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Structure and Composition of Sapphire Near-Surface Layer Implanted by $^{64}Zn^{+}$ Ions and Thermal Annealed in Oxygen

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Abstract -In this paper we present the study of structure and composition of Al_2O_3 near-surface layer implanted by $^{64}Zn^{+}$ ion with fluence of $5\times10^{16}cm^{-2}$ and energy of 100keV and annealed in oxygen at temperature range of 400-1000°C. After implantation the Zn and ZnO ion profiles concentration distribution has the Gauss form and has a maximum about 30nm. After thermal treatment in oxygen at 900°C a modification of Zn and ZnO concentration profiles from primary forms is observed. This was done by solid-state epitaxy of amorphized sapphire layer. XRD investigation follows the creation of $ZnAl_2O_4$ phase in near-surface layer after annealing at 900°C. The problem of $ZnAl_2O_4$ phase formation at annealing are discussed.

***Keywords*: ** Zn, ion implantation, sapphire, annealing, ZnO, nanoparticle

1. Introduction

The properties of metal and metal oxide nanoparticles (NPs) are comprehensively investigated because of its possible application in modern opto/microelectronic devices. Metal zinc NPs can be use in UV photo-detectors based on surface plasmon resonance phenomena. Zinc oxide NPs plays an important role, since ZnO has wide direct-band gap of 3.37eV and large exiton binding energy of 60meV. So it can be used in UV light source and electro luminescence displays. According to other ZnO unique properties it can be used in dye sensitized solar cells, gas sensors, and memory devices (memristors). There are sum attempts to form the Zn and ZnO NPs in Al_2O_3 by Zn ion implantation and thermal oxidation (C. Marques et al. (2007), J. Xu et al (2010) and Y. Shen et al (2011)). Here we present the study of structure and composition in Al_2O_3 by implanted by $^{64}Zn^{+}$ ions and thermal furnace annealed in oxygen atmosphere at elevated temperatures.

2. Samples and Experimental Technique

The Al_2O_3 wafers with orientation (-1012) were implanted by $^{64}Zn^{+}$ ions with fluence of $5\times10^{16}cm^{-2}$ and energy of 100keV. To avoid the substrate significant heating the ion beam current density was less than $0.5\mu A/cm^2$. After implantation the wafers were subjected to furnace annealing in oxygen at temperatures from 400 up to 900°C during 1h.

Impurity and its compound in depth profiles were investigated using time of flight second ion mass-spectrometer SIMS-5 (Ion TOF GmbH). The crater etching was made by Cs^{+} ion beam (for $Al_2O_3^{-}$, Al^{-}, O^{-}, ZnO^{-} analysis) and by O^{-} ion beam (for Zn^{+} analysis) with energy of 1keV, raster dimensions were

300×300μm^2. The Bi^+ ion beam for impurity and its compound ion analysis has the next parameters: energy of 30keV, ion beam current of 1,2pA and raster dimensions are 100×100μm^2. There were analyzed the next ions $^{64}Zn^+$, ZnO^- and $^{16}O^-$, $^{27}Al^-$, $^{27}Al^+$, $Al_2O_3^-$ matrix ions. Ion etching crater dimensions were measured using stylus profilemeter Alpha Step D-120 (KLA-Tencor).

The phase composition of the implanted material was identified by the X-ray diffraction (XRD) in the angular scanning angle mode 2θ-ω. In this scheme is used a position-sensitive detector, that allows to increasing the S/N ratio about 10 times compared to 2θ-θ scheme. Identification was carried out using of a Discovery Bruker D8 diffractometer with a copper anode (wavelength λ=1.54Å).

2. Results and Discussion

On Fig.1 there presented the different ion distribution in depth profiles for the as implanted sample and on Fig.2 there presented the 3D-vizualisation of these profiles.

