Erbium Related Photoluminescence of Silicon: Influence of Co-doping with Oxygen and Hydrogenation

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Abstract. This experiment deals with the influence of co-doping with oxygen and hydrogen and also annealing parameters, temperature and excitation power on the Er related photoluminescence (PL) of silicon. The ultimate goal is to optimise the PL intensity of the Er³⁺ internal transition to make room-temperature luminescence possible. Silicon is a very inefficient light emitter, because of the low radiative recombination rate due to the indirect band gap. However, by adding optically active impurities such as erbium, Si can be made luminescent. Silicon is an ideal material for the fabrication of optical waveguides that are compatible with optical telecommunication technology at 1.54µm, because of its high transparency and high refractive index at this wavelength. Co-doping with oxygen and hydrogen can enhance the initial Er luminescence. To investigate the influence of oxygen and hydrogen on the diffusion process and the luminescence intensity, samples were doped with erbium, oxygen and hydrogen at different concentrations that were implanted both on Float Zone (FZ) and Czochralski (CZ) silicon wafers. In FZ silicon, the samples implanted with both oxygen and hydrogen showed the highest luminescence yield with a six times higher peak intensity as compared to samples implanted with only erbium and a two times higher peak intensity as compared to samples with erbium and oxygen, in accordance with previous results. However, identified by the line position and contrary to previous results on CZ-Si, the luminescence stems from an erbium-oxygen impurity complex and not from the so-called cubic centre. In CZ samples doped with erbium, oxygen and hydrogen show a 3 times higher intensity as compared to samples doped only with erbium and oxygen. Although the PL lines of the cubic centre are visible, they do not exhibit the strongest luminescence. In samples doped only with erbium and hydrogen and annealed at 900°C, we observe luminescence from only the cubic centre. Although the appearance of the cubic centre in these samples is most likely due to out-diffusion of erbium in the absence of oxygen, hydrogen again enhances the luminescence intensity by a factor 2.

1. Introduction:

1.1 Optical Technology

Optical technologies are becoming more and more important in areas that have traditionally been the domain of electronics. Optical telecommunication technology is one of the key research areas in Photonics. Research in design and manufacturing of optical fibres was started in the early 1980s [1]. In the late 1980s, this effort led to the development of manufacturing process for rare-earth-doped fibres,
with the laboratory’s first Erbium Doped Fibre Amplifier (EDFA) coming out in 1991. The most important rare-earth for application in photonics is erbium, which has a strong luminescence band around 1535 nm, corresponding to the low-loss window in silica optical fibres. At present, the Erbium Doped Fibre Amplifier (EDFA) dominates the field of optical amplification, and is now a mature technology [1,2]. The possible wavelength ranges that can be used for transmission are determined by dispersion and absorption in the fibre. There are three windows with low absorption, as can be seen in Figure 1. The first window between 800 and 900 nm is mainly due to technological reasons, since powerful semiconductor emitters based on the AlGaAs/GaAs material system can be produced at low cost for this wavelength range. For short wavelengths, attenuation is mainly determined by Raleigh-scattering ($\alpha \sim \lambda^{-4}$). The dispersion in silica vanishes around 1.3 µm, which is the second transmission window. The third window is defined by the minimum of attenuation, which is at 1.5 µm. If the profile of the refractive index of the fibre is shaped in a special way (quadruple cladding), however, the range of maximal bandwidth at 1.3 µm (dispersion minimum) can be shifted to 1.5 µm [4,5].

2. Experimental Methods:

2.1 Photoluminescence

Photoluminescence (PL) is simple, versatile, and non-destructive. PL is the spontaneous emission of light from a material under optical excitation. Eventually, these excitations relax and the electrons return to the ground state. If radiative relaxation occurs, the emitted light is called PL [8,13]. This can be investigated to characterize a variety of material parameters. A typical PL set-up is shown in Figure 3.
2.2 Fourier Spectroscopy
Photoluminescence measurements were performed with a Bomem DA8.23 Fourier-transform spectrometer. A Fourier spectrometer consists essentially of an optical part to process the light signal and a computer for the Fourier transformation. The optical part is based on a Michelson interferometer; a brief description of the function is given in the Figure 4. There are two mirrors (SM1, SM2) – one moveable, another fixed and a semi-transparent beam splitter (ST), which are the core of the Fourier Spectrometer [9,10]. Photoluminescence (PL) measurements were performed by pumping with the 514-nm line of an Ar\textsuperscript{+} ion laser, which has a penetration depth of about 1µm in silicon. The pump power was varied between 10 and 200 mW. The luminescence signal was analysed with a Fourier spectrometer and detected with a liquid-nitrogen-cooled Ge detector.

