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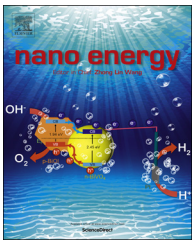

RAPID COMMUNICATION

Phosphorus-doped zinc oxide p-n homojunction thin film for flexible piezoelectric nanogenerators

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Abstract
The performance of zinc oxide (ZnO)-based piezoelectric nanogenerators (PENGs) has been largely limited by piezoelectric potential screening effect due to excess electrons in ZnO. To address this problem, we report here a method that can greatly enhance the performance of ZnO PENGs by reducing excess electrons. We formed ZnO p-n homojunction thin film, composed of unintentionally doped n-ZnO and phosphorus-doped p-ZnO, on the ITO/Ag/ITO(IAI) coated flexible substrate with a low sheet resistance of 3.03 Ω/sq and a high optical transmittance of 88.16%, where were prepared by roll-to-roll sputtering. The fabricated PENG with a p-n homojunction demonstrates the output power up to ~140 μW, which is approximately two orders of magnitude higher than that of the PENG only with ZnO. Besides, the output performance related with the p-ZnO and n-ZnO thickness ratio and the roles of p-n junction formation were also systematically investigated. The results here introduce a new method to further extend performance limit of ZnO-based PENGs.

Introduction

Harvesting energy from independent energy resources has been of interest due to its potential application in electronic devices [1]. Piezoelectric nanogenerator (PENG) in particular can generate electricity from various physical movements existing in human motions and environment [2,3]. Zinc oxide (ZnO) is one of the well-known piezoelectric materials [4,5], which has wurtzite crystal structure with a direct wide energy band gap (3.37 eV). Due to its non-toxicity and relatively low cost, ZnO have been widely studied as a piezoelectric energy harvesting material [6,7].

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However, ZnO PENG's output power is relatively low in comparison to other PENGs using different piezoelectric materials such as $BaTiO_3$ [8,9], PZT [10], due to its low piezoelectric coefficient [11,12]. Large electron concentration exhibited in ZnO due to the n-type unintentional doping by oxygen vacancies or zinc interstitials [13,14]. These electrons can screen piezoelectric potential generated by mechanical deformation or applied stress, resulting in low piezoelectric output power generation. To address this problem, several methods have been introduced to date: p-type doping [15–17], p–n junction formation [18,19], and surface treatment [20,21] have been applied to reduce excess electron concentration in ZnO in order to boost piezoelectric potential. In particular, reliable excess electron concentration reduction has been successfully demonstrated by forming a p–n junction with p-type materials and ZnO, enhancing the piezoelectric output performance. Various p-type materials including P3HT [22,23], ZnS [24], NiO [25], PEDOT:PSS [26], and p-Si [27] have been adapted to form a p–n heterojunction. However, relatively few attempts have been made to form ZnO p–n homojunction due to the absence of high quality p-ZnO film [28]. The homojunction formation is more suited for PENGs due to its chemical stability, mechanical durability, and improved piezoelectric power generation.

In this work, we fabricated the PENGs with unintentionally doped n-ZnO and phosphorus-doped p-ZnO:P [29,30] homojunction and demonstrated related performance enhancement of the PENGs. Besides, the maximum performance has been achieved by optimizing thickness ratio between ZnO and p-ZnO:P layers. The ZnO p–n homojunction PENG demonstrated the output voltage and current up to $\sim$24 V and $\sim$6 μA, respectively, at the applied force of 0.5 MPa. This is approximately two orders of magnitude higher output power in comparison to the output power of the PENGs only with a ZnO layer.

Experimental method

Transparent ITO/Ag/ITO multilayer coating on PET substrate

Flexible ITO/Ag/ITO (IAI) multilayer electrodes were sputtered on a flexible PET substrate with a thickness of 125 μm by using lab-scale roll-to-roll (RTR) sputtering at room temperature. By using an unwinding and rewinding system, the flexible PET substrate continuously passed over the rectangular ITO and Ag targets. In addition, tension of the flexible PET substrate was controlled using a load cell in the rolling system. Prior to the RTR sputtering, the surface of the PET substrate was pre-treated at a constant pulsed DC power of 550 W by irradiation of Ar^+ ions to improve the surface morphology of the PET substrate and the adhesion with the bottom ITO film. After ion-beam pretreatment of the PET substrate, a bottom ITO layer was sputtered at a constant Ar/O_2 flow ratio of 30/2 sccm, a DC power of 550 W, and a working pressure of 0.5 mTorr using a rectangular ITO target with geometry of 200×100 mm^2 placed below the rotating cooling drum at a distance of 100 mm. After sputtering of bottom ITO layer, the 12 nm thick Ag layer was also RTR sputtered on the bottom ITO layer at a constant Ar flow ratio of 30 sccm, a DC power of 380 W, and a working pressure of 1 mTorr using a rectangular Ag metal target. Finally, a top ITO layer was sputtered onto the Ag interlayer under deposition conditions identical to those used to sputter the bottom ITO layer.

ZnO layer deposition

The ZnO and p-type ZnO:P films were deposited on flexible PET substrate using RF magnetron sputtering system with multi-cathode guns at room temperature. Unintentionally doped ZnO layer was first sputtered on the IAI multilayer electrode at a constant RF power of 100 W applied to a 3 in. ZnO target, a Ar/O_2 flow rate of 20/2 sccm, and working pressure of 9 mTorr. During the RF magnetron sputtering of the ZnO layers, the PET substrate was constantly rotated at a speed of 20 rpm to ensure uniform thickness of the ZnO layers. The p-ZnO:P layer was then sputtered on the unintentionally doped n-ZnO layer using 1 wt% P_2O_5 doped ZnO ceramic target without breaking a vacuum as a function of thickness. The p-ZnO:P layer was grown under identical RF power, Ar/O_2 flow rate and working pressure to the n-ZnO layer. Fig. S1 shows continuous n-ZnO and p-ZnO:P sputtering process using tilted multi-cathode guns.

Piezoelectric nanogenerator fabrication process

Polydimethylsiloxane (PDMS) is spin-coated on a pre-cleaned ITO-coated PET substrate at 3500 rpm for 30 s. The PDMS spin-coated film is then soft-cured in oven at 85 °C for 5 min. Subsequently, soft-cured PDMS covered substrate is carefully attached on the ZnO deposited IAI substrate to avoid forming air bubbles in PDMS layer between the two substrates. Lastly, the attached device is placed in vacuum chamber to remove air bubbles in PDMS layer, followed by curing in oven at 85 °C for 3 h.

Device characterization

The output performances of our PENGs were measured using a SR 570 (Stanford Research Systems) low noise current amplifier and a Lecroy Waverunner LT 354. The electrical characteristics of diodes were measured using an Agilent 4145B semiconductor analyzer. The compressive force was periodically applied on the PENGs using the pushing machine. The crystal structure of the ZnO layers was examined by synchrotron X-ray scattering (XRS) at the GI-WAXS beam line of a Pohang Light Source (PLS) and by high-resolution transmission electron microscopy (HRTEM: JEM-2100 F). The wavelength of the incident X-rays was set to 1.243 Å by a double bounce Si (111) monochromator.

Results and discussion

The ZnO p–n homojunction PENG fabrication process is described in Fig. 1(a). The PET film is first cleaned with acetone, IPA, and deionized (DI) water, followed by bottom electrode layer deposition using RF magnetron sputtering. The bottom electrode layer on PET substrate is composed of ITO/Ag/ITO (IAI) layers. The IAI-coated PET substrate can provide