Implantation site of rare earths in single-crystalline ZnO

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(Received 4 September 2002; accepted 3 January 2003)

The lattice location of rare earth $^{167\text{m}}\text{Er}$ in single-crystalline hexagonal ZnO was studied by means of the emission channeling technique. Following 60-keV room-temperature implantation of the precursor isotope ^{167}Tm at doses of $1.3\text{--}2.8 \times 10^{13} \text{ cm}^{-2}$ and annealing up to 900°C , the angular distribution of conversion electrons emitted by the radioactive isotope $^{167\text{m}}\text{Er}$ was measured by a position-sensitive electron detector. The conversion electron emission patterns from $^{167\text{m}}\text{Er}$ around the [0001], [1102], [1101] and [2113] directions give direct evidence that the large majority of Er atoms (75-90%) occupies substitutional Zn sites.

Rare earth (RE) doped semiconductors have long been studied for possible applications as electroluminescent devices emitting in the visible or infrared ([1] and references therein). Since it was experimentally observed that the rare earth luminescence efficiency at room temperature increases with the band gap of the semiconductor [2], wide band gap materials such as GaN are especially promising for possible applications. Rare earth luminescence from Nd, Sm, Eu, Tb, Dy, Ho, Er and Tm has also been reported in the hexagonal II-VI semiconductor ZnO [3-12]. Interest in zinc oxide has recently increased due to the fact that its structural and semiconducting properties are similar to hexagonal GaN, but that, in comparison to GaN, high-quality single crystals of ZnO are easier to grow [13].

In analogy with GaN, where the optically active sites of rare earths are considered to be substitutional Ga sites [14, 15], optical activity of Er in ZnO is likely to be associated with REs occupying substitutional Zn sites. Several methods for producing RE-doped ZnO have been described in the literature, including sintering [3-5], wet-chemical synthesis [6, 11], laser ablation [7-10] and co-deposition following evaporation [12]. However, all these methods result in polycrystalline samples, and there exists evidence that the rare earths accumulate at the grain boundaries of polycrystalline ZnO [4]. Ion implantation, on the other hand, which is a widely used method in semiconductor technology for doping single crystals, has so far not been investigated for rare earth doping of ZnO.

In this letter we report on the lattice location of ion implanted rare earth atoms in single-crystalline hexagonal ZnO using the emission channeling technique [16]. For that purpose we have measured the angular distribution of conversion electrons emitted by the radioactive isotope $^{167\text{m}}\text{Er}$ ($t_{1/2} = 2.27 \text{ s}$) following implantation of the precursor isotope ^{167}Tm ($t_{1/2} = 9.25 \text{ d}$). The recoil energy of the $^{167}\text{Tm} \rightarrow ^{167\text{m}}\text{Er}$ decay is 0.7-0.9 eV only, indicating that the $^{167\text{m}}\text{Er}$ lattice site is inherited from ^{167}Tm . We have already applied this method to study the lattices sites of

$^{167\text{m}}\text{Er}$ in Si [17], GaAs [18], and InP [19]. More experimental details can be found in these previous papers.

The two ZnO samples studied were commercially available [20] single crystals, grown by seeded chemical vapor transport. Both samples were cut perpendicular to the *c*-axis, but one polished at the Zn face (sample A) and the other at the O face (sample B). Implantations of ^{167}Tm were performed 7° from the surface normal up to a dose of $1 \times 10^{13} \text{ cm}^{-2}$ (sample A) and $3 \times 10^{13} \text{ cm}^{-2}$ (sample B) using CERN's on-line isotope separator facility ISOLDE. These implantation conditions lead to maximum ^{167}Tm concentrations of $1 \times 10^{19} \text{ cm}^{-3}$ and $2 \times 10^{19} \text{ cm}^{-3}$ at a depth of $162(54) \text{ \AA}$. The emission channeling patterns from the 150, 199 and 206 keV conversion electrons emitted by $^{167\text{m}}\text{Er}$ were recorded by a position-sensitive electron detector.

