Optical and electrical doping of silicon with holmium

J.F. Suyver [a],[*], P.G. Kik [a], T. Kimura [a],[1], A. Polman [a], G. Franzò [b], S. Coffa [b]

[a] *FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands*
[b] *CNR-IMETEM, Stradale Primosole 50, 1-95121 Catania, Italy*

Abstract

2 MeV holmium ions were implanted into Czochralski grown Si at a fluence of 5.5×10^{14} Ho/cm^2. Some samples were co-implanted with oxygen to a concentration of $(7 \pm 1) \times 10^{19}$ cm^{-3}. After recrystallization, strong Ho segregation to the surface is observed, which is fully suppressed by co-doping with O. After recrystallization, photoluminescence peaks are observed at 1.197, 1.96 and 2.06 µm, characteristic for the $^5I_6 \rightarrow {}^5I_8$ and $^5I_7 \rightarrow {}^5I_8$ transitions of Ho^{3+}. The Ho^{3+} luminescence lifetime at 1.197 µm is 14 ms at 12 K. The luminescence intensity shows temperature quenching with an activation energy of 11 meV, both with and without O co-doping. The observed PL quenching cannot be explained by free carrier Auger quenching, but instead must be due to energy backtransfer or electron hole pair dissociation. Spreading resistance measurements indicate that Ho exhibits donor behavior, and that in the presence of O the free carrier concentration is enhanced by more than two orders of magnitude. In the O co-doped sample 20% of the Ho^{3+} was electrically active at room temperature. © 1999 Elsevier Science B.V. All rights reserved.

PACS: 61.72.T; 78.20.−e; 78.55.−m; 78.55.Ap
Keywords: Holmium; Luminescence; Rare earth; Silicon; Quenching; Doping

1. Introduction

The attainment of efficient light emission from silicon is of great importance to achieve integrated opto-electronic devices in which optical and electronic signal handling are performed on one Si chip. One way to achieve light emission from Si is by doping with rare earth ions. The trivalent (the preferred bonding state) ions have an incomplete 4f shell that is electrically shielded from the surrounding host material by filled 5s and 5p shells. This leads to relatively sharp and temperature independent intra 4f transitions. Doping of Si with erbium ions, that emit at 1.54 µm, an important telecommunication wavelength, has been studied extensively [1,2], and room temperature photo-and electroluminescence has been achieved [3,4]. While the emission at 1.54 µm from the Si:Er is important for the development of LED's, amplifiers and possibly lasers operating at 1.54 µm, one major disadvantage is that this wavelength cannot be detected by Si itself. It is therefore interesting to study doping with a rare earth ion that emits at a

_____
[*] Corresponding author. Tel.: +31 20 608 1234; fax: +31 20 668 4106; e-mail: suyver@amolf.nl
[1] Present address: University of Electro-Communications, Tokyo, Japan.

smaller wavelength, such as holmium (Ho^{3+}). This ion has an optical transition from the second excited state ($^5I_6$) to the ground state ($^5I_8$) at 1.197 μm [5], close to the Si bandgap (see Fig. 1). At this wavelength the absorption coefficient of Si is 0.02 cm^{-1}. This means that both creation and detection of this wavelength on the same Si chip may be possible, thus allowing for the fabrication of an all-optical chip. In this paper the incorporation of Ho in Si by ion implantation and the first measurements of the optical and electrical properties are reported.

2. Experimental

A single crystal Czochralski-grown silicon wafer ($\langle 1\,0\,0\rangle$, P-doped, 1–5 Ω cm) was implanted with 2 MeV (5.5×10^{14} ions/cm^2) Ho ions at 77 K at a pressure below 10^{-6} mbar. Part of the wafer was co-implanted with oxygen at different energies (100, 187, 316 and 600 keV) to a total dose of 1.1×10^{16} ions/cm^2 in order to obtain a flat oxygen concentration profile. The average O concentration in the Ho implanted region measured with elastic recoil detection (ERD), was $(7\pm1)\times10^{19}$ O/cm^3. The amorphized Ho-doped (O-co-doped) layers were recrystallized by solid phase epitaxy (1 h at 490°C and 3 h at 600°C). Subsequently, rapid thermal annealing at 1000°C under flowing Ar atmosphere for 60 s was performed to anneal out residual damage and activate the implanted Ho atoms. Rutherford backscattering spectroscopy (RBS) using 2 MeV He^+ was used to measure Ho depth profiles, and recrystallization was examined by performing channeling measurements.

