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Visible-light activated ZnO/CdSe heterostructure-based gas sensors with low operating temperature

Bin Wu [1], Zhangqing Lin [1], Minqi Sheng *, Songyan Hou, Jifang Xu

School of Iron and Steel, Soochow University, Suzhou, Jiangsu 215021, PR China

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ABSTRACT

Three-dimensional ZnO/CdSe heterostructure (ZnO/CdSe HS) was fabricated with large scale and its gas-sensing application with low operating temperature was explored. Combining cost-effective chemical vapor deposition with solution growth methods, ZnO nanorods were grown on the surface of CdSe nanoribbons. Scanning electron microscopy, X-ray diffraction and transmission electron microscopy were employed to confirm the formation of ZnO/CdSe HS. The ZnO/CdSe HSs were fabricated as gas sensors in the detection of ethanol at the optimum operating temperature of 160 °C. Compared with ZnO-based gas sensors, the optimum operating temperature of the ZnO/CdSe HS-based sensor was approximately 100 °C lower, while the sensitivity was 20-fold higher in the dark and 3-fold higher under visible light illumination condition. The enhancement of sensing properties was attributed to the advanced heterostructure and visible light activated CdSe.

1. Introduction

Nanomaterials have attracted enormous attention in current materials science [1–5]. Previous studies evidenced that the structure of nanomaterials had a profound influence on their properties. In recently years, nanomaterials with heterostructures have led to revolutionary new applications because they could process the accumulation of carriers and control transport properties [6–11]. Gas sensor, one of such applications, was of significant interests because of its essential role in a number of important fields, including industrial control processes, safety systems, disease diagnoses, and environmental monitoring [12,13].

ZnO nanostructure was considered to be valuable sensing material in the gas sensor field for the detection of different gases, which is a typical semiconductor with appropriate energy gap of 3.37 eV and large exciton bonding energy of 60 MeV [14–16]. Unfortunately, ZnO-based gas sensor usually held disadvantages related to high operating temperature. As a result, considerable efforts have been spent to overcome this limitation [17], such as using heterostructure materials with high surface-to-volume ratios [18], UV illumination [19], appropriate element doping [20], and surface noble metal functionalization [21]. Nevertheless, there still existed the challenge to improve the sensitivity at lower temperature. It is well-known that the gas sensing characteristics of metal oxide semiconductor sensors are generally related to the surface performance of the materials [22]. Therefore, the structure and morphology were important parameters for ZnO-based gas sensors that possessed high sensitivity levels. From the point of structure, ZnO combined with CdSe can be applied in gas sensor, providing novel properties at the interface of heterostructures.

CdSe, a short-band-gap semiconductor, has been investigated extensively for optoelectronic devices due to the excellent visible light activated property [23–26]. There are several advantages including high optical absorption, great chemical and photo stability, and the possibility of tailoring the band gap of the semiconductor [27]. Yu at al. showed that the CdSe/TiO_2 coupled system had a much higher photocatalytic activity than that of pure TiO_2 in the degradation of 4-chlorophenol under visible light illumination. Consequently, visible light illumination might be provided to improve the sensitivity of gas sensors [28].

Here, we fabricated a uniform ZnO/CdSe heterostructure (ZnO/CdSe HS) material. ZnO nanorods were grown on the surface of CdSe nanoribbons vertically via chemical vapor deposition and solution growth methods. Sensors based on this material exhibited 20-fold and 3-fold improvement of gas sensing activity in dark and under visible-light-irradiation compared with ZnO nanorod-based sensors in response to ethanol at the optimum operating temperature of 160 °C. The lower operating temperature may be due to the heterostructure and the visible light activated CdSe.

* Corresponding author.
E-mail addresses: shengminqi@hotmail.com, shengminqi@suda.edu.cn (M. Sheng).
[1] These authors contributed equally to this work.

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2. Experimental

2.1. Reagents

Ethanol, acetone, zinc nitrate, zinc acetate, methenamine were supplied by National Pharmaceutical Group Chemical Reagent Co. Ltd. and used directly without any further purification. Commercial grade CdSe (99.99%) powder was bought from Alfa Aesar. And the corresponding solutions were prepared using double-distilled water.

2.2. Fabrication of CdSe nanoribbon

The CdSe nanoribbons were synthesized through a thermal-evaporation process in a single-zone, horizontal tube furnace. In the quartz tube, an alumina boat with CdSe powder was loaded at the centre of the heating zone, and a single-crystalline silicon wafer with 2 nm gold film was placed downstream of the source in order to collect the deposited CdSe nanoribbons. The system was flushed with Ar gas for 1 h to eliminate O_2. Then the furnace was rapidly heated to 700 °C and maintained at this temperature for 2 h with a constant flow of 15 sccm (standard-state cubic centimetre per minute) Ar under 2×10^{-2} Torr pressure.

2.3. Fabrication of ZnO/CdSe HS

Firstly, the zinc acetate ethanol solution (5 mM) was spread on the surface of the CdSe nanoribbons by spin coating. Through thermal decomposition at 300 °C for 20 min, uniform ZnO seeds were grown on the nanoribbons. Then, the seeded CdSe nanoribbons were placed in an aqueous solution of zinc nitrate (0.025 M) and methenamine (0.025 M) at 90 °C for 90 min. Finally, the products were washed by deionized water and dried in air to obtain ZnO/CdSe HS.

