Nuclear Instruments and Methods in Physics Research B 106 (1995) 429–432

NIM B
Beam Interactions with Materials & Atoms

ELSEVIER

Incorporation and stability of erbium in sapphire by ion implantation

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Abstract

Precise results on the lattice site location and stability of Er implanted sapphire using the RBS/channeling technique are reported. The Er ions were implanted into ⟨0001⟩ and ⟨01$\bar{1}$0⟩ cut samples of α-Al_2O_3 single crystals, at room and liquid nitrogen temperatures, with 200 keV energy at fluences between 8×10^{13} and 4×10^{15} Er^+/cm^2. The implantation of 8×10^{13} Er^+/cm^2 (0.01 at%) at room temperature leads to the incorporation of 70% of the Er ions near the free octahedral site (0.8 Å displaced) along the c-axis. From the remaining fraction of Er ions, at least 20% can be in a tetrahedral site. At liquid nitrogen temperature the fluence of 6×10^{14} Er^+/cm^2 amorphizes sapphire, while at room temperature a fluence an order of magnitude higher produces only a damaged buried layer. The annealing at temperatures higher than 1200°C leads to the recrystallization of the amorphous layer, but the Er ions segregate to the surface or precipitate. For the samples implanted at room temperature, the annealing leads to a higher incorporation of Er in the sapphire lattice and only a small fraction segregates to the surface at 1500°C.

1. Introduction

The incorporation of rare earth elements into optical waveguide materials attracted much interest in recent years, since one obtains optical transitions with well-defined spectral lines. Such Er doped waveguides could be used as lasers or optical amplifiers operating at the Er transition wavelength at 1.5 μm [1]. Particularly, the incorporation of Er in aluminum oxide is interesting for optical waveguide applications. As the Al–O and Er–O bond lengths are very similar and both Al and Er are trivalent, it is expected that Er can be incorporated at least partially in the Al_2O_3 crystal structure [2].

Earlier measurements have shown that Er implanted Al_2O_3 films (dose of 3.7×10^{16} Er^+/cm^2 corresponding to a peak concentration of 3.6 at%, implanted at 800 keV) show room temperature photoluminescence after thermal annealing at temperatures up to 825°C [3,4]. To understand the annealing behavior and the optical properties it is important to determine the lattice site location of Er implanted in Al_2O_3.

In this work the incorporation of Er in single crystal Al_2O_3 (sapphire) by ion implantation at room and liquid nitrogen temperatures is studied. The lattice site location is discussed together with results of the annealing behavior and stability of both the room temperature and liquid nitrogen temperature implanted samples.

2. Experimental details

High purity α-Al_2O_3 single crystals with optically polished surfaces cut perpendicularly to the ⟨0001⟩ and ⟨01$\bar{1}$0⟩ directions were implanted with 200 keV Er^+ ions to fluences from 8×10^{13} to 4×10^{15} at/cm^2. The specimens were implanted at liquid nitrogen (LN) temperature and room temperature (RT). Thermal annealing was carried out for one hour at temperatures in the range of 550–1500°C in vacuum (below 1000°C) or air (above 1000°C).

After implantation and after each stage of thermal annealing, RBS/channeling studies were performed with a 1.6 He^+ beam to characterize the lattice site location of the implanted Er ions and the structural changes induced by the thermal annealing. In the channeling experiment the backscattered particles were detected at 160° and 180° using silicon surface barrier detectors with resolutions of 13 and 18 keV, respectively. During the measurements the pressure in the

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0168-583X/95/$09.50
SSDI 0168-583X(95)00746-6

chamber was of the order of 4×10^{-8} mbar and the beam current was measured using a transmission Faraday cup [5]. In order to minimize the effects of charge accumulation on the Al_2O_3 surface during analysis, the crystal was masked with a thin Ni foil with a 4 mm hole and the beam intensity was kept bellow 4 nA. Angular scan measurements were made only for the samples implanted with 8×10^{13} Er^+/cm^2, along the $\langle 0001 \rangle$, $\langle 01\bar{1}0 \rangle$, $\langle 11\bar{2}0 \rangle$ and $\langle 02\bar{2}1 \rangle$ (not shown) axes and (0001), $(10\bar{1}0)$ and $(11\bar{2}0)$ planes.

