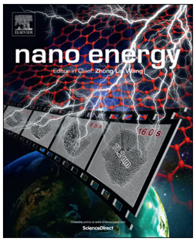
Nano Energy (2014) 9, 237–244

Available online at www.sciencedirect.com

ScienceDirect

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



RAPID COMMUNICATION

Enhanced photoresponse of ZnO nanorods-based self-powered photodetector by piezotronic interface engineering

Zheng Zhang[a,1], **Qingliang Liao**[a,1], **Yanhao Yu**[b], **Xudong Wang**[b,*], **Yue Zhang**[a,c,**]

[a]*State Key Laboratory for Advanced Metals and Materials, School of Materials Science and Engineering, University of Science and Technology Beijing, China*
[b]*Department of Materials Science and Engineering, University of Wisconsin-Madison, WI 53706, United States*
[c]*Key Laboratory of New Energy Materials and Technologies, University of Science and Technology Beijing, Beijing 100083, China*

Received 3 July 2014; accepted 22 July 2014
Available online 6 August 2014

KEYWORDS
Self-powered photodetector;
Interface engineering;
Piezotronic effect;
Metal-insulator-semiconductor;
ZnO

Abstract
Strain-induced piezopolarization can effectively engineer the interfacial electronic properties of a piezo-semiconductor junction, and thereby improve the performance of corresponding electronic devices. In this work, a metal-insulator-semiconductor (Pt/Al_2O_3/ZnO) based self-powered (SP) photodetector has been developed. The photodetector has sensitive response to the light illumination without any external bias. Applying an ultrathin dielectric layer and piezotronic effect are used as two effective strategies for interface engineering to enhance the photoresponse properties. The dielectric layer can significantly enhance the effective Schottky barrier height (SBH). In addition, the SBH can be actively modulated by the piezopolarization induced built-in electric field variation under compressive strains. Thus, the photoresponse properties of the SP photodetector are largely improved by the SBH enhancement. The responsivity and detectivity of the SP photodetector are increased by 2.77 times and 2.78 times, respectively under a compressive strain of -1.0%. According to the Schottky junction

---

[*] Corresponding author.

[**] Corresponding author at: State Key Laboratory for Advanced Metals and Materials, School of Materials Science and Engineering, University of Science and Technology Beijing, China

E-mail addresses: xudong@engr.wisc.edu (X. Wang), yuezhang@ustb.edu.cn (Y. Zhang).

[1] These authors contribute equally.

http://dx.doi.org/10.1016/j.nanoen.2014.07.019

principle, it can be concluded that the piezotronic effect occurs strongly at the interface and gradually decays towards the quasi-neutral region of the junction.

Introduction

Nanotechnology has been considered as a valid approach to solve the growing threat of global energy crises. Aiming toward highly intelligent and efficient integration, low power consumption, extremely sensitive and rapid response, and environmental benignity, a variety of novel nanodevices has been demonstrated, including solar cells [1], nanogenerators [2-4], light-emitted-diodes (LEDs) [5], sensors [6], and electronics [7]. For junction based semiconductor devices, interface engineering is an effective way to improve the performance by optimizing the crystal lattice structures, electronic band structure, barrier height, space charge region, and surface states [8]. Recently it has become a promising method to modify the interfacial physical and chemical properties at the junction area utilizing the piezotronic effect which is the coupling of semiconductor properties and piezoelectric effects [9]. For a strained piezoelectric semiconductor, such as ZnO, an ionic-displacement takes place inside ZnO inducing piezoelectric polarization that can modulate the carrier concentration, barrier height and built-in electric field at the interface [10,11]. The piezotronic effect has been used to monitor the performances of heterojunction solar cells, photoelectrochemical anodes, and LEDs [12-15].