3. Experimental Results and Discussions (FZ-Si, CZ-Si):

3.1 Photoluminescence in Float Zone – Silicon (FZ-Si)
To investigate the influence of the respective impurities on both the enhancement of the luminescence and positioning of the Er-ions, we prepared four different sets of samples in FZ-Si material. The respective preparation parameters can be found in Table 1 below.

![Table 1](image)

**Table 1.** Data of respective preparation parameters for FZ-Si substrate.

Figure 5 shows the Er\textsuperscript{3+}-related PL spectra for the FZ-Si samples in the spectral range of 1.5-1.6 µm. Spectra were taken at low temperatures, typically 7K, and with a laser pump power of 100 mW. In all cases, the spectrum shows a clear peak around 1.54 µm, characteristic of transitions between the \( ^4I_{13/2} \)
and \(^{4}I_{15/2}\) manifolds in \(\text{Er}^{3+}\). The PL spectra show the typical features of Er-O centres formed, with the most intense peak at 1.53 µm, and related peaks at higher wavelengths [14]. The oxygen co-doped samples exhibit a three times higher peak intensity (curve ‘b’) than the samples implanted with only erbium (curve ‘d’). The samples implanted with both O- and H- show the highest luminescence yield with a six times higher peak intensity (curve ‘a’) than the PL intensity of samples implanted with only erbium (curve ‘d’). From curve ‘c’, we see that implanting hydrogen alone only slightly enhances the luminescence of erbium. Co-doping with oxygen (curve ‘b’) enhances the luminescence significantly, which is to be expected, since oxygen plays an important role in the formation of the optically active erbium centres.

### 3.2 Temperature Dependence in Float Zone – Silicon (FZ-Si) Substrate

The Er-O doped samples were implanted with the three different hydrogen contents such as a) \(1\times 16\text{cm}^{-2}\), b) \(3\times 15\text{cm}^{-2}\) c) \(1\times 10^{15}\text{cm}^{-2}\), d) \(3\times 10^{14}\text{cm}^{-2}\) and e) \(1\times 10^{14}\text{cm}^{-2}\). After implantation, the samples were annealed at 900°C in \(\text{N}_2\) ambient for 20 minutes. Photoluminescence (PL) spectra were measured using the 515 nm line of an Ar\(^+\) ion laser as the excitation source at a power of 100mW.

![Figure 6](image)

Figure 6. Arrhenius plot of the temperature-dependent PL intensity of Er-O doped Si samples with different hydrogen contents in FZ-Silicon.

Figure 6 shows the temperature dependence of the integrated \(\text{Er}^{3+}\) luminescence intensity [curve (a), (b), (c), (d), (e)] of the dominant peak at 1529nm. The \(\text{Er}^{3+}\) emission at 1.53 µm exhibits a thermal quenching and becomes very weak at high temperatures. We measured the PL intensity at different temperatures between 10K and 150K. We see [Fig. 6] a weak quenching of the intensity to 20K, where a much stronger quenching sets in. The luminescence intensity rises for lower temperatures up to 15K.

In general, the quenching of the luminescence intensity in Er-doped silicon, as the temperature is increased, can be a result of two distinct processes: (1) a reduction in the excitation rate of \(\text{Er}^{3+}\) due to detrapping of electrical carriers which trapped at the \(\text{Er}^{3+}\)-related level in the Si, or (2) an increase in the de-excitation rate of excited \(\text{Er}^{3+}\) due to coupling to defect levels in the Si band gap, e.g., to the \(\text{Er}^{3+}\)-related defect.

In our cases, it can be assumed that the erbium luminescence intensity decrease is mainly caused by a reduction of the \(\text{Er}^{3+}\) luminescence efficiency due to a non-radiative energy back-transfer process. The \(\text{Er}^{3+}\) luminescence efficiency can decrease as a result of energy back-transfer from excited erbium to a trapped carrier state. Such back-transfer, followed by either exciton dissociation, or exciton recombination at the trap, decreases the \(\text{Er}^{3+}\) excited state life time, and with it the \(\text{Er}\) luminescence efficiency. Figure 7 shows the concentration dependence. We find a linear increase in the PL intensity with different concentration of hydrogen. Above this concentration, it can be assumed that the luminescence intensity will either saturate or slightly decrease. Even with more hydrogen, the amount of erbium that can be implanted without decreasing the luminescence intensity is limited to about \(10^{19}\).
cm\(^{-3}\)[15]. This limitation on the erbium and oxygen content also limits the beneficial effect of hydrogen. Still, the saturation limit was obviously not reached with the dose applied in this work, and it might be of interest to find the concentration limit for hydrogen co-doping.

