Thin Solid Films 520 (2012) 5960–5964

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

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

Transparent conductive ZnO:B films deposited by magnetron sputtering

Qian Huang, Yanfeng Wang, Shuo Wang, Dekun Zhang, Ying Zhao, Xiaodan Zhang *

Institute of Photo Electronics Thin Film Devices and Technique of Nankai University, Key Laboratory of Photo Electronics Thin Film Devices and Technique of Tianjin, Key Laboratory of Optoelectronic Information Science and Technology, Ministry of Education, Tianjin 300071, China

ARTICLE INFO

Article history:
Received 15 June 2011
Received in revised form 4 May 2012
Accepted 10 May 2012
Available online 16 May 2012

Keywords:
Zinc oxide
Boron
Doped films
Electrical properties
Optical band gap
Sputtering
Deposition conditions

ABSTRACT

This paper focuses on the preparation of boron doped ZnO (ZnO:B) films prepared by nonreactive mid-frequency magnetron sputtering from ceramic target with 2 wt.% doping source. Adjusting power density, ZnO:B film with low resistivity ($1.54\times10^{-3}\,\Omega$ cm) and high transparency (average transparency from 400 to 1100 nm over 85%) was obtained. Different deposition conditions were introduced as substrate fixed in the target center and hydrogen mediation. Hall mobility increased from 11 to above 26 $cm^2/V\cdot s$, while carrier concentration maintained almost the same, leading to low resistivity of $6.45\times10^{-4}\,\Omega$ cm. Transmission spectra of ZnO:B films grown at various growth conditions were determined using a UV–visible-NIR spectrophotometer. An obvious blue-shift of absorption edge was obtained while transmittances between 600 nm and 1100 nm remained almost the same. Optical band baps extracted from transmission spectra showed irregular enhancement due to the Burstein–Moss effect and band gap renormalization. Photoluminescence spectra also showed a gradual increase at UV emission peak due to free exciton transition near band gap. We contributed this enhancement in both optical band gap and UV photoluminescence emission to the lattice structure quality melioration.

1. Introduction

In recent years, ZnO-based transparent conduction electrodes for application in solar cell devices [1,2] have attracted much attention due to its competitive opto-electronic properties, non-toxicity, abundance of raw material, simplicity of manufacturing and stability in plasma [3,4]. Doped with group III element (B, Al or Ga), ZnO becomes an n-type semiconductor with low resistivity. Many deposition methods have been used to prepare ZnO films, such as sputtering [5], pulsed laser deposition [6], and chemical vapor deposition [7]. Magnetron sputtering from ceramic targets makes great industrial production capability due to its sufficiently high deposition rates and large-area procession [8,9]. Al-doped ZnO (ZnO:Al) thin film produced by magnetron sputtering has been widely investigated and many valuable results of low electrical resistivity, high optical transmission, and light scattering properties after wet chemical etching process have been obtained by a few research groups [10–12]. Boron dopant has been widely investigated in chemical vapor deposition method, but rarely used in sputtering process [13]. Recently, Gao et al. [14] reported ZnO:B thin films fabricated by RF-magnetron sputtering with resistivity of $7.5\times10^{-3}\,\Omega$ cm. They also showed that the band gap became narrower when boron was doped with respect to the pure ZnO film.

In this paper, we tried to meliorate the opto-electronic properties of ZnO:B films by adjusting the deposition process. Hall mobility, resistivity and optical band gap were performed to indentify film quality.

2. Experimental details

All ZnO:B films were prepared on glass substrates with the size of 26 mm × 76 mm. Planer magnetron cathode with a ceramic ZnO:B_2O_3 target (2 wt.%, 490 mm long and 94 mm wide) was operated at pulsed DC mode with the power frequency of 30 kHz. The target was positioned at a distance of 45 mm from substrate and sputtering chamber was typically pumped down to 2×10^{-4} Pa before deposition. The process pressure, argon gas flow and substrate temperature were 0.5 Pa, 50 sccm and 150 °C, respectively. The sputtering time varied from 40 to 30 min when discharge power was adjusted from 360 to 480 W.

