



Full length article

A boron and gallium co-doped ZnO intermediate layer for ZnO/Si heterojunction diodes



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ABSTRACT

ZnO (Zinc oxide)/Si (Silicon) heterojunctions were prepared by depositing *n*-type ZnO films on *p*-type single crystal Si substrates using magnetron sputtering. A boron and gallium co-doped ZnO (BGZO) high conductivity intermediate layer was deposited between aurum (Au) electrodes and ZnO films. The influence of the BGZO layer on the properties of Au/ZnO contacts and the performance of ZnO/Si heterojunctions was investigated. The results show an improvement in contact resistance by introducing the BGZO layer. Compared with the ZnO/Si heterojunction, the BGZO/ZnO/Si heterojunction exhibits a larger forward current, a smaller turn-on voltage and higher ratio of ultraviolet (UV) photo current/dark current.

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1. Introduction

Because of its unique properties such as large direct band gap (about 3.37 eV at room temperature), high exciton binding energy (60 meV), high transparency, low cost and low coefficient of thermal expansion, ZnO has attracted much attention in the past decades [1–4]. So far, due to the difficulty in obtaining stable *p*-type ZnO, the realization of homogeneous junction based on ZnO is still a challenging task [5]. Therefore, as an alternative approach, significant efforts have been executed on the development of ZnO-based heterojunctions. Some *p*-type materials such as Si [6], NiO [7], SiC [5], CuI [8], diamond [9], GaN [10] and CuO [11] and have been proposed to substitute *p*-type ZnO to form heterojunctions with intrinsically *n*-type ZnO or *n*-type doped-ZnO. Among them, *n*-ZnO/*p*-Si heterojunction have attracted great interest due to the ability to combine ZnO with the high-density circuit capabilities of Si.

In the preparation of optoelectronic devices, contact electrodes are considered to be one of the key factors affecting device performance [12]. Sometimes it is difficult to make a direct metal ohmic contact on a relatively high resistance semiconductor, such as intrinsically ZnO, with low specific contact resistance. For optoelectronic devices, transparent conducting oxides (TCOs) have been

widely investigated as electron transporting layer due to their high electrical conductivity and high transparency [13,14]. The introduction of TCO layer can improve the contact electrical properties and device performance.

Compared with commonly used TCO materials such as indium tin oxide (ITO), ZnO-based TCO films are considered to be the most promising alternative to ITO due to its unique properties and low cost [15–17]. In this work, *n*-ZnO/*p*-Si heterojunction diodes were prepared by depositing intrinsically ZnO film on *p*-type Si substrates using RF magnetron sputtering. A boron and gallium co-doped ZnO (BGZO) layer was prepared on the surface of ZnO/Si heterojunction to improve the contact characteristics and performance of the device. BGZO is considered to be a high performance transparent conductive oxide with high conductivity, high transmittance and high thermal stability [18,19]. The influence of BGZO layer on the contact properties of electrodes on ZnO/Si heterojunctions was investigated. The performance of ZnO/Si heterojunction diodes were also reported in detail.

2. Experiment details

Intrinsically *n*-ZnO films were prepared on *p*-type single crystal Si by radio frequency (RF) magnetron sputtering method with a high purity cylindrical ZnO ceramic target (purity 99.999%). Before film deposition, the silicon substrate was etched in hydrofluoric (HF) acid (20%) for 10 min to remove the surface oxide layer, and then cleaned in an ultrasonic cleaner. The ZnO target was pre-

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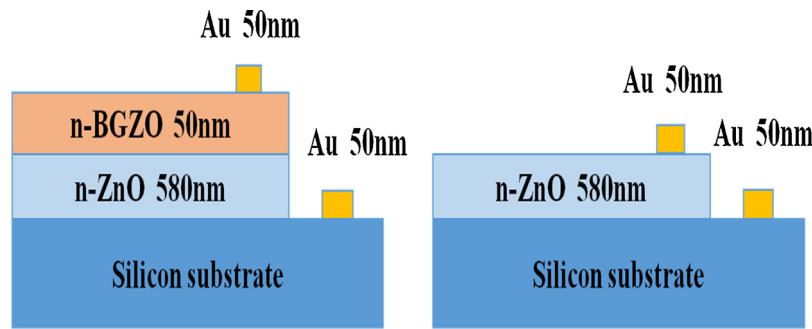


Fig. 1. Schematic of the Au/ZnO/Si and Au/BGZO/ZnO/Si heterojunction.

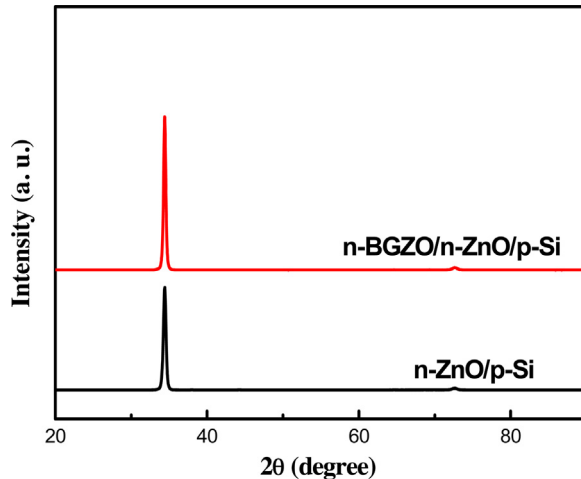


Fig. 2. X-ray diffraction patterns of ZnO/Si and BGZO/ZnO/Si structure.

sputtered for 5 min in order to remove the surface impurities of the target. The sputtering chamber was evacuated to a base pressure lower than 5×10^{-7} Torr. In the process of film deposition, the sputtering gas was pure Ar. The deposition pressure was 6 mTorr. The sputtering power was 150W. The substrate temperature was 200 °C. The thickness of the ZnO film was about 580 nm.

