EFFECT OF ANNEALING ON PROPERTIES OF GALLIUM-NITROGEN Co-DOPED ZINC OXIDE THIN FILMS PREPARED BY SPUTTERING AND ION IMPLANTATION

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1. Introduction

The group II-VI compound semiconductor zinc oxide (ZnO), exhibits superior electrical and special optical properties (high conductivity and transparency), and has been considered a promising candidate for a significant number of applications including blue and ultraviolet (UV) emitters [1], transparent electronics products, such as transparent thin film transistors (TTFT), light-emitting diodes (LED) [2], and solar cells. Nowadays, impurity-doped ZnO thin films with high conductivity and transparency are used as an electrode material for amorphous silicon (a-Si) and Cu(In, Ga)Se2 (CIGS) photovoltaic devices (PV), and have been investigated for electrodes for organic photovoltaic (PV) and organic light-emitting diodes (OLEDs) [3,4]. The major obstacle to ZnO device applications is the lack of a reliable technology for controllable and reproducible p-type doping. On the basis of the reports for obtaining p-type ZnO via nitrogen implantation [5,6] as well as our previous research on N-doped and (Al, Ga):N co-doped ZnO thin films [7], we attempted nitrogen doping in polycrystalline ZnO:Ga thin films by double-energy implantation.

In this paper we report an influence of post-implantation annealing (in O_2 and N_2 up to 600°C) on electrical and structural properties of RF sputtered ZnO:Ga thin films implanted by double energy (40 keV and 80 keV) N^+ ions.

2. Experimental Details

The ZnO:Ga thin films were prepared by rf diode sputtering from a ceramic ZnO:Ga_2O_3 (98wt%:2wt%) target with an rf power of 600 W in Ar working pressure of 1.3 Pa. The polycrystalline ZnO:Ga films of thickness ≈ 200 nm with a *c*-axes preferred orientation were deposited on Corning 7059 glass substrate. A double energy implantation of nitrogen N^+, one at 40 keV and the other at 80 keV, was performed with doses of $1x10^{15}$ and $1x10^{16}$ cm^{-2}, in order to create a nearly uniformly-doped thin film. To activate the implanted ions and repair the damaged area, the implanted films were annealed under O_2 and N_2 ambient for different times from 10 s to 30 min at temperatures varying from 200°C to 600°C, Fig. 1.

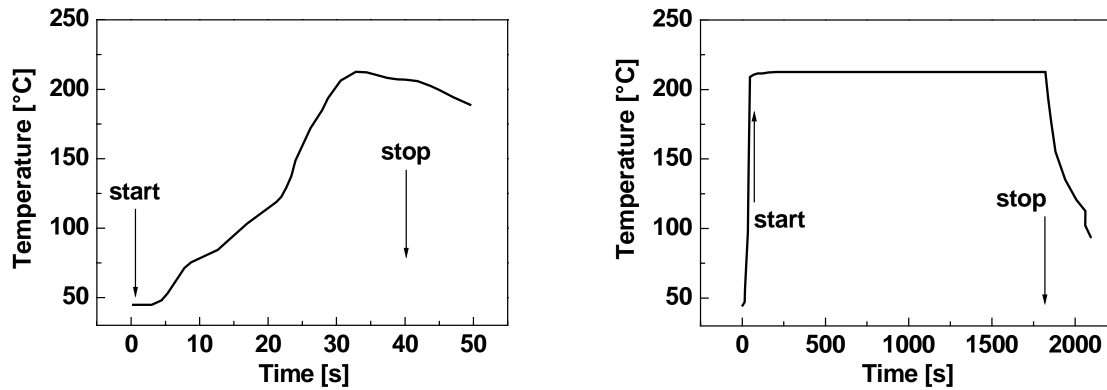

Fig. 1: *Typical annealing procedure (time-development of temperature) consisted of an initial temperature slope lasting about 30 second and the quasi-stable temperature interval remaining for 10 second or 30 min respectively*

The electrical parameters of the films were measured using a Hall-effect system with a magnetic field of 0.15 T at a room temperature (RT). The structure and preferred orientation of the crystallites were evaluated by X-ray diffraction (XRD) on X'pert Pro powder diffractometer (symmetric θ-θ geometry), equipped with an ultra-fast linear semiconductor detector PIXcel, using CuKα radiation (λ = 0.154 nm). Secondary Ion Mass Spectrometry (SIMS) depth profiles of the various ionic species were acquired with a TOF-SIMS IV analyzer (ION TOF GmbH, Muenster), using a Cs+ primary ion beam with energy of 2 keV.

