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FABRICATION AND CHARACTERIZATION p-CdS NANOWIRE

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Abstract- ***Semiconductor p-CdS nanowire arrays have been synthesized by the 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 indicate 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 p-CdS nanowire array exhibits a blue shift compared with that of bulk p-CdS. The growth mechanism and the electrochemical deposition process are discussed together with the chemical compositions analysis.***

Keywords - nanowire, electrochemical deposition, nanoparticle, p-CdS

I. 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 alumina substrates (AAS)-based synthesis is a widely used route for fabricating 1D nanostructures, because the AASs 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), one of the important semiconductor materials 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 of the fabrication of the CdS nanowire arrays. In this paper, large-scale, ordered, and single-crystalline CdS nanowire arrays have been fabricated in AAS using the electrochemical deposition technique from an aqueous solution for the first time. For the as-formed CdS NWs, systematic morphological, compositional, structural characterizations are carried.

II. EXPERIMENTAL SECTION

The AAS templates were prepared using a two-step anodization process as described previously. The pore size of the 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 $CdSO_4$, 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.

Power 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 UVvisible 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.

III. RESULTS AND DISCUSSION

The SEM images are taken for the reactant Cd and S powders for the realization of morphological difference between them. Typically, poly dispersed 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 yielded CdS particles (Figure 1). A close observation (high resolution SEM micrograph) of CdS particles shows that they are 50-300nm in diameter and closely packed. The HR-SEM image confirmed the diameters of the formed ZnSe are in the range of 100-400 nm. The existence of Cd and S elements is confirmed with an atomic ratio of S/Cd very close to 1-3. The insert plot for as-prepared CdS powder also confirmed the atomic ratio of S/Cd close to 3.

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

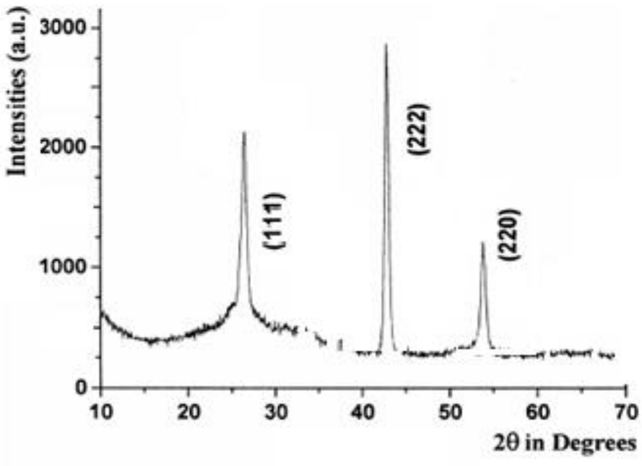

Figure 1. XRD pattern of p -CdS nanowire array.

Figure 2 shows the dependence of the (220) peak intensity of XRD patterns of the p-CdS 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.

The reduction in the peak intensity might be due to the 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 decreases with increasing pulsed time. This result indicates that the best crystallinity of the p-CdS nanowires can be obtained at the current density of about 10 mA/cm^2 and the pulsed time of about 100 ms.

Figure 3 shows SEM images of the as-prepared AAS and the p-CdS nanowire array. Figure 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 p-CdS nanowire arrays after different etching times are represented in Figure 3b-c.

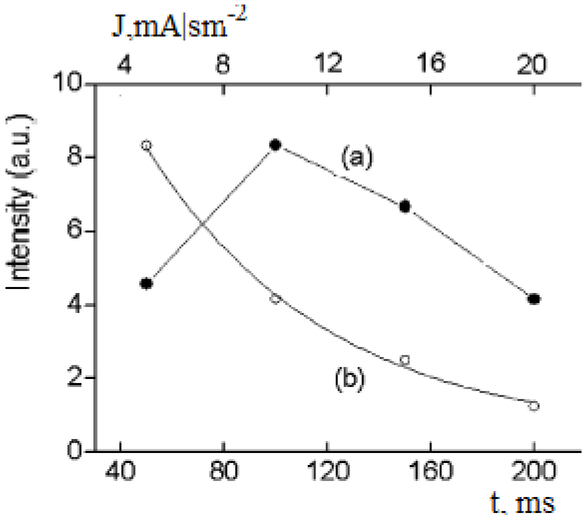

Fig. 2. Relative intensity of the (220) peak of p-CdS nanowires as a function of (a) current density (*I*) and (b) pulsed time (*t*), keeping the delayed time at 100 ms.

