Journal of Magnetism and Magnetic Materials 322 (2010) L13–L17

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Letter to the Editor

EPR study of Mn-implanted single crystal plates of TiO_2 rutile

S. Güler [a,*], B. Rameev [a,b], R.I. Khaibullin [b], O.N. Lopatin [c], B. Aktaş [a]

[a] Gebze Institute of Technology, Gebze-Kocaeli 41400, Turkey
[b] Lab. of Radiation Physics, Kazan Physical-Technical Institute, 420029 Kazan, Russia
[c] Faculty of Geology, Kazan State University, 420008 Kazan, Russia

ARTICLE INFO

Article history:
Received 31 August 2009
Available online 22 December 2009

Keywords:
Electron paramagnetic resonance
Titanium dioxide
Ion implantation
Diluted magnetic oxide
Spintronic

ABSTRACT

Single crystals of Mn-implanted TiO_2 rutile have been investigated by electron paramagnetic resonance (EPR) technique at room temperature. We have observed an EPR signal on Mn^{4+} ions ($S=\frac{3}{2}$) in the manganese-implanted single crystal TiO_2 plates. Besides, weaker EPR signals due to Fe^{3+}($S=\frac{5}{2}$, $L=0$) and Cr^{3+}($S=\frac{3}{2}$) ions have also been observed. Characteristic six-line splitting of the manganese EPR lines due to hyper-fine interaction with ^{55}Mn nuclei (spin $I=\frac{5}{2}$) has also been observed. Analysis of the EPR spectra shows that the manganese, iron and chromium ions substitute for Ti^{4+} ions in the TiO_2 rutile host. Two structurally equivalent groups of the centers have been observed in the EPR spectra in correspondence with two octahedral positions of the Ti ions in the rutile structure. Spin Hamiltonian parameters for the crystal field of orthorhombic symmetry on the Mn^{4+}, Fe^{3+} and Cr^{3+} centers have been obtained as result of computer modelling.

1. Introduction

The discovery of high-Curie temperature diluted magnetic oxides (such as transition metal doped TiO_2, ZnO, SnO_2 and others) has attracted much attention due to their potential value for the development of the spintronic devices [1,2]. A number of experimental works report on the room temperature ferromagnetism observed in various oxides [3–17]. Despite of essential progress achieved in this field, there is still an open issue: whether intrinsic or extrinsic ferromagnetism is realized in these materials.

It has been shown that the local environment of doped magnetic ions as well as nearby oxygen defects have a drastic effect on the magnetic properties of these materials. There are a few theoretical calculations showing that the magnetic state of the doped ions is expected to be very sensitive to the local crystalline structure, to the presence of various defects like interstitials and vacancies, etc. [14,15,16]. On the other hand, Electron Paramagnetic Resonance (EPR) is well-known technique to probe the local magnetic and structural properties of crystals. In particular, it is a very efficient method for the investigations of the local environment around a substitutional magnetic ion in various crystal hosts [18–29].

In this study, the local structure of Mn, Fe, Cr ions in the single crystalline TiO_2 rutile plates doped by ion-beam implantation has been studied by EPR technique. The samples under study were (1 0 0) and (0 0 1) substrates implanted by Mn and annealed at very high temperature ($T=950$ °C) to dissolve manganese clusters and to obtain highly-diluted concentration of Mn ions in the TiO_2 host. We have shown that implantation with 40 keV Mn^+ ions with subsequent annealing at high temperature results in formation of the paramagnetic Mn^{4+} centers substituting Ti^{4+} ions in the rutile structure. Besides, we have observed Fe^{3+} and Cr^{3+} centers, unintentionally created during ion-beam implantation, which also substitute the Ti^{4+} positions in the TiO_2 structure. The spin Hamiltonian parameters of the Mn^{4+}, Fe^{3+} and Cr^{3+} ions in the implanted TiO_2 rutile crystals have been obtained and discussed.

2. Experiment and results

Single crystalline (1 0 0) and (0 0 1) TiO_2 rutile substrates have been implanted on the ILU-3 ion accelerator (Kazan Physical-Technical Institute) with 40 keV Mn^+ ions to a fluence of 1.50×10^{17} ions/cm^2 at ion current density of about 8 μA/ cm^2. The sample holder was cooled by flowing water during the implantation to prevent the samples from overheating. The implanted samples have been annealed at $T=950$ °C in air during 1 h. Structural studies have revealed that annealing procedure results in the diffusion of the most of manganese impurity out of the implanted layer with thickness of about 30 nm [20]. As another result of the post-implanting thermal treatment the samples have become transparent and the colour of samples has changed from dark-grey to light-orange.

* Corresponding author.
E-mail address: sumeyra@gyte.edu.tr (S. Güler).

0304-8853/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmmm.2009.12.014