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化学气相沉积法合成高结晶度的三元系 $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ 纳米线

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摘要: 以硫化锌、硫化镉和活性碳粉作为反应物, 利用化学气相沉积方法成功合成了单晶 $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ 纳米线. 为了解产物的结构、形貌、组分、微结构以及声子振动模式, 对样品进行了扫描电镜、透射电镜、X射线衍射、能谱分析以及拉曼光谱分析. 分析显示合成的纳米线为六方铅锌矿结构, 生长方向沿着[210]方向, 长度均为 10 μm , 直径在 80–100 nm 之间, x 的值约为 0.2. 拉曼光谱分析显示产物的拉曼峰位与纯 CdS 相比发生了蓝移.

关键词: $\text{Cd}_{1-x}\text{Zn}_x\text{S}$; 纳米线; 化学气相沉积

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Synthesis of Highly-Crystallized Ternary $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ Nanowires by Chemical Vapor Deposition

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Abstract: Single crystal $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanowires were directly synthesized by a simple chemical vapor deposition process using ZnS, CdS, and C powders as starting materials. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), energy dispersive X-ray spectrum (EDXS), and Raman spectrum were used to characterize the morphology, microstructure, composition and phonon modes of the products. It was found that single crystal ternary $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanowires with a composition x of about 0.2 are highly crystallized in a wurtzite structure and grow along the [210] direction with diameters in the range of 80–100 nm and lengths of up to tens of micrometers. Raman spectrum of nanowires showed small blue shifts compared to that of CdS.

Key Words: $\text{Cd}_{1-x}\text{Zn}_x\text{S}$; Nanowires; Chemical vapour deposition

One-dimensional nanostructures, such as nanowires^[1], nanotubes^[2], and nanobelts^[3], have attracted considerable interest in recent years due to their unique physical properties and potential applications in building blocks for fabricating nanoelectronic and optoelectronic nanodevices^[4], field effect transistors (FET), logic gates, light emitting diodes (LED), nanoscale lasers^[5–8], photodetectors, nanosensor and so on. The morphology, structure,

and component of nanomaterials would greatly influence their properties, which would affect their final applications. Today, zinc sulfide, as a direct wide band gap (3.6 eV)^[9–11] and relatively high exciton binding energy material, has been extensively attracting considerable attention due to their potential applications in ultraviolet and blue optoelectronic devices^[12,13]. In the recent years, the thermal evaporation method has been widely utilized

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to grow one-dimensional or quasi-one-dimensional ZnS nanomaterial. ZnS nanobelts have been prepared by hydrogen-supported heating of the ZnS powder at 1100 °C^[9]. Deng *et al.*^[14] have also synthesized high-aspect ratio ZnS nanowires by the simple thermal evaporation at 800 °C. ZnS nanocables have been prepared by heating a mixture of ZnS and C powders to 900 °C for 1 h and then to 1100 °C for 1.5 h to obtain the ZnS nanotraps^[15]. Liang *et al.*^[16] have reported the large scale synthesis of wurtzite ZnS nanobelts by thermal evaporation of ZnS powder at a relatively lower temperature of 970 °C for 2 h in the presence of Au catalyst. Meanwhile, for one-dimensional cadmium sulfide (with a banding energy of 2.42 eV at room temperature) nanostructures, CdS nanowires have been fabricated using various methods. For example, Xu^[17], Routkevitch^[18,19], and Lee^[20] *et al.* have fabricated CdS nanowires in porous anodic aluminum membranes by electrochemical deposition. Qian *et al.*^[21,22] synthesized CdS nanowires *via* a solvothermal route and polymer-controlled growth. Duan *et al.*^[23] reported that the laser-assisted catalytic growth had been developed for the synthesis of CdS nanowires. Wang *et al.*^[24] have found catalytic growth of large scale single-crystalline CdS nanowires by physical evaporation. Jiao *et al.*^[25] have successfully obtained catalytic growth of CdS nanobelts and nanowires on tungsten substrates. Furthermore, materials with ternary alloyed nanostructures may offer more unique properties than the binary compounds^[26]. By adjusting the stoichiometry of the constituent components, their properties can be effectively tuned^[27]. For example, Cd_{1-x}Zn_xS^[28], Cd_{1-x}Zn_xSe^[29], and CdS_xSe_{1-x}^[30] could be used in optoelectronic applications and in solar energy driven devices. Although many reports are available on Cd_{1-x}Zn_xS films^[31,32], there are some reports on formation of a large scale and high quality one-dimensional ternary Cd_{1-x}Zn_xS nanowires^[33-35].