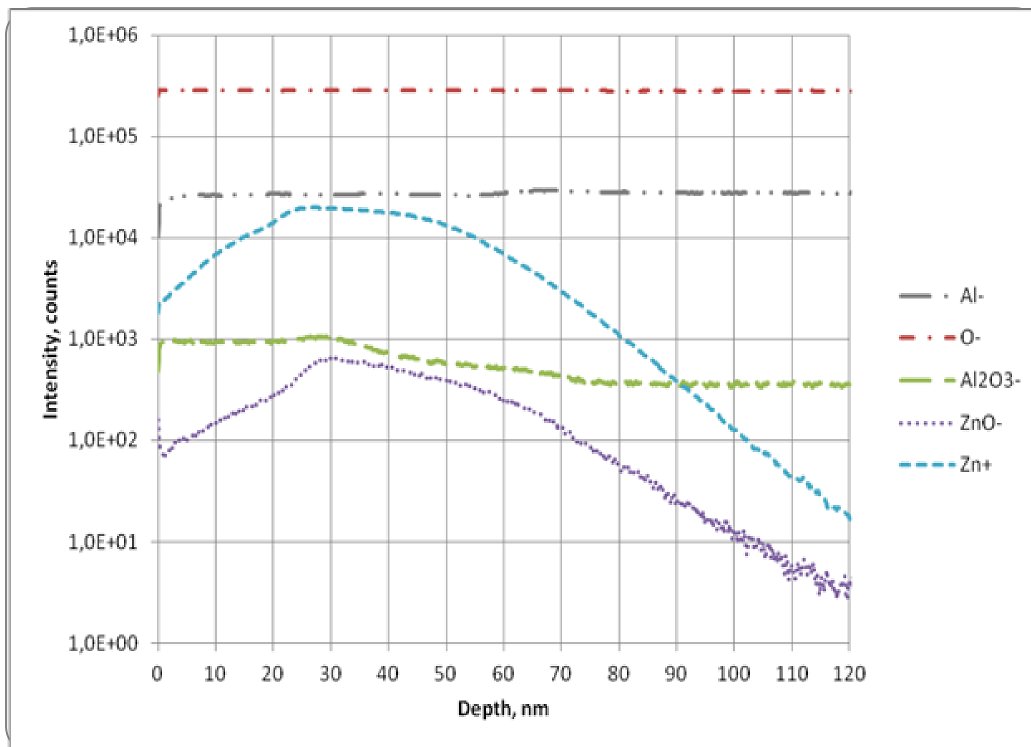

Fig. 1. Ion distribution in depth profiles for the as implanted sample.

From TR-SIMS investigations (Fig. 1) follow that Zn concentration distribution has the Gauss form and was spent along substrate depth down to 120nm with maximum near the 30nm. The ZnO compound is repeated the Zn distribution form almost. We can see the decrease in the intensity of the $Al_2O_3^-$ ions profile`. By lowering the Zn implanted impurity concentration at a depth of more than 30nm the substrate material density changed. In this regard, the output of $Al_2O_3^-$ ions from the sample surface is reduced.

On Fig. 2 there presented the different ion distribution in depth profiles for the annealed at 900°C in oxygen sample. After annealing the sample in oxygen there is observed the uphill diffusion, when Zn and ZnO atoms go towards higher concentrations. This is due to the fact that diffusion process is determined by the chemical potential gradient. The latter depends on the degree of material ordering, in particular, on the implanted layer amorphization due to radiation induced defects. The annealing of the amorphized layer is proceeds due to solid-state epitaxy, which moves away from the undamaged substrate toward its surface. The result is a failure of Zn and ZnO concentration at a depth of 40-50nm, followed by an increase in concentration.

