satellite near 2.357 eV is perhaps due to the radiative recombination of an exciton and carriers localized at the Cr-related impurities and defects.

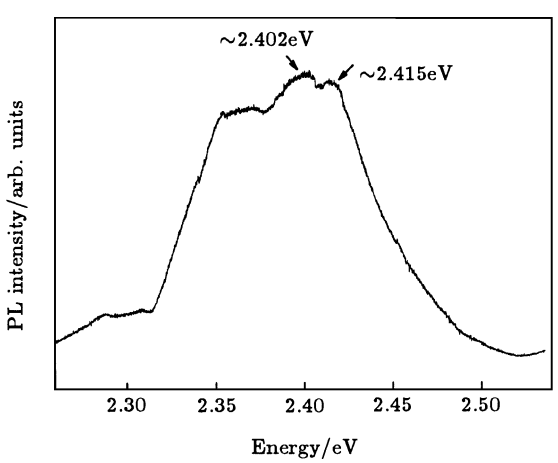


Fig.2. PL spectrum of Cr-doped CdS nanowires. The excitation wavelength is 532 nm.

The inset of Fig.3 gives a typical SEM image of a device. It is very clear that a nanowire bridges two electrodes. Note that the channel length between the electrodes is about 600 nm. The two Ti/Au electrodes function as the source and drain electrodes of the device, and the Si substrate is used as a back gate in electrical measurements. Figure 3 shows five current vs drain-source voltage (I–V_{ds}) curves obtained under different gate biases (V_g) at –20, –10, 0, 10, and 20 V. The conductance is progressively increased with the gate voltage varying from –20 to 20 V, indicating the n-type semiconductor behaviour. The room-temperature conductance of the Cr-doped CdS nanowire is about 3.44×10^{-7} S (2.90 MΩ) derived from the slopes of I–V_{ds} curves at V_{ds}=0V and V_g=0V. This high conductivity (10.96 $\Omega^{-1}cm^{-1}$) is in sharp contrast to the Bi-implanted CdS crystal,[23] CdS films,[24] and Ga-doped CdS nanowire.[25] The I-V_{ds}curves shown in Fig.3 also indicate the remarkable unsymmetric electronic transport characteristics. One possible explanation is related to the thermally assisted tunnelling which dominates over thermionic emission in the one-dimensional semiconductor / three-dimensional metal contact.[26]

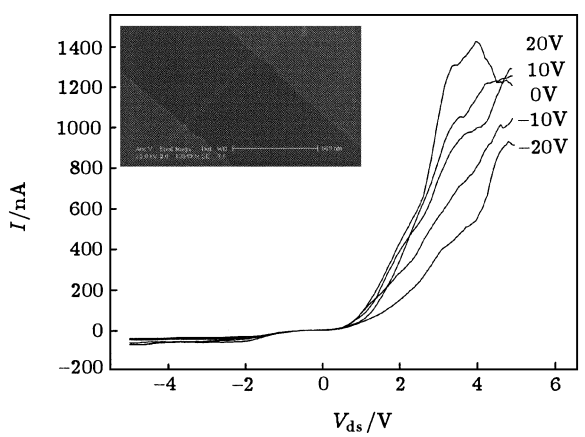


Fig.3. Room temperature I-V_{ds} curves obtained under different gate biases. The inset shows a typical SEM image of a device.

Our device consists of a semiconductor connected to two metal electrodes, which corresponds to two metal-semiconductor (MS) junctions (i.e., Schottky junctions) connected back to back. In a conventional analysis, thermionic emission dominates transport process for an ideal Schottky junction in the forward direction (i.e., the current flowing from the semiconductor to metal), especially for high barriers and/or low doping level.[27] According to thermionic emission model, a saturation current density exists for the reverse biased Schottky junction, which is always neglected. However, the total current level is very low for a nanoscale MS structure, and the reverse current is not negligible. The dominant mechanism for current injection in this case is thermally assisted

tunnelling.[26] Taking into account the influence of the reverse-biased Schottky barrier, we have put forward a modified model in which the device resistance is simplified to the reverse-biased barrier and the resistance of the nanowire itself.[28] The current density (J) is described by the following equations:

$$J(V_{\rm r},\phi_{\rm b}) = -J_{\rm s}(\phi_{\rm b})\exp\left[V_{\rm r}\left(\frac{q}{kT}-\frac{1}{E_0}\right)\right]. \qquad (1)$$

