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Site location and optical properties of Eu implanted sapphire

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Abstract

Synthetic colourless transparent (0001) sapphire crystals were implanted at room temperature with 100 keV europium ions to fluences up to 1×10^{16} cm^{-2}. Surface damage is observed at low fluences, as seen by Rutherford backscattering spectrometry under channelling conditions. Optical absorption measurements revealed a variety of structures, most probably related to F-type defects characteristic of implantation damage. Thermal treatments in air or in vacuum up to 1000 °C do not produce noticeable changes both in the matrix or the europium profiles. However, the complete recovery of the implantation damage and some redistribution of the europium ions is achieved after annealing at 1300 °C in air. Detailed lattice site location studies performed for various axial directions allowed to assess the damage recovery and the incorporation of the Eu ions into well defined crystallographic sites, possibly in an oxide phase also inferred from optical absorption measurements.

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1. Introduction

Rare-earth (RE) doped materials are very attractive due to their potential optoelectronic applications, such as optical amplifiers, in display phosphors or microlasers with a submicron dimension. This requires that the RE-based materials be synthesized and integrated with functional

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substrates, such as single crystals, ceramic microspheres, and nanofibers. On the host materials a wide range has been used, from ZnS [1], AlN [2], SiO_2 [3,4], CaO [5], CaF_2 [6] or Al_2O_3 [7]. We have used α-Al_2O_3, the most employed ceramic, due to its large optical transparency from ultraviolet to nearinfrared wavelengths, excellent mechanical properties, and good chemical and thermal stability. Similarly, among the variety of RE ions commonly used to dope different kinds of materials, europium ions have tremendous potential for its strong characteristic red emission for applications in phosphors, electroluminescent devices, optical amplifiers or lasers, and high density optical storage.

The methods that have been utilized so far to produce these RE doped systems include sol–gel techniques [8], gas phase condensation with continuous wave-CO_2 laser heating [9], sonochemical synthesis and deposition [10], co-precipitation [11] and ion implantation [4]. Ion implantation presents a powerful method of doping since it allows overcoming the low solid solubility restrictions and simultaneously also allows the precise and predictable definition of the confinement zone of the system created. Hence the structures formed and the resulting linear and non-linear properties will occur in a well defined space in the optical device. However, the intrinsic defects induced by collisions between the incoming particles and the target atoms and/or extrinsic defects resulting from the presence of the implanted ions may alter the microstructure and its properties thus requiring thermal treatments to allow relaxation to a stable system [12].

In this work Eu was implanted at low fluences into α-Al_2O_3. The structural and optical changes introduced after implantation and produced during the thermal treatments up to 1300 °C, in oxidizing and in reducing atmospheres, as well as the lattice site location were studied. To our knowledge, site location studies on Eu implanted sapphire have not been performed before.

2. Experimental details

Synthetic sapphire single crystals, 0.4 mm thick, with $\langle 0001 \rangle$ orientation (c-samples) and optically polished surfaces were implanted at room temperature (RT) with 100 keV europium ions. The nominal fluences were in the range of 1×10^{15} to 1×10^{16} cm^{-2}. The samples were tilted 8° to avoid channelling during the implantation. The expected projected range and straggling of the Eu ions were calculated using SRIM2003 [13] to be 28 and 6 nm respectively. The code also predicts the production of 1450 vacancies per incident ion. To recover from the implantation damage thermal annealings were carried out in a standard tube furnace at 800, 1000 and 1300 °C in oxidizing (ambient air) and reducing (vacuum, 2×10^{-4} Pa) atmospheres for 1 h. The samples went directly from RT to the annealing temperature and vice versa. Rutherford backscattering spectrometry (RBS) and RBS channelling (RBS-C) studies were performed with a 2.0 MeV He^+ beam after implantation and after each annealing step to characterize the structural changes. The backscattered particles were detected at 140° and close to 180° using silicon surface barrier detectors with resolutions of 13 and 18 keV respectively. The beam current was measured on the target and kept below 4 nA in order to minimize the effects of charge accumulation at the surface during analysis. Detailed angular scans were performed along $\langle 0001 \rangle$, $\langle 1\bar{2}13 \rangle$ and $\langle 1\bar{1}01 \rangle$ axes to determine the lattice site location of Eu. The optical absorption (OA) measurements were performed in the 200–900 nm wavelength range at RT, with a Varian Cary 5G UV–Vis.–NIR double beam spectrophotometer.

3. Results

3.1. Structural studies

The retained fluences measured by RBS are close to the nominal values in every case. After implantation of 1×10^{15} cm^{-2} the samples show a shallow (40 nm) damaged layer (20% minimum yield versus a typical 6% of the unimplanted matrix). This thickness coincides with the FWHM of the Eu profile, as shown in Fig. 1(a). The Eu profile peaks at 25 nm, in agreement with SRIM prediction, and displays some channelling, with a measured minimum yield of 70%. As the implantation fluence increases the