Computer simulations were performed using a Monte Carlo code previously described [6] which has been modified to accommodate the α-Al_2O_3 crystal lattice.

3. Results and discussion

3.1. The lattice site of Er in sapphire

Fig. 1 shows the angular scans of the normalized yields for the Al, O and Er ions through the three $\langle 0001 \rangle$, $\langle 01\bar{1}0 \rangle$ and $\langle 11\bar{2}0 \rangle$ axial and corresponding planar directions obtained on the as-implanted samples. The $\langle 0001 \rangle$ and $\langle 01\bar{1}0 \rangle$ samples were implanted with a dose of 8×10^{13} Er^+/cm^2 at room temperature. Although the Er and Al yields almost overlap along the

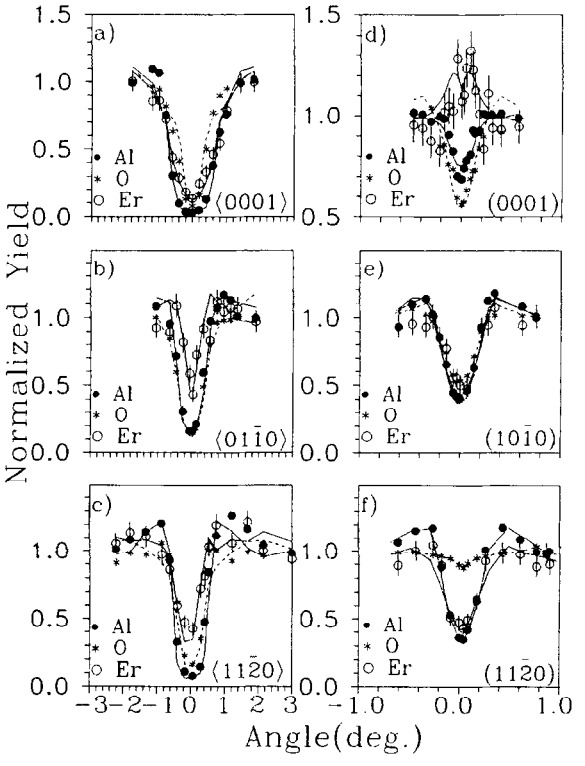

Fig. 1. Angular scans for the Al, O and Er ions in the $\langle 0001 \rangle$, $\langle 01\bar{1}0 \rangle$ and $\langle 11\bar{2}0 \rangle$ axial and corresponding planar directions. The sample was implanted with a dose of 8×10^{13} Er^+/cm^2.

$(10\bar{1}0)$ and $(11\bar{2}0)$ planar directions, it is shown that mainly a flux peak for the Er yield appears along the (0001) plane. All the three corresponding axial directions clearly show that the Er yields deviate from both the Al and O yields. Along the $\langle 0001 \rangle$ direction the Er yield overlaps with the O yield in the middle of the dip, but with the increase of the angular deviation from the c-axis it starts to overlap with the Al yield. For the $\langle 01\bar{1}0 \rangle$ axis the Er yield presents a narrow dip which clearly shows that Er cannot be in either the Al or the O sublattice.

Fig. 2 shows the projections of Al, O, and the octahedral and tetrahedral interstitial regular sites in the studied axial and planar directions. The dashed and continuous lines drawn in Fig. 1 are the theoretical fits to the data, obtained by simulating the flux of 1.6 MeV He^+ ions along the respective directions in the unit cell. The thermal vibration amplitudes considered, 0.087 Å for O, 0.067 Å for Al and 0.027 Å for Er, were obtained using the Debye model with a temperature of 950 K. Along the $\langle 0001 \rangle$ direction the interstitial sites in sapphire are shadowed by the Al or O atoms and therefore the experimental data show that the Er ions must occupy a site slightly displaced from the ideal octahedral or tetrahedral sites. The flux peak in the (0001) plane together with the very narrow peak in the $\langle 01\bar{1}0 \rangle$ axis and the wide dip in the $\langle 11\bar{2}0 \rangle$ axis show that most of the Er ions occupy a site along the $\langle 0001 \rangle$ axis but displaced 0.8 Å from the ideal octahedral site. The fraction of ions occupying that site must be of the order of 70%. However, to get the best simulation of the data we must assume that a fraction of about 20% of the Er ions is in the tetrahedral interstitial site. With these two fractions the structure of the dips is well reproduced. The remaining 10% of the Er ions are randomly distributed and no further assignment can be done.

