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Direct current electrochemical synthesis and characterization of $Cd_{1-x}Mn_xS$ nanowires

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ABSTRACT

$Cd_{1-x}Mn_xS$ (CMS) nanowire arrays were fabricated in anodic aluminum oxide (AAO) template by direct current (DC) electrochemical method. The effect of temperature and current density on the nanowire in the deposition process and the effect of different doping Mn concentration on the band gap of the nanowires were studied. The optimum deposition temperature and current density were determined as 120 °C and 2.4mA/cm^2, respectively,and the band gap of the nanowire decreased first and then increased with the increase of Mn-doped concentration.
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KEYWORDS

$Cd_{1-x}Mn_xS$ nanowires;
DC electrochemical;
AAO;
Band gap.

The II-VI group semiconductor CdS with doped by Mn ions has attracted great amount of interests because of their novel properties and potential applications in "Spintronics"[1] such as producing more efficient photo-emitters with a highly polarized electron beam, creating spin-memory devices[2], spin transistors[3], and spin filtering effect[4]. Due to the doping of Mn ions, The sp-d exchange interaction between *sp* band electrons and $3d^5$ electrons of Mn atoms will give rise to a giant Zeeman Effect which lifts the degeneracy of the spin-up and spin-down electron states.

During the past decades, GaMnN and CdMnS nanowires were successfully synthesized by chemical vapor deposition (CVD) and solution phase chemical synthesis(SPC) methods[5,6]. However, the diameter of these nanowires was not uniform,which would lead to the spin device with irreproducible function[7]. Recently, CdS nanowire arrays have been produced in porous anodic aluminum oxide(AAO) templates by ac electron deposition[8]. But there are many cracks and defects for this kind of nanowires, because the barrier of AAO template and the change of alternating current may lead to poor crystallization and many defects. In this paper, the barrier of the AAO template was removed and uniform $Cd_{1-x}Mn_xS$(CMS) nanowire arrays were fabricated by direct current electrodeposition. The influence of temperature and current density on deposition progress and the band gaps variation with the change of concentration of Mn ions was studied. The structure and morphology as well as the atomic composition of the nanowires were characterized.

The substrate materials of AAO templates were 99.9% aluminum sheets with thickness of 0.2mm, which were annealed at 500°C for 5 h. The substrate materials were degreased ultrasonically in acetone for 10min, etched in 1M /L NaOH at 60°C for 5 min to remove the native oxide layer, and electropolished to a mirror finish in a 3:1 v/v solution of Ethanol (95%)/HClO4

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(70%) at 18 V and 2°C for 1 min. Then, they were anodized in 0.3 M oxalic acid aqueous solution with graphite counter electrodes. The AAO templates were prepared by a two-step oxidation process with anodic voltage of 40 V for 9 h at 2°C. At the end of the anodizing process, the voltage was decreased from 40 to 8 V by a step of 2 V/min to reduce the thickness of the barrier before shutting off the power. After the anodization, the remained aluminum was replaced by 5% $CuCl_2$ solution, and the alumina barrier layer was removed by 1mol/L NaOH solution. As counter electrode, Au thin film was deposited for the electrochemical deposition.

CMS nanowires were deposited into the AAO templates with DC electrochemical method. The electrochemical deposition was carried out in a glass cell with platinum electrode as the anode and the AAO template as the cathode, by immersing the cell in an oil bath. The electrolyte solutions dimethyl sulfoxide (DMSO) consisted of $CdCl_2$(0.055mol/L), $MnCl_2$(0.001-0.005mol/L), S(0.19mol/L). In order to clarify the effect of temperature on the deposition process,three samples were prepared at 85°C, 100°C and 120°C with current density is 2.4mA/cm^2 respectively. The effect of current density on the deposition process was also studied,three samples were synthesised with 0.6mA/cm^2,1.0mA/cm^2 and 2.4mA/cm^2 at 120°C. After the deposition progress, the AAO templates with CMS nanowires were washed with warm DMSO, acetone and distilled water successively, and then subjected to further measurements.

