Incorporation, excitation and de-excitation of erbium in crystal silicon

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ABSTRACT

Temperature quenching of the 1.54 μm photoluminescence intensity and lifetime of Er in crystal Si was investigated between 12 K and 150 K. A p-type Czochralski-grown Si (100) wafer was doped with Er to a peak concentration of $5x10^{18}$ cm^{-3} using 1.5 MeV ion implantation. The Er doped layer was co-implanted with N to a peak concentration of $6x10^{19}$ N cm^{-3}. The sample was annealed at 490 °C for 2 hours and at 600 °C for 1 hour. The 1.54 μm photoluminescence intensity shows a weak temperature quenching between 12 and 75 K, characterised by an activation energy of 1-10 meV. For temperatures above 75 K, a strong intensity quenching with an activation energy of 210 ± 10 meV is observed. The luminescence lifetime decreases from 420 μs at 12 K to 1 μs at 170 K, and shows strong quenching behaviour above 75 K, characterised by an activation energy of 135 ± 5 meV. The results are interpreted in terms of an impurity Auger energy transfer model. The lifetime quenching is attributed to a phonon assisted backtransfer process which becomes dominant at high temperatures. Intensity quenching is attributed to both the backtransfer process and a carrier de-trapping process which reduces the Er excitation rate. Spectral response measurements on Er implanted solar cells confirm the presence of a backtransfer process at room temperature.
The relation between the Er^{3+} luminescence quenching and the phonon density of states in crystal silicon is discussed in an Appendix.

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INCORPORATION, EXCITATION AND DE-EXCITATION OF ERBIUM IN CRYSTAL SILICON

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ABSTRACT

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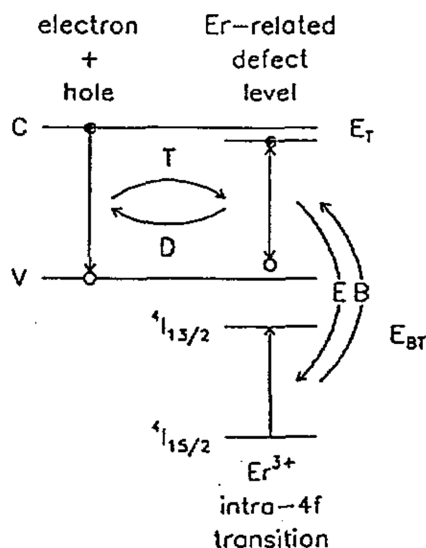

Figure 1 Schematic picture of the excitation of Er^{3+} in Si. C and V denote the Si conduction and valence band, respectively. Trapping (T), Excitation (E), De-trapping (D) and Backtransfer (B) processes are indicated.

INTRODUCTION

In recent years much research has been done on trivalent rare earth ions as possible optical dopants in optoelectronic materials. When incorporated in Si these ions could provide a solution for the problem of the indirect bandgap, which precludes efficient light emission from Si. Erbium is an interesting dopant, because the transition within the Er^{3+} 4f-shell from the first excited state ($^4I_{13/2}$) to the ground state ($^4I_{15/2}$) occurs at 1.54 μm (0.8 eV), a standard telecommunication wavelength.

Several reports on the luminescence of Er in crystal Si have been made, and strong temperature quenching of the luminescence is observed in many cases [1 - 5]. To describe this quenching behaviour a model [3] has been proposed that includes trapping (T in Fig. 1) of an electron hole pair at an Er-related defect level in the Si bandgap, followed by excitation (E) of the Er through an Auger process, as well as two quenching

mechanisms: 1) de-trapping (D) of a bound e-h pair before it can transfer its recombination energy to the Er, and 2) a non-radiative backtransfer process (B) from an excited Er^{3+} ion to an excited state in the Si electronic system. Both quenching processes are phonon-assisted and are therefore more effective at high temperature. De-trapping and backtransfer will cause a reduction in the photoluminescence (PL) intensity. Backtransfer will also cause quenching in the PL lifetime. The aim of this paper is to investigate the effectiveness of both quenching processes.

