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FABRICATION AND CHARACTERIZATION ZnCdS NANOWIRE

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Semiconductor ZnCdS nanowire arrays have been synthesized by electrochemical deposition from aqueous solutions into porous anodic alumina substrates. X-ray diffraction analyses show that the as-synthesized nanowires have a highly preferential orientation. Scanning electron microscopy indicates that high-filling, ordered, and single-crystalline nanowire arrays have been obtained. The optical absorption spectra of the nanowire arrays show that the optical absorption band edge of the ZnCdS nanowire array exhibits a blue shift compared with that of bulk ZnCdS. The growth mechanism and the electrochemical deposition process are discussed together with the chemical compositions analysis.

Keywords: Nanowire, electrochemical deposition, nanoparticle, ZnCdS.

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1. Introduction

Sulfides or selenides, as wide-band gap II-VI semiconductor materials, have been studied extensively due to their wide applications in the fields of light-emitting devices, solar cells, sensors, and optical recording materials [1–3]. ZnS is a wide band gap semiconductor, commercially used in a variety of applications, including optical coatings, solid-state solar cell windows, in thin film electroluminescent devices, photoconductors, field effect transistors, sensors, and light-emitting applications. To date, there are many methodologies available for synthesizing ZnS powders, such as laser ablation, electrochemical fabrication and solvothermal methods. The synthesis of ZnS nanowires, ZnS nanorods by a surfactant-assisted soft chemistry approach and ZnS nanocrystals in colloids are all known methods.

One-dimensional (1D) semiconductor nanostructures have received much attention due to their novel properties and potential applications in nanoscale electronics and optoelectronics [4, 5]. Among these semiconductor systems, the II-VI family of the compound semiconductors, including ZnS, CdS, and CdTe, has been widely studied because of their potential applications in solar cells, photodetectors, and light emitting diodes [6, 7]. Many attempts have been made to fabricate 1D nanostructures, such as high-temperature chemical vapor deposition (CVD) [8, 9], Among these methods, the anodic alumina substrate (AAS)-based synthesis is a widely used route for fabricating 1D nanostructures, because the AAS's possess a uniform and parallel porous structure, which can be used as templates to assemble high-quality nanowire and nanotube arrays [10, 11].

Cadmium sulfide (CdS), an important semiconductor material with a direct optical band gap of 2.4 – 2.45 eV at room temperature, has potential applications in optoelectronic and thermoelectric devices. To the best of our knowledge, there are no reports on the fabrication of the CdS nanowire (NW) arrays.

In this paper, large-scale, ordered, and single-crystalline ZnCdS nanowire arrays have been fabricated in AAS using an electrochemical deposition technique from an aqueous solution for the first time. For the as-formed ZnCdS NWs, systematic morphological, compositional, structural characterizations are carried.

2. Experimental Section

The AAS templates were prepared using a two-step anodization process as described previously. The pore size of the anodic alumina membrane (AAM) used was about 60 nm. A layer of Au film (thickness, 200 nm) was sputtered onto one side of the AAM to serve as the working electrode in a two-electrode plating cell, and a graphite plate was used as the counter electrode. The pulsed electrochemical deposition was carried out at a constant current density of 10 mA/cm^2 at 330 K. During the pulsed time, species were reduced on the pore ground. The delayed time provided time for the recovery of the ion concentration. Here, both the pulsed time and delayed time were 100 ms. The electrolyte was prepared by dissolving 10 mM $CdSO_4$, 10 mM $ZnSO_4$, 0.15 mM $Na_2S_2O_3$, 0.2 M $C_6H_8O_7$. H_2O ($H_3Cit.H_2O$), and 0.2 M NaOH in water. Due to the low solubility of $Na_2S_2O_3$ continuous heating and stirring for several hours is required. The pH of the final electrolyte was adjusted to 3.5 with H_2SO_4.