For convenience of observing the microscopic structure of the nanowire, the AAO templates with CMS nanowires were mounted on a silicon substrate with conductive adhesive. Next, they were rinsed in 1mol/L NaOH for 10-20min to remove AAO, and then washed with distilled water several times. Afterwards, they were dried naturally in air. Scanning electron microscopy (SEM) observation was carried out on Hitachi S-4800, and the conductivity of the CMS was sufficient enough so that SEM micrographs could be obtained without an additional conductive coating. High resolution transmission electron microscopy (HTEM) was carried out on FEI TECNAI G2 200 kV. For TEM imaging, the nanowire suspension was centrifuged and washed several times, then a small drop of the colloid was placed on the carbon/formvar films supported by Cu grids, and

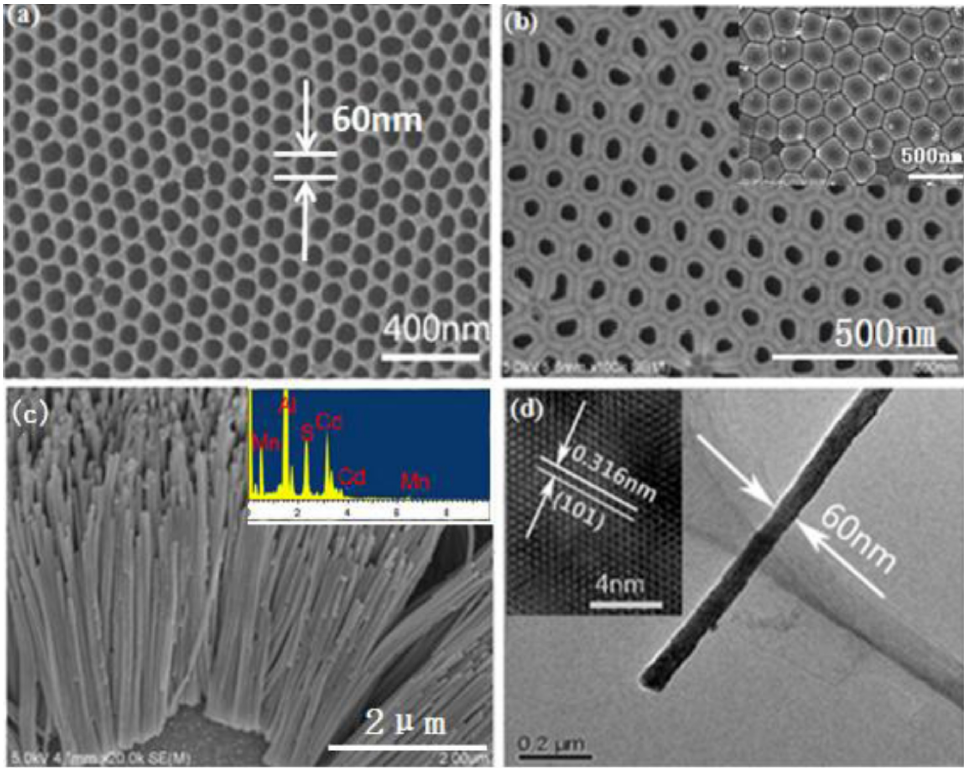

Figure 1 : Morphology and microstructure of CMS nanowires in AAO template: (a) the porous AAO template, (b) the removing barrier layer AAO template with the inset of the barrier layer, (c) SEM image of CMS nanowires exposed by dissolution of the oxide film in 1 M NaOH and EDS image (inset), and (d) the bright field image and HTEM image (inset) of the nanowire

the excess water was blotted off after 2-5 min of partial sedimentation. The X-ray diffraction analysis was carried out on D/MAX-III, with the counting time of 1.5s per step and the step size of 0.02°. The diffraction peaks of the aluminum substrate were used as an internal standard calibration, and UV visible reflection spectrum was carried out on UV-365.