Photoluminescence (PL) measurements were done using the 514.4 nm line of an Ar ion laser as a pump beam. The sample was mounted in a closed cycle helium cryostat, using silver paint to ensure good thermal contact. The PL signal was focused into a 96 cm monochromator and collected by a liquid nitrogen cooled Ge detector (wavelength range 1–1.6 μm) and a 2-stage thermoelectrically cooled PbS detector (1.6–2.3 μm). The spectra taken with the Ge detector were corrected for de-
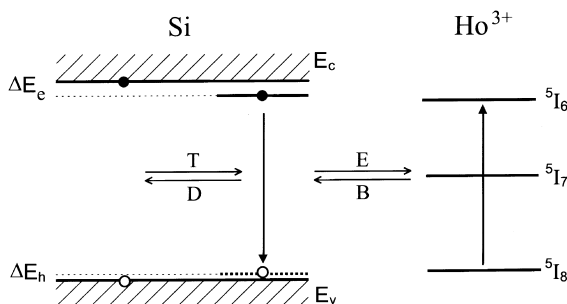

Fig. 1. Schematic model of trapping (T) and detrapping (D) of an exciton at a Ho related defect level and excitation (E) and energy backtransfer (B) of the Ho^{3+}.
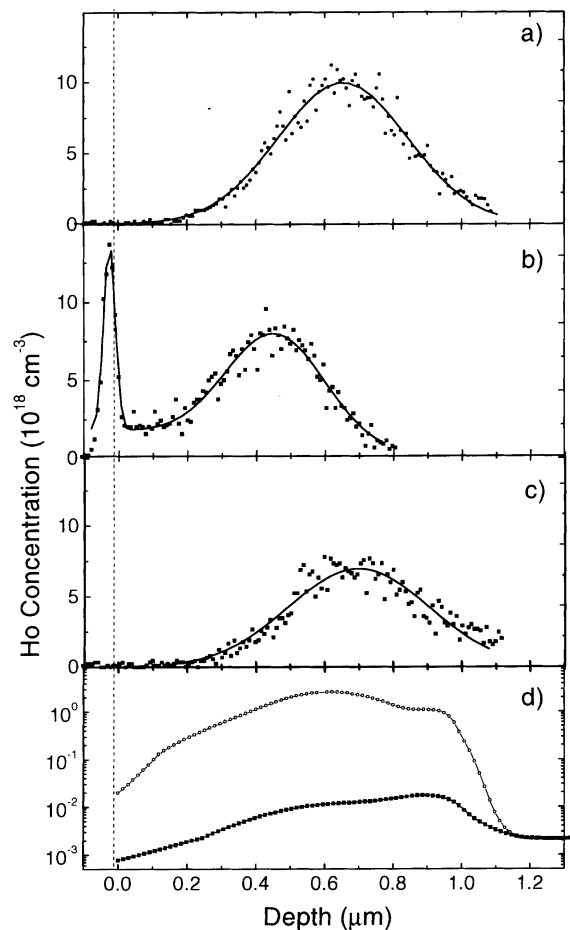

Fig. 2. RBS spectrum of Si:Ho before (a) and after (b) recrystallization and the spectrum of Si:Ho,O after (c) recrystallization. Also shown are SR profiles (d) of the Si:Ho sample (full circles) and the Si:Ho,O sample (open circles).

tector response. The signal was detected using standard lock-in techniques. Luminescence decay traces were obtained by averaging the detector signal on a digital oscilloscope. The system response time was 160 μs. Measurements were taken at temperatures ranging from 10 to 100 K.

The electrical properties of the Ho implanted layers were determined by room temperature spreading resistance (SR) measurements. The samples were beveled at an angle of 34′ and the spreading resistance data were converted into resistivity and carrier concentration using calibrated samples and a computational procedure by Berkowitz and Lux [6].

3. Results and discussion

Fig. 2 shows the Ho related signal of an RBS measurement before and after crystallization, with and without oxygen. The spectrum for the as-implanted sample (Fig. 2(a)) shows a Gaussian Ho distribution peaked at 650 nm with a full width at half-maximum of 250 nm. Channeling data (not shown) indicate that the Ho implantation causes amorphization of a 1.3 μm thick surface layer. After recrystallization (Fig. 2(b)) strong segregation of Ho to the surface was observed. This segregation is very similar to that observed previously for Er implanted Si, which was explained by a non-equilibrium segregation and trapping process, in which Er is segregated due to its low solubility in c-Si [7]. Fig. 2(c) shows the Ho profile of the O co-doped sample after recrystallization. In this case, no Ho segregation is observed. Again this is very similar to experiments on Si:Er,O. The absence of segregation is explained by the formation of strongly bound Ho–O clusters that are trapped in the growing crystal [7]. For all recrystallized samples, the channeling spectra of the Si showed good quality single crystal with a minimum yield of 5% after recrystallization.

