STRUCTURAL CHANGES OF Co-IMPLANTED ZnO SINGLE CRYSTALS AS A FUNCTION OF Co CONCENTRATION AND ANNEALING TEMPERATURE

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INTRODUCTION

The partial substitution of the nonmagnetic Zn ions in ZnO by magnetic transition metal (TM) ions (Fe, Mn, Co and Ni) were predicted to be a way towards room temperature ferromagnetism [1,2]. One of the methods for the incorporation of TM ions into ZnO matrix is ion implantation. However, for recovering the radiation-damaged ZnO lattice, post-implantation thermal treatment is needed. Such a treatment quite often may lead to the formation of secondary phase precipitates, especially in samples implanted with relatively high doses of TM. These precipitates may have considerable impact on magnetic properties of the implanted material.

In this contribution, we report X-ray diffraction (XRD) structural investigations of ZnO(0001) single crystals implanted with different concentrations of Co ions: 10%, 14%, 16%, 18% and 22% with respect to the Zn and O ions.

EXPERIMENTAL

The thickness of the implanted layers (250 nm) was calculated from the appropriate values of ion energies and fluences used during the implantation process. The XRD structural characterization was performed using synchrotron radiation at the BM25 beamline at the ESRF, the European Synchrotron. The energy of the monochromatic X-ray beam was set to 22.037 keV (λ = 0.56263 Å) and a 2D MaxiPix detector was used for the data collection. The first series of XRD measurements was performed from all as-implanted samples and next, these samples were annealed at 900°C in air and measured again. It had been repeated two times yet. The two last annealing have been done at 1200°C – after each annealing the XRD measurements were performed. The aim of such a procedure was ascertainment the thermally induced formation of new crystallographic phases, and their temperature stability.

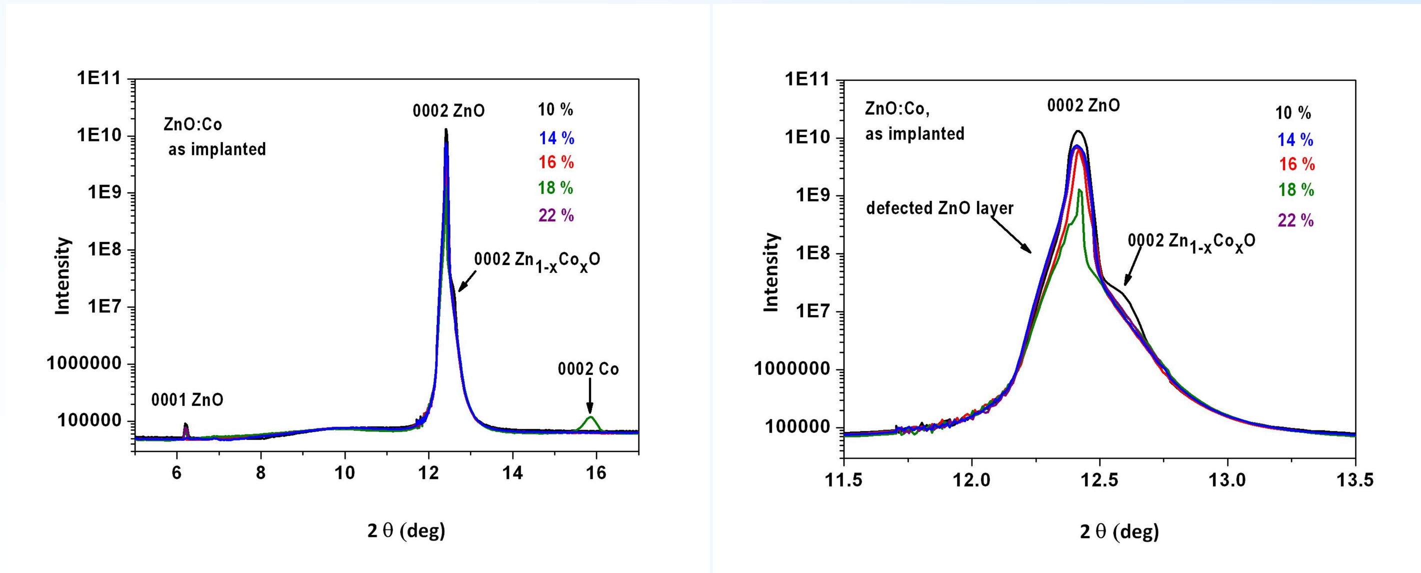
RESULTS AND DISCUSSION

During the implantation process, the implanted ions stop at a certain depth in the crystal forming a layer of some thickness depending on the implantation parameters. In our samples the implanted layers 250 nm thick are buried inside of ZnO crystal, therefore the X-ray diffraction patterns contain an information from both: ZnO matrix as well as the implanted layer.