Figure 1(a) shows the image of AAO template. It can be seen that the diameter of the highly organized nanopores is 60nm and the distance between pores is 80nm. Figure 1(b) is the back of AAO template whose barrier is removed, and the inset is the barrier which is insulator, placing restriction on producing nanowires by DC method therefore we removed it with 1mol/L NaOH. Figure 1(c) is the SEM image of nanowires, which are uniform and continuous with length of up to 5um and. Thus, it can be known that the growth of nanowires begins at the bottom of the pores and that the growth rate of the nanowire is about 1.6nm/s. The inset of Figure 1(c) presents the results of Energy Dispersive Spectrometer, and the atomic composition ratio of S to Cd is close to 1:1, which suggests Mn ions are doped in the nanowire successfully. Figure 1(d) is the bright field image of a nanowire, and the diameter of the nanowire is about 60nm, which corresponds to the diameter of the pores of the AAO membrane. The inset of Figure 1(d) is the HTEM image of the nanowire, and it can be found that there is no cracks and composition segregation in the nanowire.

The X-ray diffraction (XRD) results of the samples deposited at different temperatures are shown as Figure 2, in which *h* represents hexagonal crystal structure

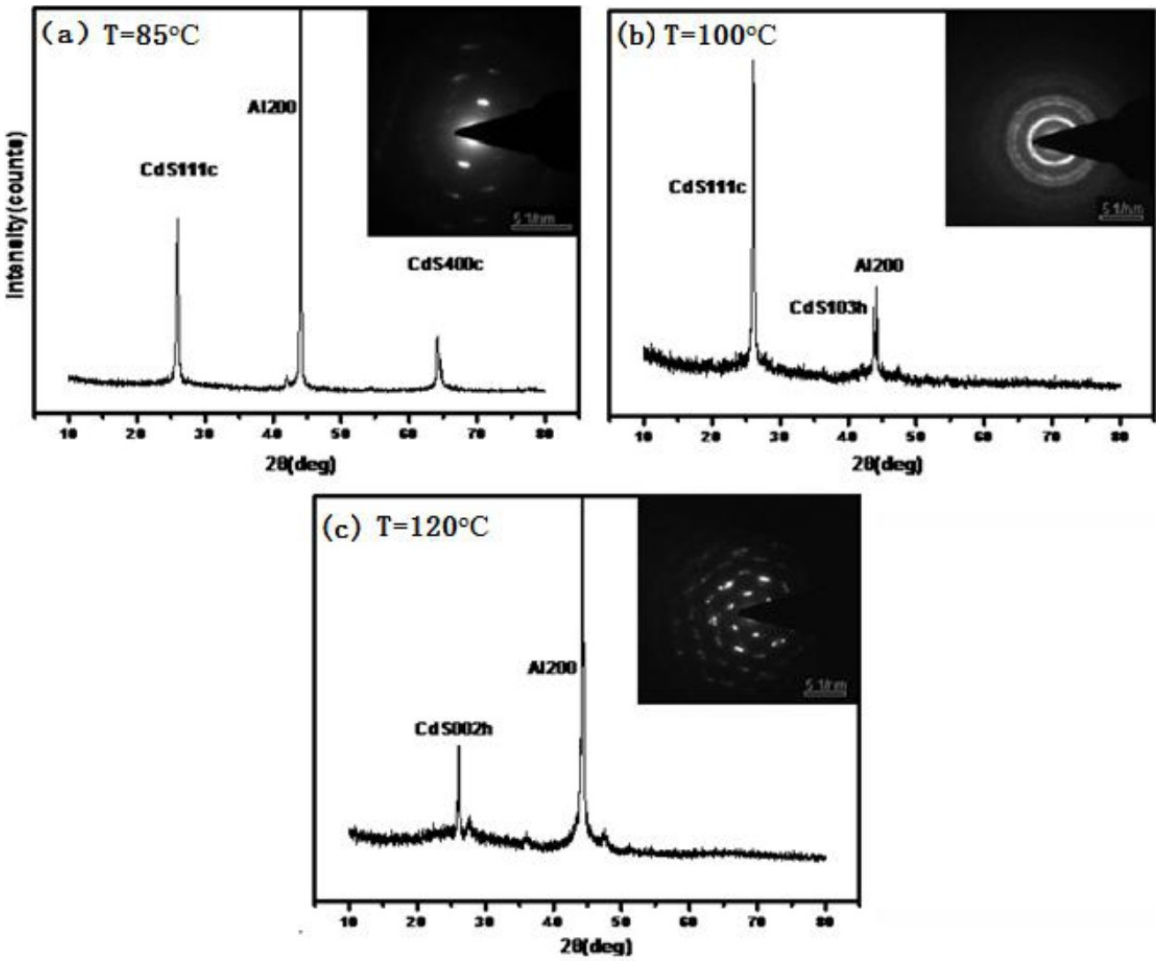

Figure 2 : The x-ray diffraction patterns of the nanowires which were deposited at different temperature. The insets of the figure are TEM electron diffraction pattern. With the increase of temperature, the structure of the nanowire change from tetragonal crystal structure to the hexagonal crystal structure, and the higher the temperature is, the better crystallization. The best deposition temperature is 120°C. From the XRD results we can know that the nanowires grow in AAO along the [002] crystal orientation at 120°C

