Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 515 (2007) 8785–8788
www.elsevier.com/locate/tsf

Influence of substrate temperature on N-doped ZnO films deposited by RF magnetron sputtering

Jinzhong Wang [a,*], Vincent Sallet [b], François Jomard [b], Ana M. Botelho do Rego [c], Elangovan Elamurugu [a], Rodrigo Martins [a], Elvira Fortunato [a]

[a] Materials Science Department, CENIMAT/I3N and CEMOP-UNINOVA, FCT-UNL, 2829-516 Caparica, Portugal
[b] Laboratoire de Physique des Solides et de Cristallogenèse, C.N.R.S., 1 Place Aristide Briand, 92195 MEUDON CEDEX, France
[c] Centro de Química-Física Molecular, Complexo Interdisciplinar, IST 1049-001 Lisboa, Portugal

Available online 30 March 2007

Abstract

Nitrogen-doped ZnO films were deposited by RF magnetron sputtering in 75% of $N_2/(Ar+N_2)$ gas atmosphere. The influence of substrate temperature ranging from room temperature (RT) to 300 °C was analyzed by X-ray diffractometry (XRD), spectrophotometry, X-ray photoelectron spectroscopy (XPS), secondary-ion mass spectrometry (SIMS) and Hall measurements setup. The XRD studies confirmed the hexagonal ZnO structure and showed that the crystallinity of these films increased with increasing substrate temperature (T_s). The optical studies indicate the average visible transmittance in the wavelength ranging 500–800 nm increases with increasing T_s. A minimum transmittance (9.84%) obtained for the films deposited at RT increased with increasing T_s to a maximum of 88.59% at 300 °C (500–800 nm). Furthermore, it was understood that the band gap widens with increasing T_s from 1.99 eV (RT) to 3.30 eV (250 °C). Compositional analyses (XPS and SIMS) confirmed the nitrogen (N) incorporation into the ZnO films and its decreasing concentration with increasing T_s. The negative sign of Hall coefficients confirmed the n-type conducting.

Keywords: ZnO thin films; Sputtering; XPS; SIMS; Hall measurement

1. Introduction

Zinc oxide (ZnO) is a multifunctional semiconductor which is fascinating as a potential material for short-wavelength optoelectronic devices such as light emitting diodes and laser diodes owing to its wide band gap (3.37 eV), large exciton binding energy (60 meV), and high optical gain (320 cm^{-1}) at room temperature [1,2]. Recently, room temperature (RT) electroluminescence was observed from ZnO p–n homo-junction [3–5]. Practically, the realization of p-type ZnO is very challenging due to its asymmetric doping limitations [6]. Based on the theoretical studies [7], many techniques were employed to obtain p-type ZnO through nitrogen (N) doping [8,9]. N is a suitable dopant for producing a shallow acceptor level in ZnO [1,7]. Various sources of N such as NH_3, N_2O and co-doping of nitrogen–gallium (N–Ga), nitrogen–beryllium (N–Be), nitrogen–indium (N–n) and nitrogen-aluminum (N–Al) were reported by various techniques [1,10–14]. Among the available N sources, an economic and non-toxic pure N_2 was widely investigated as a source of N doping [8,9]. Hitherto, only few reports [8–14] were successful in developing p-type ZnO because of the strong "self-compensation" effect caused by a large background electron concentration and low solubility of N [7]. It is well known that the dopant activity and the crystalline quality of the semiconductor films are greatly influenced by its deposition parameters, in particular the deposition temperature. We have given an attempt, in this study, to understand the influence of substrate temperature on N-doping in ZnO films through pure N_2.

2. Experimental details

Thin films of ZnO were deposited on sapphire (001) substrate with different substrate temperatures (T_s) ranging RT to 300 °C. The films were sputtered using a ceramic ZnO target

* Corresponding author. Tel.: +351 212948562x11605; fax: +351 212948558.
E-mail address: jiwa@fct.unl.pt (J. Wang).

0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2007.03.061

Table 1
Electrical parameters of the N-doped ZnO films as a function of substrate temperature

T_s	Thickness (μm)	Band gap (eV)	Bulk resistivity (Ω cm)	Mobility (cm^2/Vs)	Carrier concentration (cm^{-3})
RT	1.08	1.99	1.17×10^{-2}	30.6	1.74×10^{19}
150 °C	0.84	2.03	1.18×10^{-2}	31.2	1.70×10^{19}
200 °C	0.69	2.31	1.89×10^{-2}	25.5	1.29×10^{19}
250 °C	0.62	3.26	6.53×10^{-1}	5.66	1.69×10^{18}
300 °C	0.49	3.30	$>10^5$	-	-