2.4. Characterization

The X-ray diffraction (XRD) was carried out on a Philips X'pert PRO MPD diffractometer with Cu Kα radiation (λ = 0.15406 nm). A scanning rate of 0.05 s^{-1} was applied to record the pattern. Field emitting scanning electron microscopy (SEM, FEI Co., model Quanta-200) was employed to observe the morphology of products. Transmission electron microscope (TEM) images and energy-dispersive X-ray spectrometry (EDS) analysis were performed by a FEI Tecnai G2F20 transmission electron microscope, with an accelerating voltage of 200 kV. Spectroscopic properties were recorded by UV–vis absorption spectra (PerkinElmerLambda 750 spectrophotometer). The gas sensitive properties were measured using a static test system made by Hanwei Electronics Co., Ltd., Henan Province, China. A 350 W xenon lamp provided visible light with an adjusting high brightness cold light source. The optical output power was measured by PM100D (Thorlabs).

The gas sensor instrument is illustrated in Fig. 1. In detail, there are two gold electrodes wrapped on both ends of a ceramic tube. Each electrode was contacted with two Pt wires to connect with the test device, and the operating temperature was controlled by a Ni–Cr alloy heater in the tube. Aqueous slurry of the ZnO/CdSe HS was dropped on the ceramic tube to form a thin sensing film and dried in air at 60 °C for 10 h.

The test atmosphere was prepared by injecting ethanol gas into a chamber full of 18 L clean air, where two fans were placed to homogenize the gas. The ethanol gas concentration could be accurately confirmed by controlling the ratio of the injected volume to the chamber volume. Meanwhile, the visible light though the optical fiber irradiated on the gas sensor was controlled by the outside equipment. During the gas measuring process, the circuit voltage was 5 V and the load resistor was 1 MΩ, respectively. The sensitivity of the sensor was defined as $S = (G_g - G_a)/G_a$, where G_a and G_g are the conductance of sensor in ambient air and in the presence of target gas (ethanol). After each test, the chamber was flushed with clean air for 5 min.

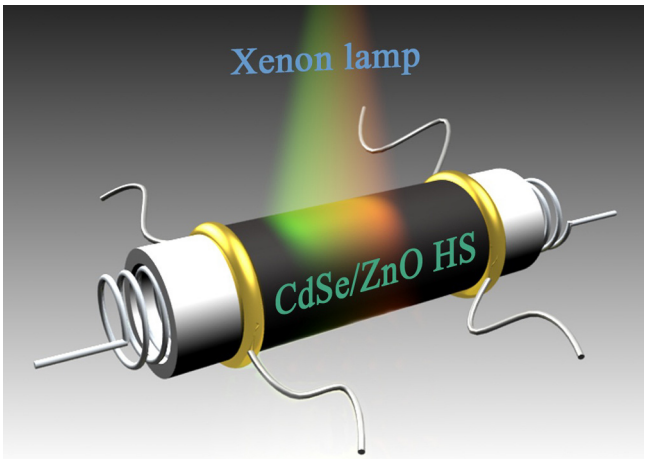

Fig. 1. The detailed schematic of gas sensor instrument.

3. Results and discussion

3.1. Morphology and structure of CdSe and ZnO/CdSe HS

The structural phases of the CdSe and ZnO/CdSe HS were identified by XRD. Fig. 2a presents a typical result with the main peaks at 23.91, 25.33, 27.09, 35.11, 41.97, 45.77 and 49.67°, which are indexed as (100), (002), (101), (102), (110), (103) and (112) planes of hexagonal CdSe (JCPDS No. 08-0459). The rest of peaks except CdSe in Fig. 2b are agreed with hexagonal ZnO (JCPDS No. 36-1451). No other impurity diffraction peaks were discovered, which confirmed that the composite was only composed of ZnO and CdSe.

A large number of CdSe nanoribbons with smooth side surfaces and uniform dimensions along their length are revealed in Fig. 3a. After the deposition of ZnO seeding layer, ZnO seeds covered on the surface of CdSe nanoribbons uniformly (Fig. 3b). Fig. 4a and b are the SEM images of ZnO/CdSe HS with different magnifications. It could be observed clearly that the products were mainly composed of branch-like nanorods with the length of several micrometers. The branch-like ZnO/CdSe HS possessed well-aligned surfaces, which were built up from compactly aggregated regular-shaped ZnO nanorods. Fig. 4c displays a typical TEM image of ZnO/CdSe HS at low magnification, which also illustrates the branch-like morphology. EDS was used to clearly indicate the parts of ZnO nanorods and CdSe nanoribbons of the ZnO/CdSe HS in Fig. 4d. The nanorods were composed of Zn and O, while the nanoribbons were made up of Cd and Se, respectively.

For comparison, the structure of the prepared ZnO nanorods was also investigated. All the XRD peaks in Fig. S1 were indexed as pure hexagonal ZnO. Fig. S2 shows the SEM images of the ZnO nanorods deposited on the silicon wafer. The average length of ZnO nanorods was approximately 1 μm, with about 50 nm in diameter.

Compared to single-phase semiconductors, the heterostructure systems possess significant advantages, such as promoting the absorption of light. As a wide band gap semiconductor, the band gap energy of ZnO was about 370 nm. However, the UV–vis spectra revealed that the absorption edge of the ZnO/CdSe HS was about 710 nm (Fig. S3). The results indicated that visible light could induce photogenerated carriers in ZnO/CdSe HS, which are beneficial for the visible-light-activation gas sensor.

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