Proceedings of the 2nd International Workshop on Materials Science (IWOMS'95), Hanoi, Oct. 1995

Emitted light of erbium-doped float-zone silicon: A photoluminescence study

D. T. Xuan Thao[a,b], T. Gregorkiewicz[a], C.A.J. Ammerlaan[a], N.N. Long[c], L.K. Binh[b], F.P. Widdershoven[d], P. Christianen[e] and J.C. Maan[e]

[a] Van der Waals-Zeeman Institute, University of Amsterdam, Valckenierstraat 65-67, NL-1018 XE Amsterdam, The Netherlands
[b] International Training Institute for Materials Science, P400 C10 DHBK, Hanoi, Vietnam
[c] Faculty of Physics, University of Hanoi, 90 Nguyen Trai Road, Hanoi, Vietnam
[d] Nederlandse Philips Bedrijven B.V., Prof. Holstlaan 4, NL-5656 AA Eindhoven, The Netherlands
[e] High Field Magnet Laboratory and Research Institute for Materials, University of Nijmegen, NL-6525 ED Nijmegen, The Netherlands

We report a photoluminescence study of a series of n-type (phosphorus-doped) float-zone silicon samples doped with rare-earth erbium by ion implantation. Photoluminescence spectra consisting of eight very sharp lines in the range between 1.54 and 1.62 μm have been observed. They are ascribed to 4f intra-shell transitions of the Er^{3+} ions. A Zeeman effect study in high magnetic fields up to 16 Tesla has been performed. In the present case, we found a new center of erbium in float-zone silicon which has a lower-than-cubic symmetry. The experimentally determined activation energies are consistent with the bound exciton mediated excitation mechanism. The decay time of the transition is determined as well and found to be approximately one millisecond.

1. Introduction

In recent years, there has been a great interest in rare-earth (RE) impurities in silicon and semiconductor compounds with respect to their physical properties and practical applications [1]. In principle for an isolated RE ion the transitions within the 4f shell are parity-forbidden. These are, however, permitted in a crystal lattice due to the presence of the ligand electric field which gives rise to the mixing of opposite parity states [2]. The knowledge of the excitation and de-excitation mechanisms allows to learn about the relation between the band structure and atomic energy levels. In ytterbium-doped InP a single optical center is believed to be formed. It is considered to consist of an Yb ion replacing an In ion on a substitutional site and behaving as an isolated trap [3]. The situation is more complicated in the case of erbium. Er ions can be incorporated on sites of different symmetries and/or in some complexes that induce different Er-related photoluminescence (PL) spectra. Although the problem related to Er-doping is still under debate, Er-based materials are already applied in the telecommunication technique because erbium PL wavelengths coincide with the minimum-loss-region of the optical fibers. In addition, many optoelectronic and integrated-circuit devices are produced from semiconductors doped with RE elements including Er as well. Previously it was reported that Er-doped Czochralski silicon (Cz-Si:Er) showed PL spectra with five lines suggesting Er ions to be incorporated on a site of cubic (T_d) symmetry. On the other hand, Er-doped float-zone silicon (Fz-Si:Er) exhibited a poor spectrum with quite different features: a broad line at about 1.54 μm and some additional not clearly visible bands at lower energies [4-6]. De Maat-Gersdorf *et al.* [7] have suggested the appearance of phonon replicas in the emission from Cz-Si:Er samples. In the present study we have observed up to eight sharp PL lines of about 12 cm^{-1} width in Fz-Si:Er samples which were prepared by the ion implantation technique. These findings can neither be explained by the Er cubic symmetry, nor by the phonon-replica theory as reported earlier; they suggest Er^{3+} ions to be on a site of a lower-than-cubic symmetry.