In Fig. 2(d) carrier concentrations derived from spreading resistance data are shown for the Ho implanted sample with and without O. The background value in the bulk of the sample corresponds to the P doping of the Si. As can be seen, Ho implantation increases the carrier concentra-

tion to 2×10^{16} cm^{-3}. Co-implantation of O leads to a further increase in the free carrier concentration to a value of 3×10^{18} cm^{-3}. A similar effect was seen before in Si:Er,O [8]. From the absence of a p–n junction, it is concluded that the doping is n-type. Comparing the SR measurements with the RBS data, an upper limit for the electrically active fraction of Ho-ions of 20% was obtained for the O co-doped sample.

Fig. 3 shows a PL spectrum of the O co-doped sample taken at 12 K. For comparison the PL spectrum of Er-implanted CZ-Si (2 MeV Er, 2×10^{15} Er/cm^2, 2×10^{16} O/cm^3) is shown. A sharp PL peak is observed at 1.130 μm in the Ho-implanted sample, which is due to a phonon assisted band to band transition in Si [9]. In addition, a clear peak is observed at 1.197 μm, which corresponds to the $^5I_6 \rightarrow {}^5I_8$ transition of Ho^{3+} [5]. Furthermore, a broad luminescence band is observed for $\lambda > 1.2$ μm, which is attributed to defects remaining in the crystal after the implantation and annealing procedure [9]. The PL decay time of this background was measured to be <160 μs, as expected for defect luminescence. Two peaks in the long wavelength section of the spectrum, at 1.96 and 2.06 μm can be identified. The arrows in the figure indicate known wavelengths of the transitions between the Stark levels of the $^5I_7$ level and those of the $^5I_8$ level measured in e.g. oxide glasses
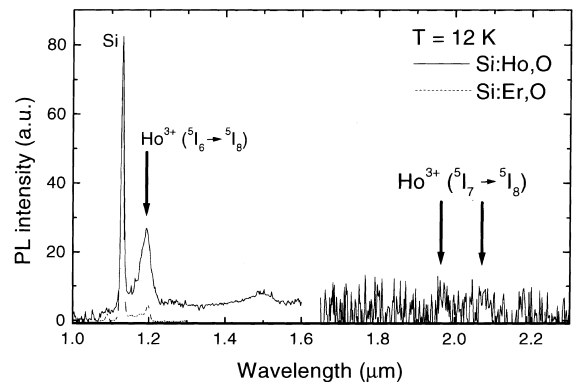

Fig. 3. PL spectrum of the Si:Ho,O sample, measured with a Ge detector ($\lambda < 1.6$ μm) and with a PbS detector ($\lambda > 1.6$ μm). Indicated by the arrows are literature values of the Ho^{3+} PL peaks [5]. The dashed line is a Si:Er,O spectrum with comparable Er and O concentrations.

[5]. They coincide with the measured peaks for the Ho-doped Si sample.

In Fig. 4, the temperature dependence of the luminescence at 1.197 μm is shown for both Ho-doped samples, with and without O. The Ho related intensity at each temperature was determined from the PL spectra by subtracting the background signal determined by interpolation of the intensities measured at 1.15 and 1.25 μm. As can be seen, both samples share an identical luminescence quenching behavior. The activation energy derived from the plot is 11 meV.

A luminescence decay trace measured at 1.197 μm at 12 K for the O co-doped sample is shown as an inset in Fig. 4. It shows a fast component that is detector-speed limited and is attributed to the background defect luminescence, and a slow component with a lifetime of 14 ms. Lifetimes in the 1–20 ms range are characteristic for rare earth ions in a variety of hosts [10]. The temperature dependence of the slow component of the lifetime was measured up to 25 K and is plotted (solid squares) in Fig. 4.