Electrical properties of the samples such as sheet resistance, Hall mobility, and carrier concentration, were measured at room temperature using the van der Pauw method in the HL5500 Hall System (Accent, York, UK). Thicknesses of all films were measured by Dektak 3030 profilometer (Veeco Instruments Inc., Woodbury, USA). The optical transmittance was measured using the Cary 5000 spectrophotometer (Varian Co., Palo Alto, USA) in a spectra range of 300 to 1100 nm. Photoluminescence (PL) measurements were carried out at room temperature in a PL-Raman microscope system (Renishaw plc., Gloucestershire, UK), excited by a He–Cd laser (325 nm) with the incident power density of 40 mW/cm^2.

* Corresponding author. Tel.: +86 22 23502778; fax: +86 22 23502778.
E-mail address: xdzhang@nankai.edu.cn (X. Zhang).

0040-6090/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2012.05.014

3. Results and discussion

Series of ZnO:B films were prepared to optimize deposition parameters. Discharge powers were adjusted from 360 to 480 W when working pressure was kept at 0.5 Pa and substrate temperature was fixed at 150 °C. The electrical properties as well as thickness with the unit of nm are shown in Fig. 1. The resistivity of ZnO:B films decreased rapidly with discharge power increasing from 360 to 420 W, and appeared saturation when changed from 440 to 480 W. A resistivity below $2\times10^{-3}\,\Omega$ cm was achieved for all films at power density more than 0.9 W/cm^2 and with the thickness changing from 900 to 1050 nm. More detailed description of the influence of discharge power on electrical properties is given in Fig. 1(b). Carrier concentration of ZnO:B films increased with increasing discharge power. This may result from the boron doping efficiency increasing.

Hall mobility increased with discharge power from 360 to 420 W and then decreased with the further increment. We anticipate this trend to be dominated by the variation of atoms impinging energy on substrate surface. With discharge power changing from 360 to 420 W, impinging energy increases leading surface migration enhanced. This may improve grain growth and lead to less scattering at grain boundaries as well as intra-grain defects [15]. At higher power, the effect caused by negative high energetic oxygen ions dominates, which may damage the growing ZnO:B film by implantation of oxygen ions. This indicates that these energetic negative oxygen ions or atoms could increase the stress or strain defects on the surface due to high energetic oxygen ions bombardment [16].

Electrical property variation with different film thicknesses is shown in Table 1. Thickness was controlled by changing sputtering time from 4 to 40 min, when discharge power was kept at 440 W. The resistivity of ZnO:B films decreased rapidly with film thickness increasing from 107 to 313 nm, and appeared saturation with thickness larger than 540 nm. The resistivity attenuation is caused by crystal imperfections on the initial stages of thin film growth. Being front contact in thin film solar cells, resistivity as well as sheet resistance of ZnO films must be low enough to reduce the series resistance losses. Thus, we have to search after the effective way to improve electrical property and then reduce the needed film thickness which may reduce the series resistance and optical absorption losses simultaneously.