The XRD patterns performed from implanted samples are shown in Fig.1: the highest peak (0002 ZnO) originates from ZnO matrix while the asymmetries visible in the lower part of this peak (Fig.1b) originate from the implanted layer as follows: the right-hand asymmetry testifies about partial substitution of Zn ions by Co ions in the ZnO lattice resulting in the formation of $Zn_{1-x}Co_xO$ solid solution inside the implanted layer and the left-hand asymmetry comes from the layer damaged by the implanted ions. The weak green peak visible in Fig.1a in the vicinity of 2θ ≈ 16 deg indicates on existence of Co precipitates in the implanted layer.

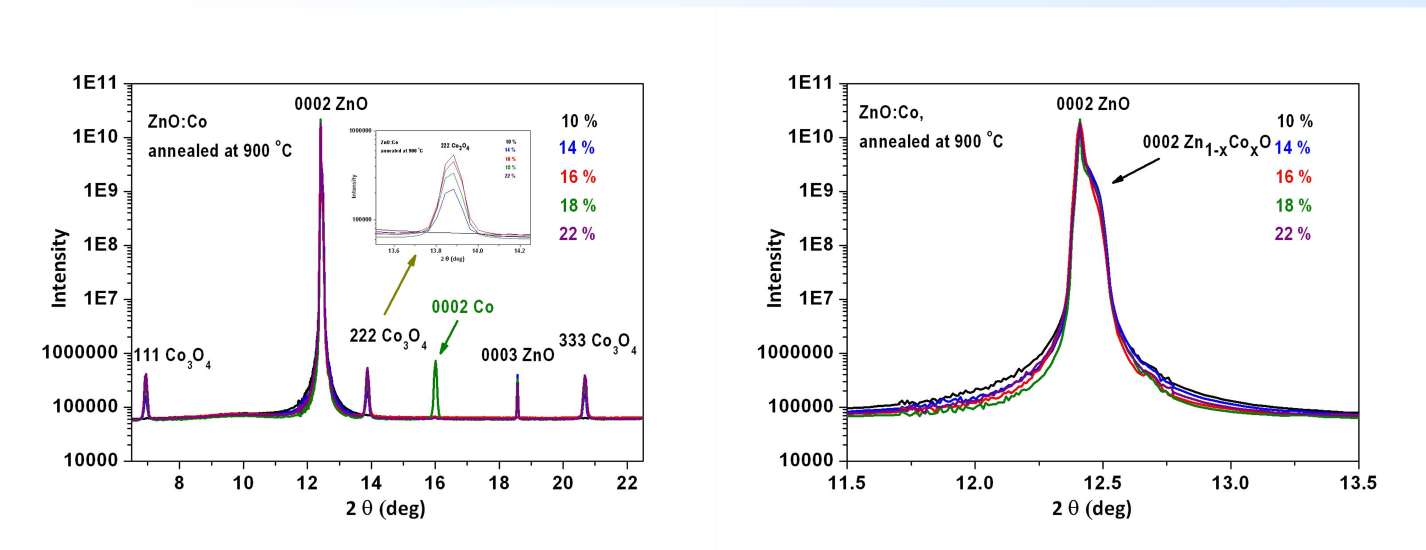
The first annealing at 900°C caused the evident structural changes of the implanted layers such as vanishing of the damage layers and creation of secondary phase (except for the sample with 10% Co concentration) which can be attributed to the cubic Co_3O_4 structure (see Fig.2a,b). The inset picture in Fig.2a confirms the lack of Co_3O_4 phase for sample with 10% Co concentration. The shape of right-hand asymmetry of the 0002 ZnO peak is the same for all samples what testifies that the solubility limit of Co in ZnO for solid solution $Zn_{1-x}Co_xO$ is $x \approx 0.1$. Any changes of this structure have not been observed after next annealing at 900°C.

