

Homojunction photodiodes based on Sb-doped *p*-type ZnO for ultraviolet detection

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(Received 19 October 2005; accepted 20 January 2006; published online 28 February 2006)

ZnO-based *p-n* homojunctions were grown using molecular-beam epitaxy. Sb and Ga were used as dopants to achieve the *p*-type and *n*-type ZnO, respectively. The mesa devices were fabricated by employing wet etching and standard photolithography techniques. Al/Ti metal was deposited by electron-beam evaporation and annealed to form Ohmic contacts. Current-voltage measurements of the device showed good rectifying behavior, from which a turn-on voltage of about 2 V was obtained. Very good response to ultraviolet light illumination was observed from photocurrent measurements. © 2006 American Institute of Physics. [DOI: 10.1063/1.2178470]

ZnO is a II-VI wide-band-gap semiconductor that has been widely studied in the recent years due to its intrinsic properties suitable for optoelectronic applications.^{1,2} One of the big challenges toward good ZnO-based optoelectronic devices is the difficulty of reliably making *p*-type ZnO. Undoped ZnO usually shows *n*-type conduction due to presence of zinc interstitials and oxygen vacancies; therefore, the acceptor carriers get compensated for easily. For this reason, considerable studies on ZnO-based optoelectronic devices were carried out by fabricating heterojunctions^{3–6} employing *n*-type ZnO with other *p*-type materials. There has already been a great deal of efforts on the fabrication of *p*-type ZnO by mono-doping group V elements, such as N,⁷ P,⁸ As,⁹ and co-doping^{10,11} of III-V elements. Most of the films are still not reliable, leading to the fact that their homojunction devices have issues such as very small breakdown voltages, large leakage currents, poor rectification, or large turn-on voltages.^{10–14} Recently, our group showed that Sb, another group V element is an efficient dopant for producing reliable and reproducible *p*-type ZnO films. The electrical¹⁵ and optical properties¹⁶ of these films along with the Sb doping mechanisms were studied. Following this, ZnO heterojunction diodes based on Sb-doped *p*-type ZnO layers and *n*-Si (100) substrates were fabricated,¹⁷ which has shown great potential of Sb-doped films for optoelectronic devices. Nevertheless, the disadvantage of heterojunction devices is that the use of multiple materials introduces complexities and the lattice mismatch between two different semiconductors introduces a lot of dislocations, which degrades the device performance. Besides the dislocations, the SiO₂ formation at the interface of Si and ZnO also poses problems, which can be easily avoided in the case of homojunction devices. In this letter, ZnO *p-n* homojunctions—using Sb-doped *p*-type ZnO and Ga-doped *n*-type ZnO—were fabricated, which show good electrical and optical properties.

ZnO films were grown on *p*-Si (111) substrates (resistivity 10–40 Ω cm) at 550 °C using a Perkin–Elmer 425B molecular-beam-epitaxy (MBE) system. The reason for choosing Si (111) substrates is that the hexagonal atom arrangement of Si (111) favors the formation of wurtzite ZnO

films. Prior to growth, the Si substrates were cleaned by the Piranha-HF method and dried with nitrogen, which was followed by a thermal cleaning at 650 °C in the MBE chamber. Zn, Ga, and Sb sources were provided by effusion cells while oxygen plasma was generated by an electron-cyclotron-resonance tube. An ultrathin Zn layer was first deposited on the Si substrate before introducing oxygen plasma in order to minimize SiO₂ formation. Then a 0.5 μm thick Sb-doped ZnO layer was grown. A postgrowth annealing at 800 °C was carried out for 30 min to activate the Sb acceptor dopants. Subsequently, an *n*-type Ga-doped ZnO layer of 0.5 μm thick was grown on top to form the *p-n* homojunction. Another reference sample was grown with the same above conditions but without the Ga-doped ZnO layer in order to characterize the electrical properties of the Sb-doped ZnO layer of the homojunction. Al/Ti bilayer metal contacts of thickness 400 nm/10 nm were deposited at room temperature and annealed at 550 °C for 30 s in nitrogen environment to form Ohmic contacts for facilitating Hall and resistivity measurements using van der Pauw configuration. Results showed that the Sb-doped ZnO layer had a hole concentration, mobility, and resistivity of $1 \times 10^{16} \text{ cm}^{-3}$, $10 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, and $6 \text{ } \Omega \text{ cm}$, respectively, while the Ga-doped layer had an electron concentration, mobility, and resistivity of $1 \times 10^{18} \text{ cm}^{-3}$, $6 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, $0.9 \text{ } \Omega \text{ cm}$, respectively.