EXPERIMENTAL

A single crystal Czochralski-grown (CZ) Si wafer (p-type [100], B doped, 1.0 - 10 Ωcm), was implanted with Si, Er and N at room temperature at a base pressure below 10^{-6} mbar. To avoid channelling effects all implantations were performed at an angle of 7° off the surface normal. The sample was first implanted with 3.5×10^{15} cm^{-2} 450 keV Si to form a 700 nm thick buried amorphous layer, starting 160 nm below the surface. 225 keV N was implanted to a dose of 1×10^{15} cm^{-2}. 1.46 MeV Er ions were implanted into the buried amorphous layer to a dose of 1.6×10^{14} cm^{-2}. After implantation the sample was annealed at 490 °C for 2 hours to sharpen up the amorphous-crystal interfaces, followed by a 600 °C anneal for 1 hour to recrystallize the amorphous region from both sides. The anneals were done in a vacuum furnace at a background pressure of 10^{-7} mbar. Er depth profiles were measured with Rutherford backscattering spectrometry (RBS) using a 2 MeV He^+ beam at a scattering angle of 165° with a detector resolution of 14 keV. N depth profiles were measured using secondary ion mass spectrometry (SIMS) using a 6 keV O_2^+ beam.

PL measurements were done using the 515 nm line of an Ar ion laser as a pump beam. The laser beam was modulated using an acousto-optic modulator. The peak pump power ranged from 1 mW to 100 mW in a 1 mm diameter spot. The sample was mounted in a closed-cycle helium cryostat, using silver paint to ensure good thermal contact. The temperature was varied between 12 and 150 K. The luminescence signal was collected by a 48 cm monochromator in combination with a liquid nitrogen cooled Ge detector using standard lock-in techniques. The spectral resolution was 3 nm. Luminescence lifetimes were measured using 1 ms pump pulses with a power of 1 W and a repetition frequency of 20 Hz, by monitoring the detector signal on an averaging digital oscilloscope. The overall system response time was 0.5 μs.

In this paper we also analyse spectral response measurements on passivated emitter, rear locally-diffused (PERL) Si solar cells, which were implanted with 3.5 MeV Er ions to doses of 1×10^{13} cm^{-2} and 3×10^{13} cm^{-2} and were annealed at 1060 °C for 60 min. and 1000 °C for 75 min. The solar cells were made at the University of New South Wales, and their detailed electrical characteristics are reported in ref. [6]. From these measurements the absolute external quantum efficiency was determined, defined as the number of electron-hole pairs collected per incoming photon.

RESULTS

Figure 2 shows the Er depth profile after annealing (solid line). The Er distribution is described by a Gaussian profile peaking at a depth of 490 nm, showing a full width at half maximum (FWHM) of 310 nm and a peak concentration of 5×10^{18} cm^{-3}. No difference was observed between random or channelling RBS spectra in the Er part of the spectrum, indicating that the Er is distributed randomly in the Si.

The N concentration profile is also shown in Fig. 2, as indicated by the dashed line. It shows a peak concentration of 6×10^{19} cm^{-3} at a depth of 580 nm and a FWHM of 200 nm. No redistribution of the Er [7] was observed after recrystallizing the a-Si. This is

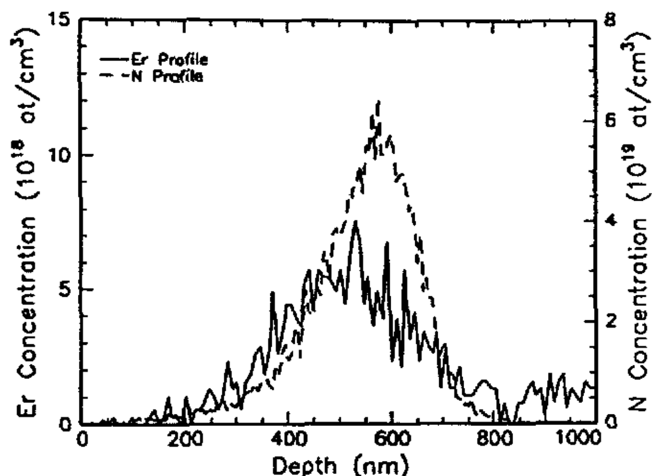

***Figure 2** Er concentration profile as measured by RBS (solid line), and N concentration profile as measured by SIMS (dashed line).*