In order to identify the lattice sites of Er, we have compared the experimental channeling yields to simulated patterns for $^{167\text{m}}\text{Er}$ emitter atoms on substitutional Zn sites (S_{Zn}) and substitutional O sites (S_{O}) with varying root mean square (rms) displacements. Besides, we also considered a large variety of interstitial sites the location of which has been described in Ref. [21] for the case of hexagonal GaN. Among them are the interstitial T and O_i sites which are positions that are centered in the wide-open interstitial regions of the wurtzite lattice. Note that the O_i sites should not be confused with substitutional oxygen sites S_{O} .

The electron channeling simulations were carried out with the "many beam" formalism using a number of 20 beams, i.e. representing the electron wave functions by 21×21 Fourier components. In order to describe the crystal structure of ZnO, we adopted two different structural models. While in both models lattice constants of $a = 3.2495 \text{ \AA}$ and $c = 5.2069 \text{ \AA}$ [22] were used, the first approach assumed the Zn-O *c*-axis bond length to be $z = 0.375 c$, as in an ideal wurtzite structure. In addition, this approach used isotropic root mean square (rms) displacements of $u_1(\text{Zn}) = 0.082 \text{ \AA}$ and $u_1(\text{O}) = 0.085 \text{ \AA}$ [23], which would correspond to Debye temperatures of $T_{\text{D}}(\text{Zn}) = 320 \text{ K}$ and

FIG. 1. Angle-dependent conversion electron emission yields from $^{167\text{m}}\text{Er}$ in ZnO sample A around the [0001] (a), [1102] (b), [1101] (c) and [2113] (d) axes. Since there were only slight changes up to an annealing temperature of 600°C, we have compiled in this figure patterns measured with best statistics but following different annealing temperatures [200°C (c), 300°C (a), 400°C (d), and 600°C (b)] Panel (e)-(h): best fits of simulated channeling patterns for S_{Zn} sites to the experimental yields, corresponding to 89%, 97%, 97% and 87% of Er on S_{Zn} , respectively.

$T_{\text{D}}(\text{O}) = 696 \text{ K}$. The second approach consisted of a more refined model, which applied a c -axis bond length of $z = 0.382 c$ and anisotropic rms displacements of $u_{\parallel}(\text{Zn}) = 0.0780 \text{ \AA}$, $u_{\parallel}(\text{O}) = 0.081 \text{ \AA}$, $u_{\perp}(\text{Zn}) = 0.090 \text{ \AA}$ and $u_{\perp}(\text{O}) = 0.092 \text{ \AA}$ [24], where $u_{\parallel}$ and $u_{\perp}$ represent one-dimensionally projected rms displacements parallel and perpendicular to the c axis, respectively. However, the best fit results for the Er fractions and rms displacements obtained from both approaches differed only by a few percent and less than $0.02 \text{ \AA}$, respectively.

Following room temperature implantation of $^{167\text{m}}\text{Tm}$, sample A was subjected to an annealing sequence up to 900°C in steps of 100 K under vacuum. Following each 10 min annealing step, the conversion electron emission channeling patterns around the [0001], [1102], [1101] and [2113] crystal directions were recorded. Figure 1 (a) shows the [0001] pattern following the annealing step at 300°C. The channeling effects along the c axis and along the major crystal planes give direct evidence that the majority of $^{167\text{m}}\text{Er}$ atoms occupy sites which are located within the c -axis atomic rows. The best two-fraction fit of the theoretical yields to the experimental data is shown in Fig. 1 (e)

FIG. 2. Simulated patterns for emitter atoms on substitutional oxygen sites S_{O} (a-d) and the so-called interstitial O_{i} sites (e-h).

and corresponds to 89% of Er atoms along the c axis, and 11% on random (R) sites, which are characterized by an isotropic emission yield. However, since, e.g., also S_{O} and T sites are aligned with the atomic rows along the c axis, [0001] patterns alone do not provide unambiguous site identification and additional crystal directions must be taken into account. Suitable directions in that respect are, e.g., the [1102], [1101] and [2113] axes [21]. The emission channeling patterns of these three directions are shown in Figs. 1 (b), (c) and (d). In all cases a combination of substitutional Zn sites and random sites provided the best two-fraction fit, as is shown in Figures 1 (f), (g) and (h).

