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Novel rib-like $Zn_xCd_{1-x}S$ whiskers in silica matrix

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ABSTRACT

$Zn_xCd_{1-x}S$ whiskers in silica matrix with novel rib-like structure have been synthesized in high yield by a solid–vapor decomposition route. The whiskers are composed of $Zn_xCd_{1-x}S$ rod-arrays grown closely parallel to each other with uniform diameter and length. The photoluminescence spectrum of the whiskers revealed a strong blue light emission peak at 469 nm and a weak one at 533 nm, suggesting their potential applications in short wavelength optoelectronic nanodevices.

1. Introduction

$Zn_xCd_{1-x}S$, an important ternary chalcogenide semiconductor, has a band gap tunable from 2.4 to 3.7 eV with x from 0 to 1 and, hence, can emit at different wavelengths (different band-to-band transitions). Such tenability leads to their wide applications as window materials in solar cells [1,2] and photo-catalysts in hydrogen production under visible light [3]. In 2005, Lee et al. reported the tunable lasing emission within 340–390 and 485–515 nm of a single $Zn_xCd_{1-x}S$ nanoribbon with a broad range of x [4]. After that, the interest in studying one-dimensional (1D) $Zn_xCd_{1-x}S$ nanostructures with new geometric configurations has been steadily increased, owing to their large potential capacities for next-generation optoelectronic applications [5–8]. For example, zigzag-shaped $Zn_xCd_{1-x}S$ nanowires were fabricated via metal-organic chemical vapor deposition [5]. ZnCdS nanotubes were synthesized through a thermochemical process [6]. And $Zn_xCd_{1-x}S$ nanorods were prepared from molecular precursors [7,8]. To date, in order to widen the use of these 1D nanostructures, it is still of significance to prepare a greater assortment of structures.

Moreover, when nanomaterials are capped inside a dielectric matrix, quantum confinement may be achieved with attractive optical properties. Several literatures have reported the quantum size effect and nonlinear optical effects of $Zn_xCd_{1-x}S$ nanocrystals embedded into a host matrix [3,9–11]. Through a continuing effort, we report here the synthesis of novel rib-like $Zn_xCd_{1-x}S$ whiskers embedded in silica matrix in bulk quantities by a solid–vapor decomposition process. The characterization of photoluminescence (PL) revealed that the prepared whiskers own an intensive broad blue light emission peak at 469 nm, suggesting their potential applications in short wavelength optoelectronic nanodevices. In addition, such silica-coated $Zn_xCd_{1-x}S$ whiskers will be very useful for biological labels because they allow surface conjugation with some organic functional groups which in turn can be linked to biomolecules.

2. Experimental procedure

The proposed $Zn_xCd_{1-x}S$ whiskers were synthesized in a two-heaters horizontal quartz-tube furnace, as described in detail elsewhere [12]. Specifically, the furnace temperature decreases gradually from the entrance end of the gas flow to the outlet, giving three temperature regions at high (H. T.), medium (M. T.), and low temperature (L. T.), respectively. In an optimum processing, 5 g of commercially available ZnS (4 g, Alfa Aesar, Product no. 40091) and CdS powder (1 g, Alfa Aesar, Product no. 41511) mixture was selected as source material, which was loaded in an alumina boat and positioned at the H. T. region. Several pieces of Au-coated silicon wafers were positioned at the M. T. region (the connection of the two heaters) to collect the products. High-purity Ar was injected into the quartz tube with a constant flow rate (100 SCCM) to eliminate the remanent O_2 inside for several times before heating. After that, the flow rate of Ar carrier gas was adjusted to 30 SCCM, and the furnace was then ramped up at a rate of 10 °C/min to 950–1100 °C at H. T. zone and 600–750 °C at L. T. zone. The time for synthesis was 30 min. A total pressure of 500 Torr was maintained throughout the whole heating process. Finally, the furnace was cooled naturally to room temperature. It is worth to point out that the optimum processing parameters were

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determined by simple trial and error approach. The as-synthesized products were collected from the silicon wafers and characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) with an X-ray energy dispersive spectrometer (EDS) and PL spectroscopy.

3. Results and discussion

The controlled thermal evaporation resulted in a white–yellow wool-like product on the silicon wafers in high yield. SEM images show that the as-synthesized products are composed of rib-like whiskers. The low magnification image as shown in Fig. 1(a) reveals that the whiskers are in a wood-shavings state and most of them are curved. Some straight ones were also found as shown in Fig. 1(b)–(d). The whiskers have a uniform cross-section with widths of 3–6 μm along their length that can extend to several tens of microns. Detailed examinations show that each whisker is composed of numerous and highly self-assembled rods. The rods have no catalytic droplets at their tips, implying their growth was dominated by a vapor–solid mechanism instead of vapor–liquid–solid one [13], and embed in another material with a lighter color that can be proved by the streak-like surface in Fig. 1(b) and (c) and some extrusive rods in Fig. 1(d). All the rods are of uniform diameters (30–50 nm) and quite long in lengths (3–6 μm). They grew side-by-side at nearly the same rate and direction, and simultaneously stopped growing. So, it can be concluded that this product is not a monolithic "whisker", but a nanocomposite one.