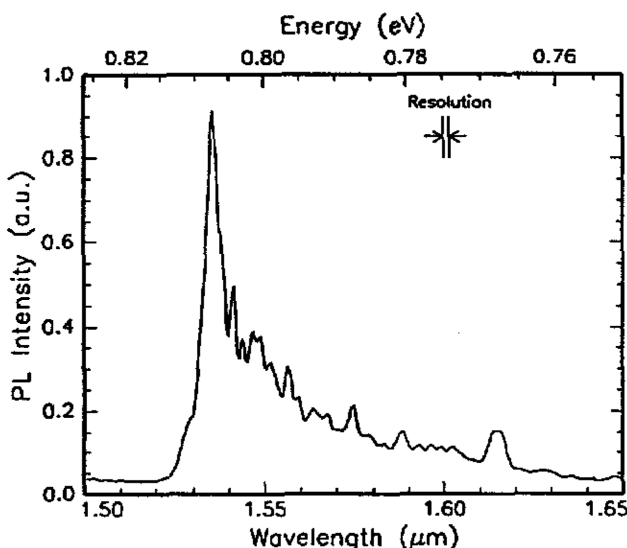

***Figure 3** PL spectrum of Er doped Si measured at 12 K, at a pump power of 20 mW and a spectral resolution of 3 nm.*

attributed to the fact that N, like other impurities as O and C, prevents Er segregation [4, 8].

Figure 3 shows the PL spectrum of the sample at 12 K, pumped with a laser power of 20 mW. The main peak around 1.536 µm is due to radiative decay from the first excited state ($^4I_{13/2}$) to the ground state ($^4I_{15/2}$) of Er^{3+}. The luminescence lifetime at 1.54 µm is 420 µs. The small peak around 1.615 µm has a lifetime shorter than 30 µs and is known from heavy-ion irradiated CZ Si [9] and is probably not related to Er. The remaining structure in the spectrum is due to transitions between the different Stark-split levels in the manifolds. Measurements of PL spectra at various temperatures between 12 and 150 K show that no significant shift in the peak wavelength occurs as function of temperature.

Figure 4 shows the 1.54 µm integrated Er^{3+} luminescence intensity as a function of temperature. All intensity measurements were made in a pump power range which showed a linear dependence of the PL intensity on pump power, i.e. no saturation effects occurred. Measurements at different temperatures were made at different pump powers, but all intensity measurements were normalised to the value for a fixed pump power for the whole temperature range. As can be seen in Fig. 4 the PL intensity quenches by 3 orders of magnitude between 12 and 150 K.

Figure 4 also shows the PL lifetime as a function of temperature. The measured Er decay traces were not single exponential, therefore the lifetimes in Fig. 4 are defined as 1/e decay times. As can be seen from the figure, the lifetime decreases from 420 µsec at 12 K to 1 µsec at 170 K. The quenching behaviour for lifetime and intensity show a similar trend. This shows that lifetime quenching, i.e. a backtransfer process (see Fig. 1), plays a significant role in the intensity quenching.

Figure 5 shows spectral response measurements at 300 K of PERL solar cells implanted with either 1×10^{13} Er cm^{-2} or 3×10^{13} Er cm^{-2} taken from ref. [6]. A spectral shape typical for Er absorption is observed for wavelengths around 1.54 µm. The dashed lines indicate a background which is also seen in Si implanted solar cells and is attributed to implantation defects [6]. Implantation of a 3 times higher Er fluence results in a 3 times