The device fabrication was carried out using conventional photolithography. Mesa structures of size $250 \text{ } \mu\text{m} \times 250 \text{ } \mu\text{m}$ were patterned by wet etching, using a diluted solution of 1: 1: 160 of acetic acid: phosphoric acid: water. Al/Ti electrodes were placed on the Ga-doped ZnO and Sb-doped ZnO layers of the *p-n* homojunction diode by electron-beam evaporation and standard lift off. The schematic of the fabricated device is shown as the inset of Fig. 1. Annealing at 550 °C for 30 s in nitrogen environment yielded Ohmic contacts. Figure 1 shows the current-voltage (*I-V*) curves measured for a pair of contacts on the top Ga-doped ZnO layer (open circles) and the bottom Sb-doped ZnO layer (solid squares) using Agilent 4155C parameter analyzer and Signatone probe station. The linear trend shows the establishment of Ohmic contacts. The intercontact resistances are obtained from the slopes of the curves to be about 2 kΩ and 1.6 kΩ only for the top and bottom contacts, re-

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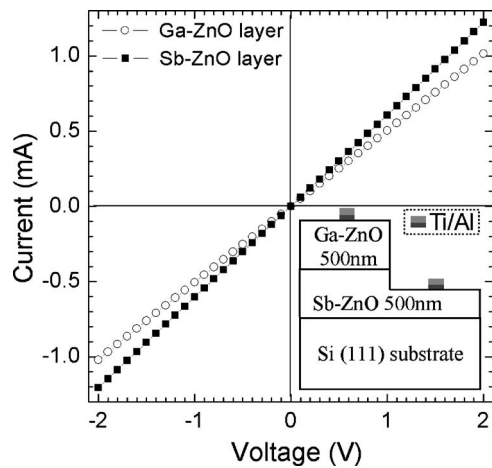


FIG. 1. I - V curves of the contacts on Ga-doped and Sb-doped ZnO layer of the device showing Ohmic characteristics. Inset gives the cross-sectional view of the fabricated device.

spectively, suggesting that the contact resistances are in the order of several hundred ohms or less. After ensuring Ohmic characteristics for the metal-semiconductor interface, I - V of the ZnO p - n homojunction was measured. The measurement results are shown in Fig. 2, where clear rectifying behavior can be observed with and without ultraviolet (UV) illumination. The band diagram of the junction at equilibrium is shown as the inset of Fig. 2. The turn-on voltage of the diode is around 2 V as seen from the I - V characteristics, from where the exponential increase in current approximately begins. Based on the doping profile of this homojunction device, the built-in potential (turn-on voltage) of about 2 V can be obtained if the intrinsic carrier concentration of $1 \times 10^{10} \text{ cm}^{-3}$ is used, which is reasonable due to the wide-band gap of ZnO according to Ref. 2. The increase in current is not sharp over a range of voltages larger than 2 V due to presence of considerable series resistance. The dark current density is about 4.8 mA/cm^2 at 3 V reverse bias. The large magnitude of dark current density indicates that there are considerable defects and dislocations in the ZnO film grown on Si substrate, which is a typical result of heteroepitaxy between largely mismatched materials. However, very good response to UV illumination can be seen from Fig. 2 (dashed lines) in the reverse biased condition due to the photo-generation of additional electron-hole pairs. The magnitude

