IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Co-doping of aluminium and gallium with nitrogen in ZnO films deposited by RF magnetron sputtering

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys.: Condens. Matter 20 075220

(http://iopscience.iop.org/0953-8984/20/7/075220)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 129.252.86.83
The article was downloaded on 29/05/2010 at 10:35

Please note that terms and conditions apply.

J. Phys.: Condens. Matter **20** (2008) 075220 (4pp) doi:10.1088/0953-8984/20/7/075220

Co-doping of aluminium and gallium with nitrogen in ZnO films deposited by RF magnetron sputtering

Jinzhong Wang[1,4], **Elangovan Elamurugu**[1], **Nuno Pessoa Barradas**[2], **Eduardo Alves**[2], **Ana Rego**[3], **Gonçalo Gonçalves**[1], **Rodrigo Martins**[1] **and Elvira Fortunato**[1]

[1] Material Science Department, CENIMAT-I3N and CEMOP-UNINOVA, FCT-UNL, Campus de Caparica, 2829-516 Caparica, Portugal
[2] Ion Beam Laboratory, Physics Department, Instituto Tecnologico e Nuclear EN, 10, 2686-953 Sacavém, Portugal
[3] Centro de Química-Física Molecular, Complexo Interdisciplinar, IST 1049-001 Lisboa, Portugal

E-mail: jiwa@fct.unl.pt

Received 17 November 2007, in final form 24 December 2007
Published 28 January 2008
Online at stacks.iop.org/JPhysCM/20/075220

Abstract
N, (N + Ga) and (N + Al) doped ZnO films were deposited on *c*-plane sapphire substrates by RF magnetron sputtering at room temperature. The samples were characterized by their structural, surface morphological, compositional and optical properties. The x-ray diffraction studies confirmed the co-doping of (N + Ga) and (N + Al) besides showing improvement in the crystallinity when compared with the single N doping. The surface of the films becomes rougher after co-doping. The x-ray photoelectron spectroscopy and Rutherford back-scattering analysis indicate that the co-doping changes the chemical states and varies the amount of nitrogen (N) in ZnO. The amount of 'N' has been greatly increased for (N + Ga) co-doping, indicating that it is the best co-doping pair for p-type ZnO. Additionally, co-doping has increased the average visible transmittance (40–650 nm) and the optical band gap is shifted towards shorter wavelength. In the case of (N + Al) co-doping, the band gap becomes wider than that of undoped ZnO.

1. Introduction

ZnO is a promising optoelectronic material that is effective in the UV or blue light region due to its direct wide band gap (3.37 eV) and large exciton binding energy (∼60 meV) and has been studied by a variety of growth techniques [1–4]. It is a well known fact that undoped ZnO is n-type conducting or highly resistive. Furthermore, n-type ZnO with high electron concentration and low resistivity can be easily obtained by doping group III elements [5, 6]. The main barrier for the ZnO applications in UV/blue light emitting diodes or laser diodes is obtaining the p-type conductivity with high hole concentration and low resistivity. In order to overcome this barrier, different elements such as nitrogen (N), phosphorus (P), arsenic (As) and lithium (Li) etc were tried doping the ZnO [7–10]. Among these acceptor doping elements, N is demonstrated as the ideal candidate [1, 11]. However, it is complicated to obtain better p-type ZnO through single N doping due to its solubility limit and the appearance of $(N_2)_O$ defects at high doping concentrations [12]. In order to solve these problems, one novel theoretical method of co-doping was proposed by Yamamoto *et al*, and several co-doping pairs such as (N + Ga) and (N + Al) were suggested [13, 14]. Further, the (N + Ga) co-doping pair was considered as the optimal candidate for p-type doping in ZnO. Since then, many researchers have obtained encouraging results through (N + Ga) or (N + Al) co-doping pairs in ZnO [15, 16]. However, there is no detailed experimental report on comparative studies between (N + Ga) and (N + Al) co-doping in ZnO. Hence, an attempt is made in the present study to investigate the effect of (N + Ga)

[4] Author to whom any correspondence should be addressed.

 © 2008 IOP Publishing Ltd Printed in the UK

Table 1. Parameters obtained from the ZnO (002) peak. FWHM—full width at half maximum.