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and *c* represents cubic structure. From the XRD patterns, we know that the structure of the nanowire is cubic structure at 85°C, a mixed structure of cubic and hexagonal at 100°C and hexagonal crystal structure at 120°C. Combined with the TEM image, it can be concluded that the crystal structure is best when the temperature is 120°C, and the nanowires grow in AAO template along the [002] crystal orientation. Therefore, the appropriate deposition temperature is 120°C.

In order to clarify the effect of current density on the deposition process, three samples were deposited with current density of 0.6mA/cm^2, 1.0mA/cm^2 and 2.4mA/cm^2 at 120°C for 15 min. Figure.3 shows XRD patterns of the nanowires deposited at different current density. It is found that there is nothing deposited in the template with current density of 0.6mA/cm^2, while cadmium is discovered when the current density is 1.0mA/cm^2. All diffraction peaks of the template deposited with current density of 2.4mA/cm^2 can be assigned to CdS, Al and AAO, without any trace of elemental Cd, S, Mn or other compounds, which confirms that the as-deposited nanowire corresponds to highly crystalline wurtzite CdS-type structure.

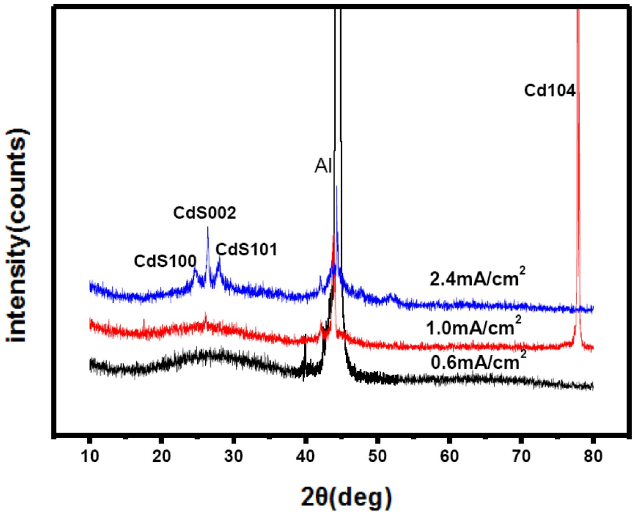

Figure 3 : X-ray diffraction patterns of the nanowires which were deposited at different current density. It is found that there is nothing deposited in the template at current density is 0.6mA/cm^2, and when the current density is 1.0mA/cm^2, the main deposition is cadmium. The appropriate current density is 2.4mA/cm^2, All diffraction peaks of the template deposited is assigned to CdS, Al, and AAO, without any trace of elemental Cd, S, Mn or other compounds