The reverse current density ($J_{\rm s}$) is a slowly varying function of the applied bias, which has the form

$$J_{\rm s} = \frac{A^*T(\pi qE_{00})^{1/2}}{k}\left\{q(V_r-\xi) + \frac{q\phi_0}{\cosh^2(qE_{00}/kT)}\right\}^{1/2} \times \exp\left(-\frac{\phi_{\rm b}}{E_0}\right), \qquad (2)$$

in which A^* is the Richard constant of the semiconductor, ξ is the distance between the Fermi energy and the conduction band, $\phi_{\rm b}$ is the Schottky barrier height, k is Boltzmann's constant, q is the electron charge, and

$$E_0 = E_{00}\cos th\left(\frac{qE_{00}}{kT}\right),$$

where

$$E_{00} = \hbar/2\left(\frac{N_{\rm d}}{m^*\varepsilon_{\rm s}}\right)^{1/2},$$

m^* and $\varepsilon_{\rm s}$ are the effective mass of an electron and the permittivity of the semiconductor nanowire, respectively. $N_{\rm d}$ is the donor concentration.

Employing this modified model, we have fitted the I–$V_{\rm ds}$ curve for the same nanowire device and obtained reasonable fit as shown in Fig.4. The empty circles represent the experimental results and the line represents the calculated I-V curve. In our simulation, the Schottky barrier heights of 0.32 and 0.68 eV, and the resistance of nanowires are extracted from the I-V curves.[28] Other specific parameters are taken from bulk parameters of CdS crystals,[29] including effective mass $m^*(0.2m_{\rm e})$, band-gap (2.40 eV) etc. From the analyses presented above, it can be safely concluded that the current transports through the MS junctions in the present nanowire devices are governed by thermally-assisted tunnelling.

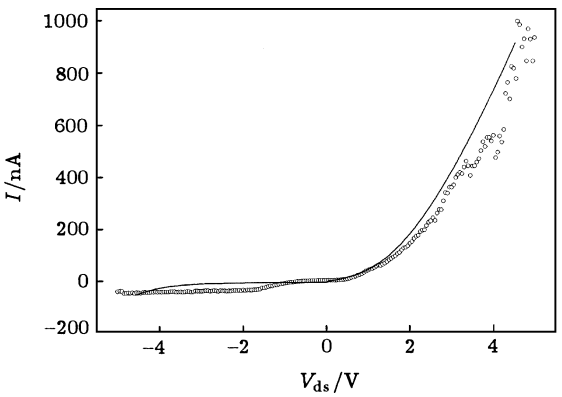


Fig.4. Theoretic and experimental I-$V_{\rm ds}$ curve of the device at room temperature. The empty circles represent the experimental data and the line represent the theoretical results.

4. Conclusion

In conclusion, Cr-doped CdS nanowires have been synthesized in large scale via thermal co-evaporation of CdS and metal Cr powder mixtures. The nanowires are about tens of microns in length and 20 nm in average diameter. The CdS still has a single phase hexagonal crystalline structure with a rather low Cr concentration. Devices consisting of individual Cr-doped CdS nanowires were fabricated and they exhibited remarkable rectifying characteristics. The results of I–$V_{\rm ds}$ measurement of individual Cr-doped CdS nanowire devices demonstrate that the nanowires are n-type doped and have high conductivity. This work indicates that the Cr-doped CdS nanowires have potential applications in building nano- and/or optoelectronic devices.

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