Powder X-ray diffraction (XRD, D/MAX-rA), field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F), transmission electron microscopy (TEM, H-800), selected area electron diffraction (SAED), and high-resolution transmission electron microscopy (HRTEM, JEOL-2010) were used to study the crystalline structure and morphology of nanowire arrays. The chemical compositions of the nanowires were determined by energy dispersive spectrometer (EDS). The band structure of the nanowires was obtained by measuring the optical absorption spectra on UV-visible spectrophotometer (Cary-5E). For XRD and optical absorption measurements, the overfilled nanowires on the surface of the AAM and the back Au film were mechanically polished away using Al_2O_3 nanopowders. For SEM observation, the AAM was partly dissolved with 0.5 M NaOH solution and then carefully rinsed with deionized water several times.

The SEM images and elemental compositions [energy-dispersive X-ray analysis] of the ZnCdS NWs were analyzed by scanning electron microscope (HR-SEM, JSM, 7000F). The particles' morphology and structure were also studied by transmission electron microscopy (TEM) with a JEOL-2010HRTEM instrument. The 632.8 nm line of an He–Ne laser was used as the excitation source, focused to a $1 - 2$ μm spot size. The X-ray diffraction patterns of the products were measured with a Bruker AXSD* Advance Powder X-ray diffractometer (using CuKR) 1.5418 Åradiation). The collection of the emission was done through an objective with 40× magnification, then into an optical fiber connected to a SHAMROCK spectrometer SR-303I-A from ANDOR Technology onto a cooled CCD camera, connected to a computer.

3. Results and Discussion

The SEM images were taken of the reactant Zn, Cd and S powders for the realization of morphological difference between them. Typically, poly dispersed Zn and Cd particles possess spherical shape, submicron size and smooth surfaces. The Cd submicrometer sized particles reacted with an S vapor environment at 450 °C in a closed reactor, yielding ZnCdS particles (Fig. 1). A close observation (high resolution SEM micrograph) of ZnCdS particles showed that they were $50 - 300$ nm in diameter and closely packed. The HR-SEM image confirmed the diameters of the formed ZnCdS are in the range of $100 - 400$ nm. The existence of Zn, Cd and S elements was confirmed with an atomic ratio of S/Zn, Cd very close to $1 - 3$. The insert plot for as-prepared ZnCdS powder also confirmed the atomic ratio of S/Zn, Cd close to 3.

Figure 1 shows the XRD pattern of the as-prepared ZnCdS nanowire array. The intensity of the (220) diffraction is much higher than all the other peaks, indicating that the ZnCdS nanowires have a preferential orientation along the [220] direction, which will be further conformed by HRTEM analysis. In addition, no diffraction peaks for elemental Cd and S can be detected.

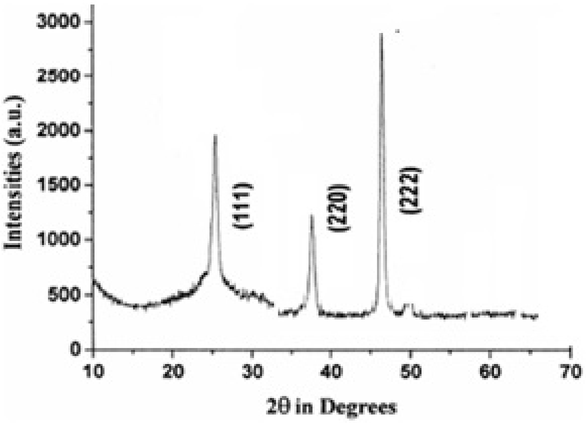

FIG. 1. XRD pattern of ZnCdS nanowire array

Figure 2 shows the dependence of the (220) peak intensity of XRD patterns of the ZnCdS nanowires on the current density and pulsed time. One can see that the peak intensity first increases, after reaching a maximum value at the current density of 10 mA/cm^2, and then decreases with further increasing of the current density.