The reflection spectra of UV - visible spectrophotometer is shown in Figure 4(a), It is found the absorption edge of nanowires with different Mn concentrations are 451.9nm(0%), 488.2nm(1%), 460.8nm(2.4%) and 452nm(6.3%), respectively. According to the formula $(\alpha E_p)^2 = K(E_p - E_g)$ [9], where α is absorption coefficient, *K* is a constant, *Ep* is the photonic energy and *Eg* is the energy gap of the sample, we can obtain the value of the band gap of CMS with different Mn-doped concentrations. As Fig.4(b) shows, It is found that there is a bowing of band gap *Eg* with the small concentration of Mn ions. This consequence is probably caused by *sp-d* exchange interaction, The energy gap is $E_g(x,T) = E_g(CdS) + Dx - b\chi T$ [10],where, *D* and *b* are a constant which is related to the materials, T is temperature and $\chi = (C_M x)/(T + \Theta x)$, $C_M(x)$ is the Curie constant and Θ (x) is the Curie-Wiess tem-

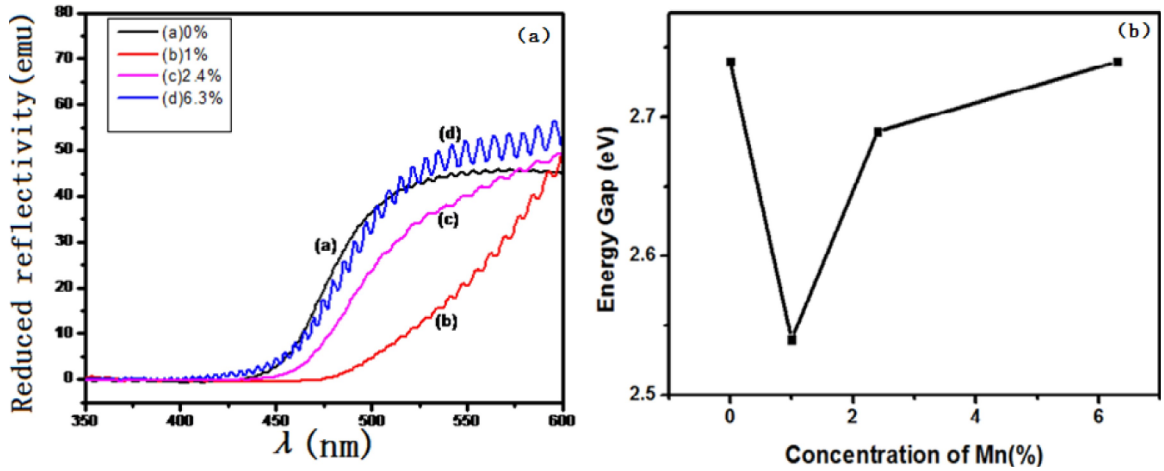

Figure 4 : (a) Reflection spectra of CMS with different concentration of Mn ion and (b) the band gap of CMS with different Mn-doped concentration, the energy decrease first and then increase with increasing of concentration of Mn.

perature, both of which can be obtained from the high-temperature susceptibility data for a sample with a given x value. Therefore, the value of energy gap of CMS is tunable by changing the Mn-doped concentration, the energy gap of the nanowire decrease when the concentration of doping Mn less than 1%, and then increase with the concentration more than 1%.

CONCLUSIONS

In conclusions, CMS nanowires were deposited in AAO by DC electrochemical method. The effects of temperature and current density on the deposition progress were studied, and the appropriate deposition temperature and deposition current density were determined as 120°C and 2.4mA/cm^2 respectively. At the optimum temperature and current density, the uniform CMS nanowire arrays with length of up to 5um and diameters of 60 nm could be obtained, and the nanowires grew in AAO along the [002] crystal orientation. By changing the concentration of doping Mn ions, the value of energy gap can be tunable, and because of sp-d exchange interaction the band gap decreases first and then increases with the increasing of concentration of Mn-doped concentration.

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