Then, BGZO films with a thickness of about 50 nm were deposited on the surface of ZnO films by RF magnetron sputtering method with a BGZO ceramic target (97 wt% ZnO with 2.5 wt% Ga₂O₃ and 0.5 wt% B₂O₃, purity 99.99%). A reference sample is also grown on a glass substrate in order to investigate the optical properties of BGZO/ZnO films. The properties of the films were characterized by UV–vis spectrophotometer (Shimadzu UV-2501PC), scanning electron microscopy (SEM, JEOL JSM-7500F) and X-ray diffractometer (XRD D/MAX-2200 V, Cu K_{α1}, $\lambda = 0.15406$ nm).

ZnO/Si heterojunction diodes were fabricated by depositing Au contacts on ZnO layers and Si substrates, respectively. Fig. 1 shows the schematic of the Au/ZnO/Si and Au/BGZO/ZnO/Si heterojunction.

The contacts properties of Au on ZnO or BGZO were characterized using a Keithley 4200/SCS digital semiconductor characterization system and transmission line model (TLM) method. The performance of the heterojunction diodes was analyzed using Keithley 4200/SCS and PTI optical system. A Xe-arc lamp and monochromator combination provided the light source.

3. Results and discussion

X-ray diffraction patterns of *n*-ZnO/*p*-Si and *n*-BGZO/*n*-ZnO/*p*-Si structure are shown in Fig. 2. Only one XRD peak with high intensity located at about 34.4°, corresponding to (002) reflection of ZnO

hexagonal wurtzite structure, is observed for both samples [20]. The full width at half maximum (FWHM) of (002) peaks is about 0.34° and 0.38° for ZnO/Si and BGZO/ZnO/Si structure, respectively. The highly *c*-axis orientation and peak with relatively low FWHM indicate a higher quality of prepared films. From the Scherrer's formula [19], the calculated crystallite size of ZnO and BGZO films is about 24.9 nm and 22.5 nm, respectively.

Fig. 3a and b show the SEM images of ZnO/Si and BGZO/ZnO/Si structure, respectively. As can be seen from the figure, the films are homogeneous and compact with cylindrical grains. Compared with ZnO/Si, the crystalline size of BGZO film on ZnO/Si structure is slightly smaller and denser, which is consistent with the results of XRD. Fig. 3c and d show the cross-section SEM images of ZnO/Si and BGZO/ZnO/Si structure, respectively. From the figure, ZnO films show a clear columnar structure, which is consistent with XRD results. The thickness of the ZnO films are about 580 nm. For BGZO/ZnO/Si structure, a ~50 nm thickness of BGZO film was deposited on the ZnO film.

In order to characterize the optical properties of the films, the ZnO and BGZO/ZnO samples were also prepared on glass substrate and the process parameters for sample preparation on glass are the same as those prepared on silicon. The transmittance and absorption spectra of the films on glass substrate are shown in Fig. 4a. Both films show higher transmittance above 80% including substrates in the range of 300–700 nm. Compared with ZnO films, BGZO/ZnO films have relatively higher optical transmittance due to a denser and smoother surface.

From the absorption spectra, the optical band gap (E_g) of the films could be estimated by Tauc's formula [21]:

$$\alpha h\nu = C(h\nu - E_g)^{1/2} \quad (1)$$

Where α is the optical absorption coefficient, h is Planck's constant, ν is the frequency of incident photon and C is a constant. From the $(\alpha h\nu)^2$ versus $h\nu$ plots as shown in Fig. 4b, the extrapolation of the linear portion of plots to $\alpha = 0$ leads to the optical band gap of about 3.47 eV and 3.49 eV for ZnO films and BGZO/ZnO films, respectively. The band gap energy of the prepared ZnO films is greater than the visible photon energy (<3.1 eV or >390 nm), therefore the film is transparent to the visible light and the UV photons (>3.49 eV or $\lambda < 356$ nm) could be absorbed in the films.

In order to characterize the characteristic electrical property of ohmic contacts, the transmission line method (TLM) is employed to quantify the contact resistivity (ρ_c , also called specific contact resistance) of Au/ZnO contacts and Au/BGZO/ZnO contacts. The TLM structure on the surface of ZnO films is prepared by the photolithography, as shown in Fig. 5(a). The gap spacings of the contact pads are from 80 to 720 μ m. The total resistance (R_T) between two adjacent electrodes can be expressed as the following equation [22,23]:

$$RT = 2RC + \frac{Rsh \cdot \ell}{W} \quad (2)$$

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