On the other hand, piezoelectric nanogenerator is a direct application of piezoelectric effect in ambient mechanical energy harvesting, which leads to a mass of self-powered (SP) nanodevices and nano-systems [16,17]. A series of SP nanodevices composed of nanogenerators and sensing units have been developed to detect vibration [18], magnetism [19], and photons [20]. The most effective SP device is to integrate the powering and sensing functions in the same building block. Based on this concept, a new type of fast and sensitive SP photodetector was demonstrated using the built-in electric field at the junction area of a pn junction [21,22] or a metal-semiconductor (MS) contact [23,24] to separate the photogenerated electron-hole pairs (EHPs) under illumination without a bias [23,25]. For an MS photodetector, the deep depletion region formed in the semiconductor provides strong built-in electric-field to separate EHPs [26,27]. Furthermore, a thin insulator layer can be employed between semiconductor and metal electrode forming a metal-insulator-semiconductor (MIS) contact, where the insulator layer reduces the tunneling current from metal to semiconductor and improves the reliability and performance. The performance of a ZnO based SP photodetector might be effectively improved by the strain-induced piezopolarization at the ZnO-Pt interface.

In this work, an MIS based SP photodetector was developed, where the insulator layer was an Al_2O_3 thin film prepared by atom layer deposition (ALD). The photoresponses of the SP photodetector were enhanced by the modulation of barrier heights and built-in electric field as a result of piezo-induced negative polarization, which was further evidenced by the investigation of the resistance variation at junction area under compressive strains.

Experimental sections

Growth of ZnO Nanorod arrays (NRAs)

The ZnO NRAs were grown on FTO substrates using hydrothermal method. The colloid seed solution was prepared by dissolving zinc acetate $[Zn(CH_3COO)_2 \cdot 2H_2O]$ in ethanol with a concentration of 0.05 M. Several drops of colloid seed solution were applied onto a cleaned FTO substrate to cover the entire substrate surface. The substrate was dried at room temperature and then annealed at 350 °C in air for 30 min. The precursor solution was prepared by dissolving Zinc nitrate hexahydrate $[Zn(NO_3)_2 \cdot 6H_2O]$ and hexamethylenetetramine (HMTA) $[(CH_2)_6N_4]$ in deionized water with an equal concentration of 0.1 M. The substrate coated with ZnO seed layer was immersed in the precursor solution at 95 °C for 6 h without stirring.

Deposition of Al_2O_3 layer by atomic layer deposition (ALD)

A home-made ALD system was applied to carry out the thin film coating of Al_2O_3 on ZnO NR surface. The amount of trimethylaluminum and H_2O vapor supply were controlled by two solenoid valves. The target substrate was loaded in a quartz tube and placed at the position 5 cm away from the precursor inlet nozzle. N_2 gas with 40 sccm flow rate was introduced into the chamber to serve as the carrier gas and provide 3.3 Torr system base pressure. During the coating process, the system temperature was kept at 100 °C. Trimethylaluminum and H_2O was pulsed into the reaction chamber separately with a pulsing time of 500 ms and followed by 60 s N_2 purging. Therefore, one deposition cycles involves 500 ms of H_2O pulse+60 s of N_2 purging+500 ms of trimethylaluminum pulse+60 s of N_2 purging. After 20 cycles of deposition, the chamber was allowed to cool down naturally under N_2 flow.

Device fabrication

The Pt electrode was prepared by depositing a thin film of Ti/Pt onto a highly conductive Si substrate. The Si substrate with a resistivity of 0.001–0.005 Ω/cm was sliced into 1.5 mm × 1.5 mm square pieces. The Si substrate was cleaned by Piranha solution (H_2SO_4:H_2O_2=60: 1, 100 °C), SC-1 (NH_4OH: H_2O_2: DI=1: 1: 5, 75 °C), SC-2 (HCl: H_2O_2: DI=1: 1: 5, 75 °C), and diluted HF (HF: DI=1: 50) solution. The substrate was then loaded into CHA metal evaporator for oxide free surface. The Ti/Pt (20/130 nm) film was deposited by e-beam evaporation under the base pressure of less than 2.1×10^{-6} Torr. The evaporation rate