3.2. Thermal stability of Er in sapphire and annealing implantation induced radiation damage

Fig. 3 shows the variation of the minimum yields along the $\langle 0001 \rangle$ axis with the annealing temperature for two $\langle 0001 \rangle$ samples implanted at 200 keV with a dose of 8×10^{13} Er^+/cm^2 at RT and LN temperatures. Changes of the minimum yields are observed in the range between 800 and 1200°C. At 1500°C, although the minimum yield of Al improves, the yield for Er increases drastically in both samples. This increase is a clear indication that although the Er concentration is very low, precipitation occurs at high temperatures.

Fig. 4 shows the RBS results for a sample implanted at LN temperature with a dose of 6×10^{14} Er^+/cm^2 and Fig. 5 shows the RBS results for a sample implanted at RT with a dose of 4×10^{15} Er^+/cm^2. These two significant examples were selected to show that a complete amorphization of sapphire was obtained at

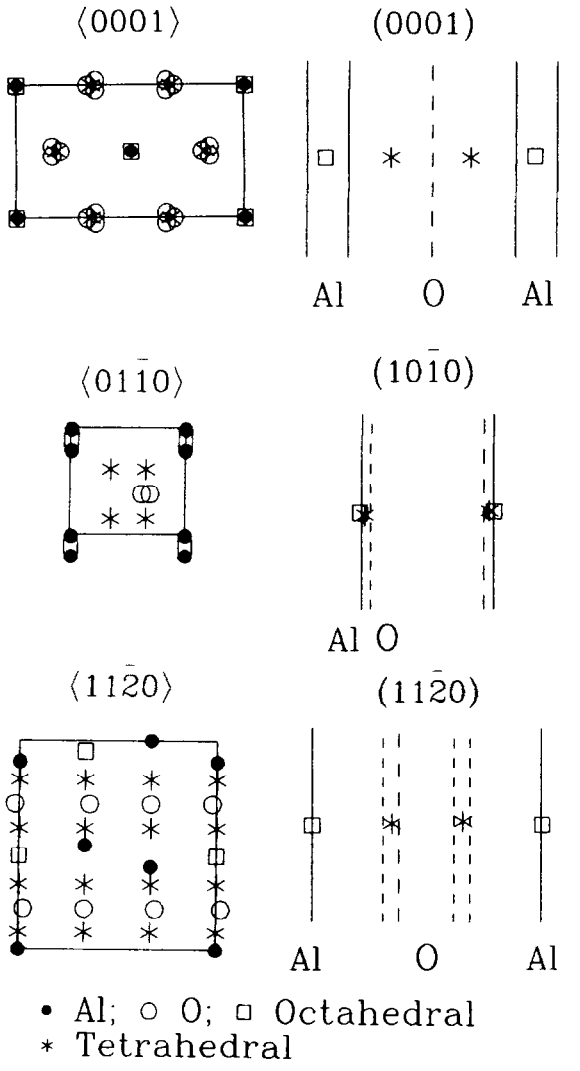

Fig. 2. Projections of Al, O, and octahedral and tetrahedral interstitial regular sites in the ⟨0001⟩, ⟨00$\bar{1}$0⟩ and ⟨11$\bar{2}$0⟩ axial and corresponding planar directions.

LN temperature for a dose of 6×10^{14} Er^+/cm^2, while a dose one order of magnitude higher at room temperature does not amorphize sapphire. Radiation damage is, however, clearly visible in the aligned spectrum along the ⟨0001⟩ axis both in the Al and O profiles, at a depth corresponding to the Er range. Between the narrow surface peak and the maximum in the radiation damage profile the crystal has a quite good minimum yield.