Herein, we reported a successful synthesis of highly crystallized ternary Cd_{1-x}Zn_xS nanowires using a simple catalyst-free thermal evaporation technique. The morphology, crystal structure, and the Raman spectrum of the Cd_{1-x}Zn_xS nanowires were studied.

1 Experimental

The samples were prepared by a thermal evaporation and

transport deposition technique. In a typical run, a graphite wafer was used as a substrate for the growth of Cd_{1-x}Zn_xS nanowires. The graphite substrate was cleaned using a standard treatment in piranha solution (30% H₂O₂/20% H₂SO₄/50% H₂O, φ), rinsed with de-ionized water. CdS (99.99%), ZnS (99.99%), and C powders with a molar ratio of 4:4:1 were mixed as source materials. The mixed powders were put into an alumina boat, and the graphite substrate was placed next to the source powders along the downstream side of the flowing argon. The alumina boat was placed in the middle of the alumina tube that was inserted in a horizontal tube furnace. Prior to heating, the system was evacuated by a pump and flushed with high-purity Ar for 1 h to eliminate oxygen. Then under a constant Ar flow of 300 cm³·min⁻¹, the furnace was heated to 1100 °C for about 110 min, held at this temperature for 60 min, and subsequently cooled to room temperature naturally. It was observed that yellow-white sponge like products had appeared on the surface of the graphite wafer.

The morphology and structure of synthesized products were characterized using scanning electron microscopy (SEM, EDXS Philips XL 30 FEG, Netherlands), X-ray diffraction (XRD, Japan Mac science 18kw X-ray diffraction meter with Cu K_α radiation, Japan) and energy-dispersed X-ray spectrometry (EDXS). The microstructure of samples was examined by transmission electron microscopy (TEM), selected-area electron diffraction (SAED) on a JEOL 2010 TEM (Japan) operating at 200 kV. The high resolution transmission electron microscopy (HRTEM) imaging and electron energy-loss (EEL) elemental maps were performed by FEI Tecnai F20 FEG TEM (Netherlands) operated at 200 kV. Room temperature Raman spectrum of the sample was recorded by a laser Raman scattering spectrometer (HR800, GY, France) with the 532 nm line of a laser and 2.5 mW output power.

2 Results and discussion

The XRD patterns shown in Fig.1(a) reveal the overall crystal structure of the products. As references, the standard reflections of wurtzite-structured Cd_{0.8}Zn_{0.2}S and CdS are displayed in Fig.1 (b). All the peaks are very close to those of the hexagonal Cd_{0.8}Zn_{0.2}S in the JCPDS data file (No.49-1302; *a*=0.4137 nm and *c*=0.6650 nm). Based on the careful examinations of the stan-

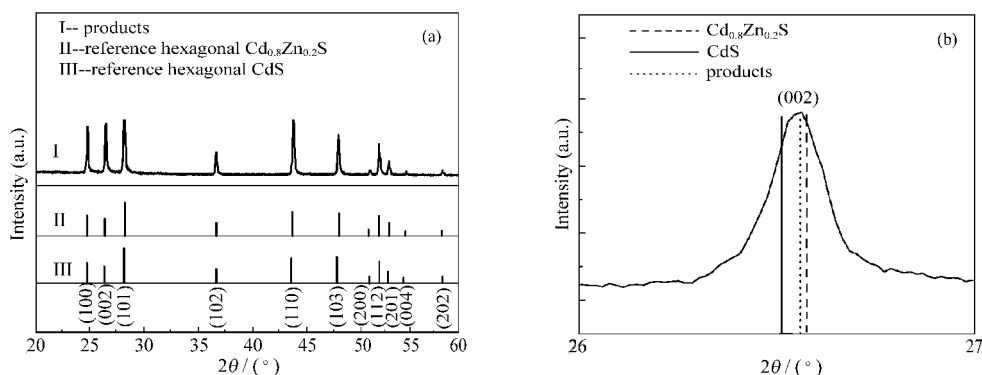


Fig.1 (a) XRD patterns of the products; (b) (002) reflection of the products and the corresponding reflection locations of CdS and Cd_{0.8}Zn_{0.2}S