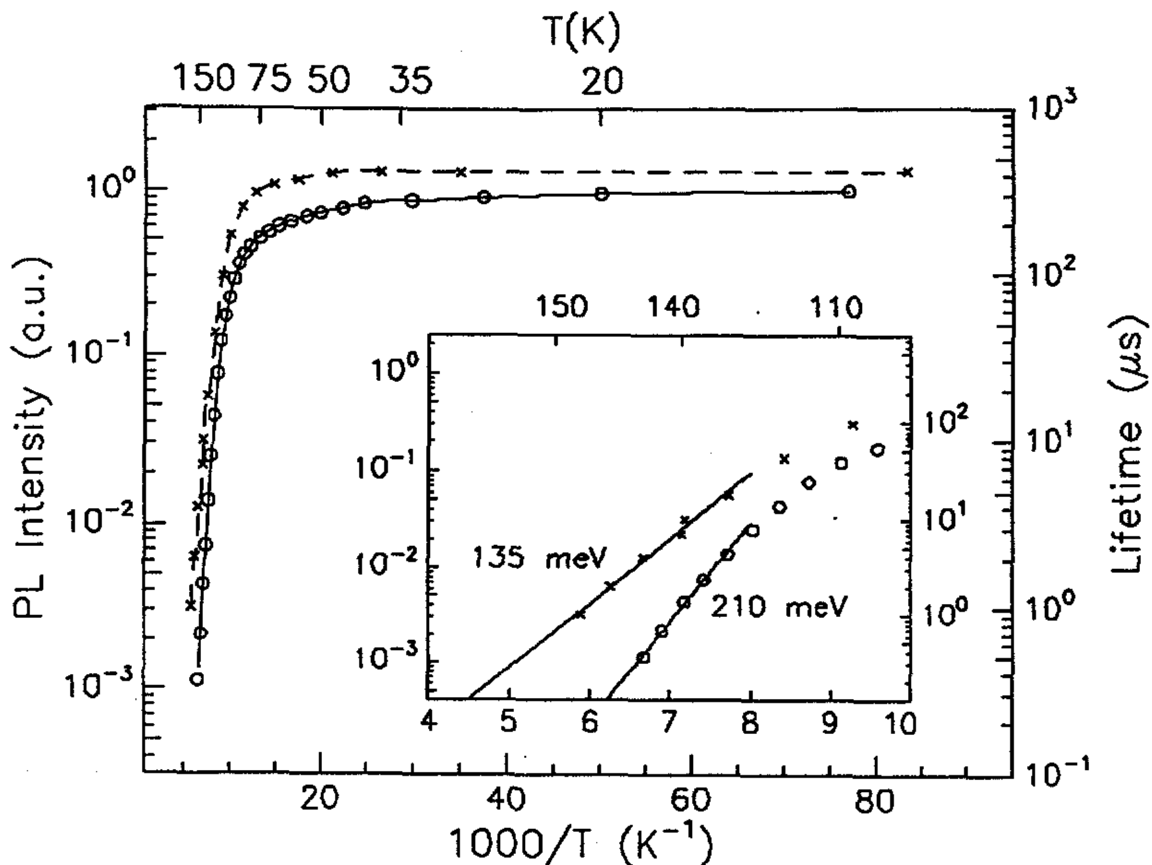

Figure 4 Arrhenius plot of the integrated Er^{3+} luminescence intensity (open circles) and lifetime (crosses). The lines through the data are guides to the eye. The inset shows the high temperature data in detail. The lines are linear fits to the data, to determine the quenching activation energies.

higher absorption. These data indicate that optically excited Er generates free carriers that are collected in the solar cell. This is direct experimental evidence for the existence of a non-radiative quenching process in which excited Er decays by the generation of a free electron-hole pair.

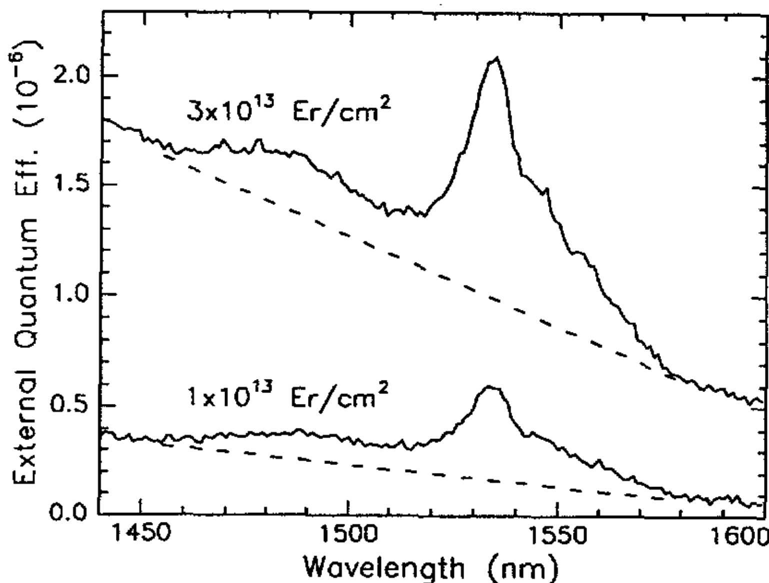

Figure 5 Spectral response of PERL solar cells implanted with $1x10^{13}$ Er cm^{-2} and $3x10^{13}$ Er cm^{-2}. From ref. [6].