2. Experiment and discussion

Samples used in this study were prepared from n-type, phosphorus-doped, (100) oriented silicon wafers that were grown by the float-zone method. The room temperature resistivity of the material is about $0.7-0.9$ Ωcm. Er^{2+} ions at an energy of 1.1 MeV have been implanted into the samples at a temperature of 500 °C. Doses in the range of 1×10^{12} to 5×10^{15} cm^{-2} were applied. No further annealing has been performed. The photoluminescence was excited by the 514 nm line of an Ar^{+}-ion laser (Spectra-Physics Stabilite 2016-05s) with excitation power typically of 100 mW. The emitted light was dispersed by a high-resolution monochromator (Jobin-Yvon THR 1500) 1.5m F/12 and detected by a liquid-nitrogen cooled North-Coast EO-817 germanium detector. For all experiments the samples were mounted on a copper block in an Oxford Instruments cryostat (Spectromag 4) that can reach 2.1 K by pumping on the liquid-helium bath.

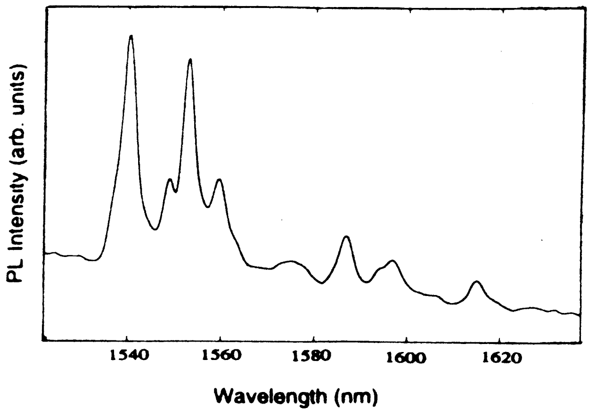

Fig.1: Typical photoluminescence spectrum of Fz-Si:Er. The spectrum was measured at 4 K.

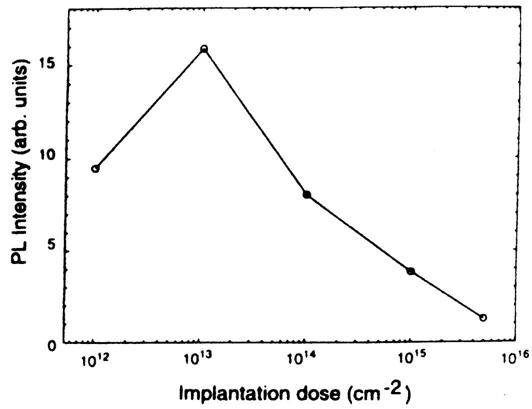

Fig.2: Photoluminescence intensity versus implantation dose taken for the line at 1540.2 nm.

A typical Er-related PL spectrum at 4 K is shown in Fig.1. For all the samples the spectrum consists of eight sharp lines with wavelengths of 1540.2, 1548.8, 1552.7, 1559.3, 1574.3, 1586.5, 1595.6 and 1615.1 nm, respectively. As can be seen, the PL intensities first increase when the implantation doses increase from 1×10^{12} to 1×10^{13} cm^{-2} (the Er top concentrations are about 4×10^{16} and 4×10^{17} cm^{-3}, respectively, as revealed by Rutherford back-scattering (RBS) and Secondary ion mass spectrometry (SIMS) results), then decrease with further-increasing Er doses (Fig.2). The PL spectra taken at different temperatures show a common feature that their intensities increase with increasing excitation power but saturate at powers near 400 mW. From the temperature dependence, shown in Fig.3, one can see that the PL intensities remain constant in the temperature range from 4 K to about 15 K, and then rapidly decrease as the temperature is raised. At 70 K the PL intensities drop to only about 10% of those observed at 4 K. As shown in Fig.4, the intensity of the 1540.2 nm line depends on the chopper frequency by an exponential law. The signal-to-noise ratio is best at a frequency of 125 Hz. The PL intensity is monotonously reduced when the chopper frequency increases from 30 to 1200 Hz. Therefore the lifetime of the Er center in this material is suggested to be in the millisecond-range [8]. Er emission has also been measured in high magnetic fields up to 16 Tesla. The preliminary results of these measurements are shown in Fig.5. Upon increase of the magnetic field the strongest line, at 1540.2 nm, shifts towards higher energy and simultaneously lowers its intensity. This most probably indicates that the line is inhomogeneous [9] and its individual components split differently upon the applied field. Some other bands of the spectrum split for higher field values. More studies are needed to clarify the effect. In general, for Er the ground state is split into 16 levels; an equal number of lines should appear in the spectrum.

