MODIFICATION OF PHYSICAL PROPERTIES OF SPUTTERED ZINC OXIDE THIN FILMS BY INTRODUCTIN OF GALLIUM AND NITROGEN

Krasimira Shtereva[1,2], Vladimir Tvarozek[1], Ivan Novotny[1], M. Milosavljević[3], P. Sutta[4], Sona Flickyngerova[1]

1. Department of Microelectronics, Faculty of Electrical Engineering and Information Technology, Ilkovičova 3, 812 19 Bratislava, Slovakia

2. Department of Electronics, University of Rousse, Studentska 8, 7017 Rousse, Bulgaria

3. VINČA Institute of Nuclear Sciences, Laboratory for Atomic Physics, 11001 Belgrade, Serbia

4. New technologies-Research Center, University of West Bohemia 30614 Plzen, Czech Republic

E-mail:vladimir.tvarozek@stuba.sk

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1. Introduction

Recently, impurity-doped zinc oxide (ZnO) thin films of good quality have gained considerable attention as a promising material for transparent electrodes in thin film solar cells and liquid crystal displays (LCD), a channel layer in transparent thin film transistors and for application in transparent optoelectronic devices [1,2]. Some applications demand ZnO with unipolar conduction, but in order to realize *p-n* junction and ZnO-based devises, high quality of both *n*- and *p*-type ZnO materials are needed. Ion implantation is an important technique for controllable introducing of doping elements in groups IV and III-V semiconductors. Georgobiani et al. [3] obtained hole conductivity in N^+ implanted ZnO films after annealing in oxygen radicals at 600°C.

Our previous investigations showed that nitrogen doping had a great impact on microstructure, electrical and optical properties of sputtered ZnO thin films [4,5]. Aims of current research are to investigate the influence of nitrogen implantation and post-implantation annealing on physical properties of sputtered ZnO:Ga thin films and once more to attempt *p*-type doping.

2. Experimental

Gallium-doped zinc oxide (ZnO:Ga) thin polycrystalline films with a thickness of ~ 500 nm were deposited on Corning 7059 glass substrates by rf diode sputtering. A ceramic $ZnO:Ga_2O_3$ (98wt%:2wt%) target, a mixture of ZnO (99.99% purity) and Ga_2O_3 (99.99% purity), was used. The sputtering was carried out at 1.3 Pa working pressure in Ar (99.999% purity) atmosphere with an rf power of 600 W, the deposition time was 30 min. Nitrogen ions were implanted at 180 keV under normal incidence in ZnO:Ga films. The ion implantation was performed in Danfysik equipment. The ion current density was ~1 $\mu A/cm^2$. The nitrogen doses were $1x10^{15}$, $5x10^{15}$, $1x10^{16}$ and $2x10^{16}$ cm^{-2}. The projected range (R_P) at 180 keV was calculated to be 340 nm. The implanted films were subjected to annealing treatment in O_2 at 550°C for 30 min. The structure and film orientation were evaluated by X-ray diffraction (XRD, Model X'pert Pro using CuKα radiation, $\lambda = 0.154$ nm). The electrical parameters were measured using a Hall system and software at a room temperature. Optical spectrophotometry measurements were carried out from the UV region to the near IR region by an Ava Spec-2048 Fiber Optic Spectrometer.

3. Results and discussion

The electrical parameters of non-implanted ZnO:Ga and N^+-implanted ZnO:Ga:N films, as-deposited and annealed in O_2 at 550°C for 30 min, are listed in table 1.

Tab. 1. *Electrical parameters of non-implanted and N^+-implanted ZnO:Ga thin films*

Dose (cm^{-2})	Resistivity (Ωcm)		Concentration n/p (cm^{-3})		Mobility (cm^2/Vs)	
	As-deposited	Annealed	As-deposited	Annealed	As-deposited	Annealed
non-implanted	$7.8x10^{-2}$	$3.6x10^{-3}$	$n\sim6.5x10^{19}$	$n\sim7.5x10^{19}$	1.2	23
2.10^{16}	3.7	$5.8x10^{-3}$	$n\sim4x10^{17}$	$n\sim5.1x10^{19}$	4.2	21
1.10^{16}	0.8	$4.8x10^{-3}$	$n\sim9.4x10^{18}$	$n\sim6x10^{19}$	0.8	21
5.10^{15}	0.62	$4.2x10^{-3}$	$p\sim1.8x10^{18}$	$n\sim6.4x10^{19}$	5.5	23
1.10^{15}	1.23	$3.5x10^{-3}$	$p\sim1x10^{19}$	$n\sim7.6x10^{19}$	0.5	23

The non-implanted ZnO:Ga samples are *n*-type and have almost uniform parameters, resistivities of the order ~ 10^{-2} Ωcm and carrier concentration of the order ~ 10^{19} cm^{-3}. After implantation of N^+ ions, the carrier concentration decreased more than two orders of magnitude and consequently resistivity increased, while mobility changed insignificantly. The higher resistivity in implanted samples can be explained with (i) nitrogen introduction and formation of N_O acceptors that partly compensate donor defects in the film, and (ii) the damage caused by ion implantation. As-deposited samples implanted with low N^+ doses showed unstable *p*-type behavior, while those implanted with higher doses were *n*-type. All samples exhibited *n*-type conductivity after annealing treatment in O_2 and their resistivity is decreased by more than an order of magnitude (Fig. 1).