Sample	Peak Position (deg)	Diffraction intensity (counts)	FWHM (deg)	Lattice constant *c* (nm)	Grain size (nm)
S1	33.96	861.8	0.234	0.5273	35.1
S2	34.27	4069.6	0.186	0.5227	44.2
S3	34.25	1436.8	0.292	0.5230	28.2

and (N + Al) co-doping in RF sputtered ZnO films, besides comparing the results with the single N doping.

2. Experimental details

The ZnO films were deposited on sapphire(001) substrates at room temperature by RF magnetron sputtering. The ceramic targets of pure ZnO (99.99%), ZnO (95 wt%):Ga_2O_3 (5 wt%) and ZnO (98 wt%):Al_2O_3 (2 wt%) were used for preparing undoped and doped films. The chamber was evacuated initially to $\sim 2 \times 10^{-6}$ mbar. The partial pressures of nitrogen and argon were maintained at $\sim 1.5 \times 10^{-3}$ mbar and 6.0×10^{-3} mbar, respectively. All the films were sputtered with a constant power of 100 W at a total pressure of 1.2×10^{-2} mbar for 30 min. The target–substrate distance was kept at 10 cm. The samples doped with N, (N + Ga) and (N + Al) are denoted as S1, S2 and S3, respectively. The thickness of the films was measured using a surface profilometer (Dektak3) with an accuracy of ±20 nm. The details of the sputtering apparatus and the other characterization techniques such as XRD, AFM, XPS, RBS, Hall measurements and optical spectrophotometry can be found in [1].

3. Results and discussion

The thicknesses of S1, S2 and S3 are 0.80, 0.82 and 0.32 μm, respectively. It is noticeable that the thickness of S1 and S2 are similar, which indicates that there is no influence of (N + Ga) co-doping on the growth rate compared with that of N-doped ZnO films. However, the thickness of S3 is obviously decreased compared to S1 and S2. This implies that the growth rate of N-doped ZnO films is decreased effectively on co-doping Al with N. X-ray diffraction (XRD) patterns of the films were recorded in the 2θ range 30°–75°. Two diffraction peaks obtained at around 34.2° and 36.1° are confirmed to be (002) and (101) peaks of ZnO by comparing with the standard data (ICDD file 36-1451). The (002) peak is a high intense one and clearly shows a tendency for preferential growth. A weak diffraction from the (004) plane that is a secondary diffraction of (002) was obtained at 2θ around 72°. A strong diffraction peak obtained at 2θ around 42° from the sapphire substrate concealed the visibility of other diffraction peaks. In order to show the diffraction peaks and the influence of co-doping clearly, XRD patterns in the 2θ range 30°–40° are shown in figure 1. It can be noticed that the samples (S1) doped with N show diffraction peaks from (002) and (101) planes. The (101) diffraction is suppressed for the co-doping (N + Ga) and (N + Al), whereas the (002) peak is shifted to higher 2θ, that presumably indicates the change in strain.

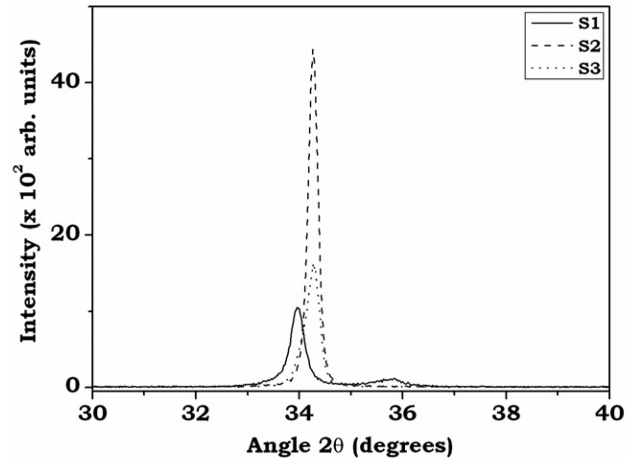

Figure 1. XRD spectra of S1, S2 and S3.

