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Ultra-violet photo-response characteristics of p-Si/i-SiO$_2$/n-ZnO heterojunctions based on hydrothermal ZnO nanorods

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ABSTRACT

Hydrothermal zinc oxide (ZnO) nanorod (NR)-based p-Si/n-ZnO and p-Si/i-SiO$_2$/n-ZnO heterojunctions were fabricated, and the effects of interfacial native SiO$_2$ (~4 nm) on the I-V characteristics of heterojunctions under dark and ultra-violet illumination conditions were investigated. First, the structural and optical properties of ZnO seed crystals grown by sol-gel method and hydrothermal ZnO NRs on two different substrates of p-Si and p-Si/i-SiO$_2$ were examined, and more improved optical and crystalline quality was obtained as revealed by photoluminescence and X-ray diffraction. The p-i-n heterojunctions showed ~3 times greater forward-bias currents and enhanced rectifying property than those of p-n junctions, which is attributed to the role of native SiO$_2$ in carrier confinement by promoting the electron-hole recombination current through the deep level states of ZnO crystal. The measured ratios of photocurrent to dark current of the p-i-n structure were also greater under reverse bias (92–260) and forward bias (2.3–7.1) conditions than those (28–225 for reverse bias, 1.6–6.8 for forward bias) of p-n structure, and the improved photosensitivity of the p-i-n structure under reverse bias is due to lower density of recombination centers in the ZnO NR crystals. Fabricated ZnO NR heterojunction showed repeatable and fast photo-response transients under forward bias condition of which response and recovery times were 7.2 and 3.5 s for p-i-n and 4.3 and 1.7 s for p-n structures, respectively.

1. Introduction

The nanotechnology has been enriched with a wide variety of new emerging semiconductor materials for the improved precision in fabrication, higher efficiency, and faster response time of the nanoelectronic sensors and actuators. One of the most extensively investigated materials is zinc oxide (ZnO) for its unique properties of a direct band gap of 3.37 eV and a high exciton binding energy of 60 meV enabling the excitonic emission processes to persist even at room temperature (RT) [1,2]. It is also non-toxic and biocompatible, and the material stability under elevated temperature and chemical environment enabled the ZnO material to be considered as a viable candidate in various types of high-efficiency ultraviolet (UV) photodetectors for the bio-medical and military applications. For example, extensive research has been reported for the ZnO-based passive devices such as p-n junction [3], p-i-n Schottky diodes [4], metal–semiconductor–metal photodetectors [5], and heterojunction structures as well as active-type sensors and actuators [6]. Moreover, pioneering research on the piezoelectric, photonic, and piezo-phototronic applications based on ZnO nanostructures has been successfully demonstrated for the environmental, industrial, and military applications [7]. In recent decades, an excessive amount of research work has been made on ZnO using the various challenging but practical synthesis methods for the ZnO-based nanomaterials. Among these synthesis procedures, the aqueous solution method can be preferred because it can synthesize many different geometrical morphologies of ZnO nanostructures with a high degree of crystallinity and a controlled orientation at temperature lower than 100 °C.

As-grown ZnO nanostructures grown via hydrothermal route has been regarded as a source of unintentional n-type conductive semiconductor due to native point defects such as zinc interstitials and oxygen deficiencies [8]. Since high quality and stable p-type doping has been a problem for a long time, to develop a reliable p-n ZnO-based homojunction device has remained as a challenge [3]. An alternative approach is to utilize p-type substrates of different materials such as p-GaN [6], p-SiC [9], p-Si [3,4], and p-NiO [10] which are commercially available at low cost and large area. The potential problem in the formation of ZnO heterojunction using these p-type substrates is the large lattice mismatch between the two different junction materials and the high-density interface states [11]. Especially, the recombination centers at the interface of two different materials significantly degrade the performance of the electrical and optical properties of the hetero-