4. Ho excitation model

In general, the excitation of rare earth ions in Si is thought to occur through a mechanism indicated
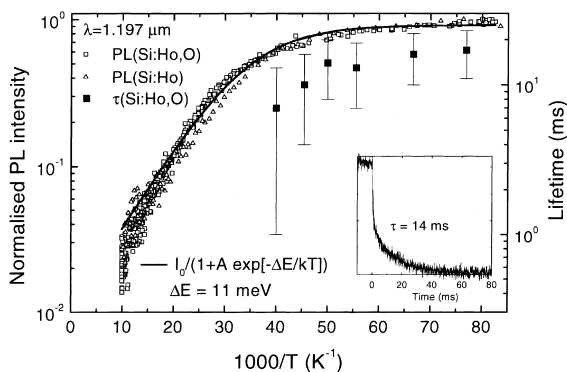

Fig. 4. Temperature dependence of the 1.197 μm PL intensity for the Si:Ho (triangles) and the Si:Ho, O (open squares) samples. Indicated with solid squares is the 1/e lifetime of the slow component of the 1.197 μm luminescence of the Si:Ho, O sample. The inset shows the corresponding decay trace measured at 12 K.

schematically in Fig. 1. An electron–hole pair is trapped (T) at a rare earth related defect level in the Si bandgap. Subsequently, the rare earth can be excited (E) by energy transferred through an impurity Auger process. Quenching processes in this model are energy backtransfer (B) from the excited rare earth to the defect state, and dissociation (D) of the electron hole pair. An additional quenching process of the Er population that was recently identified for Si:Er is Auger energy transfer to free carriers that are then excited higher in the conduction band [11].

Fig. 4 shows comparable luminescence quenching behavior with and without O while the carrier concentrations in these samples are very different (Fig. 2(d)). Note that Si:Er co-doped with high concentrations of P (with similar free carrier concentrations as in Fig. 1(d)) does show large Auger quenching. The difference between Si:Er and Si:Ho may be caused by a much smaller Auger coefficient or by a very large ionization energy of Ho, so that no free carriers are created up to 100 K. It is therefore concluded that the observed PL quenching in Fig. 4 is not due to Auger quenching to free carriers. This leaves only backtransfer and dissociation (see Fig. 1) as possible processes that could be the cause of the observed PL quenching.

5. Conclusions

Ho implanted crystalline Si layers, (some co-doped with O) were regrown by solid phase epitaxy. Photoluminescence peaks are observed at 1.197, 1.96 and 2.06 μm, characteristic of the $^5I_6 \rightarrow {}^5I_8$ and the $^5I_7 \rightarrow {}^5I_8$ transitions of Ho^{3+}. Up to 100 K, the 1.197 μm luminescence of the Si:Ho and the Si:Ho,O samples quenches with temperature with a typical energy of 11 meV. The Ho^{3+} luminescence lifetime at 1.197 μm at 12 K is 14 ms. An increment of two orders of magnitude in the free carrier concentration is observed when samples are co-doped with O. It is concluded that the observed PL quenching is not caused by Auger quenching to free electrons, but rather by a backtransfer or an electron–hole dissociation process.

Acknowledgements

References

[1] J. Michel, J.L. Benton, R.F. Ferrante, D.C. Jacobson, D.J. Eaglesham, E.A. Fitzgerald, Y.-H. Xie, J.M. Poate, L.C. Kimerling, J. Appl. Phys. 70 (1991) 2672.

[2] F. Priolo, G. Franzò, S. Coffa, A. Polman, S. Libertino, R. Barklie, D. Carey, J. Appl. Phys. 78 (1995) 3874.

[3] G. Franzó, F. Priolo, S. Coffa, A. Polman, A. Carnera, Appl. Phys. Lett. 64 (1994) 2235.

[4] B. Zheng, J. Michel, F.Y.G. Ren, L.C. Kimerling, D.C. Jacobson, J.M. Poate, Appl. Phys. Lett. 64 (1994) 2842.

[5] Sh.N. Gifeisman, A.M. Tkachuk, V.V. Prizmak, Opt. Spectrosc. (USSR) 44 (1978) 68.

[6] H.L. Berkowitz, R.A. Lux, J. Electrochem. Soc. 18 (1981) 1137.

[7] A. Polman, J.S. Custer, P.M. Zagwijn, A.M. Molenbroek, P.F.A. Alkemade, J. Appl. Phys. 81 (1997) 150.

[8] F. Priolo, S. Coffa, G. Franzò, C. Spinella, A. Carnera, V. Bellani, J. Appl. Phys. 74 (1993) 4936.

[9] G. Davies, Phys. Rep. 176 (1989) 83.

[10] A. Polman, J. Appl. Phys. 82 (1997) 1.

[11] F. Priolo, G. Franzò, S. Coffa, A. Carnera, Phys. Rev. B 57 (1998) 4443.