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Controlled synthesis of highly orientation-ordered single crystal $Cd_{1-x}Zn_xS$ nanorod array

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ABSTRACT

In this article, a catalyst-free method for the preparation of orientation-ordered single-crystal $Cd_{1-x}Zn_xS$ nanorod arrays on graphite substrates has been reported. The morphology and crystal structure of the $Cd_{1-x}Zn_xS$ nanorod arrays were studied using scanning electron microscopy and transmission electron microscopy. The results showed that the nanorods with 40–100 nm in diameter and 2000 nm in length grew along the [001] direction of the hexagonal crystalline phase. A vapor–solid (VS) growth mechanism was proposed for the formation of the $Cd_{1-x}Zn_xS$ nanorod arrays. The photoluminescence characterizations showed a strong blue emission at 420 nm for the $Cd_{1-x}Zn_xS$ nanorod arrays when the value of x is 0.5. Thus, with a simple CVD technique, the high-density and orientation-ordered nanorod arrays would become a promising candidate in many applications such as building blocks for optoelectronics.

1. Introduction

Recently, II–VI compound semiconductor nanowires (NWs) have been attracting extensive research interest in applications of field effect transistors (FETs), lasers, light-emitting diodes (LEDs), photodetectors, solar cells, chemical/biosensors, and thermoelectric devices [1–7]. Among them, materials with ternary alloyed nanostructures may offer more unique properties than the corresponding plain and binary compounds [8]. By adjusting the stoichiometric compositions, their properties can be effectively tuned [9]. For example, $Cd_{1-x}Zn_xS$ nanowires [10,11], $Cd_{1-x}Zn_xSe$ nanowires [12], and CdS_xSe_{1-x} nanobelts [13] were shown to possess color tunable emissions by adjusting the compositional ratios of Cd to Zn and S to Se of the nanostructures, respectively.

Various methods have been employed in the epitaxial growth of 1-D nanostructure arrays. For instance, Xu et al. fabricated CdS nanowire arrays in porous anodic luminum membranes by electrochemical deposition [14]. Lee and co-workers synthesized large-scale homoepitaxial single-crystalline cross ZnS nanowire arrays on CdS nanoribbon substrates by the metal-catalyzed vapor–liquid–solid growth method [15]. These methods could be roughly divided into two general categories: template assisted and gas-phase methods. By the template assisted electrochemical deposition, single-crystalline product with good quality is hardly prepared. On top of that, it is troublesome to remove the template and/or to clean the product. On the other hand, the gas-phase process for synthesizing 1-D nanostructure arrays is so complicated, which often involves a catalyst seed for an inducted anisotropic growth of the desired materials. The catalyst seed may interfere with the potential application of the products. In addition, the removal of the seed may damage or contaminate the nanostructure.

In this article, we reported a systematic study of the simple direct heteroepitaxial and catalyst-free growth of vertically aligned $Cd_{1-x}Zn_xS$ nanorod arrays in large scale on cheap graphite substrates using chemical vapor deposition (CVD) method. The effect of the growth parameter on the growth yield and morphology of $Cd_{1-x}Zn_xS$ nanorod arrays is studied in detail. The morphology and structural properties of the nanorod arrays are investigated by field-emission scanning electron microscope (SEM), transmission electron microscope (TEM), and selective-area electron diffraction (SAED). The growth mechanism is also discussed.

2. Experiments

2.1. Preparation of the samples

The CVD apparatus for sample preparation is illustrated in Fig. 1.

The raw materials were high pure ZnS (99.99%) and CdS (99.99%) powders. An alumina boat loaded with a molar ratio of ZnS to CdS in 1:1 was placed in the heating center of a horizontal alumina tube furnace. After being cleaned by piranha

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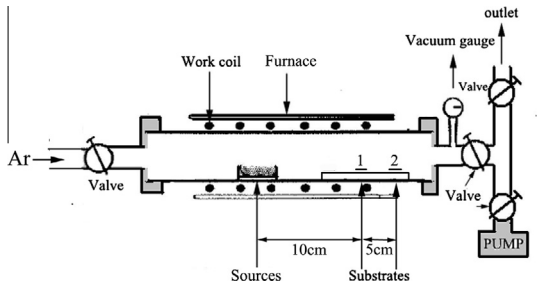

Fig. 1. Schematic illustration of the furnace used in the experiments.

solution (30%H_2O_2/20%H_2SO_4) and de-ionized water, the graphite wafers were placed to downstream as deposition substrates for materials growth. The distance between the first graphite substrate (sample 1) and the source materials was 10 cm, and the distance between the first graphite substrate (sample 1 on it) and the second substrate (sample 2 on it) was 5 cm. Prior to heating, the system was evacuated and flushed with high pure Ar for 1 h to eliminate oxygen. Then the furnace was heated up to 1200 °C within 130 min and held at this temperature for 60 min, and then cooled down to room temperature naturally under a constant flow rate of 300 SCCM Ar.

2.2. Characterization

The morphologies and elemental compositions of the samples were observed by scanning electron microscope (SEM, Philips XL 30 FEG) and energy-dispersive X-ray spectroscope (EDS). An X-ray diffraction meter (XRD, Japan Mac science) with Cu Kα radiation was used to obtain phase compositions of the samples. A JEOL 2010 transmission electron microscope (TEM) with selected-area electron diffraction (SAED) was used to analyze the morphology and microstructure. A Hitachi F-7000FL spectrophotometer was used to measure the room temperature photoluminescence (PL).