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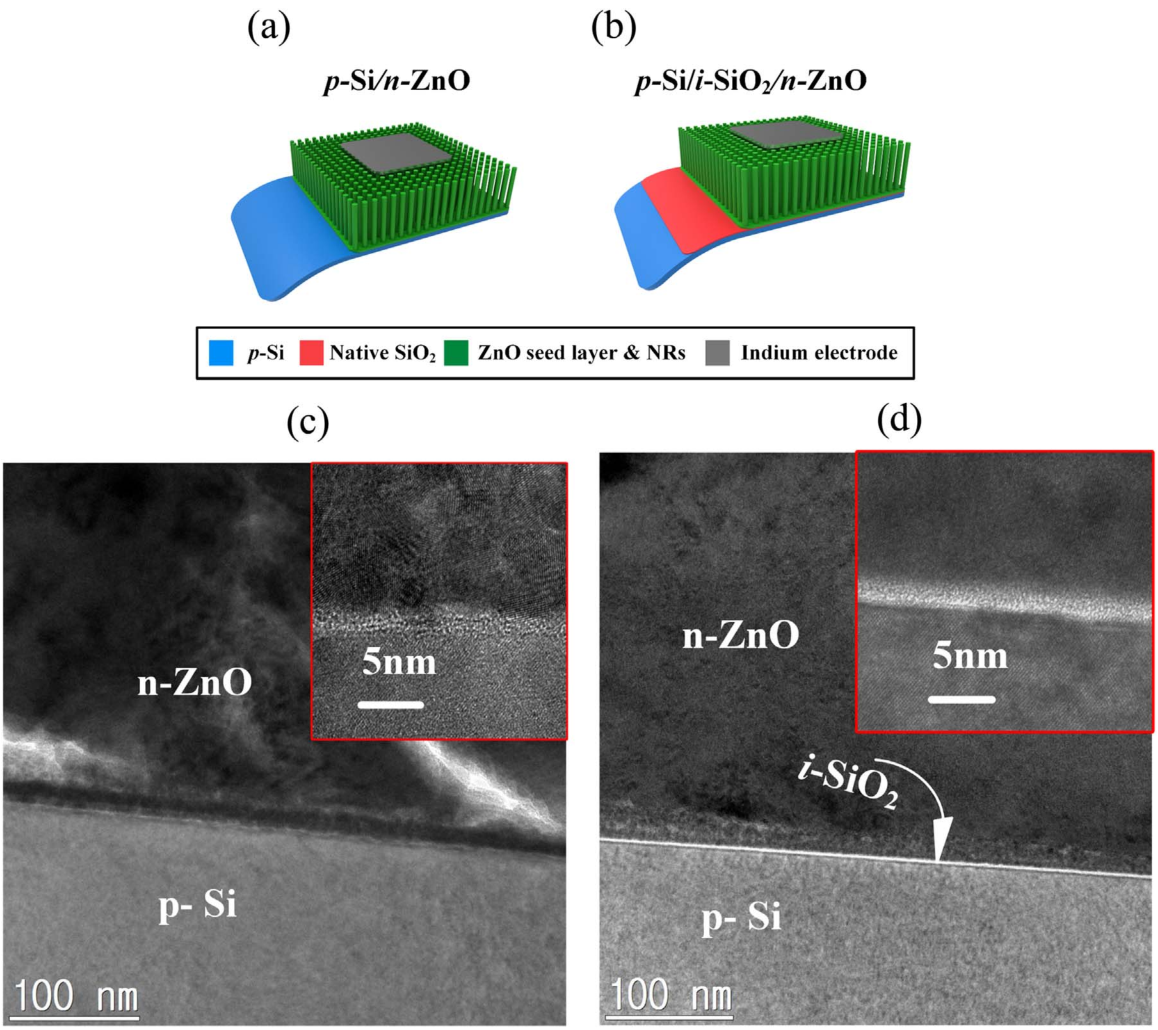

Fig. 1. Schematic illustrations of (a) *p*-Si/*n*-ZnO NRs and (b) *p*-Si/*i*-SiO_2/*n*-ZnO NRs heterojunctions. HR-TEM images of interfaces for the (c) *p*-Si/*n*-ZnO NRs and (d) *p*-Si/*i*-SiO_2/*n*-ZnO NRs heterostructures are shown.

junction devices of our concern.

Schematics of two different heterojunction structures examined in this study were shown in Fig. 1(a) and (b). In the case of *p*-*i*-*n* structure, a very thin native SiO_2 was introduced intentionally at the interface between the *p*-Si substrate and ZnO seed layer. It was reported that a thin in-situ MgO layer (~8 nm) at the interface of *n*-Si/*n*-ZnO was successfully grown in a metal organic chemical vapor deposition (MOCVD) system without vacuum pause [12]. The presence of this current blocking layer enabled the growth of high density MOCVD ZnO NRs with an enhanced vertical alignment and showed significantly improved UV photo-sensing performance. However, the role of this interface oxide in the crystalline quality improvement for the vertically grown NRs were not clearly understood, especially for the hydrothermal ZnO nanostructures.

In this study, we examined how the presence of native silicon oxide grown on the surface of silicon in air ambient condition affects the performance of our heterojunction devices as well as structural and optical properties of the ZnO NRs to be grown thereupon. As shown in Fig. 1(d), the high-resolution transmission electron microscopy (HR-TEM) micrograph shows the presence of uniform native oxide on the Si substrate of which thickness is ~4 nm in the case of *p*-*i*-*n* structure, whereas no interfacial oxide is observed in the case of *p*-*n* structure as shown Fig. 1(c). X-ray diffraction (XRD) and room temperature (RT) photoluminescence (PL) have been carried out to compare the crystalline quality of ZnO nanostructures of two different heterojunction structures. Comparative study was also performed through the analysis of transient UV photo-response and I-V characteristics of the *p*-*n* and *p*-*i*-*n* heterojunctions under dark and UV illumination conditions.

2. Experimetal procedure

To fabricate the *n*-ZnO NR-based heterojunction, we used p^+-Si (100) substrate (1×1 cm^2) of a resistivity of 0.01 Ω-cm with typical boron doping. The NRs were synthesized by using a low temperature hydrothermal method of the following two respective process steps for the seed layer and NRs. All the chemicals used in this work were of reagent grade from Sigma-Aldrich and used without any further purification.

First, a colloidal solution was prepared by dissolving 0.06*g* of zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$] in 30 mL n-propanol [$C_3H_8O$] to form a 0.2 mol concentrated solution. The solution was then sonicated for 30 min at RT and spun onto the substrate to deposit the ZnO seed layer. Prior to the deposition of ZnO seed layer, the surface of *p*-Si substrate was cleaned by acetone and isopropyl alcohol respectively for 5 min, rinsed by de-ionized (DI) water, and dried with nitrogen purge. For the heterojunction of *p*-Si/*n*-ZnO (no interfacial native oxide), the substrate was put into the buffer oxide etchant (BOE) for 5 min to remove the native oxide grown on the silicon surface. In the case of *p*-Si/*i*-SiO_2/*n*-ZnO heterojunction (with interfacial native oxide), no BOE etching was performed, but the *p*-Si substrate was preheated at 300 °C for 10 min in an ambient condition to grow a uniform silicon oxide of ~4 nm. The grown oxide film thickness was quite repetitive in