ard data listed in JSPDS database, it can be found that there are very small shifts between the reflections of hexagonal CdS (JCPDS No.49-1302, $a=0.4140$ nm and $c=0.6719$ nm) and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$. Considering the obvious discrepancy of the reflections of ZnS (JCPDS file NO. 36-1450), it is easy to exclude the existence of ZnS in the products according to the XRD pattern. The reflections of the products show a slight shift to high angle compared with those of hexagonal CdS, as seen from Fig.1(b). The values of full width at half maxima (FWHM) of the reflections are much larger than the differences between the reflections of CdS and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ (as shown in Fig.1(b), FWHM of (002) peak is about 0.174, while the corresponding reflections of CdS and $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ are at 26.50° and 26.53° , respectively). Hence, it can be concluded that the products consist of pure hexagonal CdS or $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$, or the mixture of them. No XRD diffraction peaks from Cd, S, Zn, or other impurities are observed in the products.

Fig.2(a, b) are low- and high-magnification SEM images, indicating that the products are composed of a large number of nanowires with high aspect ratio on a large scale. The length of the nanowires reaches about tens of micrometer and diameters in the range of 80–100 nm. It can be found from Fig.2(b) that most nanowires have smooth surfaces and tops. The inset of Fig.2(a) is an EDXS spectrum taken on a region randomly selected from the surface of the products. It can be seen that there are mainly Cd, S, and Zn elements existing in the sample. The trace amount of Se is probably due to impurity or detecting error. The quantitative analysis demonstrates the molar ratio of $n(\text{Cd}):n(\text{Zn}):n(\text{S})$ is about 46:4:50.

The morphology and microstructure of the products are further checked using TEM. Fig.3(a) is a TEM image of the prod-

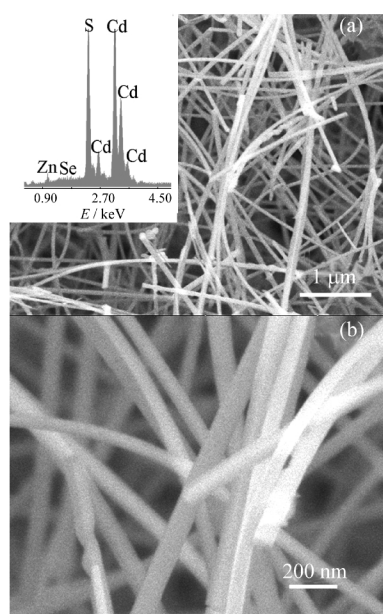


Fig.2 Low-(a) and high- magnification (b) SEM images of the as-synthesized nanowires obtained from thermal evaporation at 1100°C

The inset of (a) is EDXS spectrum taken from the products.

ucts, showing some long and straight nanowires. Their width is in the range of 70–120 nm. Fig.3(b) is a selected area electron diffraction (SAED) pattern taken from one nanowire. The SAED pattern can be indexed based on a hexagonal structure with electron beam along [001] direction, revealing the single crystal nature of the nanowire. Some diffraction spots which separated a little were attributed to the angle of diffraction.

Examinations of the elemental mappings and TEM-EDXS analysis were employed to further reveal the compositional high homogeneity of these composite nanowires. Fig.4(a) shows a bright-field TEM image of a segment of a straight nanowire, which reveals a clear and uniform surface, and the diameter of the nanowires is 80 nm. The S, Cd, and Zn elemental mappings from this composite nanowire (Fig.4(b–d)) further demonstrate that the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanowire has a well-defined compositional profile. The chemical compositions of sixteen nanowires randomly selected were analyzed by EDXS. It was found that two kinds of nanowires, i.e., pure CdS and ternary $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanowires, coexisted in the products. The number ratio of the two kinds of nanowires is 1:1 and the $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanowires have an average composition x about 0.2. The result of detailed composition analysis is consistent with that of XRD. Fig.5 shows typical EDXS spectra of one $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ and one pure CdS nanowires. The overall composition ratio of $n(\text{Cd}):n(\text{Zn}):n(\text{S})$ in the sample can be easily calculated to be 44:5:51, which matches the SEM-EDXS result quite well.