In order to illustrate that substitutional O sites S_{O} and interstitial sites are responsible for distinctively different emission patterns, Figs. 2 (a-d) show the theoretical patterns for 100% of emitter atoms on S_{O} sites, and Figs. 2 (e-h) for 100% on interstitial O_{i} sites. Comparing to the experimental results of Figs. 1 (a-d) it is clear that large fractions of Er on these sites can be ruled out. In general, allowing for Er on other than substitutional Zn and random sites did not significantly improve the quality of fit.

Annealing sample A up to 600°C did not result in substantial changes in the fraction of Er on S_{Zn} sites [Fig. 3 (a)]. For higher annealing temperatures, however, the substitutional Er fraction decreased considerably. Sample B was only measured in the as-implanted state, with the fraction of Er on S_{Zn} sites (75%) being lower than in sample A. Since the implanted dose was twice as high as the one of sample A, the smaller substitutional fraction is most likely due to more severe lattice damage.

FIG. 3. Fraction of Er atoms on substitutional Zn sites (a) and their room temperature rms displacements perpendicular to the indicated crystal directions (b) following isochronal (10 min) annealing steps. The dashed and dotted lines indicate the room temperature rms displacements of Zn and O atoms.

Figure 3 (b) shows the root mean square (rms) displacements of Er from the perfect substitutional Zn positions derived from the room temperature measurements following the different annealing steps. As can be seen the rms displacements of Er are clearly larger than those of Zn and O atoms. With increasing annealing temperature up to 700°C, the rms displacements of Er showed a slight tendency to decrease, and to increase again for higher annealing temperatures. The most likely reason for this increase and the decrease of the substitutional Er fraction is rare earth diffusion. This was indicated by additional Rutherford backscattering studies [25] where ZnO samples were implanted with Er doses of 5×10^{14} – 5×10^{15} cm $^{-2}$ at 150 keV, leading to depth profiles of 314(99) Å and maximum concentrations of 2×10^{20} – 2×10^{21} cm $^{-3}$. Following 1050°C annealing in air for 30 min these experiments showed good recovery of the implantation damage and no substantial decomposition of the surface region, while already 50% of Er had segregated to the crystal surface.

Our results on the lattice sites of implanted rare earths may be compared with the X-ray absorption fine structure (XAFS) experiments of Ishii et al [10] on Er in laser-ablated and 700°C annealed ZnO. While emission channeling allows determining the position of probe atoms with respect to the crystal lattice, it is not particularly sensitive to their immediate neighborhood. XAFS, on the other hand, gives information on the distance of neighboring atoms but not on their geometrical arrangement. The XAFS data showed that the nearest neighbors of Er are six O atoms, one at a distance of 2.136 Å, four at 2.378 Å, and one at 3.028 Å. This differs from ideal Zn sites in an undistorted crystal, for which one would expect only 4 nearest O neighbors at distances of 1.98–1.99 Å. The u_1 values observed in our emission channeling experiments following 700°C annealing would be well in accordance with a static Er displacement of 0.22–0.26 Å along the c axis. While the Er-O distances observed in XAFS could be explained by such a displacement and an outward relaxation of surrounding O atoms, the presence of two additional O nearest neighbors indicates a more complicated defect structure.

Summarizing, we have given direct evidence that the majority of rare earth atoms are incorporated on substitutional Zn sites following room temperature ion implantation into ZnO. Fractions of Er on other highly symmetric lattice sites must be small. Annealing up to 600°C did not affect the substitutional Er fraction, whereas for higher annealing temperatures the substitutional Er fraction decreased, probably related to rare earth diffusion.

This work was funded by the FCT, Portugal (project CERN/FIS/43725/2001) and by the European Union (Large Scale Facility contract HPRI-CT-1999-00018). U. Wahl, E. Rita, and J.P. Araújo acknowledge their fellowships supported by the FCT, Portugal.

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