3. Results and Discussion

Nitrogen ions were implanted under normal incidence in *n*-type ZnO:Ga thin films. Hall-effect measurements showed the dispersion of electrical data before annealing due to implantation induce defects. XRD patterns of the N-implanted ZnO:Ga films reveal a preferred orientation of the crystallites in a (002) plane, Fig. 2.

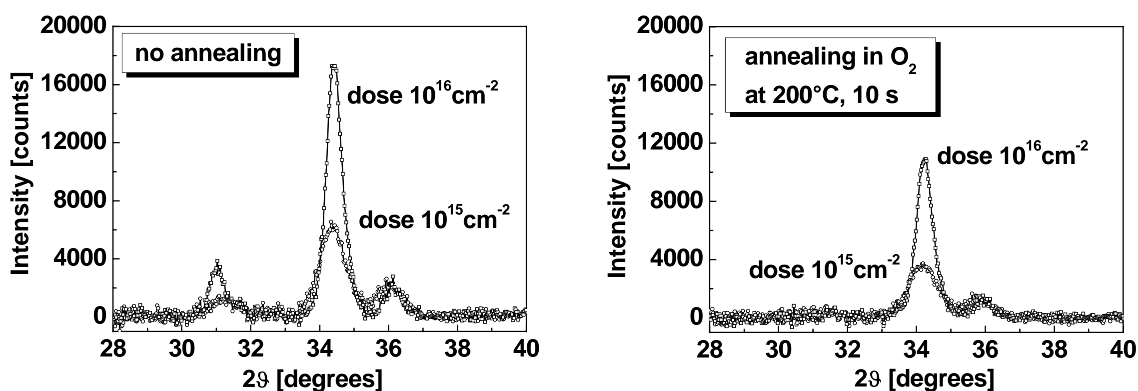

Fig. 2: *XRD diffraction patterns of ZnO:Ga:N films before and after annealing (in O_2 at 200ºC for 10 second)*

The SIMS depth profile of the complex $^{30}NO^{-}$ ions in *p*-type ZnO:Ga:N films confirmed homogeneous depth distribution of nitrogen and its compounds after double

energy implantation and followed by annealing in O_2 at 200ºC during 10 second, Fig.3 (doses of $1x10^{15}$ cm^{-2}, *n*-type ZnO:Ga:N and $1x10^{16}$ cm^{-2}, *p*-type ZnO:Ga:N).

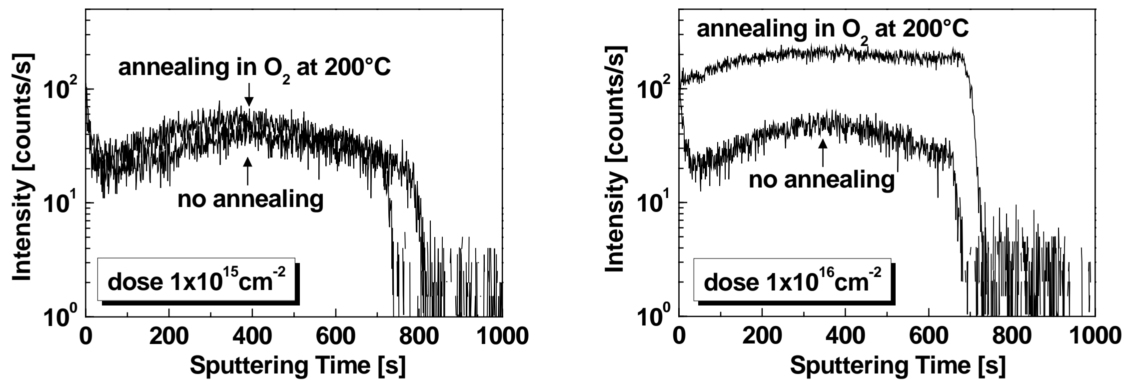

Fig. 3: *The SIMS depth profile of the complex $^{30}NO^{-}$ ions in ZnO:Ga:N films implantated by double energy nitrogen N^{+} before and after annealing in O_2 at 200ºC for 10 second*