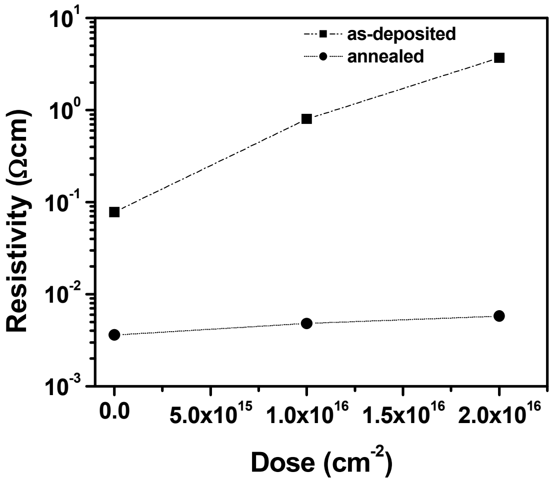

Fig.1: *Resistivity of as-deposited and annealed samples as a function of N^+ dose.*

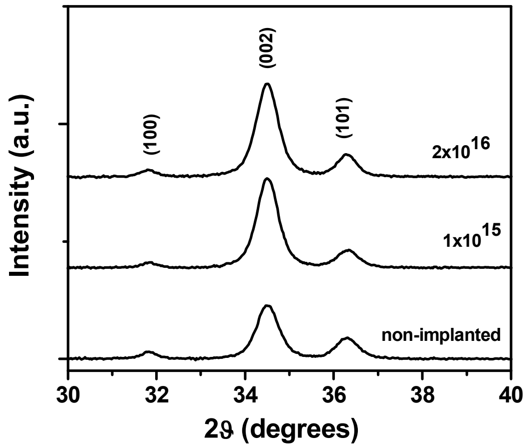

Fig. 2: *XRD patterns of annealed ZnO:Ga:N films implanted with different N^+ doses.*

Fig. 2 shows XRD patterns of annealed samples. The strong (002) diffraction line and weak (100) and (101) lines indicate the c-axis preferential orientation of these films. There is a rise in the integrated area of (002) diffraction line with implantation and increasing N^+ dose.

The average transmittance (including glass substrate) in the wavelength range of $390 < \lambda < 1100$ nm is higher than 80% and increased after annealing in O_2 (Fig. 3). Blue shift of the band edge of the annealed samples is consistent with the increase in carrier concentration.

4. Conclusions

The physical properties of polycrystalline sputtered ZnO:Ga thin films were modified by implantation of N^+ ions with energy of 180 keV and doses ranging from $1x10^{15}$ to $2x10^{16}$ ions/cm^2. As-deposited samples implanted with low N^+ doses showed unstable *p*-type behavior, while those implanted with higher doses were *n*-type. The higher resistivity in implanted samples resulted from the formation of N_O acceptors that partly compensate donor defects in the film, and the damage caused by ion implantation. All samples became *n*-type after annealing treatment in O_2 and their resistivity is decreased by more than an order of magnitude. XRD patterns revealed preferential growth in the (002) direction in ZnO:Ga:N films. The optical properties are closely related to microstructure and electrical properties of the films. Blue shift of the band edge for annealed ZnO:Ga:N samples compared to as-deposited ones, is consistent with the increase in carrier concentration.

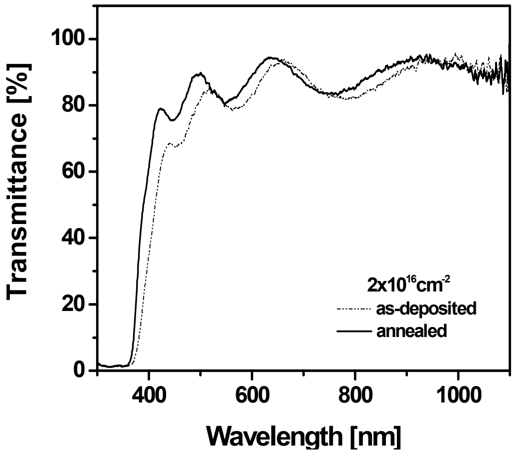

Fig. 3: *Optical transmittance spectra of ZnO:Ga:N films implanted with* N^+*-dose of* *1x*10^{16} *cm*$^{-2}$ *as-deposited and annealed in* O_2.

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