Nuclear Instruments and Methods in Physics Research B 268 (2010) 1842–1846

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Damage recovery in ZnO by post-implantation annealing

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ARTICLE INFO

Article history:
Available online 25 February 2010

Keywords:
ZnO
Ion implantation
RBS/channeling
SIMS
Radiation damage
Dopant diffusion

ABSTRACT

ZnO bulk samples were implanted with 200 keV-Co ions at room temperature with two fluences, 1×10^{16} and 8×10^{16} cm^{-2}, and then annealed in air for 30 min at different temperatures up to 900 °C. After the implantation and each annealing step, the samples were analyzed by Rutherford backscattering spectrometry (RBS) in random and channeling directions to follow the evolution of the disorder profile. The RBS spectra reveal that disorder is created during implantation in proportion to the Co fluence. The thermal treatments induce a disorder recovery, which is however, not complete after annealing at 900 °C, where about 15% of the damage remains. To study the Co profile evolution during annealing, the samples were, in addition to RBS, characterized by secondary ion mass spectrometry (SIMS). The results show that Co diffusion starts at 800 °C, but also that a very different behavior is seen for Co concentrations below and above the solubility limit.

1. Introduction

Diluted Magnetic Semiconductors (DMS) are semiconducting materials in which transition metals (TM), or appropriate rare earth ions are substituted onto cation sites which couple with the free charge carriers to yield ferromagnetism via indirect interaction [1]. This ferromagnetic property has triggered a great interest for the DMS due to their application potential in spintronics [2,3]. One of the major problems for spintronic devices is the Curie temperature which must be above room temperature (RT) to have practical applications. The mean-field Zener model, proposed by Dietl et al. [4], predicts that wide band gap semiconductors, as ZnO, doped with TM ions exhibit ordering temperatures above 300 K, provided there is a sufficient charge carrier density [5]. Several experiments have shown promising results, however, the results differ from one experiment to another depending for instance on the TM doped ZnO synthesis technique. Some of them have shown ferromagnetic properties with a Curie temperature above RT [6], whereas other experiments exhibit spin-glass [7], or paramagnetic behavior [8]. These studies reveal also that the ferromagnetism in DMS requires a high carrier concentration as well as a high TM dopant concentration substituting the cations [4]. Moreover, the crystalline quality and the residual defects seem to have an impact on the ferromagnetic properties [9]. Another problem is the presence of TM precipitates and/or the formation of secondary phases. In many cases, the ferromagnetism observed is due to the presence of TM precipitates which present superparamagnetic properties, rather than from carrier mediated magnetic dopants [10,11].

One method to introduce TM dopants into bulk ZnO crystals is the ion implantation technique which provides several advantages, namely reproducibility, precise control of the fluence, use of an isotopically pure beam and the possibility to overcome the solubility limit of atoms in a material [5]. As the ferromagnetic strength depends on the TM concentration in the DMS, this ion implantation method seems interesting for the study of ferromagnetic properties in DMS. However, this method also presents several drawbacks. The major one is the generation of structural defects in the lattice which are detrimental not only for a proper inclusion of implanted TM ions on substitutional sites [9], but also for compensating the free carriers. A possibility to prevent the disorder creation in the crystal during ion implantation is to increase the implantation temperature. However, this is not the case in ZnO crystal; an implantation temperature increase to 623 K induces a significant suppression of point defects at the surface, but is not able to decrease the disorder rate in the bulk [5]. In this material, a post-implantation annealing at high temperature is necessary to completely recover the lattice structure [12]. A drawback of post-implantation annealing at high temperature is the possible diffusion of the implanted ions and the formation of nano-clusters.

The aim of this work is to study the disorder recovery and possible diffusion of the implanted species during thermal annealing. To do that, ZnO samples were implanted with Co atoms and subsequently annealed at different temperatures. Two Co fluences were chosen in order to observe how the Co concentration affects the ZnO disordering and the Co diffusion. The disorder was studied with Rutherford backscattering spectrometry in the channeling

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doi:10.1016/j.nimb.2010.02.032

direction (RBS-C). To analyze the Co diffusion, we used the RBS and SIMS techniques. The results show a disorder recovery, but also Co diffusion during annealing at temperatures above 800 °C.

2. Experimental

Commercial ZnO bulk single-crystalline samples with a wurtzite structure (ZnOrdic AB) were implanted with 200 keV-Co ions from the implanter of the Ion Technology Centre at Uppsala University. The projected range is around $R_p = 90$ nm according to the SRIM code. Two fluences (1×10^{16} and 8×10^{16} cm^{-2}) were used in order to introduce a maximum atomic concentration of ~1% and ~9%, respectively (SRIM code [13]). These doses are intended to be below and above the solid solubility limit of Co in ZnO, which is around 6.5 at.% [14]. During implantation, the samples were tilted ~7° relative to the incident ion beam to minimize channeling. As the increase of the implantation temperature seems to promote the formation of Co clusters and does not reduce the damage production [5], the implantations were performed at RT. The samples were subsequently annealed up to 900 °C, for 30 min, in air in order to avoid a loss of oxygen [15]. No thermal treatments were preformed above 900 °C to prevent the implanted layer decomposition [16].

After the implantation and after each annealing step, the samples were analyzed by Rutherford backscattering spectrometry in random (RBS) and channeling (RBS-C) direction using the tandem accelerator at Uppsala University. The spectra were collected with a 2 MeV-He^+ beam at a backscattering angle of 170°. To collect the RBS-C spectra, the samples were mounted on a goniometer, which allows aligning of the He beam with the (0 0 0 1)-axis. The spectra were analyzed with the SIMNRA program [17]. The χ_{min} is the ratio of the minimum backscattering yield at channeling condition to that of a random beam. It indicates the degree of disorder in the sample and in our virgin samples, χ_{min} was around 2%, which indicates a very high crystalline order.