Although the samples were held at a temperature of 500 °C during implantation it is expected that at higher implantation doses some residual implantation damage will be built up. In RBS channeling experiments this becomes visible at 1×10^{15} cm^{-2} [10]. The change in the PL intensities versus Er doses can be attributed to the building-up of this residual implantation damage.

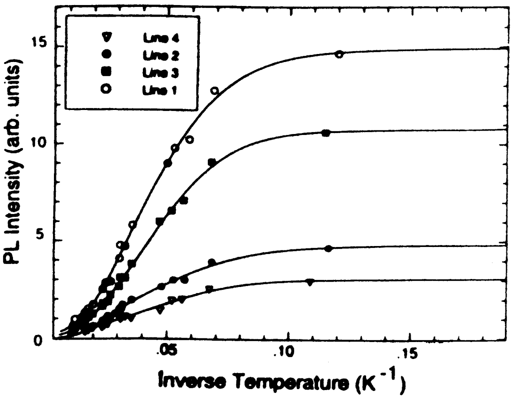

Fig.3: Photoluminescence intensities versus inverse temperature. The solid line is a fit (see text).

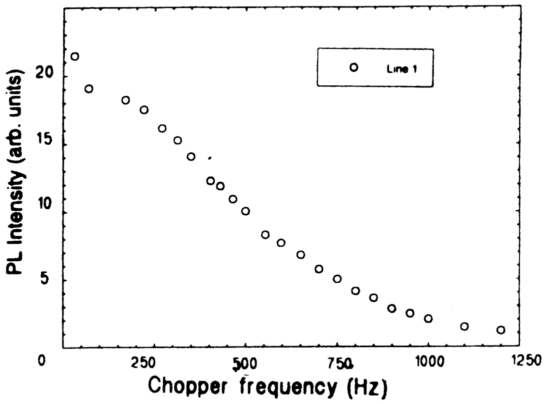

Fig.4: Photoluminescence intensity versus chopper frequency. The feature is similar for all lines.

Group theory shows when Er is incorporated in silicon at a cubic-symmetry (T_d) site the ground state is split into three quartet Γ_8, one doublet Γ_7 and one doublet Γ_6 levels and the first excited state is split into one Γ_7, two Γ_6 and two Γ_8 levels. The Er-related PL lines at low temperature are due to the dipole transitions from the lowest level of the first excited state to levels of the ground state, thus giving rise to five lines in the spectrum. In Fig.1 we observed, however, eight lines. This implies that Er ions are incorporated not only on a site of cubic symmetry. The lower-symmetry crystal field will lower the degeneracy of the ground state levels. As a result, every quartet Γ_8 is split into two doublet levels. The spectrum will therefore contains eight lines consistent with Fig.1. Angular scan experiments with a He-beam gave evidence for Er-atoms to be sited at the coordinates (0.375, 0, 0) and equivalent points in the Si unit cell.

Since the 4f shell of Er ions is well shielded by the outer electrons, a temperature-independent emission is expected. The observed temperature dependence is ascribed to the excitation and/or de-excitation mechanisms. To fit these results, as shown in Fig.3, the following equation is applied:

$$I(T) = \frac{I(0)}{1 + A_1 \exp(-\frac{E_1}{kT}) + A_2 \exp(-\frac{E_2}{kT})} \quad (1)$$

As can be seen in Table 1 the four most prominent lines have similar activation energies suggesting that they are related to the same center. The Er-related emission is presumably mediated by a recombination of an exciton bound to an Er ion and/or a donor impurity of silicon. Recombination energy is transferred to the 4f shell of the Er ions inducing the excitation of the ground state to the excited states. Dipole transitions within the 4f-shell

