Fabrication and optical properties of InP/Cu$_2$O nanojunctions

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Abstract. The InP/Cu$_2$O nanojunction hybrid materials are fabricated by a facile method via electrodeposition of Cu$_2$O nanoparticles on the ordered one dimensional InP nanopore arrays. The morphology and element composition of the InP/Cu$_2$O heterostructures are characterized. Experimental results indicate p-type Cu$_2$O nanoparticles homogenously covered on the surface of n-type InP nanopore arrays and formed efficient heterogeneous structure. Compared to the pristine InP nanopore arrays, the InP/Cu$_2$O nanoheterojunction structure have advantageous of the separation of photogenerated electron-hole pairs.

1. Introduction

Semiconductor nanostructures have attracted significant attention in the fields of energy and environment, because they possess versatile and unique properties [1, 2]. Indium phosphide (InP) is an ideal material to be employed as nanostructured photoelectrodes because of its small band gap and high carrier mobility [3, 4]. Recently, InP nanostructures have received increasing attention as promising multifunctional building blocks for future advanced energy conversion and storage devices. Semiconductor nanostructures, however, can lead to severe carrier recombination loss due to their extremely large surface areas [5]. Constructing semiconductor heterojunction is an effective method to enhance electron-hole separation [6, 7], since heterojunction can significantly boost the synergistic effects between the components. Generally, when the n- and p-type semiconductors contact with each other, a p-n junction formed at the interfaces because of the differences in band level. Driven by the strong internal electric field, the photogenerated holes will quickly move to the valence band of the p-type semiconductor, whereas the electrons will transfer to the conduction band of the n-type semiconductor [8, 9]. Therefore, it is highly desirable to construct heterojunctions with large interface area to facilitate the charge separation and transfer.

Cuprous oxide (Cu$_2$O) is a small band gap metal oxide-based semiconductor (band gap 2.0-2.2 eV) [10, 11]. Furthermore, as a typically p-type semiconductor, Cu$_2$O has been widely used to couple with n-type semiconductors to improve their photoelectric efficiency in PEC water splitting [10, 12, 13]. Yet, up to date, there are few researches about InP nanostructures coupled with Cu$_2$O. The purpose of this paper is to prepare InP heterostructure possessing a highly ordered nanojunction structure. We achieve this by using InP nanopore arrays as a substrate to deposit Cu$_2$O nanoparticles. The InP nanopore arrays used in this study are prepared by anodization of n-InP substrates, which generates closely packed arrays
of n-type InP nanopore [14, 15]. The p-n junction formed between the n-type InP and p-type Cu2O in the InP/Cu2O heterojunction is beneficial for reducing the rate of electron-hole recombination and facilitate the charge transfer between Cu2O and InP.

In this study, we construct InP/Cu2O heterojunction and investigate its morphologies, composition and photoluminescence properties. In order to deposit a Cu2O on InP nanopore arrays surfaces, we employ a electrodeposition method that can allow for a conformal coating. Experimental results indicate that Cu2O nanoparticles cover on the surface of InP nanopores uniformly and the heterogeneous structure is formed efficiently.

2. Experimental section

2.1. Preparation of InP nanopores arrays

The fabrication process of InP/Cu2O arrays as follows. The highly ordered InP nanopores arrays were prepared in two steps as our previous report [14]. Firstly, the InP nanopores were synthesized by electrochemical anodization of n-type InP (100) single crystals (0.6 mm thickness, 99.9% purity) in 1 M HCl aqueous solution. Prior to the anodization, InP wafer were ultrasonically cleaned in alcohol, acetone and distilled water sequentially. The anodization was performed at 7 V for 60 min in a two-electrode cell with graphite foil as the counter electrode and InP wafer as working electrode at room temperature. In order to form ohmic contacts, indium films were sputtered on the back side using magnetron sputtering. After anodization, the above InP specimen were transferred into a mixture of pure HCl and H3PO4 (HCl: H3PO4= 1:3 v/v) to remove the top irregular layer. After maintained at room temperature for a few minutes, the ordered porous InP templates with uniform and square pore arrays were obtained. The obtained samples were washed with distilled water for several times and then dried overnight in air.

2.2. Fabrication of InP/Cu2O arrays heterojunction

The InP/Cu2O arrays heterojunction were synthesized by electrodeposition process equipped with a three-electrode system. An Ag/AgCl electrode was used as the reference electrode, a platinum foil as the counter electrode and the obtained InP nanopores arrays as the working electrode. The highly ordered InP nanopores arrays was transferred into the Cu2O deposition bath containing 0.4 M CuSO4 and 3 M lactic acid. The pH of the solution was adjusted to 12 by 5 M NaOH solution. The electrodeposition process was conducted at 50°C with an applied potential of -0.4 V vs Ag/AgCl for different time. After the electrodeposition process, the substrates were immediately rinsed with distilled water and absolute ethanol for several times to remove impurity ions remaining in the samples and then naturally dried in air.

2.3. Characterization

The morphologies and the microstructures of InP/Cu2O arrays were characterized by field emission scanning electron microscopy (FE-SEM, FEI Sirion 200) combined with an energy-dispersive X-ray spectrometer. The crystalline structures of the InP /Cu2O arrays were identified by X-ray diffraction (XRD) (XRD: D8 ADVANCE X-ray diffractometer, Bruker, Germany) at 40 kV and 200 mA. The chemical state of component elements in the samples was investigated by X-ray photoelectron spectroscopy (XPS), which is carried out on Kratos AXIS Ultra DLD XPS instrument equipped with an Al Kα source. The binding energies were normalized to the signal for adventitious carbon at 284.8 eV. The room temperature photoluminescence (PL) spectra were obtained by the Jobin Yvon LabRam HR 800 UV system at an excitation wavelength of 514.5 nm.