DISCUSSION

To quantitatively analyse the observed temperature quenching of the Er^{3+} luminescence in Si in Fig. 4, the model of Fig. 1 is used. In this model a small fraction of the e-h pairs generated by the laser are trapped (T in Fig. 1) at an Er related defect level. With this trapping process an energy difference E_T is associated. The bound e-h pair can either recombine and excite the Er (E) or it can dissociate again (D). An excited Er^{3+} ion can decay by emission of a 1.54 μm photon or by backtransfer (B) of the energy to a state in the Si electronic system. With this backtransfer process an activation energy E_{BT} is associated. The decay rate W of an excited Er^{3+} ion is given by :

$$W = W_{rad} + W_{BT} \cdot e^{-E_{BT}/kT} \tag{1}$$

where W_{rad} is the radiative decay rate, W_{BT} is a pre-factor for the backtransfer process, k is Boltzmann's constant and E_{BT} is the activation energy for backtransfer. Priolo et al. [3], have developed a rate equation model which takes into account the de-trapping, but assume a constant W. Substituting Eqn. (1) in their model we find in the low pump power regime :

$$I \propto \frac{1}{W} \cdot \frac{1}{1 + C \cdot e^{-E_T/kT}} \tag{2}$$

in which E_T is the activation energy for de-trapping an e-h pair and C is given by :

$$C = \frac{\sigma_n \cdot N_C}{\sigma_p \cdot G_L \cdot \tau_C} \tag{3}$$

with σ_n and σ_p the capture cross-sections for an electron and a hole at the Er-related defect level, N_C the effective density of states at the bottom of the conduction band, G_L the optical generation rate and τ_C the minority carrier lifetime. In general C is a function of temperature, as both N_C and τ_C are temperature dependent. If we take $N_C \propto T^{3/2}$ [10] and $\tau_C \propto T^{1/2}$ by assuming that the carrier lifetime is determined by uni-molecular recombination, then $C \propto T$.

The inset of Fig. 4 shows the quenching behaviour for high temperatures in more detail. According to Eqns. (1) and (2), the slope for the high temperature lifetime data should yield E_{BT} and the slope for the intensity data should yield $E_{BT} + E_T$. Linear fits to the 5 highest temperature data points result in $E_{BT} = 135 \pm 5$ meV and $E_T = 75 \pm 10$ meV. Fitting the data to Eqns. (1) and (2) for high temperatures, and varying the temperature dependence of C from constant to $\propto T$ yields the same result for the activation energies within the error bars. Fitting the lifetime data to Eqn. (1) yields an estimate of $W_{BT} = 10^8$-10^{10} s^{-1}.

Below 75 K the intensity shows a very small quenching characterised by an activation energy of 1-10 meV, which is not seen in the lifetime quenching and is attributed to a second de-trapping process, possibly the dissociation of the weakly bound hole.

The energy difference between the Si bandgap (1.12 eV) and the Er excitation energy (0.81 eV) is around 300 meV. However, in this experiment the observed activation energies add up to only 215 ± 10 meV. This suggests that the excitation and de-excitation processes involve different defect levels. Also, it is possible that the levels are broader then indicated in Fig. 1.

The spectral response measurement in Fig. 5 can be used to estimate the quantum efficiency (QE) for the backtransfer process. Assuming a smoothly decreasing background for the sample implanted with 3×10^{13} Er cm^{-2}. The external QE at 1.54 μm is found to be 10^{-6}. This external QE is the product of the probability for absorption of a photon by an

Er^{3+} ion and the probability for an excited Er^{3+} ion to de-excite and generate a free e-h pair. The probability for absorbing a photon is given by: $N_{Er} \cdot \sigma_{abs}$, with N_{Er} the optically active Er fluence and σ_{abs} the absorption cross-section. Assuming that all implanted Er is optically active and taking a typical value for the cross section (6×10^{-20} cm^2 [11]), the absorption probability is be estimated to be 2×10^{-6}. The QE for de-excitation can then be estimated to be on the order of 50 %, showing that the de-excitation process for Er can be quite efficient. The above estimate can be taken as an upper limit for the QE for de-excitation, as internal reflections in the solar cell were neglected. In reality, multiple reflections will take place in these PERL solar cells [12], which can significantly reduce the 50 % estimate.

CONCLUSIONS

The 1.54 μm Er^{3+} luminescence intensity in crystal Si, co-doped with 6×10^{19} N cm^{-3}, quenches by three orders of magnitude as the temperature is increased from 12 K to 150 K. The luminescence lifetime decreases from 420 μs at 12 K to 1 μs at 170 K. An impurity Auger model, which involves trapping of carriers at an Er related defect level, followed by energy transfer to the Er^{3+} ion, is used to describe the data. Carrier de-trapping, characterised by an activation energy of 75 ± 10 meV, results in a reduction in the Er excitation rate at high temperature. In addition, a non-radiative de-excitation process, with an activation energy of 135 ± 5 meV reduces the Er luminescence efficiency at high temperature. Spectral response measurements on Er-implanted Si solar cells provide direct evidence for such a non-radiative quenching process, in which excited Er^{3+} decays by the generation of a free electron-hole pair.