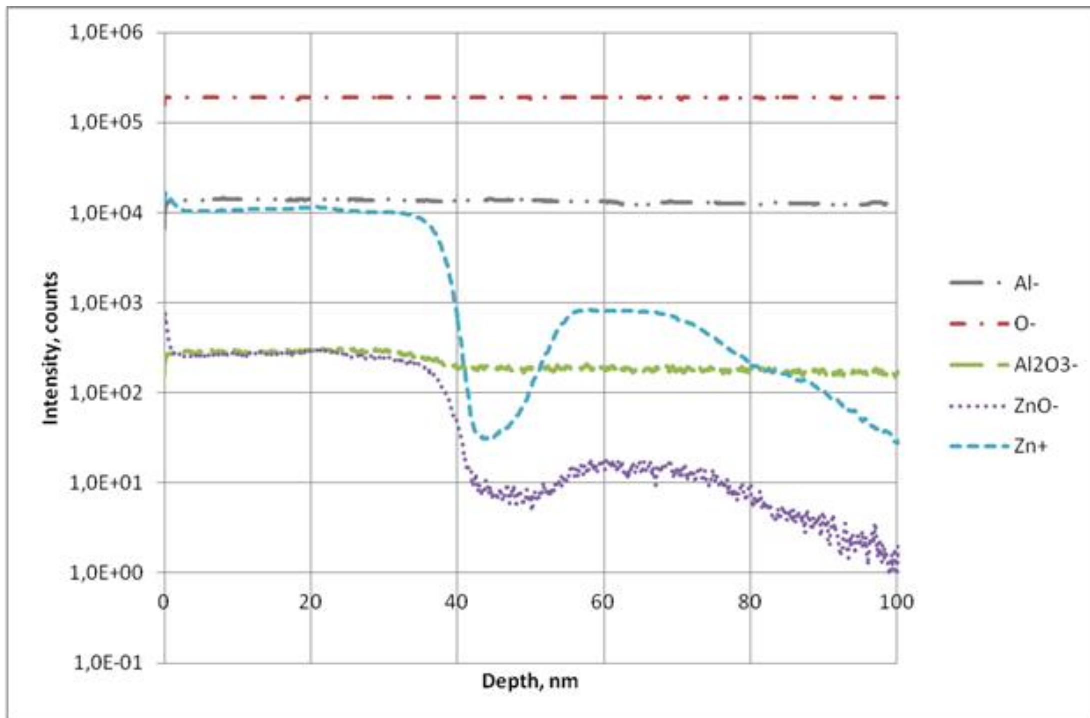

Fig. 2. Ion distribution in depth profiles for the annealed at 900ºC in oxygen sample.

With regard to the presence of $ZnAl_2O_4$ compounds say anything it is difficult. On the one hand, there is a small peak corresponding to this compound (Fig. 3). Although it is difficult to say it really or not, because sample is charged, and all the peaks are shifted towards smaller mass (left on the spectrum), and this one is a bit more to the right. On the other hand, there is no full compliance with the isotopic ratios (Fig. 4).