The annealing of the radiation damage has a different mechanism in the two samples. For the sample implanted at LN temperature the oxygen sublattice is almost fully recrystallized after the annealing at 825°C, but the Al sublattice is not. Both sublattices are totally reorganized at 1200°C. The Er peak, however, shows that above 1200°C, part of the Er migrates to the surface, and some structure appears. The segregation of Er to the surface is related with the epitaxial regrowth of the amorphous layer. During this process Er moves to the surface and precipitation occurs. On the contrary, in the crystal implanted at RT the radiation damage in the O and Al sublattices disappears only above 1200°C and a small Er surface peak can be seen after annealing at 1500°C. Also, at this temperature an improvement in the minimum yield of the Er ions at the depth of the maximum concentration is observed. This is clearly due to the formation of coherent precipitates of an Er compound. When the implanted dose of Er is very low, like in the case shown in Fig. 3, these precipitates are not observed.

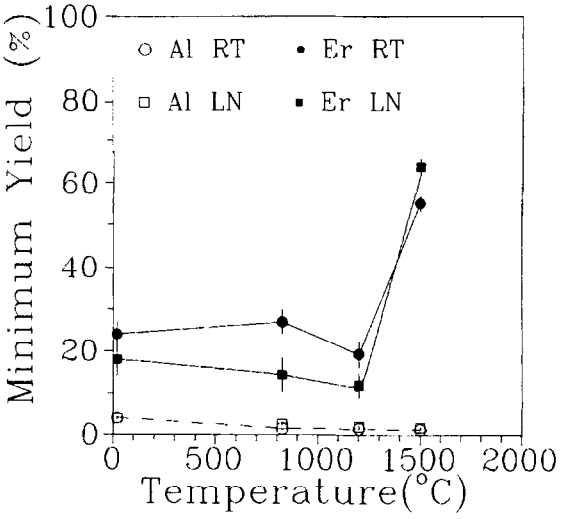

Fig. 3. Variation of the minimum yields with the annealing temperature for two samples implanted at 200 keV at room and liquid nitrogen temperatures with a dose of 8×10^{13} Er^+/cm^2.

4. Conclusions

The implantation of Er ions in Al_2O_3 follows the general trends concerning radiation damage and recrystallization previously seen with other implanted species [7].

After implantation of 8×10^{13} Er/cm^2 and before annealing a high fraction of the Er ions (~ 70%) are 0.8 Å displaced from the free octahedral site along the c-axis. This lattice site is different from the site occupied by Hf after implantation, which substitutes Al [8]. Since there exists also evidence that In^{3+} does not occupy the Al site after implantation [9], and both In^{3+} and Er^{3+} have big ionic radii (0.81 and 0.88 Å, respectively) it is possible that the ionic radii associated with the valence effect play an important role in the occupation of the interstitial site.

At liquid nitrogen temperature the fluence of 6×10^{14} Er^+/cm^2 amorphizes sapphire, while at room

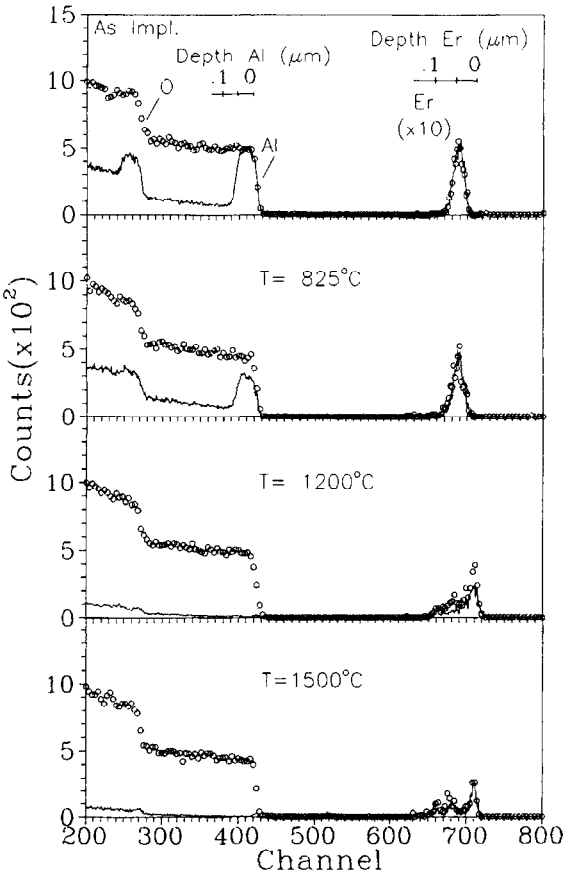

Fig. 4. RBS spectra for a sample implanted at 200 keV at liquid nitrogen temperature with a dose of 6×10^{14} Er^+/cm^2 in the as-implanted state and after annealing treatments at 825, 1200 and 1500°C.