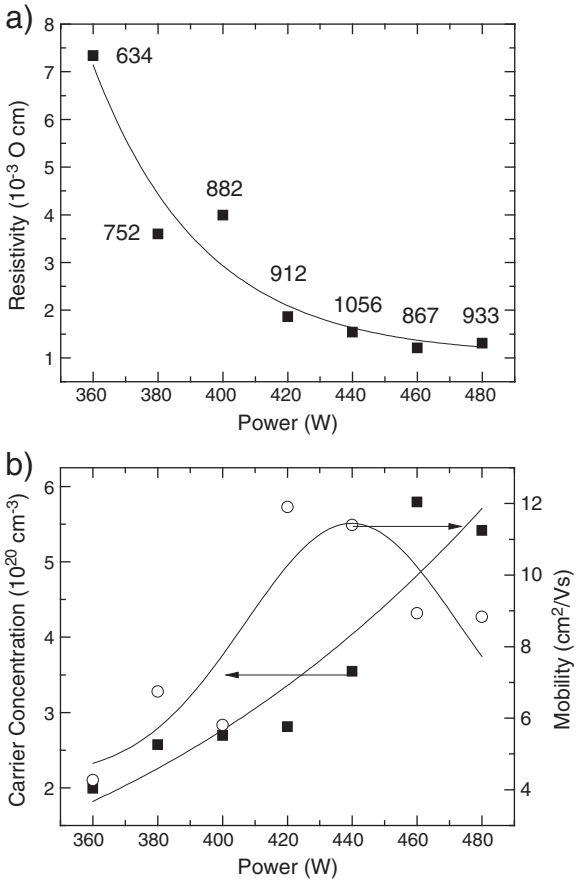

Fig. 1. Resistivity (a) as well as carrier concentration and Hall mobility (b) as function of discharge power.

Table 1
Electrical properties of films with different thicknesses. Thickness was controlled by changing sputtering time from 4 to 40 min, when discharge power was kept at 440 W. The process pressure, argon gas flow and substrate temperature were 0.5 Pa, 50 sccm and 150 °C, respectively.

No.	Thickness (nm)	Sheet resistance (Ω/sq)	Carrier concentration (cm^{-3})	Mobility ($cm^2/V\cdot s$)	Resistivity (Ω cm)
1	107	483.38	2.44×10^{20}	5.3	47.8×10^{-3}
2	313	69.78	3.97×10^{20}	7.8	2.02×10^{-3}
3	540	31.94	4.89×10^{20}	8.0	1.59×10^{-3}
4	828	22.40	3.36×10^{20}	10.8	1.71×10^{-3}
5	1056	14.54	3.55×10^{20}	11.4	1.54×10^{-3}

High transmittance is the most important feature to reduce optical losses. We focused on transmittance in visible and near infrared wavelength region. High transmittance in near infrared wavelength is not important for amorphous silicon (a-Si:H) absorber layers, but makes a big difference in microcrystalline silicon (μc-Si:H) solar cells and modules, as here the light spectrum up to 1100 nm can be utilized and contributes to overall photo current. The transmittance of ZnO:B film with discharge power of 440 W is given in Fig. 2. High transmittance at both visible and near infrared region was obtained with average transmittance above 85% from 400 to 1100 nm. Even at 1100 nm, no obvious decrease appeared in transmittance spectra which show low free-carrier absorption. This superior long-wavelength transparency is suitable for microcrystalline silicon solar cell whose spectrum response has been extended to 1100 nm.

Indicated by first-principle calculations, the Fermi level shifts up into the conduction band and the band gap becomes narrower in ZnO:B compared to the pure ZnO film [17]. These lead to their low resistivity and low transmission in the 300–400 nm region. Annealing process has been used to enhance the conductivity and widen the optical band gap of ZnO:B thin films. In the present study, we tried to meliorate the opto-electronic properties by adjusting the deposition process. Films were deposited by different conditions: sample A, substrate swung side by side (used as dynamic mode [18]); sample B, substrate was fixed in the target center (used as static mode [18]); sample C, 2 sccm H_2 was added into sputtering atmosphere with substrate fixed in the target center. Other working conditions were all the same: pressure was kept at 0.5 Pa, substrate heater temperature was fixed at 200 °C, discharge power was 440 W, and argon gas flow was 50 sccm.

Electrical properties of these samples are described in Table 2. Low resistivity and high carrier mobility were obtained when substrate was fixed in the target center (sample B) or H_2 introduced into atmosphere (sample C). The worst electrical quality observed for dynamically sputtered film can partly be attributed to various deposition conditions under magnetron cathode for the moving substrate. Resistivity difference of magnetron sputtered aluminum-doped zinc oxide (ZnO:Al) films along the target cross-section has been reported by Kluth et al. [17]. Ten times higher resistivity has been recorded at the position opposite to the racetrack of the target. It is reasonable that dynamic deposition leads to a higher resistivity ($1.54\times10^{-3}\,\Omega$ cm) of a factor of two compared to the minimum resistance ($7.03\times10^{-4}\,\Omega$ cm) of the static point, while dynamic film can be understood as a stacked multilayer film subsequently grown with the properties of static print from left to right. The reason for preferable resistance of static mode is mainly related to high carrier mobility as shown in Table 1. Mobility increases from 11 to above