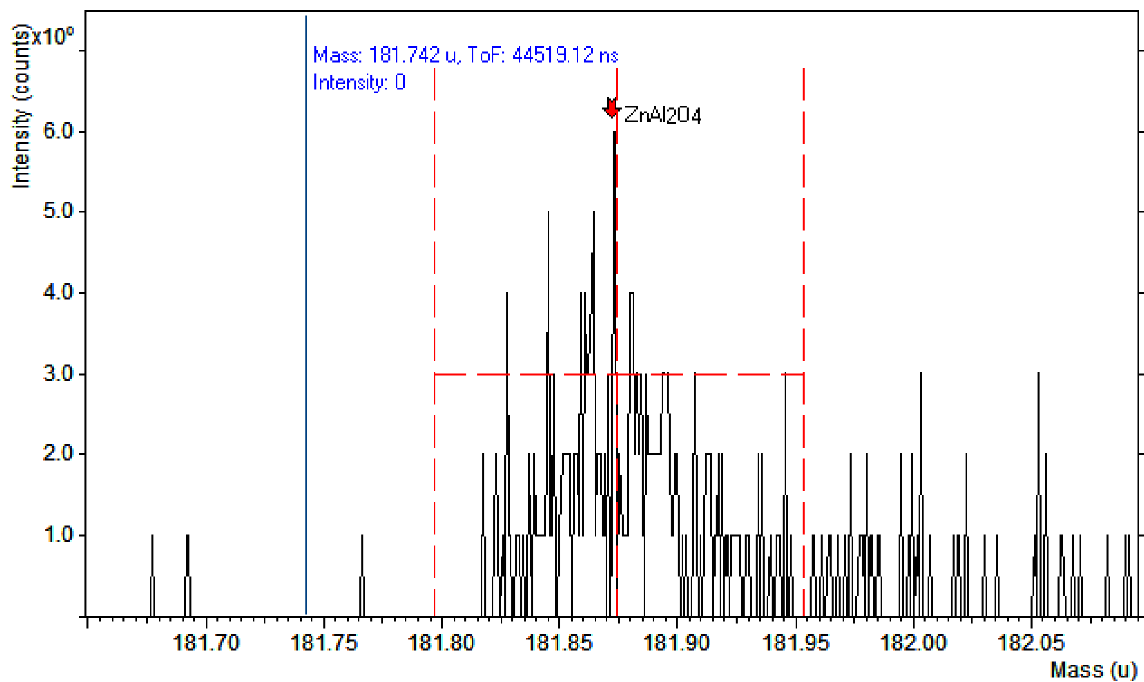

Fig. 3. Mass $ZnAl_2O_4$ peak.

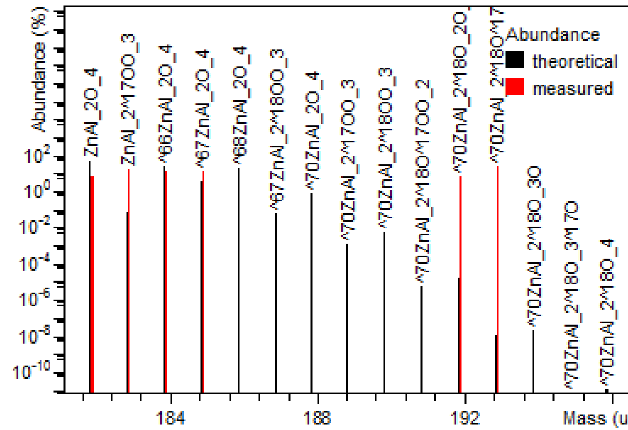

Fig. 4. The isotopic composition of the $ZnAl_2O_4$ compound. Black color is presented theory peaks of the mass spectrum, the red - the peaks of the experimental spectrum.

On Fig.5 there are presented the XRD curve in 2θ-ω mode for the as implanted sample (1) and for sample annealed at 1000ºC. On curve the peak at 36.5 degree is correspondent to ZnAl2O4 phase. Other peaks are correspondent to sapphire (012) plane which paralleled to substrate surface.

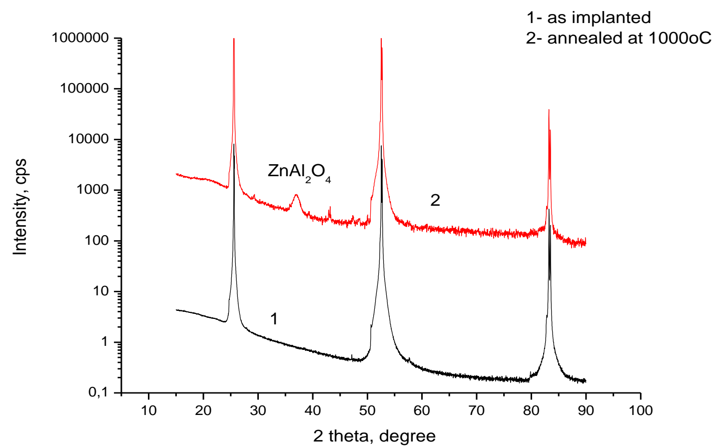

Fig. 5. XRD curve

3. Conclusion

1) By Zn ion implantation with subsequent thermal annealing in oxygen atmosphere in temperature range from 600 up to 900ºC ZnO NPs were obtained in substrate.

2) After Zn ion implantation and thermal annealing at temperature low than 400ºC the Zn metal NPs in amorphous state were existed in sapphire substrate.

2) After thermal annealing at temperature of 1000ºC the ZnO NPs were disappeared and the $ZnAl_2O_4$ phase was formed in Al_2O_3 substrate.

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