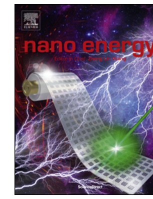
Nano Energy 26 (2016) 417–424

Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen



Interface engineering on p-CuI/n-ZnO heterojunction for enhancing piezoelectric and piezo-phototronic performance

Caihong Liu, Mingzeng Peng, Aifang Yu, Jingyu Liu, Ming Song, Yang Zhang *, Junyi Zhai *

Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences; National Center for Nanoscience and Technology (NCNST), China

ARTICLE INFO

Article history:
Received 5 February 2016
Received in revised form
18 May 2016
Accepted 26 May 2016
Available online 2 June 2016

Keywords:
Interface engineering
Energy harvesting
Piezocharges
Piezo-phototronic effect
UV photosensing

ABSTRACT

The enhanced piezoelectric and piezo-phototronic performance of ZnO-based thin film devices has been achieved by interface engineering. The piezoelectric performance of ZnO thin film is significantly boosted due to the formation of CuI/ZnO heterojunction, which effectively reduce the unfavorable piezopotential screening effect induced by free electrons in n-type ZnO. Furthermore, taking the advantage of the piezo-phototronic effect, the mechanically generated piezocharges lowers the barrier height which largely facilitates the charge transport across the CuI/ZnO heterojunction/interface and the performance of as-fabricated device were further enhanced by external strains. The photosensing behaviors of the CuI/ZnO photodetector are systematically investigated under different strain and illumination conditions. Under compressive strain, the optimum performance of flexible CuI/ZnO thin film as UV photodetector is attributed to the formation of pn heterojunction, which further modulated through the piezo-phototronic effect and improves the efficiency of charge separation as a result. Our works demonstrate merits of piezoelectric and piezo-phototronic effects for the design of energy harvesting and optoelectronic nanodevices by engineering piezoelectric/semiconductor materials interface.

1. Introduction

The heterojunction/interface between two nanostructured semiconductors plays an essential role in the design of modern nanodevice, which significantly influences the performance of integrated nanomaterials. Uniquely, by coupling the piezoelectric, semiconducting and optical characteristics of semiconductors, the piezotronic and piezo-phototronic effect has been considered as an effective approach to modulate the charge carrier generation, separation, transport and recombination at heterojunction/interface [1–14]. Within a group of non-centrosymmetric semiconductors, wurtzite-structured ZnO has been experimentally and theoretically investigated in constructing the heterojunction which modulate the performance of piezotronic and optoelectronic devices.

By taking full advantage of the piezo-phototronic effect, the construction of semiconductor/metal or semiconductor composites comprising piezoelectric component is regarded as an effective strategy for the measurement of ultraviolet and/or visible light under external strain condition. The interface engineering based on Schottky junction formed between piezoelectric material and metal electrode has been reported for the construction of UV photodetectors [7,15–17]. Most of recent works demonstrated single ZnO or GaN micro/nanowire-based photodetectors, the performance of Schottky junction based photodetector can be tuned by piezocharges at the metal/semiconductor heterointerface. In contrast to the Schottky junction-based photodetector, the approach of utilizing heterojunction/interface was performed to improve the collection of photogenerated carriers and reduce the electron-hole pairs recombination in the prototype of core/shelled CdS/ZnO coaxial micro/nanowire [18,19]. Core/multi-shell architecture was then progressed by employing carbon or optical fiber as flexible support, which enhances their light harvesting efficiency [9,10].

The key characteristic of the piezo-phototronic effect is that the carrier generation, transport, separation and/or recombination at the heterojunction/interface can be tuned by modulating the piezopotential which created and further tuned by externally applied strain. Therefore, one method to enhanced piezo-phototronic effect is increasing piezoelectric charge at the interface. Recently, considerable efforts have been paid to improve the piezoelectric performance of ZnO nanomaterials. Chemical doping has been revealed as a distinctive strategy for improving the efficiency of piezoelectric energy harvesting, which facilitates the piezocharges separation under the applied stress.[20–22] Most important, the construction of pn heterojunction turned out to be another key factor in enhancing the device performance. Typically, excess

* Corresponding authors.
E-mail addresses: zhangyang@binn.cas.cn (Y. Zhang), jyzhai@binn.cas.cn (J. Zhai).

http://dx.doi.org/10.1016/j.nanoen.2016.05.041
2211-2855/

amount of free electrons from n-type ZnO can screen the piezopotential along its polar *c*-axis generated by externally applied force, which greatly lower the piezoelectric performance of ZnO nanomaterials. A formation of pn heterojunction has a remarkable contribution towards reducing the number of free electrons in n–type ZnO. It has been reported that p-type materials were employed to deposit on the surface of ZnO nanostructures, including poly(3-hexylthiophene), CuO, Cu_2O and NiO [23–26].

Another method to improve piezo-phototronic effect is reducing charge carrier recombination probability, the design of semiconductor composites heterojunction/interface should take into account their band positions and band gap [27]. For instance, forming the heterostructure in CdS-shell/ZnO-core micro/nanowire extended the photoresponse spectra from UV to visible range attributable to the intrinsic property of CdS with smaller band gap. Wide band gap semiconductors such as undoped ZnO and GaN are inherently visible blind and mainly focus on the detection of UV light. Additionally, the band positions of non-piezoelectric semiconductors play a critical role in the in-depth study of piezo-phototronic effect as well, which has contribution to the light adsorption and photogenerated charges transfer progress [27,28]. Under different strain conditions, photogenerated electrons can be controllably transferred between piezoelectric and non-piezoelectric semiconductors due to the favorable energetics of the relative positions of the conduction band and band bending at the heterojunction/interface.

