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ScienceDirect
Acta Materialia 57 (2009) 2291–2299
Acta MATERIALIA
www.elsevier.com/locate/actamat

Mn behaviors in Mn-implanted ZnO

Y. Wang [a], J. Zou [a,*], Y.J. Li [b], B. Zhang [b], W. Lu [b]

[a] School of Engineering and Centre for Microscopy and Microanalysis, The University of Queensland, Brisbane, Qld 4072, Australia
[b] National Lab for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, 500 Yu Tian Road, Shanghai 200083, China

Received 25 November 2008; received in revised form 25 January 2009; accepted 27 January 2009
Available online 27 February 2009

Abstract

The behavior of Mn when doped into ZnO by ion implantation was investigated by scanning transmission electron microscopy, electron energy loss spectroscopy and energy dispersive X-ray spectroscopy. Unlike the previously reported case of Co/Ni-implanted ZnO (where Co/Ni nanocrystals were observed), Mn implantation has been found to induce an O deficiency in ZnO, which results in the formation of hexagonal Zn nanocrystals when the implantation dose is sufficient. Further annealing of the high-dose Mn-implanted ZnO promotes the formation of $ZnMn_2O_4$ compounds near the surface and a porous structure within the implanted region. The fundamental reasons behind these physical phenomena are discussed.

Keywords: ZnO; Mn implanted; Ion implantation; Zn precipitate

1. Introduction

In conventional semiconductor and information technology, it is well established that, on one hand, the existing integrated circuits made of semiconductors only make use of the charge of electrons in semiconductors; while on the other hand, the mass storage of information (such as hard disks, magnetic tapes and magneto-optical disks) merely utilizes the spin of electrons in ferromagnetic materials. The idea of taking advantage of both the charge and the spin of electrons pushes diluted magnetic semiconductors (DMSs) to the top of both academic and industrial interests [1–5]. One noticeable feature of DMSs is that another degree of freedom (spin) can be added compared with conventional semiconductors, which allows tremendous applications in spintronic devices in the future [1–5]. As a consequence, considerable effort has been devoted to turning this into reality and extensive investigations have been carried out in II–VI and III–V based DMSs in the last few years [6–11]. Although III–V based DMSs such as GaAs:Mn have been successfully achieved, their low magnetic ordering temperatures (~170 K) limit the application of such materials [8,12]. As an alternative, ZnO:Mn DMSs have also attracted considerable attention due to the fact that ZnO doped with transition metals (such as Mn, Co and Ni) [12–21] could be ferromagnetic with a Curie point well above room temperature. Many attempts have been dedicated to obtaining room-temperature ferromagnetic ZnO:Mn DMSs with high concentrations and uniformly distributed Mn. However, the conclusions drawn from previous studies [12–21] are rather controversial. Some reported paramagnetic properties of Mn-doped ZnO [16], some found antiferromagnetic features for the ZnO:Mn compound [17], and others claimed that their ZnO:Mn DMSs displayed ferromagnetism at over 400 K [9]. The diversity of these results is believed to be at least partially due to the growth conditions and/or the post processing methods used. Although several methods have been established to secure ZnO:Mn DMSs (such as pulsed laser deposition and sputtering), ion implantation, as a mature doping technique, has been recognized as one of the most versatile techniques for acquiring ferromagnetism in ZnO doped with transition metals [12,13].

On the other hand, the issue of whether Mn is incorporated into the ZnO matrix or is segregated to form Mn-rich

* Corresponding author.
E-mail address: j.zou@uq.edu.au (J. Zou).

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doi:10.1016/j.actamat.2009.01.033

clusters is of critical importance since the distribution of Mn atoms can significantly affect their charge state and magnetic coupling [22,23]. Therefore, knowledge of the nature of Mn distribution is essential to understanding the origin of ferromagnetism in ZnO:Mn DMSs. It has been reported that Mn-doped ZnO may lead to the formation of various Mn-related oxide precipitates or secondary phases such as MnO_2 [16], Mn_2O_3 [18] and $ZnMnO_3$ [15]. These precipitates inevitably impact on the magnetic properties of ZnO:Mn DMSs, making it more complicated to understand the origin of the ferromagnetism of ZnO:Mn DMSs. Most of the previous studies have been concentrated on the structural and magnetic properties of these Mn-rich clusters. For example, Xu et al. [22] reported that most Mn atoms were located on substituted Zn sites when the Mn concentration is below 20%, and they claimed that the ferromagnetism with the Curie temperature of 45 K is an intrinsic characteristic of the ZnO:Mn. However, a secondary-phase MnO was found when the Mn concentration reached 20%. Liu et al. [15] revealed that nanosized $ZnMnO_3$ clusters with a round shape and $MnZn_3O_6$ precipitates with a hexagonal shape can be formed in ferromagnetic Mn-doped ZnO fabricated by magnetron sputtering. On the other hand, Venkataraj et al. [16] found that MnO_2-like precipitates were formed in the Mn-implanted ZnO and observed paramagnetism. Nevertheless, little attention has been paid to the behavior of Mn in ZnO:Mn DMSs, especially in terms of the effect of the implantation with different doses and the effect of the annealing process on the ion implantation. Such information is of great significance, both scientifically and technologically.

