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ScienceDirect
Thin Solid Films 515 (2007) 8780–8784
www.elsevier.com/locate/tsf

Influence of the reactive N_2 gas flow on the properties of rf-sputtered ZnO thin films

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Available online 30 March 2007

Abstract

Nitrogen (N)-doped ZnO thin films were RF sputtered with different N_2 volume (ranging from 10% to 100%) on sapphire (001) substrates. The influence of N_2 vol.% on the properties of ZnO films was analyzed by various characterization techniques. The X-ray diffraction studies showed that the films grow along the preferential (002) crystallographic plane and the crystallinity varied with varying N_2 vol.%. The films sputtered with 25 vol.% N_2 showed better crystallinity. The transmittance was decreased with increasing N_2 volume until 25% and was almost constant above 25%. A maximum optical band gap (2.08 eV) obtained for 10 vol.% N_2 decreased with increasing N_2 volume to reach a minimum of 1.53 eV at 100%. The compositional analysis confirmed the incorporation of N into ZnO films, and its concentration increased with increasing N_2 volume to reach a maximum of $\sim 3.7 \times 10^{21}$ atom/cm^3 at 75% but then decreased slightly to 3.42×10^{21} atoms/cm^3. The sign of Hall coefficient confirmed that the films sputtered with ≤ 25 vol.% N_2 possess p-type conductivity which changes to n-type for >25 vol.% N_2.

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

1. Introduction

Due to wide direct-band-gap (3.37 eV) and large exciton binding energy (~ 60 meV), the importance of ZnO thin films in opto-electronic devices have attracted more attention. Many growth techniques such as sputtering, molecular beam epitaxy, metal–organic chemical vapor deposition, pulsed laser deposition, etc., have been employed to study ZnO in detail [1–4]. Among these techniques, sputtering has been widely used to study ZnO films owing its low cost, simplicity, low processing temperature and easy doping. The difficulty in obtaining p-type ZnO, which is a barrier for their applications in short-wavelength light-emitting or laser diodes, is still being explored. In order to realize p-type ZnO films, various group-I and -V elements in the periodic table have been employed [1,2,5–7] and some research groups have claimed that p-type ZnO has been obtained. However, few available reports [2,6,8] including a recent report on the RT electroluminescence from ZnO p–n homo-junction do not show both high hole concentration and mobility. A theoretical study shows that nitrogen (N) dopant is the optimal candidate for obtaining p-type ZnO [9]. Further, many N sources such as N_2, NO, N_2O and NH_3 have also been studied [2,8,10–13]. Among the available N sources, an easy getting, economic and non-toxic N_2 has been widely used in sputtering techniques [12,13]. Hitherto, a systematic investigation on the influence of nitrogen volume percentage (N_2 vol.%) on the properties of ZnO was not carried out. In this context, N-doped ZnO films have been RF sputtered with different N_2 vol.% at room temperature. The influence of N_2 vol.% on the structural, morphological, optical, compositional and electrical properties of ZnO films was studied in detail.

2. Experimental details

ZnO films were RF sputtered on sapphire (001) substrate at room temperature from a ceramic ZnO target. The films were studied as a function of N_2 vol.%, which was estimated from the N_2 and Ar gas flows during sputtering. The ratio of N_2 and Ar

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0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2007.03.062

gas flows was maintained at 4:36, 10:30, 20:20, 30:10 and 40:0 sccm for obtaining the N_2 vol.% of 10, 25, 50, 75 and 100, respectively. In each case, the total flow of the gas was fixed at 40 sccm. The chamber was evacuated initially to $\sim 2\times10^{-6}$ mbar. All the films were sputtered with a constant power of 100 W at a total pressure of 1.2×10^{-2} mbar for 60 min. A radiofrequency power generator (13.6 MHz) from Advanced Energy (Model: RFX 2500) was used for sputtering the target. 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) in Bragg–Brentano geometry ($\theta/2\theta$ coupled). 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 detected 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. The electrical parameters were estimated using a Hall measurements setup (Bio-Rad HL5500 Hall system) with a permanent magnet of 5 kG in van der Pauw configuration.