In respect of the long-term toxicity of cadmium and its compounds, exploitation of new type of non-piezoelectric components in the heterojunction has become progressively urgent for the sustainable development of piezotronic and piezo-phototronic nanodevice. Optimum band positions, long-term chemical stability, non-toxicity of the semiconductor candidates are highly desirable for improving the photoresponsivity [29–32]. Amongst few p-type semiconductors, CuI (γ-phase) is an important one with wide band gap ($E_g \sim 3.1$ eV) and receives particular attention due to its good p-type conductivity and high transparency in the visible range [33–35]. Previous work reported that photodetectors based on heterojunction between ZnO and small band gap semiconductors such as p-Si (1.12 eV), CuO ($\sim$1.35 eV), Cu_2O ($\sim$2.17 eV) and CdS ($\sim$2.4 eV) [9,27,36,37]. However, the detecting performance of UV photodetector (PD) will be lowered due to the disturbance of visible light. Comparing to the heterojunction formed by n-type CdS/ZnO composite, the depletion width of CuI/ZnO pn heterojunction can be effectively tuned by the thickness of the p-type CuI layer, which can remarkably improve the piezoelectric performance of ZnO-based nanodevices. In this work, we demonstrate that interface engineering leads to: i) enhanced piezoelectric output by the formation of a p-CuI/n-ZnO heterojunction from 0.8 V to 5.0 V; ii) piezo-phototronic effect enhanced relative changes of photoresponsivity (384%) based on CuI/ZnO pn heterojunction with a staggered band alignment; iii) the simplified and environmental friendly fabrication process is more suitable for scalable, flexible and 3D-structure piezo-phototronic device production with high performance and low-cost.

2. Experimental sections

2.1. Material synthesis and characterization

Cu film was deposited by using a high purity Cu target (99.99% purity). The iodization of the Cu film was carried out by exposing the Cu side to the iodine source. After the synthesis of CuI layer, we transfer the samples into the RF magnetron sputter system immediately. The time that exposed to the air is less than 2 min. ZnO layer was synthesized by a standard RF magnetron sputter deposition using a high purity ZnO target (99.99%) and Ar/O_2 (flow rate was fixed at 8:1) as the sputtering gases at 20 °C. The morphology of the CuI/ZnO film was examined by SEM (Hitachi 8020) and TEM (F20). The crystal structure of the CuI/ZnO film was conducted by XRD using a Bede D1 ZM-SJ-001 diffractometer. The XPS characterization was conducted by Thermo Scientific ESCALAB 250Xi. The UV–vis absorption characterization was performed by a Shimadzu UV-3600 spectrophotometer.

2.2. Device fabrication

The fabrication of CuI/ZnO PENG was fulfilled by sputtering Cu (99.99% purity) electrodes on the top of ZnO film and on the bottom of PET substrate. The output voltage and current of as-fabricated PENG was characterized by LeCroy 610Zi oscilloscope, Stanford Research System SR 570 low noise current amplifier. The CuI/ZnO PDs were fulfilled by sputtering ITO (99.99%) as transparent electrodes. The room temperature electrical property was measured by a semiconductor characterization system (Keithley 4200-SCS).

3. Results and discussion

Fig. 1 represents the characterization of CuI thin film, which is fabricated by iodizing of a Cu film on top of substrate [38]. The SEM image (Fig. 1a) demonstrates that the CuI layer is uniformly synthesized on Si substrate. In order to illustrate CuI/ZnO multilayer structure, the cross-sectional SEM and TEM images are presented in the Fig. S1 in the Supporting Information, respectively. Basing on our SEM and TEM characterizations, different phase and interface of CuI/ZnO can be unambiguously identified. The crystal structure of as-prepared CuI film with different thickness was characterized by XRD measurement, as exhibited in Fig. 1b. It can be clearly identified that the six signals corresponding to a cubic phase γ-CuI (111), (200), (220), (311), (222) and (400), respectively [39,40]. These assigned sharp diffraction peaks confirm the phase purity of the samples and their high crystalline quality. The presence of Cu and I element was confirmed by EDX and XPS spectra as shown in Fig. 1c and d. The XPS spectra were employed to determine the valence states of as-synthesized CuI film as well. The observation of characteristic peaks for Cu $2p_{3/2}$, Cu $2p_{1/2}$, I $3d_{5/2}$ and I $3d_{3/2}$ agrees well with previous studies [40,41]. For the preparation of CuI layer, iodine vapor reacts at top surface of Cu layer and then the whole Cu layer. In order to exclude the presence of Cu° in the CuI layer, we performed the Cu LMM Auger spectrum due to Cu $2p_{3/2}$ XPS (~932 eV) signal cannot differentiate between Cu^+ and Cu^0, see Fig. S2. The auger spectrum indicates only Cu^+ peak (~570 eV) was detected in the sample and no Cu^0 peak was found. The UV–vis absorption spectrum of CuI is shown in Fig. 1e. The as-prepared CuI film is transparent in the visible region, also confirmed by Fig. 1f and S3 (see Supporting Information). The room-temperature PL spectrum of CuI film exhibits a strong peak at 410 nm can be assigned to near band edge emission, which was irradiated by a 325 nm excitation light [39]. We characterized the CuI samples which synthesized and stored 8 months ago at ambient condition in comparison with freshly synthesized samples. The UV–vis and PL spectra reveal no decomposition or oxidation is observed, see Fig. S4 in Supporting Information.

The device structure is schematically presented in Fig. 2a, as well as the comparison of their piezoelectric performances. The PET layer plays an important role in the designing flexible PENG due to its elastic feature to bear an applied stress and insulating characteristic to avoid electron leakage, see Fig. S5 in Supporting Information. After applying a stress (1 MPa) to the surface of ZnO PENG, the positive and negative piezocharges are generated and