The intensity of the (002) peak is increased on co-doping and the increment is very significant for the (N + Ga) co-doping. The parameters obtained from the XRD patterns such as peak positions, full width at half maximum (FWHM), lattice constant *c* and grain size (Scherrer and Bragg formula) are given in table 1. The lattice constant *c* of 0.5273 nm obtained for the single N doping is decreased when co-doped with Ga or Al, which probably indicates a decrease in tensile strain. Further, the grain size of 35.1 nm obtained for single N doping is increased to 44.2 nm for (N + Ga) co-doping, but decreased to 28.2 nm for (N + Al) co-doping. The samples deposited with single N doping and (N + Al) co-doping showed high resistivity ($>10^5$ Ω cm), and correspondingly Hall coefficients were not detectable. However, the Hall coefficients of the films deposited with (N + Ga) co-doping showed a bulk resistivity of 6.2×10^{20} Ω cm, mobility of 0.14 $cm^2\ V^{-1}\ s^{-1}$ and carrier concentration of 7.24×10^{16} cm^{-3}.

The surface microstructures obtained from AFM analysis are shown in figure 2. The surface of S1 is composed of inconsistent spherical shaped crystallites, the size of which varies between 20 and 70 nm. However, the crystallites are packed tightly and the surface seems to be compact, with an RMS roughness value of 3.17 nm. When Ga is co-doped with N (S2), the crystallite size is increased a bit to range between 40 and 70 nm. It can be noticed that the crystallites are loosely packed in comparison with S1, which has presumably increased the RMS roughness to 4.17 nm. On the other hand, when the films are co-doped with Al (S3), the surface becomes very interesting, with the crystallite size reducing to range between 15 and 40 nm. Further, the shape of the crystallites changes from spherical to conform. The crystallites are more

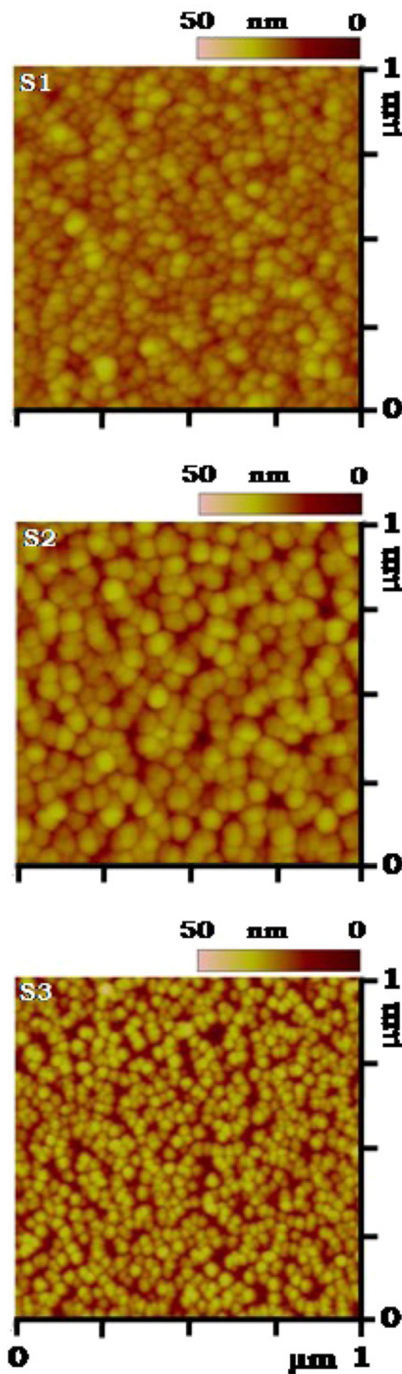

Figure 2. AFM pictures of S1, S2 and S3.
(This figure is in colour only in the electronic version)

loosely packed than the surface of S2, and consequently the RMS roughness is increased to 5.79 nm. The foregoing discussion indicates that the shape, size and RMS of the surface microstructures are influenced by the co-doping.