The resistivity, carrier`s concentration and mobility of implanted films before and after annealing under O_2 and N_2 ambient for 10 s at temperatures 200÷400°C are shown in Fig. 4 and 5. Resistivity decreases with an increase of annealing temperature. Relationship of carrier concentration vs annealing temperature indicated a minimal value at 200°C in both O_2 and N_2 ambient. Simultaneously, the carrier mobility showed a maximum due to lower scattering by the ionized impurities and improvement of crystalline structure. The relationship electrical-structural properties was confirmed by our previous observations [8] on XRD pattern changes for ZnO:Ga thin films annealed in-situ in vacuum at temperatures from RT to 400ºC. The shift of (002) diffraction lines, improvement of their symmetry and intensity – all demonstrate better texture, lower biaxial stresses and more ordered crystalline structure. Independently of the parameters of ion implantation and annealing conditions (time 30 sec-30 min, temperature up to 600°C), the films annealed at temperatures > 400°C remained *n*-type. They showed the lowest resistivity $2x10^{-2}$ Ωcm and carrier mobility 3 cm^2/Vs after annealing in N_2 at 600°C. Unstable *p*-type ZnO:Ga:N films were measured on double energy implanted samples with dose $1x10^{16}$ cm^{-2} annealed during 10 s: (i) at 400°C in N_2 (resistivity 0.5 Ωcm, hole mobility 0.8 cm^2/Vs and concentration $1.6x10^{19}$ cm^{-3}); (ii) at 200°C in O_2 (resistivity 20 Ωcm, hole mobility 1 cm^2/Vs and concentration $3.2x10^{17}$ cm^{-3}).

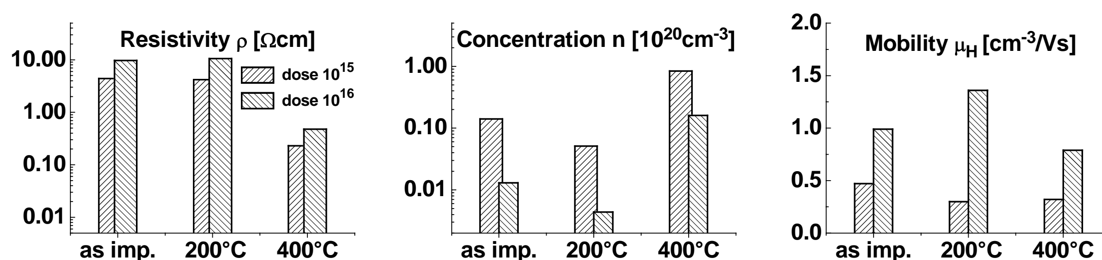

Fig. 4: *Electrical properties of implanted films before and after annealing under N_2 ambient for 10 s at temperatures 200°C and 400°C*

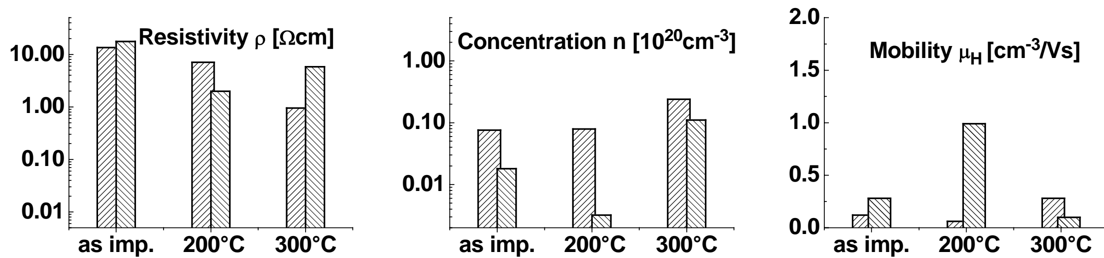

Fig. 5: *Electrical properties of implanted films before and after annealing under O_2 ambient for 10 s at temperatures 200°C and 300°C*

4. Conclusion

A double energy implantation of nitrogen N^+ (one at 40 keV and the other at 80 keV, with doses of $1x10^{15}$ and $1x10^{16}$ cm^{-2}) created more uniform-doped ZnO:Ga:N thin films in comparison with single energy implantation. Post-implantation annealing (in O_2 and N_2 up to 600°C) changed their electrical and structural properties but in generally it did not alter mostly the *n*-type conductivity. Double energy implanted ZnO:Ga:N thin films converted to unstable *p*-type semiconductor after annealing at 400°C in N_2, resp. at 200°C in O_2, for 10 second. It means that chosen processing parameters and post-implant annealing do not provide conditions to create a sufficient amount of acceptors in order to overcome the donors and to obtaining a *p*-type ZnO:Ga.

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