3. Result and discussion

The typical SEM images of the obtained $Cd_{1-x}Zn_xS$ nanostructures were shown in Fig. 2. Fig. 2a gives an overall view of the sample, revealed the product was well-aligned nanorod arrays with high density over a large area. Fig. 3b and c shows the high-magnification SEM images of region 1 and region 2 which marked with two white rectangles in Fig. 3a, respectively. It can be seen that the vertically aligned nanorod arrays formed on the inner surfaces of the pyramid, and each nanorod is perpendicular to the inner surface. The diameters of the nanorods range from 40 to 100 nm with the uniform length of 2 μm. In most cases, there exist two clear features: one is that it can be found no catalyst tips at the end of the nanorods. The most other one is that the diameters on the top of the $Cd_{1-x}Zn_xS$ nanorods are bigger than the bottom. The XRD pattern shown in Fig. 2d reveals the overall crystal structure of the products. As references, the standard reflections of wurtzite-structured ZnS (JCPDS No. 36-1450; $a = 0.386$ nm and $c = 0.626$ nm) and $Cd_{0.8}Zn_{0.2}S$ (JCPDS No. 49-1302; $a = 0.414$ nm and $c = 0.667$ nm) are displayed in pattern *b* and *c*, respectively. It is clearly seen that the crystallographic phase of the nanorod arrays is good agreement with the typical hexagonal wurtzite crystals. According to Vegard's law [12,15], for $Cd_{1-x}Zn_xS$ compounds, the lattice parameters have a linear dependence on composition *x*, according to $C_x = C_{CdS} + (C_{ZnS} + C_{CdS})_x$, where C_{ZnS}, C_{CdS}, and C_x are the respective *c*-axis lattice constants of the hexagonal structures of the ZnS, CdS, and $Cd_{1-x}Zn_xS$. The composition *x* of the nanorod arrays can be determined from Vegard's law using the lattice parameters deduced from the XRD data. We estimate that the composition *x* of the nanorods could be determined to 0.5.

Fig. 3 gives SEM images, EDS and XRD pattern of sample 2, which was placed about 15 cm away from the source materials. From Fig. 3a, a large number of products with pyramid structure can be observed. Fig. 3b indicates that the inner surface of the pyramid is flat, and only a little of short nanorods over the surface. The inset of Fig. 3b, which was the EDS measurements taken from the pyramid, indicating that the pyramid is only composed of Cd, Zn and S with an atomic ratio of 4:1:5. Fig. 3c shows the high-magnification SEM image of region which marked with a white rectangle. In Fig. 3b, the nanorod has a clear hexagonal cross section as

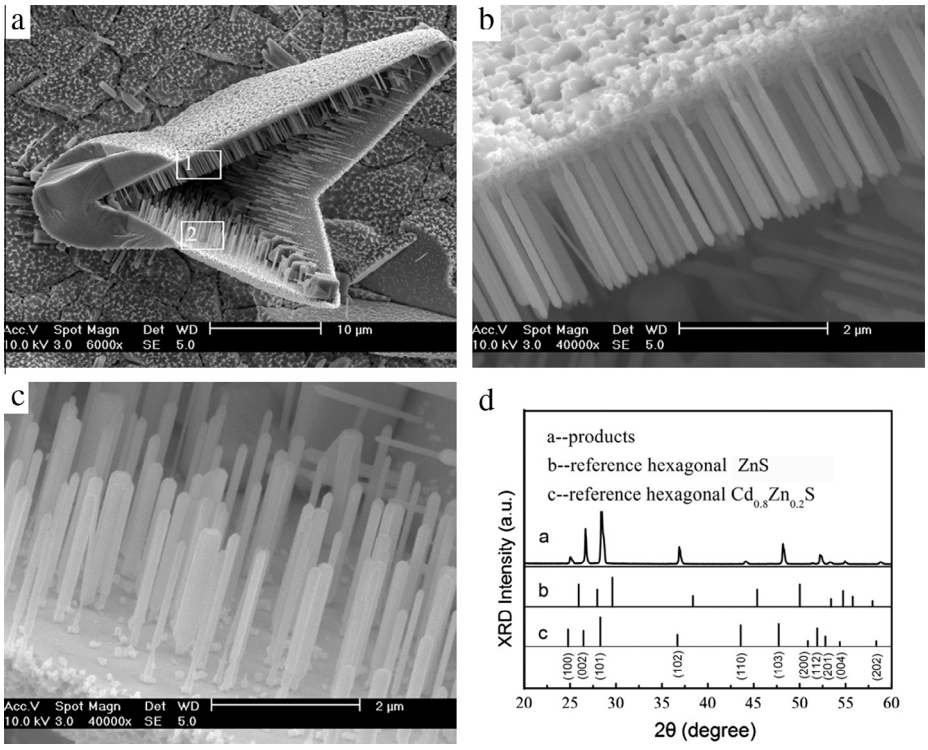

Fig. 2. SEM images of sample 1. (a) Low-magnification; (b) middle-magnification; (c) high-magnification; and (d) XRD pattern of nanorod arrays; inset (c) the corresponding EDS spectrum of image (c).