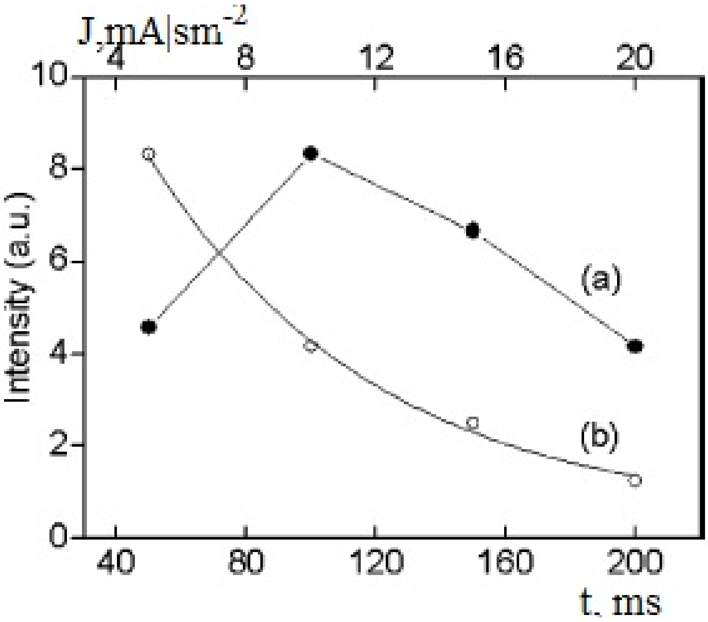

FIG. 2. Relative intensity of the (220) peak of ZnCdS nanowires as a function of (a) current density (I) and (b) pulsed time (t), keeping the delayed time at 100 ms

The reduction in the peak intensity might be due to hydrogen evolution at larger current densities, which suppresses the growth of the nanowires along the (220) orientation. Keeping the delayed time at constant 100 ms, the (220) peak intensity always decreased with increasing pulse time. This result indicates that the best crystallinity of the ZnCdS nanowires can be obtained at a current density of ∼ 10 mA/cm^2 and pulse time of about 100 ms.

Figure 3 shows SEM images of the as-prepared AAS and the ZnCdS nanowire array. Fig. 3a is a typical image of the as-prepared empty AAS. One can see that the AAS has a highly ordered pore array with an average pore size of about 60 nm. The morphologies of the ZnCdS nanowire arrays after different etching times are represented in Fig. 3b-c. Parts b and c of Fig. 3 are the surface images of the nanowire arrays after etching for 10 and 20 min, respectively.

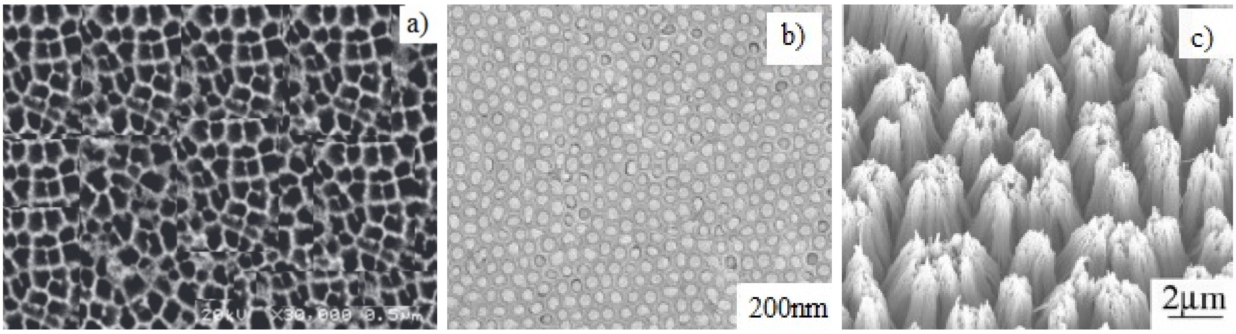

FIG. 3. SEM images of empty AAS (a) and ZnCdS nanowire arrays: (b and c) top views of the ZnCdS nanowire array after etching for 10 and 20 min

Apparently, the nanowires are highly filled (nearly 100%) and the exposed parts of the nanowires increase with increasing etching time. The length of the nanowires is the same as the thickness of the AAS used, because the deposition of the nanowires starts at the Au cathode on the bottom of the pores, and then the nanowires grow along the pores until the top of the AAS. It is noted that all the ZnCdS nanowires have the same length, implying that the electrodeposition process is well-controlled and all the nanowires grow along the pores at the same rate. It is evident that the ZnCdS nanowires with a smooth surface and a high aspect ratio still inside the nanochannels of AAM can be clearly seen. The diameters of the nanowires are uniform and equal to the pore size of the AAS used. One can see that the nanowire is dense and uniform in diameter corresponding to the pore size of the AAS. Some contrast variations were observed along the nanowires. The variation in the intensity of the individual spots might arise from slight structural deformation along the length in the release process of the nanowires from the substrate. The lattice-resolved image of the nanowire further reveals that the nanowire is structurally uniform and single-crystalline, with an interplanar spacing corresponding to the (220) plane of cubic ZnCdS. This result indicates that the growth direction of ZnCdS nanowire is along the [220] direction, which is in agreement with XRD results.