Fig. 2(a) and (b) displays two typical TEM images of the as-prepared rib-like whiskers, showing the whiskers are composed of rod-arrays arranged in parallel. All the rods are of uniform diameters (30–50 nm) and length (3–6 μm). No catalytic droplets were found at the tips, which is in agreement with the SEM results. Moreover, these rods are connected by a junction layer with a lighter color that possesses a different phase compositions from the whisker. The image with higher magnification in the inset of Fig. 2(b) further reveals that each rod is coated with a uniform sheath, including the end of the rod. Some rods separate from others because of the ultrasonic effect during TEM sample preparation, which are also confirmed by the TEM image of an incomplete whisker segment (shown in Fig. 2(c)). The well-alignment of the nanorods may be controlled by thermodynamic/kinetic process due to the stronger vapor pressure at M. T. region [14].

To confirm their compositions, EDX micro-analyses at different spots on the whisker were carried out. Two typical spectra are shown in Fig. 2(d). The upper spectrum was recorded from a spot as indicated by part I on the nanorod shown in Fig. 2(c), which clearly presents the characteristic peaks of Zn, Cd, S, O and Si. EDX quantitative analysis further revealed that the atomic percentages of Zn, Cd, and S were about 37.30%, 12.09% and 50.61%, respectively. Thus, it was estimated that the composition x of the nanorod as shown in Fig. 2(c) is about 0.76. Within experimental errors, this composition agrees with that determined by XRD which will be discussed below. The nether spectrum was taken from a spot on the sheath layer as marked by part II in Fig. 2(c), revealing that here it consists of only two kinds of elements, Si and O, and the atom ratio of Si and O is close to 1:2. The oxygen for forming SiO_2 matrix might be the remnants in the substrate, furnace and/or Ar gas carrier [10]. The Cu and C peaks in both spectra came from the TEM sample grid.

High-resolution (HR) TEM image as shown in Fig. 2(e), taken from the rectangular area as designated in Fig. 2(c), reveals that the nanorods consist of crystalline core and amorphous shell. The lattice spacings of 0.334 and 0.635 nm in the HRTEM image correspond to the inter-planar ones of the $(10\bar{1}0)$ and (0001) crystal planes of hexagonal $Zn_{0.78}Cd_{0.22}S$ alloy, respectively. This result, together with the selected area electron diffraction (SAED) pattern shown in

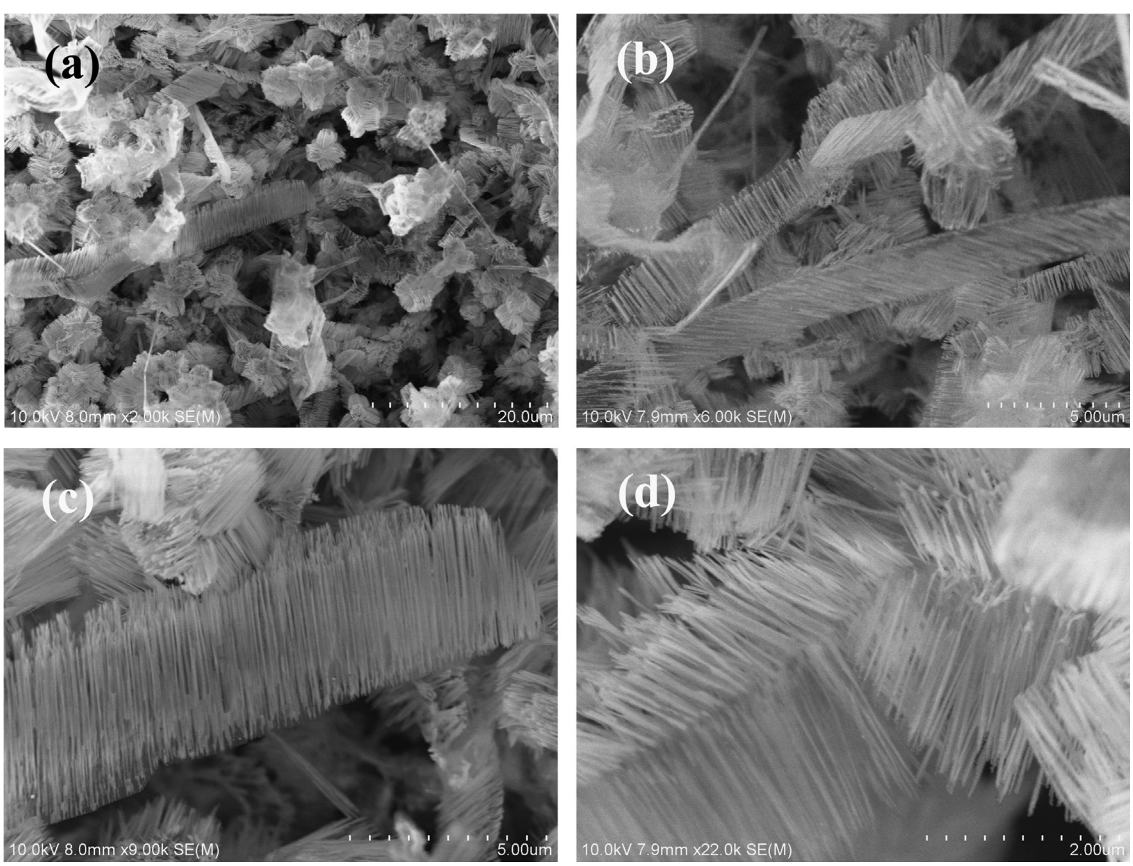

Fig. 1. SEM images of the rib-like whiskers with different magnifications.