3. Results and discussion

The morphology and structure of the as-obtained materials were observed using field-emission scanning electron microscopy. As shown in the inset of figure 1a, the pristine InP nanopores array were viewed to be vertically aligned on the surface of the InP substrate with uniform nanopores that have an average
diameter of 50-80 nm. This observation indicates that the surface of the InP nanopore array is smooth, as shown previously. After the electrodeposition process, the side facets of the InP nanopores array demonstrated a rough appearance with a large amount of minute particles inlaid (figure 1b). This latter observation implies that the Cu2O nanoparticles were deposited into the surface of the InP nanopores by electrodeposition. The bottom layers of the figure 1a were zoomed in and shown in figure 1b. Obviously, the Cu2O nanoparticles were homogeneously formed on the surface of the InP nanopores array. Figure 1c displays the top view of InP nanopores array right after the Cu2O modification, it is observed that a large quantity of Cu2O nanocubes are on the surface of the InP nanopores. The size of these nanocubes was determined to be 1-2 µm. More interestingly, a high magnification SEM image (figure 1d) indicated that Cu2O was composed of vast quantities of minute particles with sizes of several nanometers, and these particles aggregated together to from the nanocubes structure.

Figure 1. (a) Cross-sectional SEM image of the InP@Cu2O nanopore arrays; (inset) Cross section SEM of the InP nanopore arrays. (b) Amplification of the bottom layer in panel a. (c) Top-view SEM image of the InP@Cu2O hybrid structure. (d) HRSEM images of the Cu2O.

X-ray diffraction was performed to identify the phase composition and crystal structure of the as-obtained samples. Figure 2 shows the XRD patterns of the InP/Cu2O arrays. It can be seen from the curves that the two peaks located at 30.4° and 63.8° for InP nanopore arrays were observed, which can be indexed to (100) and (200) crystal faces of the cubic InP (JCPDS Card No. 01-070-2513), respectively. Besides these peaks, four additional sharp peaks located at 29.4°, 36.5°, 42.3° and 61.5° were observed, which can be assigned to (110), (111), (200), and (220) planes of the cubic Cu2O (JCPDS 65-3288), respectively.[16, 17] In addition, the (220) peak is stronger than other peaks from Cu2O, indicating the preferential growth of Cu2O along the [110] direction. No diffraction peak of CuO or Cu could be found in their XRD pattern.
Figure 2. XRD pattern of InP/Cu2O

Figure 3 shows high-resolution XPS spectra of InP@Cu2O arrays heterojunction. The peaks located at 444.3 eV and 452.1 eV (Figure 3a) can be ascribed to the In 3d5/2 and In 3d3/2 from InP, respectively.[18] The peaks in the P 2p region (Figure 3b) centered at 129.3 and 128.5 eV can be attributed to those of P 2p1/2 and P 2p3/2 from InP, respectively.[18] An additional component at ca. 133.3 eV could be ascribed to In(POx)y, which could arise from easy oxidation of InP even at room temperature.[19] Cu 2p (932.1 eV for Cu 2p3/2 and 952.0 eV for Cu 2p1/2) core levels for the sample exhibits the typical features for bulk Cu2O [20, 21]. In addition, the O 1s peak located at 531.1 eV (Figure 3d) further confirms the formation of Cu2O.[20] Note that metallic Cu cannot be excluded, but it is not practical to differentiate it from Cu2O based only on the XPS data due to their very close binding energies[20, 22].

Figure 3. High-resolution XPS spectra of (a-d) In 3d, P 2p, Cu 2p and O 1s
The room-temperature PL spectra of the synthesized nanomaterials are shown in Figure 4. The spectrum of pure InP nanopores exhibits only a single narrow PL peak centered at about 910 nm, which could be attributed to the band band PL phenomenon with the energy of light approximately equal to the band energy of InP. Compared to that of the pure InP nanopores, the PL peak of the InP nanopores in the InP/Cu2O composite structure exhibits a little red shift. In addition, the emission intensity decreased, which indicates that the InP/Cu2O composites exhibit slower electron-hole recombination rate compared with pure InP nanopores. There is another PL peak at about 625 nm in the InP/Cu2O heterojunctions. The direct band gap recombination transitions for Cu2O can only be observed at very low temperatures or in high quality material [23]. With respect to the InP/Cu2O heterojunction architecture, energy band bending exists at the interface, which induces a new position of the energy level. Moreover, interfacial defects are formed due to the large difference of the crystal lattice constant between InP and Cu2O. These have an impact on the band bending. Therefore, the peak located at 625 nm may be ascribed to the new built interfacial energy band transition in nanoheterojunction.

![Figure 4](image_url)

**Figure 4.** Room-temperature photoluminescence spectra of InP nanopore arrays and InP/Cu2O arrays films.

4. Conclusions

In conclusion, the InP/Cu2O nanoheterojunction composites are constructed via anodic etching combined with electrodeposition method. Experimental results indicate Cu2O nanoparticles homogenously covered on the surface of 1D InP nanopore arrays and formed the efficient heterogeneous structure. The InP/Cu2O nanoheterojunction structures have advantageous of the separation of photogenerated electron-hole pairs. The InP/Cu2O nanoheterojunction would be expected to have significant applications in the fields of energy and environment.

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