Fig.6(a) shows one $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanowire with a smooth flat surface. The composition of this nanowire was determined by EDXS to be $\text{Cd}_{0.78}\text{Zn}_{0.22}\text{S}$. The corresponding HRTEM image in Fig.6(b) displays clear lattice fringes, demonstrating the high crystallinity of the nanowire. The lattice spacing between the adja-

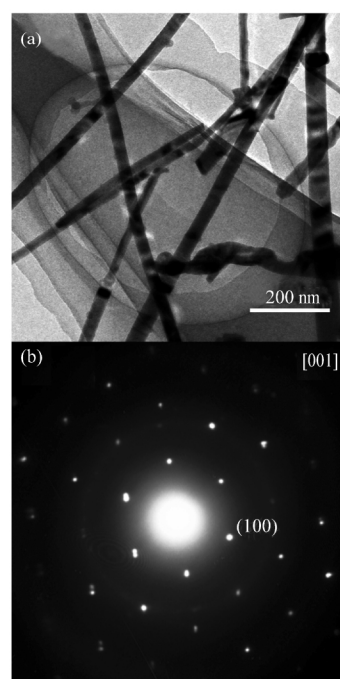


Fig.3 (a) TEM image of obtained nanowires and (b) SAED pattern of one nanowire in the hexagonal structure

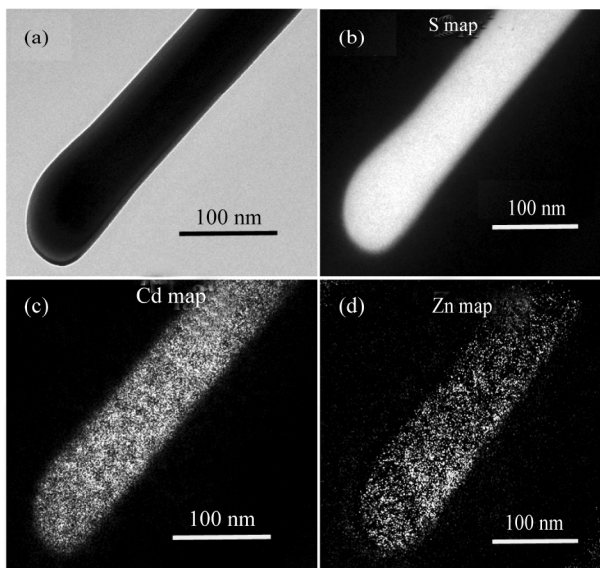


Fig.4 Bright-field TEM image of a Cd_{1-x}Zn_xS nanowire (a) and elemental mappings of S (b), Cd (c), and Zn (d)

cent planes is 0.355 nm, which corresponds to {100} planes of wurtzite Cd_{1-x}Zn_xS. So the growth direction of the Cd_{1-x}Zn_xS nanowire is [210], as indicated by the arrow in Fig.6(b).

The SEM and TEM observations presented above show that the growth of the nanowires should not be dominated by the vapor-liquid-solid (VLS)^[36] process which involves metal particles as

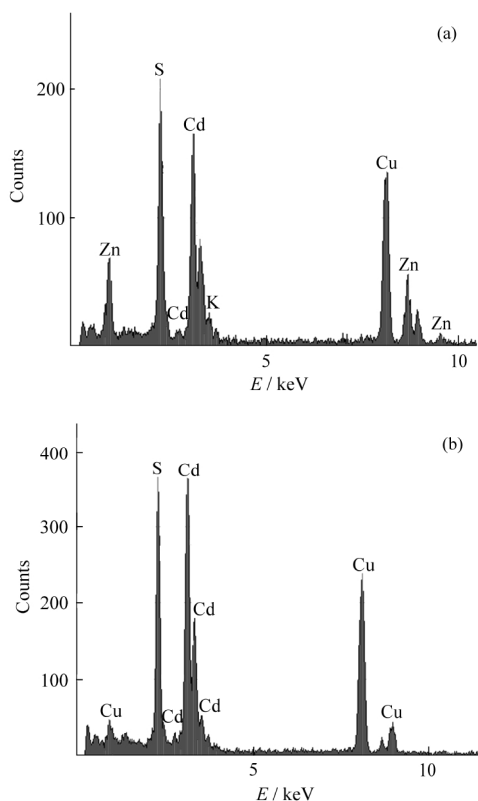


Fig.5 EDXS spectra recorded from a Cd_{1-x}Zn_xS (a) and a pure CdS nanowire (b)