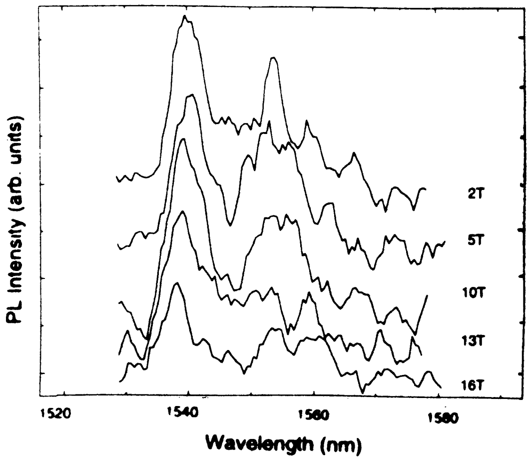

Fig.5: Photoluminescence spectra measured in different applied magnetic fields.

Table 1: Fitting parameters in eq.1 of the temperature dependence of Er emission lines: A_1 and A_2 are the coupling coefficients, E_1 and E_2 are the activation energies.

Line	Wavelength (nm)	A_1	A_2	E_1 (meV)	E_2 (meV)
1	1540.2	13.5	102	5.51	19.86
2	1548.8	9.2	557	4.33	20.96
3	1552.7	17.8	170	5.56	17.14
4	1559.3	12.9	1350	4.92	31.34

are responsible for the erbium PL. At low temperatures, the activation energies are found to be from 4 to 6 meV, which could then be related to the exciton formation. At higher temperatures also the binding of the exciton to a donor level mediating the Er excitation can be influenced [11]. This gives rise to an activation energy of about 20 meV. At still higher temperature the back-transfer between the excited 4f-shell and a bound exciton system should be expected. This is, however, at this moment still in progress.

3 Conclusion

We detect relatively strong PL in Fz-Si:Er. The optical center has a decay time of approximately 1 ms and lower-than-cubic symmetry. The activation energies as determined from the temperature dependence of PL are consistent with a bound exciton mediated excitation mechanism of the Er-related center.

Reference

[1] *Rare-Earth Doped Semiconductors*, eds. G.S. Pomrenke, P.B. Klein and D.W. Langer (Materials Research Society, Pittsburgh, 1993), Vol. **301**.

[2] S. Hufner, *Optical Spectra of Transparent Rare-Earth Compounds* (Academic, New York, 1978).

[3] H.J. Lozykowski, *Phys. Rev.* **B48** (1993) 17758.

[4] J. Michel, L.C. Kimerling, J.L. Benton, D.J. Eaglesham, E.A. Fitzgerald, D.C. Jacobson, J.M. Poate, Y-H. Xie and R.F. Ferrante, *Mater. Sci. Forum* **83-87** (1992) 653.

[5] Y.S Tang, K.C. Heasman, W.P. Gillin and B.J. Sealy, *Appl. Phys. Lett.* **55** (1989) 432.

[6] H. Ennen, J. Wagner, H.D. Müller and R.S. Smith, *J. Appl. Phys.* **61** (1987) 4877.

[7] I. de Maat-Gersdorf, T. Gregorkiewicz, C.A.J. Ammerlaan and N.A. Sobolev, *Semicond. Sci. Technol.* **10** (1995) 666.

[8] A. Polman, G.N. van den Hoven, J.S. Custer, J.H. Shin, R. Serna and P.F.A. Alkemade, *J. Appl. Phys.* **77** (1995) 1256.

[9] W. Jantsch, H. Przybylinska, Yu. Suprun-Belevich, M. Stepikhova, G. Hendorfer and L. Palmetshofer, to be published.

[10] F.P. Widdershoven, Ph.D. thesis, Twente University (1991).

[11] H. Efeoglu, J.H. Evans, T.E. Jackman, B. Hamilton, D.C. Houghton, J.M. Langer, A.R. Peaker, D. Perovic, I. Poole, N. Ravel, P. Hemment and C.W. Chan, *Semicond. Sci. Technol.* **8** (1993) 236.