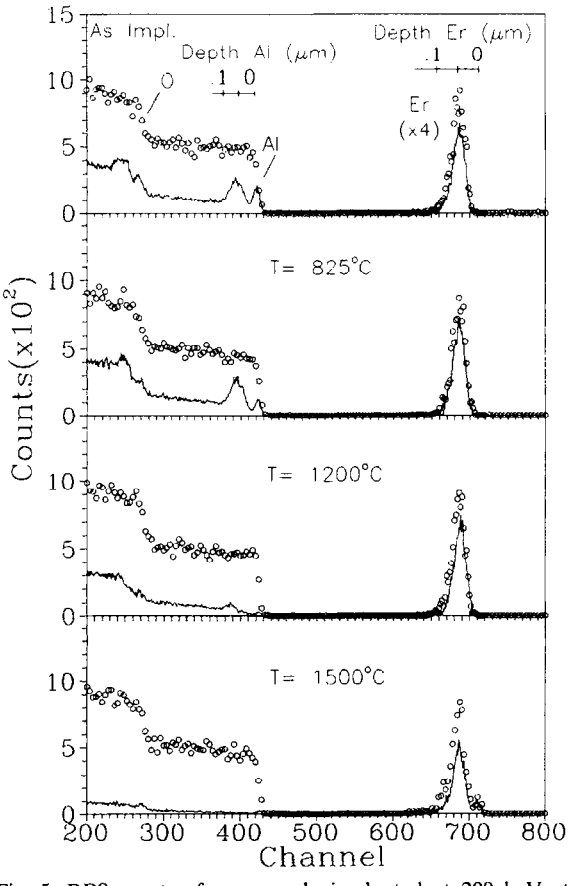

Fig. 5. RBS spectra for a sample implanted at 200 keV at room temperature with a dose of 4×10^{15} Er^+/cm^2 in the as-implanted state and after annealing treatments at 825, 1200 and 1500°C.

temperature a fluence an order of magnitude higher produces only a damaged buried layer. The annealing at temperatures higher than 1200°C leads to the recrystallization of the amorphous layer, but the Er ions segregate to the surface or precipitate. For the samples implanted at room temperature, the annealing leads to a higher incorporation of Er in the sapphire lattice and only a small fraction segregates to the surface at 1500°C.

Acknowledgements

This work has been partially funded by the Junta Nacional de Investigação Cientifica e Tecnológica, Portugal, through projects CERN/CA/982/92 and CA/1021/93. Work at FOM is financially supported by NWO, IOP Electro-Optics and STW.

References

[1] A. Polman, Mater. Res. Soc. Symp. Proc. 316 (1994) 385.
[2] P. Villars and L.D. Calvert, Pearson's Handbook of Crystallographic Data for Intermetallic Phases (American Society for Metals, Metals Park, OH, 1986) pp. 1047, 2177.
[3] G.N. van den Hoven, E. Snoeks, A. Polman, J.W. van Uffelen, Y.S. Oei and M.K. Smit, Appl. Phys. Lett. 62 (1993) 3065.
[4] M.K. Smith, G.A. Acket and C.J. Laan, Thin Solid Films 138 (1986) 171.
[5] P. Pászti, A. Manuaba, C. Hadjn, A.A. Melo and M.F. da Silva, Nucl. Instr. and Meth. B 47 (1990) 184.
[6] L. Rebouta, P.J.M. Smulders, D.O. Boerma, F. Agulló-López, M.F. da Silva and J.C. Soares, Phys. Rev. B 48 (1993).
[7] G.C. Farlow, P.S. Sklad, C.W. White and C.J. McHargue, J. Mater. Res. 5 (1990) 1502.
[8] J.G. Marques, A.A. Melo, J.C. Soares, E. Alves, M.F. da Silva and K. Freitag, these Proceedings, (IBMM-95) Nucl. Instr. and Meth. B 106 (1995).
[9] G.C. Farlow, C.W. White, C.J. McHargue and B.R. Appleton, Mater. Res. Soc. Symp. Proc. 27 (1984) 395.