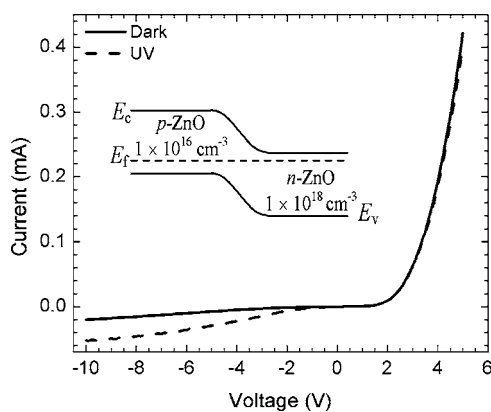


FIG. 2. I - V characteristics of the Ga-doped ZnO/Sb-doped ZnO p - n homojunction showing clear rectifying behavior. The I - V obtained in dark and UV is shown as solid and dashed lines, respectively. The inset shows the band diagram of the homojunction.

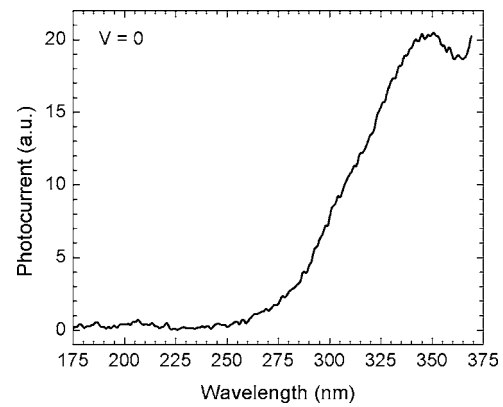


FIG. 3. PC spectrum of the homojunction diode in the photovoltaic mode of operation. Good response in the UV region is evident.

of photocurrent increases with the increase of applied reverse bias due to enhanced carrier collection.

To study the response of the device to the individual wavelengths, devices were packaged on TO5 cans using conductive epoxy and photocurrent (PC) measurements were carried out using a home-built system. The PC system consists of an Oriel Xe arc lamp as the UV source. The light from the lamp passes through an Oriel 0.25 m monochromator, which produces a specific wavelength light at its output port. After chopping, the light is then cast on the device. The generated PC signal is amplified by a home-built operational amplifier and fed to a digital lock-in amplifier from where the data is collected. Figure 3 shows the PC spectrum of the homojunction device operating in the photovoltaic mode. The device indeed shows response as a result of the photocarriers generated by the absorption of light in the space-charge region. The response extends from 250 nm and steadily increases up to 350 nm ($\sim 3.54 \text{ eV}$), which corresponds to the effective band gap of ZnO. There is a dip at 365 nm ($\sim 3.39 \text{ eV}$) in the spectrum corresponding to the actual band gap of ZnO beyond which there is an increase in response into visible region. This dip is the absorption edge of ZnO where ideally the response from the device should end. But, it continues to exist in the visible region due to the collection of photogenerated carriers in the Si substrate.

In summary, p -type and n -type ZnO thin films were grown via Sb and Ga doping, respectively, using MBE. ZnO p - n homojunction devices were fabricated using conventional photolithography based on the ZnO:Ga/ZnO:Sb sample. Al/Ti metal was used to form Ohmic contacts on both the p -ZnO and n -ZnO layers. The rectifying I - V characteristics show the existence of the ZnO p - n homojunction and the turn-on voltage is around 2 V. The I - V curves also show very good response to UV light, which was further studied by carrying out PC measurements. Evident photoreponse was observed in the UV region of the PC spectra. To enhance the performance of these devices, a higher doping concentration of the p -type layer may be utilized. Further optimizing the device by improving the crystalline quality would be effective to reduce the leakage current. This can be achieved by growing the homojunction structures on other substrates, such as sapphire, GaN, and ZnO wafers.

The authors acknowledge the financial support from DARPA/DMEA through the UCR Center for Nanoscience AIP license or copyright, see <http://apl.aip.org/apl/copyright.jsp>

and Innovation for Defense (CNID) under Award No. H94003-04-2-0404.

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