3. Results and discussion

The average value of film thickness found varying between 1.5 and 2.2 μm. A minimum thickness (1.5 μm) obtained for 10 vol.% N_2 increased with increasing N_2 volume and reached a maximum of 2.2 μm at 100%. X-ray diffraction (XRD) patterns of the films were recorded in the 2θ ranging 30°–75°. A strong diffraction peak from the sapphire substrate at 2θ around 42° concealed the visibility of other peaks to noise levels. Hence, the samples were scanned at two discrete 2θ ranges of 30°–40° and 45°–75°, respectively. In the 45°–75° 2θ range, a very weak peak obtained at around 72° (10 vol.% N_2) was confirmed as a secondary diffraction peak from (002) by matching with a standard hexagonal ZnO (ICDD card no. 36-1451). This peak was disappeared when the N_2 vol.% increased to 25. To authenticate the influence of N_2 vol.% on the samples, the XRD patterns in the 30°–40° 2θ range are shown 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 peak. For 10 vol.% N_2 films, a strong peak was obtained from ZnO (002) plane showing a preferential orientation. Additionally, two other peaks from (100) and (101) planes were obtained. When the N_2 vol.% increased to 25, the intensity of (002) peak increased by about an order of magnitude and the (100) and (101) diffraction peaks disappear. The increased intensity of preferred <002> orientation substantiates the improvement in crystallinity. The intensity of (002) peak decreases with increasing N_2 volume above 25% and the peak perceptibly shifts towards lower 2θ angle side, which probably suggests that the crystallinity decreases due to the increase in N defects concentration and tensile stress in the films. In addition, at high N_2 volume (>25%), two peaks around 32°and 38° (broad peak) were obtained. These additional peaks were not matched either with the standard data or with previous reports. The XRD data are summarized in Table 1 together with the electrical properties. The lattice parameter (5.26 Å) obtained for ≤25 vol.% N_2 increased with increasing N_2 volume to a maximum of 5.33 Å at 100 vol.% N_2. The crystallite size calculated using peak width increased from 25.05 to 36.85 nm for the increase in N_2 volume from 10% to 25%, but then decreased with increasing N_2 volume and reached a minimum of 15.66 nm at 100%. The variation in crystallite size probably indicates that the low N_2 volume (≤25%) promotes the grain growth and reduces the tensile stress. This may probably due to the effect of compensation of N defects by O vacancies at low N_2 concentration. When the N_2 volume increased above 50%, the grain growth is suppressed by the increased tensile stress [13].

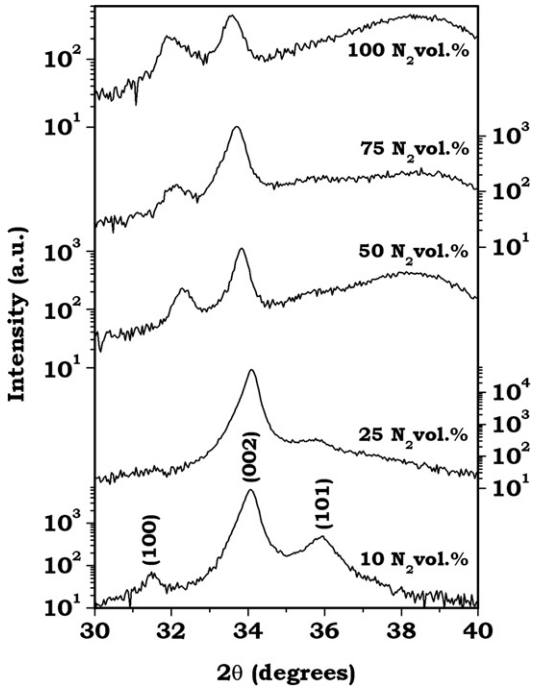

Fig. 1. XRD patterns of the N-doped ZnO films as a function of N_2 vol.%.

Table 1
Comparison of structural and electrical parameters of N-doped ZnO films

N_2 (vol.%)	Data obtained from (002) diffraction peak				Data from Hall measurements		
	Angle, 2θ (deg)	c (Å)	FWHM (deg)	Crystallite size (nm)	ρ (Ω cm)	μ (cm^2/V s)	n (cm^{-3})
10	34.06	5.26	0.328	25.05	1.90×10^{2}	257	$+1.27\times10^{14}$
25	34.08	5.26	0.223	36.85	5.57×10^{0}	22	$+5.18\times10^{16}$
50	33.84	5.29	0.325	25.27	3.29×10^{-1}	17	-1.10×10^{18}
75	33.72	5.31	0.389	21.10	2.06×10^{-1}	15	-2.01×10^{18}
100	33.59	5.33	0.524	15.66	1.30×10^{-1}	19	-2.48×10^{18}

c – lattice parameter; FWHM – full-width at half-maximum; ρ – bulk resistivity; μ – Hall mobility; n – carrier concentration.

The surface morphology obtained from SEM studies is comparatively shown in Fig. 2 for various N_2 volume. For 10 vol.% N_2 films, spherical shaped grains with the size varying between ~15 and 40 nm are seen on the surface. The grains are