The surface chemical states and composition analyses of these films were characterized by XPS and RBS techniques. Figure 3 shows the N_{1s} XPS spectra of S1, S2 and S3. The broad N_{1s} photoelectron peaks should be composed of three minor peaks positioned at around 396, 398 and 402 eV, respectively. The corresponding peak positions, named N1, N2 and N3, are probably derived from N–Zn, N–H and NO_2, respectively [17]. It can be noticed that the N2 peak of sample S1 is clearly identified from peak N1. For sample S2, the N1 peak position is hardly changed. The obvious variation is the peak area, which has been increased significantly when compared with that of S1, which implies that the N concentration in S2 greatly increases, whereas in sample S3 peak N2 becomes one shoulder of the N1 peak, and the position of the N1 peak shifts slightly towards the lower binding energy. The compositions obtained from XPS and RBS techniques are given in table 2. It is noticeable that the N concentration in S2 is increased about twofold when compared with S1. Further, the N3 peak disappears in the spectra of S2. Although the total N concentration decreases slightly in S3, the N1 concentration increases and the concentration of N2 and N3 obviously decreases compared with S1. The N composition values obtained through the RBS technique are very different from that of XPS measurements. The probable reason is that the XPS measurements are carried out on the surface, whereas the RBS measurements are carried out on the bulk. However, the trend of N variation in the films is similar, as observed from the two measurement techniques: N concentration in the (N + Ga) co-doped film is the highest and it becomes the lowest in the (N + Al) co-doped film. In addition, hydrogen atoms are found in all films by RBS measurements.

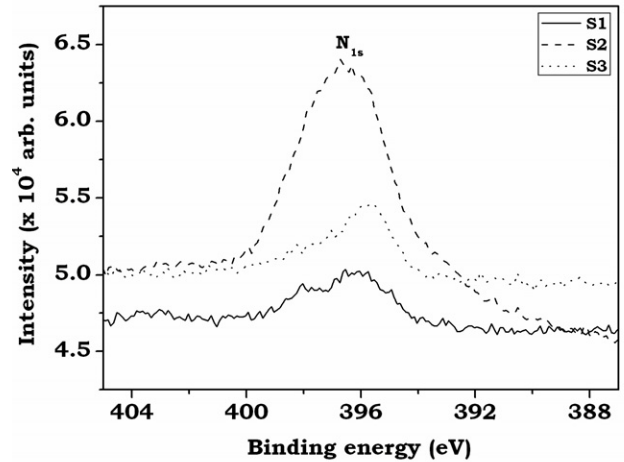

Figure 3. N_{1s} XPS spectra of S1, S2 and S3.

Table 2. Composition of S1, S2 and S3 obtained from XPS and RBS measurements.

Sample	Nitrogen (N) content (%)			
	XPS analysis			RBS analysis
	N1	N2	N3	N
S1	1.2	0.6	0.3	6.4
S2	3.1	2.2	0.0	6.8
S3	1.4	0.4	0.1	3.9

Figure 4 shows the transmittance spectra recorded in the wavelength range 300–900 nm. Compared with S1, the optical absorption edge of S2 shifts slightly towards shorter wavelength. The absorption edge shift of S3 is very obvious

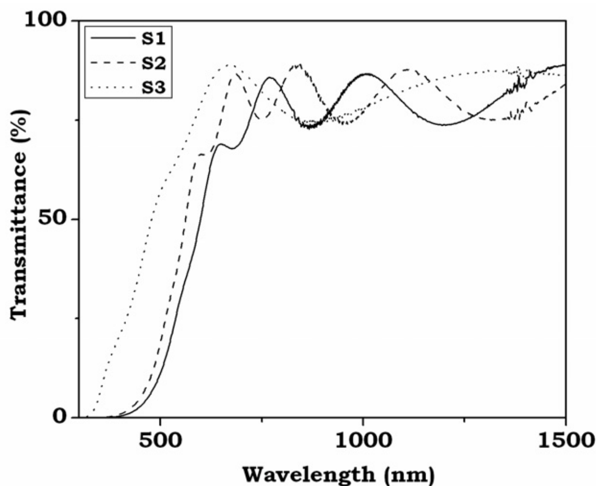

Figure 4. Transmittance spectra of S1, S2 and S3.

and larger. The average optical transmittance calculated in the wavelength range 400–650 nm for S1, S2 and S3 is about 26, 34 and 59%, respectively. The optical band gap calculated from the absorption coefficient [18] is 2.31, 2.41 and 3.48 eV for samples S1, S2 and S3, respectively. After co-doping, the optical band gap becomes wider, which indicate that the co-doping affects not only the N chemical state and composition but also the band gap. Especially for (N + Al) co-doping, the band gap become wider than even that of undoped ZnO [19]. Hence, (N + Al) doping may be useful in changing the optical properties of ZnO, especially the band gap, to fabricate optoelectronic devices to be useful in the shorter wavelength region.