Parts b and c of Figure 3 are the surface images of the nanowire arrays after etching for 10 and 20 min, respectively. Apparently, the nanowires are high filling (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 p-CdS 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 p-CdS 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. It is noticed that there are some contrast variations along the nanowires. The variation in the intensity of the individual spots might come from slightly 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 structural uniform and single-crystalline, with an interplanar spacing corresponding to the (220) plane of cubic p-CdS. This result indicates that the growth direction of p-CdS nanowire is along the [220] direction, which is in agreement with the XRD result.

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

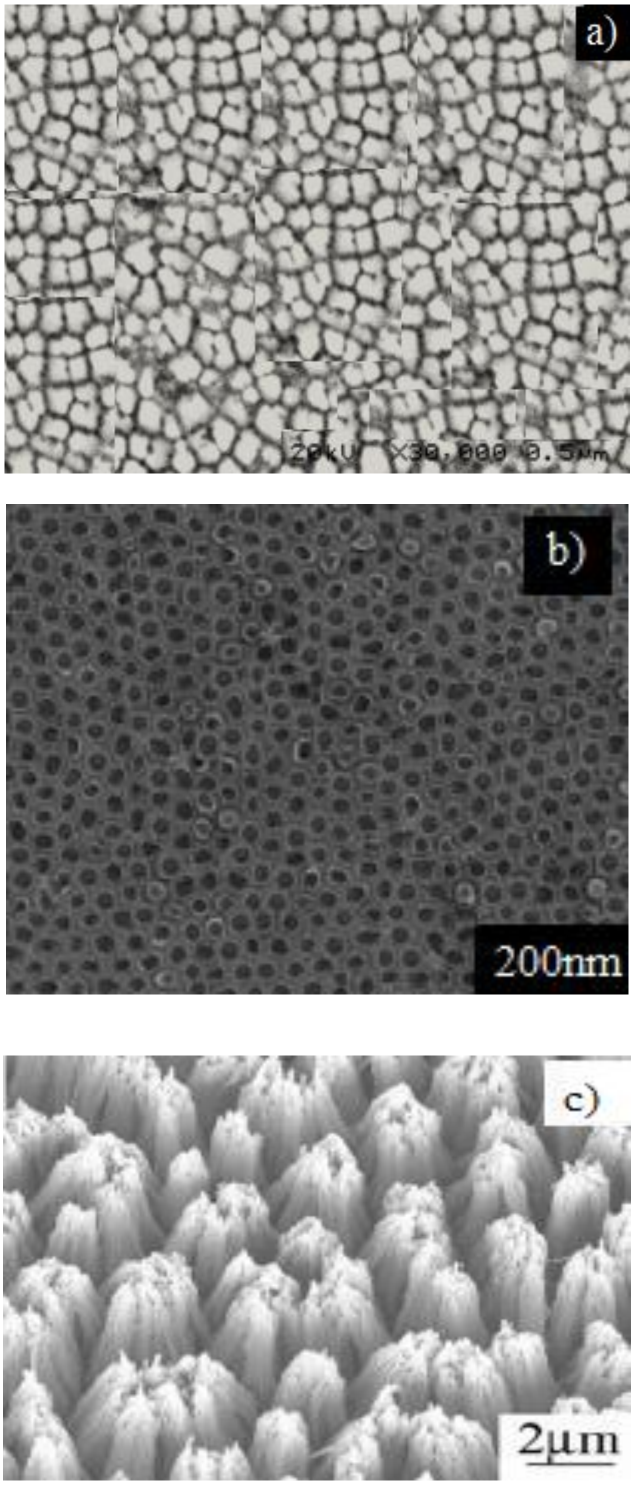

Fig. 3. SEM images of empty AAS (a) and p-CdS nanowire arrays: (b and c) top views of the p-CdS nanowire array after etching for 10 and 20 min

That the compositions of the nanowires are stoichiometric in despite of a wide range of the Cd^{2+} concentration in the electrolytes, which indicates that we can use a high Cd^{2+} concentration in the electrolyte to co-deposit a p-CdS nanowire array. It is worthy to note that the potential has a very important influence on the compositions of p-CdS nanowires. It was found that the p-CdS nanowires deposited at about -2.0 V exhibited a stoichiometric composition with Cd/S ratio of 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.