In this article, through detailed scanning transmission electron microscopy (STEM), energy-filtered TEM (EFTEM), energy-dispersed X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) investigations, the behavior of Mn in Mn-implanted ZnO and the annealing effects on Mn behavior are comprehensively investigated. The fundamental reasons behind the new physical phenomena observed are discussed.

2. Materials and methods

Commercial single-crystal wurtzite-structured (0 0 0 1) ZnO used in this study was purchased from the MTI Company. Mn ion implantation was carried out in an accelerator (LC-4 high-energy ion implanter) at an energy of 200 keV and with a beam flux of $\sim 2.3 \times 10^{13}\,cm^{-2}\,s^{-1}$ [24]. During implantation, ZnO samples were held at room temperature and tilted 7° from the beam axis to minimize the channelling effect. Two ion doses, i.e. $1 \times 10^{17}\,cm^{-2}$ (sample A) and $5 \times 10^{16}\,cm^{-2}$ (sample B), were used. After implantation, parts of both these samples were further annealed at 725 °C for 5 min in a flowing N_2 atmosphere in order to study the effect of annealing.

To understand the structural and chemical characteristics of as-implanted and annealed samples, cross-sectional TEM (XTEM) investigations were carried out. XTEM specimens were prepared using a tripod technique, including mechanical grinding, followed by a final thinning using a Gatan precision ion polishing system. The TEM investigations were carried out in a FEI Tecnai F30 equipped with a Gatan Image Filter (GIF) system, operating at 300 kV. The EELS profiles (both zero-loss and core-loss spectra) were acquired in the image mode (diffraction coupled) and no objective aperture was inserted. The EELS spectra were processed by the Gatan's software (DigitalMicrograph with the EELS package for energy scale calibration, background subtraction and plural scattering removal). The EDS experiments were preformed on a Philips F20 in STEM mode, operating at 200 kV.

3. Results

3.1. Conventional TEM and EFTEM studies

Fig. 1a is a typical low-magnification XTEM image of the as-implanted sample A, showing its general morphology. As can be seen from this figure, a uniform damage layer is clearly distinguished and the surface of the implanted ZnO is relatively flat. To examine the Mn distribution within the Mn-implanted layer, EFTEM was performed [23,25]. Fig. 1b is a high-magnification bright-field TEM image; its corresponding EFTEM Mn elemental map is shown in Fig. 1c. In Fig. 1b many moiré fringe areas can be seen (one of these is marked by an arrow). It is of interest to note that vertical column-like regions seen in Fig. 1b can also be observed in the Mn map (Fig. 1c) with the bright column-like areas in Fig. 1c corresponding to Mn-rich areas. Based on Fig. 1c, the depth of Mn penetration can be estimated as 120 nm. It should be noted that the actual depth might be larger than this value due to the limitations of EFTEM. The whole damage layer can be roughly measured from Fig. 1a to be 200 nm. In addition, the low Mn concentration around the surface area can be observed in Fig. 1c. Fig. 2a is a typical low-magnification XTEM image of the annealed sample A, in which a damage layer can be clearly seen. Interestingly, a rough surface with voids just below the surface is noticeable in Fig. 2a, which is significantly different from that of the as-implanted case (Fig. 1a), but similar to that in the ion-implanted GaN [26]. In order to understand the Mn distribution after annealing in the Mn-implanted ZnO, a similar EFTEM experiment was performed on the annealed sample and the results are shown in Fig. 2b and c, respectively. As can be noted, significant Mn redistribution took place. Interestingly, Mn is located on the two sides (top and bottom) of the voids and, based on Fig. 2c, the depth of Mn penetration can be estimated to 160 nm, which is about 40 nm deeper than that of the as-implanted case. It should be mentioned that although voids were formed, moiré fringe areas are still observed in the annealed ZnO. These moiré fringes were verified to be the same type as that in the as-implanted case. However, the size of the moiré fringe