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Letter

High performance ultraviolet detector based on TiO_2/ZnO heterojunction

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ABSTRACT

TiO_2 nanowires array is synthesized on the FTO via hydrothermal method, which is modified with ZnO prepared by using the crystallization method. The fabricated ultraviolet detector based on TiO_2/ZnO heterojunction possesses high photoelectric performance evaluated by the photo-to-dark current ratio, which has been demonstrated to reach 4 orders of magnitude. The separation of electron–hole pairs is facilitated by the built-in electric field in heterojunction, resulting in a large photocurrent as well as a high responsivity, which can attain 150 A/W. Compared with the pure TiO_2 device, The red shift in both absorption spectrum and photo response provides a potential application for the TiO_2/ZnO device.

1. Introduction

Wide band gap semiconductors are widely used in ultraviolet (UV) detectors, especially oxide semiconductors such as TiO_2, ZnO, and NiO, which are environmental friendly as well as thermally and chemically stable [1]. Amongst the different materials studied thus far, Titanium dioxide (TiO_2), an n-type semiconductor (anatase 3.2 eV and rutile 3.0 eV) has an extremely wide range of application field due to the ease it can be used to fabricate various one-dimensional nanostructures including nanotubes, nanoribbons and nanowires [2–4]. Recently TiO_2 nanowires (NWs) have attracted extensive research attention because of their unique microstructure and diversified functional properties, for instance the high surface-to-volume ratios [5] and superior charge transport [6]. Zinc oxide (ZnO, 3.37 eV) is another wide band gap semiconductor with high sensitivity in adsorbing oxygen on the surface and large binding energy at room temperature [7]. As one of the key electronic and photonic material, ZnO exhibits promising applications in optoelectronics devices [8–10]. The diversity of nanostructures and synthesis methods of ZnO leads more and more people to focus on the study about UV detectors based on ZnO. However, the performance of traditional UV detectors based on single material is defective, some important photoelectric properties are limited by the nature of the material itself, for example the absorption spectrum is defined or the photo responsivity is low. In order to overcome these weaknesses, some UV detectors are prepared by composite materials [11,12]. Researchers have paid more attention to the coupling of semiconductors, especially a heterojunction based on two kinds of semiconductors with different energy band structures to improve the sensitivity of photodetectors [13,14]. It has been proved that the heterojunction can improve the separating results of charges effectively. TiO_2 and ZnO are good candidates to form a heterostructure with better properties than individual ones resulting from the coupling of different energy level structures. The built-in electric field has been generated and provides more efficient charge separation which can result in a growth in the number of carriers and an increasing of the carrier lifetime. Moreover, nowadays people pay not enough attention to the fact that the adjustment of detection range of the UV detectors based on heterojunction is feasible, so we take the issue into thought in our research.

In this study, we pioneered the use of relatively simple synthesis methods to form the TiO_2/ZnO heterojunction, and applied the heterojunction to the UV detection. The TiO_2/ZnO based UV detector was fabricated with the structure of metal–semiconductor–metal (MSM). Au was selected as Schottky contact metal. Compared with the device based on pure TiO_2 NWs array, significant improvements of photoelectric performance in the TiO_2/ZnO heterojunction device were realized. The photo-to-dark current ratio reached 4 orders of magnitude, improved from 2 orders of magnitude of the pure TiO_2 device. A great leap of the responsivity from 12 A/W up to 150 A/W had been measured under 380 nm UV illuminated. On the other hand, a considerable improvement in responsivity was also observed in contrast with those devices based on some other composite materials in the recent reports,

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for example, ZnO with CuO [15] and TiO_2 with SnO_2 [16]. Furthermore, we have taken notice of the spectral selection characteristic of the devices. A slight red shift could be observed in the absorption spectrum after modifying ZnO on the TiO_2 NWs. The enhancement of the detection range provided potential application for the TiO_2/ZnO heterojunction device.

2. Experimental details

The TiO_2 NWs array was prepared by the hydrothermal method. 10 mL of toluene was first added as a solvent. Then 1 mL of tetrabutyl titanate and 0.2 mL of titanium tetrachloride were added in sequence. Thereafter, 1 mL of hydrochloric acid was added into the precursor solution dropwise. Subsequently, the whole mixture solution was transferred into a 23 mL Teflon-lined stainless-steel autoclave, and one piece of FTO substrate was immersed in the solution. After a reaction at 150 °C for 5 h, the autoclave had a natural draft cooling, and the FTO was dried in the air at room temperature.

The crystallization method was used to synthesize ZnO nanoparticles. Firstly, FTO covered by the TiO_2 NWs array was put into the 0.25 M Zinc acetate dehydrate ethanol solution. After an immersion for several minutes, the overmuch solution on the TiO_2 NWs array was removed by using the method of spin-coating with speed of 1000 rpm and time of 20 s, dried for 10 min at 60 °C, followed by the thermally annealing at 500 °C for 1 h in an atmospheric oven, then cooled down to room temperature.

The circular Au electrodes in radius of 2 mm were fabricated by the magnetron sputtering technique. X-ray diffraction (XRD) analysis of the materials was carried out with a Shimadzu XRD-6000 diffractometer. The morphology was shown by the scanning electron microscope (SEM; XL30 ESEM FEG). The absorption spectra were measured on a Shimadzu UV-1700 Pharma Spec UV spectrophotometer. The current–voltage (*I*–*V*) characteristics and responsivity of the devices were measured using a Keithley 2601 source meter together with a UV power meter. A 30 W deuterium lamp was used as the light source and the monochromatic light was provided by a monochromator.