Significant structural changes in the implanted layers are observed after annealing at 1200°C (Fig.3a,b). The previously identified phases $Zn_{1-x}Co_xO$ and Co_3O_4 disappeared, and new not recognized peaks appeared.



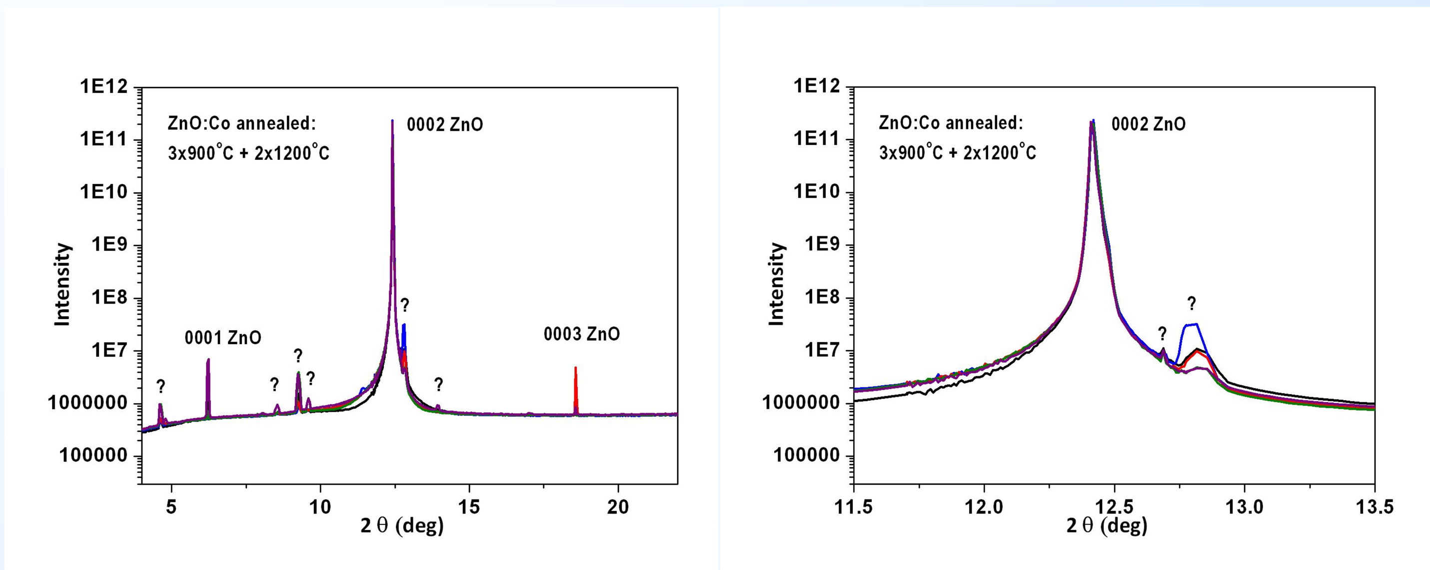
(a) (b)

Fig.1 The superimposed XRD patterns of as-implanted ZnO:Co samples with different Co concentrations. The patterns from respective samples are shown in different colours according to description in the figures; (a) – the patterns in wide range of 2θ angles; (b) – the zoom of these patterns in the vicinity of 0002 ZnO reflection.



(a) (b)

Fig.2 The superimposed XRD patterns of ZnO:Co samples after first annealing at 900°C: (a) – the patterns in wide range of 2θ angles; (b) – the zoom of these patterns in the vicinity of 0002 ZnO reflection.



(a) (b)

Fig.3 The superimposed XRD patterns of ZnO:Co samples after second annealing at 1200°C: (a) – the patterns in wide range of 2θ angles; (b) – the zoom of these patterns in the vicinity of 0002 ZnO reflection.

REFERENCES

1. T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science 287, 1019 (2000)
2. K. Sato and H. Katayama-Yoshida, Jpn. J. Appl. Phys. 40, L334 (2001)