Analysis of depth distribution of cobalt was made by secondary ion mass spectrometry (SIMS) utilizing a Cameca ims 4f instrument. A primary sputter beam of 8.2 keV $^{32}(O_2)^+$ ions was applied and secondary ions of $^{59}Co^+$ were detected. In addition, a primary beam of 4.5 keV Cs^+ ions has been used and secondary ions of $^{59}Co^{133}Cs^+$ were detected. For the depth profiling, the primary ions were rastered over an area of 200×200 μm^2 and secondary ions were detected from the central part of this area (~60 μm in diameter).

3. Results and discussion

The RBS spectrum recorded in random direction after implantation of a Co fluence of 1×10^{16} cm^{-2} at RT is shown in Fig. 1a (full line). The SRIM code gives a maximum atomic concentration of ~1.1 at.%, which is below the Co solubility limit of ~6.5 at.% in ZnO [14]. The Zn and Co surfaces are indicated by the arrows in the RBS spectrum. According to SIMNRA, the peak corresponding to the implanted Co atoms should be centered at 1490 keV. In this spectrum, this Co peak cannot be seen, which means that the fluence is too low to be detected by RBS. To study the damage in the Zn sublattice, RBS spectra were recorded in channeling direction along the (0 0 0 1) axis on the as-implanted sample and after annealings at 500, 600 and 800 °C (see Fig. 1a). The RBS-C spectrum recorded on the as-implanted sample exhibits a large peak around 1480 keV, which is due to the superposition of the displaced Zn atoms and the incorporated Co atoms. But in this sample, the Co fluence is low and the Co atoms contribution can be neglected, as it is indicated by the random spectra. For this dose, we consider the wide peak at 1480 keV to represent mainly the damage in the Zn sublattice. The maximum of this damage peak does not reach the level of the random spectrum, which means that the sample is only partially disordered. This absence of amorphization is in accordance with previous results observed after implantation of heavier ions, or at higher temperature [5,15,18]. After annealing at 500 and 600 °C, no changes were observed concerning the damage peak on the RBS-C spectra. After annealing at 800 °C, however, the RBS-C spectrum exhibits a huge decrease of the damage peak. That means that the disorder recovery in this sample starts between 600 and 800 °C. The analysis of the RBS-C spectra allows the determination of the disorder amount and the conversion of the energy scale into depth in the material. The results of this analysis (Fig. 2a) show that the disorder maximum is centered at ~100 nm as predicted by SRIM. Before annealing, the maximum disorder was around 45%. No decrease of the disorder rate was observed after annealing at 500 and 600 °C, but after annealing at 800 °C, the disorder decreases to ~17%.

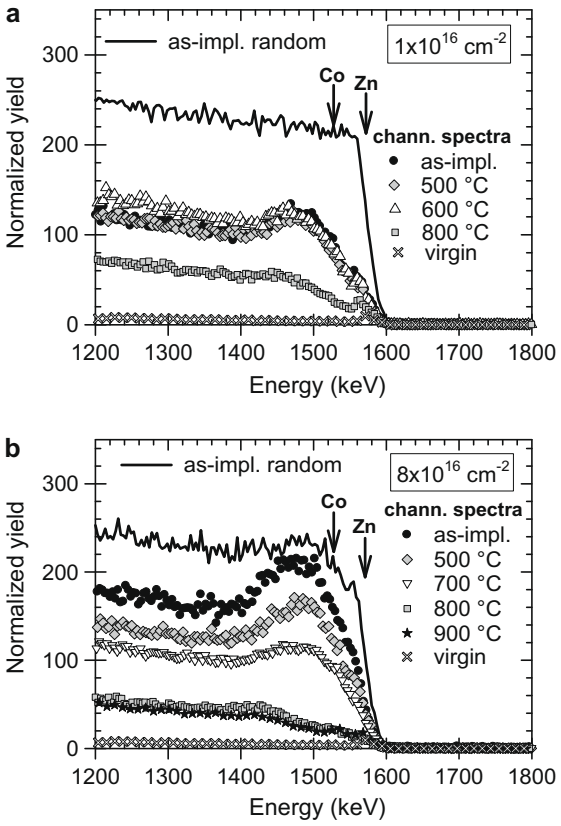

Fig. 1. RBS spectra recorded in random (full line) and channeling direction (other symbols) on ZnO single-crystals implanted at RT with 200 keV-Co ions at 1×10^{16} cm^{-2} (a) and 8×10^{16} cm^{-2} (b) and subsequently annealed in air at different temperatures for 30 min.

In order to increase the Co concentration in ZnO, another sample has been implanted with a higher fluence (8×10^{16} cm^{-2}) at RT. In this sample, the maximum Co concentration (~9 at.%) overcomes the Co solubility limit in ZnO (~6.5 at.%). Fig. 1b presents the RBS spectra recorded in random and channeling directions for this sample. The RBS spectrum recorded in random direction in the as-implanted sample exhibits a peak at 1490 keV, which is related to the Co atoms. This Co peak will be discussed later, but it indicates that in this sample the Co implanted fluence is too high to be neglected in relation to the damage. As a consequence, the broad peak at 1480 keV on the RBS spectra recorded in channeling direction is due to the superposition of two contributions: the damage in the Zn sublattice and the implanted Co atoms occupying