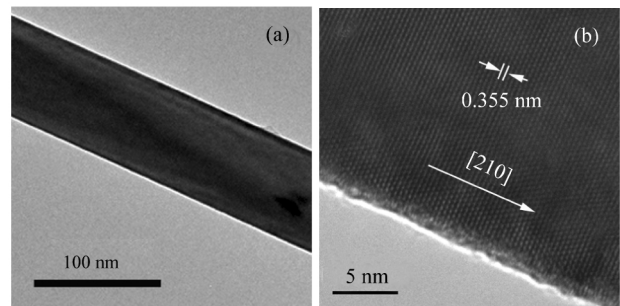


Fig.6 (a) TEM image of an individual Cd_{1-x}Zn_xS nanowire and (b) HRTEM image taken from the nanowire

catalyst to define the one-dimensional growth of nanowires. No catalyst was purposely introduced in our synthesis and no obvious evidence demonstrated the existence of liquid phase in the growth of the nanowires. So the growth of the nanowires should be dominated by the vapor-solid (VS) mechanism^[37-39].

Raman spectroscopy was employed to characterize phonon modes of the products. Wurtzite-structure CdS and Cd_{1-x}Zn_xS belong to C_{6v}⁴ (P6₃mc) space group with a two formula unit primitive cell. All the atoms occupy the C_{3v} sites and there are following normal lattice vibration modes: $\Gamma_{\text{opt}} = A_1 + 2B_1 + E_1 + E_2$ ^[40]. The A₁, E₁ and E₂ are Raman active whereas B₁ is forbidden. Fig.7 shows Raman spectrum of the products. Because of the strong fluorescence background, the Raman intensities are very weak. It can be seen that there are eight modes observed in the spectrum, which are centered at 207.4, 418.2, 1143.3, 1167.5, 1263.7, 1276.3, 1744.5, and 1767.3 cm⁻¹, respectively. The present Raman spectrum is quite different from previous reports on pure CdS nanowires, which are commonly dominated by the longitudinal optical (LO) phonon at about 304 cm⁻¹ and its overtones, such as 2LO (608 cm⁻¹), 3LO (907 cm⁻¹) and so on^[25,41,42]. Tell and co-workers^[43] observed 207 cm⁻¹ phonon mode in bulk CdS crystal and assigned it to multiphonon process with A₁ symmetry. Nusi movici and co-workers^[44] pointed out the phonon should be two phonons Raman-scattering at M of Brillouin zone. The phonon at 418 cm⁻¹ observed here should be overtone of it. The six high energy phonons over 1000 cm⁻¹ in the spectrum can be divided into 3 pairs with small shifts (about 24.2, 12.6, and 22.8 cm⁻¹, respectively). Considering the phonons of wurtzite ZnS have high-

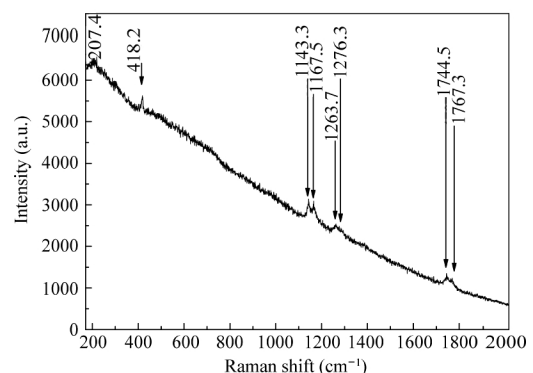


Fig.7 Room-temperature Raman spectrum of the products

er energy than those of CdS, the phonons of Cd_{1-x}Zn_xS ($x \approx 0.2$) would have small blue shifts compared with those of CdS in the Raman spectrum. So the phonons should be attributed to CdS and Cd_{1-x}Zn_xS, respectively. To the best of our knowledge, no report about the high energy phonons was found. As to the exact assignment of the phonons, more detailed examinations are necessary to clarify those high energy phonons observed here.

3 Conclusions

In summary, Cd_{1-x}Zn_xS nanowires were successfully synthesized *via* a simple thermochemical process using ZnS, CdS, and C as the starting materials at a temperature of 1100 °C. The single crystal Cd_{1-x}Zn_xS nanowires were crystallized in wurtzite-structure with high crystallinity, and ranged about tens of micrometers in length and several tens to hundred of nanometers in diameters and grew preferably along the [210] direction. Examinations of the elemental mappings and EDXS analysis showed the compositional high homogeneity of these alloy nanowires. The Raman spectrum of the nanowires showed small blue shifts compared with those of CdS.

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