3.3 Photoluminescence in Czochralski – Silicon (CZ-Si)

In the case of CZ growth we used Si as substrate with high oxygen content (10\(^{18}\) cm\(^{-3}\)). The implanted ions are erbium, oxygen and hydrogen in different concentrations. We prepared five different samples for the CZ-Si material. The respective preparation parameters can be found in Table 2:

| CZ-Si Samples | Implanted Impurities | Dosis of Impurities (cm\(^{-2}\)) | Annealing Temp (°C) | Duration of Annealing (hr) | Energy at (eV) |
|---------------|----------------------|-----------------------------------|---------------------|--------------------------|---------------|
| CZ1           | Er+O                 | 1×14 cm\(^{-2}\) (Er) 1×15 cm\(^{-2}\) (O) | 600/900             | 15/20                    | 300/950       |
| CZ2           | Er+H                 | 1×14 cm\(^{-2}\) (Er) 1×15 cm\(^{-2}\) (H) | 600/900             | 15/20                    | 300/030       |
| CZ3           | Er+O+H               | 1×14 cm\(^{-2}\) (Er) 1×15 cm\(^{-2}\) (O) 1×4 cm\(^{-2}\) (H) 3×14 cm\(^{-2}\) (O) 1×15 cm\(^{-2}\) (H) | 600/900             | 15/20                    | 300/030       |

Table 2. Data of respective preparation parameters for CZ-Si substrate.

Figure 8 (a) shows the PL spectrum at 7K of CZ-Si sample implanted at 300 keV with the highest ion dose applied (1×14 cm\(^{-2}\)) and a hydrogen ion dose of (1×15 cm\(^{-2}\)) at 30 keV. The sample was annealed at 900°C for 20 min. The solid (labelled C) arrows indicate the positions of Er\(^{3+}\) centres with cubic site symmetry. We observed the maximum PL intensities in CZ-Si substrates in these samples (CZ3).

Figure 8 (b), (c) depicts the PL spectrum of a CZ-Si sample and FZ-Si sample. In FZ-Si we see more intense PL lines visible at smaller wavelengths as compared to the main cubic transition (6504.8 cm\(^{-1}\) (1.54 µm), denoted with C), which are related to Er\(^{3+}\) centres with lower site symmetry. The same emission lines appear also in CZ-Si. The difference of intensities in FZ and CZ material can be explained by the high oxygen content of approximately 10\(^{18}\) cm\(^{-3}\) in CZ material and the low oxygen content of approximately 10\(^{16}\) cm\(^{-3}\) in FZ material. It is assumed that the high optical activity of Er implanted into CZ-Si is related to erbium forming complexes with oxygen.

Figure 8 (a) shows the PL spectrum with high intensities of a CZ-Si substrate. The arrows labelled C indicate the positions of four transitions related to the Er\(^{3+}\) centre with cubic site symmetry. There are two possible explanation, such as 1) either erbium is diffused during annealing, lower erbium concentration in deeper regions of sample are responsible for luminescence and can explain appearance of cubic centre or 2) presence of interstitial oxygen can explain appearance of cubic centre. This presence of interstitial oxygen – although at a lower concentration than in CZ-Si - can explain these results: hydrogen mobilises the interstitial oxygen and when oxygen moves out of the interstitial lattice site, the lattice is locally widened and the big Er\(^{3+}\) ion can move into the interstitial sites.

4. Conclusion:

Samples were prepared on FZ and CZ silicon wafers with a resistivity of 10 – 24 Ωcm. The samples were doped with Er, O and H with different concentrations to investigate the influence of hydrogen on
the luminescence and diffusion process. In FZ silicon, the samples implanted with both oxygen and hydrogen showed the highest luminescence yield with a six times higher peak intensity as compared to samples implanted with only erbium and a two times higher peak intensity as compared to samples with erbium and oxygen, in accordance with previous results. However, identified by the line position and contrary to previous results on CZ-Si [15,16], the luminescence stems from an erbium-oxygen impurity complex with lower symmetry and not from the cubic symmetry site. Measurements of the luminescence intensity on excitation power revealed an increased number of optically active erbium centres. Investigations on the temperature dependence of the luminescence showed a rise in intensity up to 15 K, a weak quenching up to 20 K, at which point a stronger quenching sets in. These results are attributed to the much lower impurity concentration in FZ silicon, especially to a much lower concentration of interstitial oxygen as compared to CZ Si. The additionally implanted oxygen in these samples has a statistical distribution of positions in the lattice and might not be mobilised during the out-diffusion of hydrogen. The observed enhancement of the Er$^{3+}$-related PL can be due to another effect of hydrogen, the formation of complexes with oxygen at impurities. Future work would involve finding the concentration limit for hydrogen co-doping of the FZ silicon sample to attain the position of Er$^{3+}$ centres with cubic site symmetry as was found in the CZ silicon sample.

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