in 75% of $N_2/(Ar+N_2)$ gas atmosphere. The chamber was evacuated initially to $\sim2\times10^{-6}$ mbar. The partial pressure of argon and nitrogen were maintained at $\sim1.1\times10^{-3}$ and 8.0×10^{-3} mbar respectively. All the films were sputtered with a constant power of 100 W in a total pressure of 1.2×10^{-2} mbar for 30 min. The target–substrate distance was kept at 10 cm. A radio frequency power generator (13.6 MHz) from Advanced Energy (Model: RFX 2500) was used for sputtering. The thickness of the films was measured using a surface profilometer (Dektak3). The crystal structure of the films was confirmed using an X-ray diffractometer (DMAX-III C from Rigaku; sealed tube, Cu K_α radiation). The electrical parameters were estimated using a Hall measurements setup (Bio-Rad HL5500 Hall system) with a permanent magnet of 5 kG. Optical transmittance (T) was measured using a double beam spectrophotometer (Shimadzu UV-3100). The surface morphology was analyzed using scanning electron microscopy (SEM). The nature of chemical surface was understood through X-ray photoelectron spectroscopy (XPS). The profile of the composition Vs depth was determined by secondary-ion mass spectrometry (SIMS) using Cs^+ primary beam.

3. Results and discussion

The average value of the film thickness found varying between 490 and 1075 nm. A maximum thickness of ~1075 nm obtained for the films sputtered at RT decreased with increasing T_s to a minimum of ~490 at 300 °C. The increasing T_s decreases the film's growth rate from 0.59 to 0.27 nm/s. The reason may probably due to the fact that the increased thermal scattering at higher T_s prevents the sputtered species from reaching the substrate, and as well due to the lower absorption of particles. The thickness values are summarized in Table 1 along with the optical and electrical properties. X-ray diffraction patterns of the films were recorded in the 2θ ranging 30–75°. As a strong diffraction at 2θ around 42° concealed the visibility of other reflections to the noise level, the samples were scanned at two discrete 2θ ranges of 30–40° and 42–75° respectively, and are shown cumulatively in Fig. 1. It may be noteworthy that the y-axis is given in logarithmic scale due to the very high intensity (several thousands arbitrary units) of (002) diffraction at high T_s. A strong diffraction peak is observed at around 34° for all the films regardless of substrate temperature (T_s). This peak showed a strong orientation along (002) plane, which was indexed by matching with a standard hexagonal ZnO (ICDD card no. 36-1451). The shifting of (002) diffraction peak towards higher 2θ side implies that the tensile strain in the film decreases with increasing T_s. The intensity of (002) diffraction peak was increased with the increasing T_s, which suggests that the crystallinity increases. A secondary diffraction peak observed from (002) plane at around 72° which is very weak for those deposited at RT becomes eminent at high temperatures.

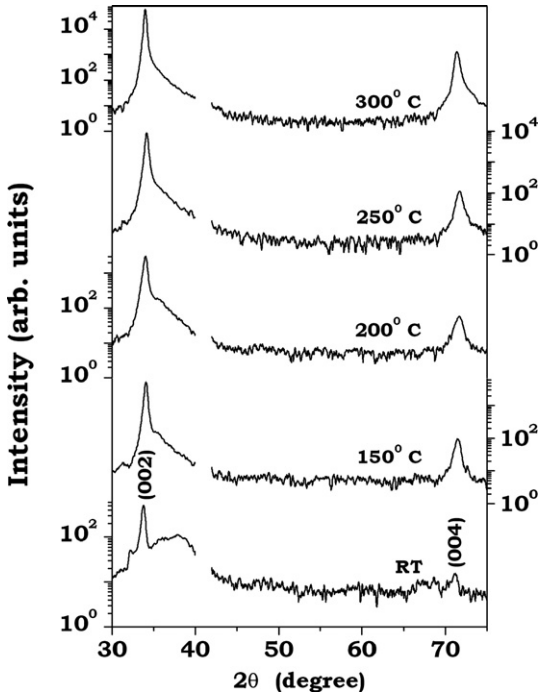

Fig. 1. XRD patterns of the N-doped ZnO films as a function of substrate temperature.

The transmission spectra of the films recorded in the wavelength ranging 350–1500 nm are shown in Fig. 2. It is perceptible that the average visible transmittance in the wavelength ranging 500–800 nm increases with increasing T_s.

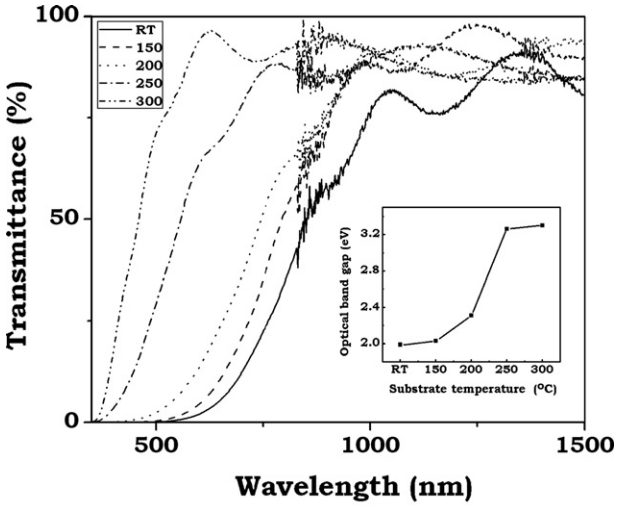

Fig. 2. Transmission spectra of the N-doped ZnO films as a function of substrate temperature; insert shows the variation of band gap.