The EDS spectrum of ZnCdS nanowires is shown in Fig. 4, which proves that the nanowires consist of only Zn, Cd and S. Quantitative analysis of the EDS spectrum indicates that the atomic ratio of Zn/Cd/S is close to 1:1:1. It is well-known that a high Zn, Cd^{2+} concentration in the electrolyte is necessary for the deposition of ZnCdS thin films in order to bring the electrode potentials of the Cd^{2+} closer to S^{2+}. To confirm the feasibility for nanowire growth, electrolytes with different Cd^{2+} concentrations were used to grow ZnCdS nanowires.

That the compositions of the nanowires are stoichiometric despite the wide range of Cd^{2+} concentration in the electrolytes, which indicates that we can use a high Cd^{2+} concentration in the electrolyte to co-deposit a ZnCdS nanowire array. It is worth noting that the potential has a very important influence on the compositions of ZnCdS nanowires. The ZnCdS nanowires deposited at about -2.0 V were found to exhibit a stoichiometric composition with Zn/Cd/S

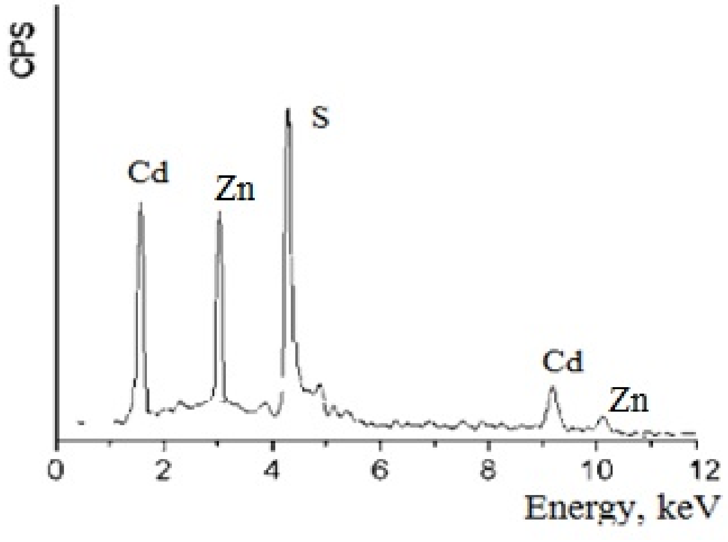

FIG. 4. EDS spectrum of the ZnCdS nanowire array

ratio of 1:1:3, and that deposited at more negative potentials (< -2.1 V) exhibited a Cd-rich phase, while that deposited at more positive potentials (> -1.5 V) revealed a S-rich phase. Fig. 5 shows the optical absorption spectra of the ZnCdS nanowires/AAS assembly system with the diameter of 60 nm and 40 nm. The absorption spectrum of the ZnCdS nanowires/AAS assembly system was shown to be quite different from that of the blank AAS, which is due to the absorption of ZnCdS nanowires. The relationship between the absorption coefficient (α) near the absorption edge and the optical band gap (E_g) for direct interband transitions are known to obey the following formula: $(\alpha h\nu)^2 = A(h\nu - E_g)$, where A is the parameter that related to the effective masses associated with the valence and conduction bands, and $h\nu$ is the photon energy. Hence, the optical band gap for the absorption edge can be obtained by extrapolating the linear portion of the plot $(\alpha h\nu)^2$ versus $\alpha = 0$. The two insets (topright corner in Fig. 5) show the $(\alpha h\nu)^2$ versus $h\nu$ plots for the two samples. For all samples, the optical absorption in the edge region can be well-fitted by the relation $(\alpha h\nu)^2 \sim h\nu - E_g$, which shows that the ZnCdS nanowires embedded in the AAS have a direct band gap. The band gap of nanowires with diameters of 60 and 40 nm is about 2.83 and 2.88 eV, respectively. The shift of 40 nm nanowires is higher than that of 60 nm nanowires. This result indicates that the optical band edge of the ZnCdS nanowires embedded in AAS exhibits a marked blue shift with respect to that of the bulk and thin-film ZnCdS (2.83 – 2.88 eV). The blue shift could be attributed to the quantum size effect, which has also been observed in other semiconductor nanosystems.