3. Results and discussion

Fig. 1(a) displays typical scanning electron microscopy (SEM) image of the as-synthesized pure TiO_2 material, which reveals the formation of 1D wire-like nanostructure with diameters of 20–40 nm. The image of TiO_2/ZnO composite structure is shown in Fig. 1(b). Under the same magnification, more adhesions on the surface are discovered after depositing ZnO. This can be explained that ZnO adsorbs to the sidewall of the TiO_2 NWs and the NWs array forms several nanoclusters. Fig. 1(c) and (d) illustrates the X-ray diffraction (XRD) patterns of the as prepared pure TiO_2 material and TiO_2/ZnO hybrid material. Fig. 1(c) shows that all of the reflection peaks of pure TiO_2 can be indexed to the rutile TiO_2 phase (JCPDS Card No. 21-1276), and no impurity peaks are observed, indicating that the final product is pure phase compound. The XRD pattern of the hybrid material is shown in Fig. 1 (d). There are two diffraction peaks around $2\theta = 32°$ and $34°$ on the basis of rutile phase, representing the (100) and (002) crystal planes of zincite ZnO phase (JCPDS Card No. 36-1451). We confirm that the composite material consisting of TiO_2 and ZnO is synthesized. Fig. 1(e) shows the structure diagram of the device. Both of the devices based on TiO_2 and TiO_2/ZnO are consist of two back-to-back Schottky junctions connected by FTO. Because of the symmetry of the device structure, the direction of the applied bias has no effect on the operation of the device. When testing the photoelectric performance, the device is illuminated by UV light from the back side of FTO glass. The working area of the device is equal to the total area of the two Au electrodes. The distance between the two Au electrodes is far enough, and the working regions are connected by the FTO.

Fig. 2(a) shows the *I*–*V* characteristics of UV detectors based on TiO_2/ZnO heterojunction and pure TiO_2. Both of them exhibit nonlinear behavior due to the rectifying action. Regardless of the direction of the applied voltage, all currents are rising with the increase of the voltage. At 6 V bias, the dark current of TiO_2/ZnO device is 17 nA, which is lower than that of the pure TiO_2 device of 68 nA. Under the illumination of 380 nm UV light with the power of 3.5 μW/cm^2, the photocurrent of the TiO_2/ZnO device reaches

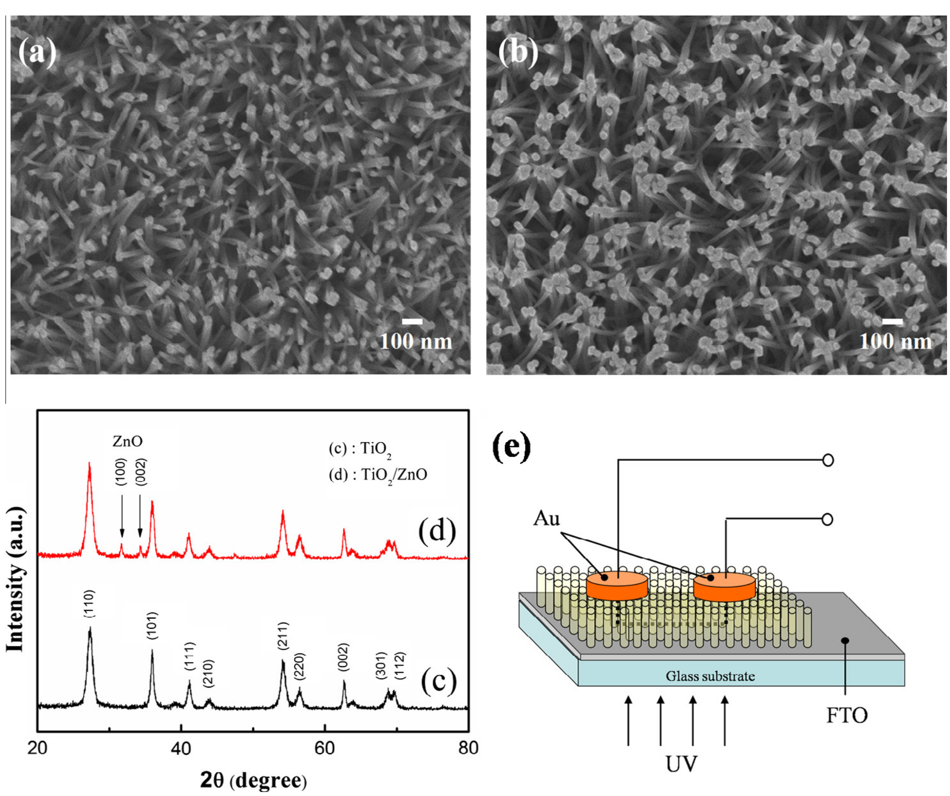

Fig. 1. SEM images of (a) TiO_2 NWs array, (b) TiO_2/ZnO composite structure, a comparison of X-ray diffraction (XRD) patterns of (c) pure TiO_2 material and (d) TiO_2/ZnO hybrid material, (e) the structure diagram of the device.