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High-dose V^+ implantation in ZnO thin film structures

A.F. Vyatkin [a,*], V.I. Zinenko [a], Yu.A. Agaphonov [a], A.N. Pustovit [a], D.V. Roshchupkin [a], F. Reuss [b], C. Kirchner [b], R. Kling [b], A. Waag [b,c]

[a] *Russian Academy of Sciences, Institute of Microelectronics Technology, 142432 Moscow district, Chernogolovka, Institutskaya, 6 IPMT RAS, Russia*

[b] *University of Ulm, D-89069 Ulm, Germany*

[c] *University of Braunschweig, D-38023 Braunschweig, Germany*

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Abstract

In the last two decades, diluted magnetic semiconductors have attracted great attention as promising materials for spintronics applications. [K. Sato, H. Katyama-Yoshida, Jpn. J. Phys., Part 2 39 (2000) L555] theoretically predicted that ZnO doped with V, Cr, Fe, Co, and Ni can be ferromagnetic. This has been recently confirmed experimentally for vanadium doped ZnO films which were grown on sapphire substrates, using laser deposition technique [H. Saeki, H.N. Tabata, T. Kawai, Solid State Commun. 120 (2001) 439]. In the present work, high-dose vanadium implantation was used to produce $Zn_{1-x}V_xO$ ($x \sim 0.10$) thin film structures (250 nm thick) that had been epitaxially grown on sapphire substrates. Implantation with the dose $2 \times 10^{16}\ cm^{-2}$ was performed to reach a maximum vanadium concentration of 10 at%. To avoid ZnO film amorphization due to radiation damage accumulation [S.O. Kucheyev, J.S. Williams, C. Jagadish, J. Zou, C. Evans, A.J. Nelson, A.V. Hamza, Phys. Rev. B 67 (2003) 094115], all implants were done at elevated temperatures 300 and 400 °C and ion current density 10 μA/cm^2. X-ray diffraction, SIMS and photoluminescence techniques were exploited to study the implanted samples. No luminescence was observed in the implanted samples after implantation procedures. However, annealing at 800 °C for 30 min gave rise to ZnO crystal structure improvement. This implies that healing of implantation induced defects is possible even after heavy-ion bombardment. As a result, the photoluminescence peak at 3.359 eV related to the donorbound exiton was detected.

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* Corresponding author. Tel.: +7 095 962 8038; fax: +7 095 962 8047.
E-mail address: Vyatkin@ipmt-hpm.ac.ru (A.F. Vyatkin).

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1. Introduction

There is a steady growing interest in ferromagnetic semiconductors at or above room temperature (RT). ZnO doped with transition metals (TM) like V, Cr, Fe, Co, and Ni seems to be a very promising candidate according to Sato et al. [1]. Experimental work was presented by Saeki and coworkers [2], which claimed ferromagnetic ZnVO at RT. Furthermore, experimental work that claimed ferromagnetism of ZnO doped with TM like Mn or Co are published [4,5]. Ion implantation was also applied to incorporate Mn into the ZnO matrix [6], resulting in a ferromagnetic phase up to 250 K. In order to exploit the ferromagnetism in device applications, the ferromagnetic coupling should be carrier mediated. This requirement was not unambiguously proved by any of the published works. A straightforward method that proves carrier mediated ferromagnetism would be the detection of the anomalous Hall effect. To our knowledge this has not be reported for ZnO based semiconductors. Our approach to obtain magnetic semiconductors will be ion implantation of TMs into high quality epitaxial ZnO thin films.

Ion implantation can be used to dope ZnO semiconductors with high concentration of transition metals. However, the problem with doping by ion implantation is obviously related to dopant activation efficiency and undesirable effects of ion-beam-produced lattice defects on electrical, optical, and magnetic properties of the semiconductors. A recent detailed study of the lattice defect evolution in single-crystal ZnO bombarded with light (^{29}Si) ions and heavy (^{197}Au) ions at 77 and 300 K has demonstrated a very unusual behavior of the radiation defects accumulation [3]. In particularly, it was shown that ZnO exhibits a very strong dynamic annealing and remains crystalline even after a very high-dose of heavy ^{129}Au ion bombardment. However, pronounced stoichiometric imbalance with a preferential loss of O in the near-surface region took place during high-dose heavy ion implantation. In contrast to heavy ion implantation, relatively light ^{29}Si ions being implanted into ZnO with high-doses induced a non-equilibrium crystalline-to-amorphous phase transition. In this case, an amorphous phase is effectively stabilized by implanted Si atoms due to chemical effects.

In the present work, we studied $^{51}V^+$ ion implantation into ZnO thin films to create a ferromagnetic semiconductor. In comparison with Au and Si atoms, ^{51}V atoms have some intermediate mass. Therefore, it is not clear a priori what kind of radiation damage accumulation would occur in ZnO when a high-dose of V^+ ions implantation is used.

2. Experiment

ZnO thin films are grown by metal organic vapor phase epitaxy (MOVPE) [7]. With additional Ga doping n-type carrier concentrations of almost 1×10^{21} cm^{-3} are possible. Two sets of samples, ZnO and ZnO:Ga films with a thickness of 250 nm were applied for the V implantation. Samples were implanted with 180 keV $^{51}V^+$ ions at 300 or 400 °C with a beam flux of 4.65×10^{13} cm^{-2} s^{-1} and dose of 2×10^{16} cm^{-2} using Extrion 1000 Varian machine. During implantation, samples were tilted by ~7° relative to the incident ion beam to minimize channeling phenomenon. Implantation with the dose 2×10^{16} ion/cm^2 was chosen to reach a maximum vanadium concentration about 10 at%. Indeed, TRIM and SUSPRE calculations showed that the maximum vanadium concentration in the ZnO film at the dose applied was 10.5 and 12.9 at%, respectively. Ion implantation at elevated temperatures was performed to avoid possible amorphization effect and to enhance the probability of dynamic annealing of radiation damages.

After implantation the composition, structural and optical properties of the samples were analyzed by SIMS, high resolution X-ray diffractometry (HRXRD) and low temperature photoluminescence (PL). An annealing step at 700 °C and 800 °C for 30 min in a closed ZnO sinterbody was applied to anneal implantation induced damage.

3. Results and discussion

A SIMS spectrum taken from the as-implanted sample at 300 °C is shown in Fig. 1. It can be seen