Therefore, ZnCdS nanowires have a relatively strong quantum confinement effect and exhibit a marked blue shift. The shift for 40 nm ZnCdS nanowires is larger than that for 60 nm ZnCdS nanowires. Simple electrochemical calculation indicates that the formation of ZnCdS alloy can be realized by using the basic electrochemical reactions for the simultaneous co-deposition of Zn, Cd and S, as described in the present experimental conditions. To obtain a highly-filled, uniform, and single-crystalline ZnCdS nanowire array by the electrochemical deposition into the nanochannels of the AAS, several factors should be considered. First, before electrodeposition the AAS should be treated ultrasonically in water for a few minutes to remove the impurities and air bubble inside the nanochannels, because the ZnCdS ions will preferentially nucleate and grow at the sites of the impurities, causing the inhomogeneous growth of nanowires, and the air bubbles will hinder ion diffusion into the nanopores of the AAS,

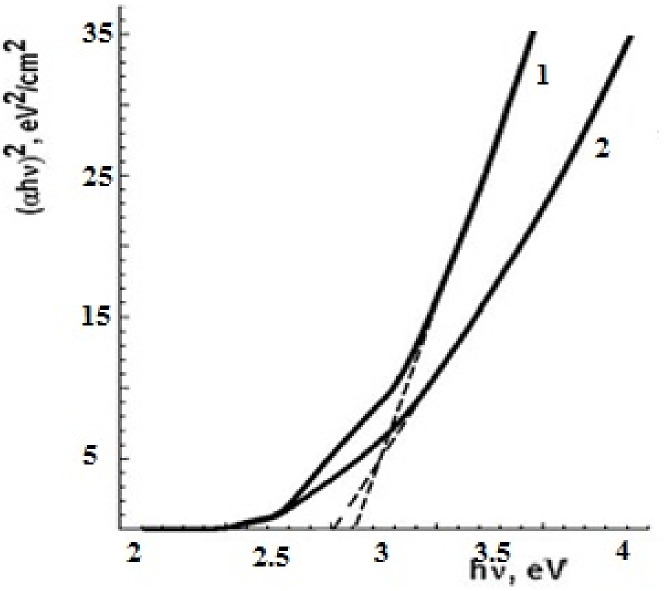

FIG. 5. Optical absorption spectra of the ZnCdS /AAS nanowire arrays with different diameters: (1) 60 and (2) 40 nm

causing the electrodeposition on the surface of the AAS. Second, a suitable deposition rate is critical to obtain dense, ordered, and singly-crystalline nanowires. To avoid rapid nucleation and growth and inhomogeneous concentration gradient in the nanopores, a pulsed electrodeposition technique is employed, which allows a better control over the deposition parameters, such as deposition rate and ion concentration at the deposition interface, as compared with the direct and alternating current deposition. In this paper, the pulsed time in each pulse cycle was so short (100 ms) that only a small number of metal ions at the interfaces were consumed. The delayed time (100 ms) provided enough time for the concentration of the metal ions at the pore tips to achieve steady state through diffusion. No evident concentration gradient near the reaction interface exists during the deposition, and the pulsed time controls the atom-by-atom deposition of nanowires, which improves the homogeneity of the deposition and makes the deposited nanowires have a highly preferential orientation and good crystallization. The proper choice of electrolyte pH value and deposition potential is also important.

4. Conclusions

In summary, highly-filled and ordered ZnCdS nanowire arrays have been prepared from aqueous solutions by the electrochemical deposition into the pores of AAS. The ZnCdS nanowires are single-crystalline and have a preferential orientation along the [220] direction. The optical absorption band edge of ZnCdS nanowires exhibits a marked blue-shift compared with that of bulk ZnCdS due to quantum size effect. We believe that the ZnCdS nanowire arrays will find interesting applications in optoelectronic and thermoelectric nanodevices in the future.

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