4. Conclusion

(N + Ga) and (N + Al) co-doped ZnO films were deposited on sapphire substrate by RF magnetron sputtering at room temperature. The XRD patterns indicate that the (002) diffraction peak is the strongest orientation, and the crystallinity is increased on co-doping either Ga or Al with N. Further, the strain in the doped films was almost relaxed completely. The surface microstructures obtained from AFM analysis confirmed the change in the crystallite size, shape and RMS roughness following co-doping. The compositional analysis shows that the N chemical states and concentration have been changed by co-doping. Especially for (N + Ga) co-doping, the N concentration has been greatly improved. The transmittance spectra indicate that after co-doping the film transmittance increases and the optical band gap shifts towards short wavelength. Especially for (N + Al) co-doping, the band gap becomes wider than even that of undoped ZnO.

Acknowledgments

This work is funded by Fundação para a Ciência e a Tecnologia through grant SFRH/BPD/12020/2003, project POCTI/CTM/55945/2004, 'CPU—Actions universitaires intégrées LUSO-Françaises' and CRUP—Acções Integradas Luso-Francesas-2006, no F-28/06.

References

[1] Wang J, Sallet V, Jomard F, Botelho do Rego A M, Elangovan E, Martins R and Fortunato E 2007 *Thin Solid Films* **515** 8780
[2] Wang J, Du G, Zhao B, Yang X, Zhang Y, Ma Y, Liu D, Chang Y, Wang H, Yang H and Yang S 2003 *J. Cryst. Growth* **255** 293
[3] Look D C, Reynolds D C, Litton C W, Jones R L, Eason D B and Cantwell G 2002 *Appl. Phys. Lett.* **81** 1830
[4] Guo X, Tabata H and Kawai T 2001 *J. Cryst. Growth* **223** 135
[5] Fortunato E, Assuncao V, Marques A, Goncalves A, Aguas H, Pereira L, Ferreira I, Fernandes F M B, Silva R J C and Martins R 2004 *Adv. Mater. Forum II Mater. Sci. Forum* **455/456** 12
[6] Musat V, Teixeira B, Fortunato E and Monteiro RCC 2006 *Thin Solid Films* **502** 219
[7] Sun J W, Lu Y M, Liu Y C, Shen D Z, Zhang Z Z, Li B H, Zhang J Y, Yao B, Zhao D X and Fan X W 2006 *Solid State Commun.* **140** 345
[8] Kim K K, Kim H S, Hwang D K, Lim J H and Park S J 2003 *Appl. Phys. Lett.* **83** 63
[9] Sun J C, Zhao J Z, Liang H W, Bian J M, Hu L Z, Zhang H Q and Liang X P 2007 *Appl. Phys. Lett.* **90** 121128
[10] Zeng Y J, Ye Z Z, Xu W Z, Li D Y, Lu J G, Zhu L P and Zhao B H 2006 *Appl. Phys. Lett.* **88** 062107
[11] Kobayashi A, Sankey O F and Dow J D 1983 *Phys. Rev.* B **28** 946
[12] Lee E C, Kim Y S, Jin Y G and Chang K J 2001 *Phys. Rev.* B **64** 085120
[13] Yamamoto T and Hiroshi K Y 2001 *Physica* B **302/303** 155
[14] Yamamoto T 2002 *Thin Solid Films* **420/421** 100
[15] Kumar M, Kim T H, Kim S S and Lee B T 2006 *Appl. Phys. Lett.* **89** 112103
[16] Zhu L, Ye Z, Fei Z, Yuan G and Lu J 2005 *Surf. Coat. Technol.* **198** 354
[17] Petravic M, Deenapanray P N K, Coleman V A, Jagadish C, Kim K J, Kim B, Koike K, Sasa S, Inoue M and Yano M 2006 *Surf. Sci.* **600** 81
[18] Futsuhara M, Yoshioka K and Takai O 1998 *Thin Solid Films* **322** 274
[19] Meyer B K, Alves H, Hofmann D M, Kriegseis W, Forster D, Bertram F, Christen J, Hoffmann A, Strabburg M, Dworzak M, Haboeck U and Rodina A V 2004 *Phys. Status Solidi* b **241** 231