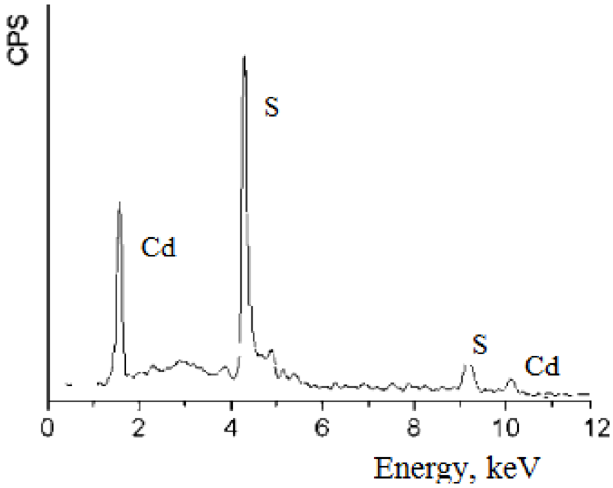

Fig. 4. EDS spectrum of the p-CdS nanowire array.

Figure 5 shows the optical absorption spectra of the p-CdS nanowires/AAS assembly system with the diameter of 60 nm and 40 nm. It can be seen that the absorption spectrum of the p-CdS nanowires/AAS assembly system is quite different from that of the blank AAS, which is due to the absorption of p-CdS nanowires. It is known that the relationship between the absorption coefficient (α) near the absorption edge and the optical band gap (E_g) for direct interband transitions obeys the following formula: $(\alpha hv)2\ ) = A(hv - Eg)$ where A is the parameter that related to the effective masses associated with the valence and conduction bands, and hv is the photon energy. Hence, the optical band gap for the absorption edge can be obtained by extrapolating the linear portion of the plot $(\alpha hv)^2$ versus α) 0. The two insets (topright corner in Figure 5) show the $(\alpha hv)^2$ versus hv plots for the two samples. For all samples, the optical absorption in the edge region can be well-fitted by the relation $(\alpha hv)^2 \sim hv - Eg$, which shows that the p-CdS nanowires embedded in the AAS have a direct band gap. The band gap of nanowires with diameters of 60 and 40 nm is about 2.43 and 2.52 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 p-CdS nanowires embedded in AAS exhibits a marked blue shift with respect to that of the bulk and thin-film p-CdS (2.43-2.52 eV). The blue shift could be attributed to the quantum size effect, which has also been observed in other semiconductor nanosystems.

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

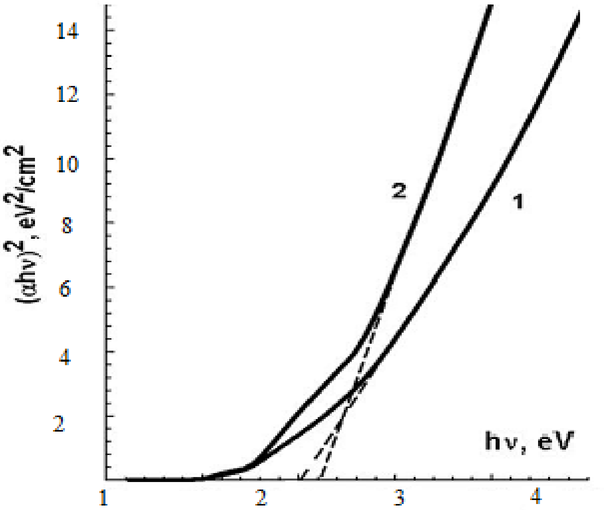

Fig. 5. Optical absorption spectra of the p-CdS /AAS nanowire arrays with different diameters: (1) 60 and (2) 40 nm.

Second, a suitable deposition rate is critical to obtain dense, ordered, and single-crystalline nanowires. To avoid the rapid nucleation and growth and inhomogeneous concentration gradient in the nanopores, the 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 are 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. Proper choice of the pH value of the electrolyte and deposition potential is also important.

IV. CONCLUSIONS

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

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