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APPENDIX I: Er^{3+} LUMINESCENCE QUENCHING AND THE PHONON DENSITY OF STATES IN CRYSTAL SILICON

The temperature quenching of the 1.54 μm luminescence of Er^{3+} in Si is described by an impurity Auger energy transfer model. In this model the quenching is attributed to the dissociation of bound excitons, trapped at an Er-related defect, and a backtransfer process from excited Er^{3+} to an excited state in the Si electronic system [1]. Both quenching processes require the annihilation of phonons. When considering such a phonon assisted process one should take into account the occupation of phonon modes n_q as a function of frequency ω. The occupation of phonon modes is given by the expression:

$$n_q = \frac{g(\omega)}{\exp(h\omega / 2\pi kT) - 1} \tag{1}$$

in which $g(\omega)$ is the phonon density of states. In general this $g(\omega)$ is a function with several singularities for certain values of ω, the so called van Hove singularities [2].

The phonon density of states can be calculated from the dispersion relation $\omega(\mathbf{k})$ as given by eq. (2) [2]:

$$g(\omega) = \frac{V}{(2\pi)^3} \int \frac{dS_\omega}{|\nabla_k \omega(k)|} \tag{2}$$

where V is the volume of the crystal and the integration is carried out over a constant frequency surface in **k**-space. To calculate an estimate of this phonon density of states which shows some of the important singularities, the dispersion relation $\omega(\mathbf{k})$ is needed. Figure 1 shows 4 branches along three directions of the dispersion relation in crystal Si as taken from ref. [3]. The crosses are the measured data points, with a smooth fit through the data points as indicated by the solid lines. The bottom axis shows **k** divided by 2π/a, with a the lattice constant, in vector notation, indicating the (100), (110) and (111) directions. The top axis indicate **k** in terms of symmetry points in the irreducible part of the Brillouin zone. Γ is the zone center, and X, K and L are points on the zone boundary in the (100), (110) and (111) directions [4]. The lines through the data points are spline fits to the data in order to obtain more points of $\omega(\mathbf{k})$ for further calculations. The proper way to obtain more points of $\omega(\mathbf{k})$ is to fit the data to a dispersion relation obtained by a shell-model [5]. By using spline fits one only considers three symmetry directions, whereas a shell-model includes the whole Brillouin zone, including possible saddlepoints in the dispersion relation. These saddlepoints can contribute significantly to the real phonon density of states, but are omitted in this approach.

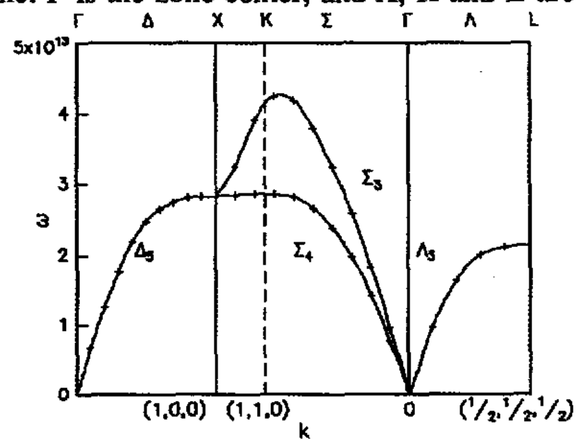

*Figure 1: The dispersion relation ω(**k**) along three directions as taken from ref. [3]. The bottom axis shows **k** in vector notation (divided by 2π/a). The top axis is in symmetry point notation in the irreducible part of the Brillouin zone [4]. The lines through the data points are spline fits to the data.*

The estimate of the phonon density of states consists of four contributions from the four different branches shown in Fig. 1. In order to

add up the contributions of the three different directions, the dispersion relations were scaled by the length of the **k** vectors, i.e. √2 in the (110) and √3 in the (111) direction. From these dispersion relations the inverse function of $\omega(k)$ was calculated numerically by exchanging x and y values. From this inverse function the absolute value of the partial derivative with respect to ω is taken. This derivative is then put into eq. (2) because :

$$\left|\frac{\partial}{\partial\omega}(\omega(k))^{-1}\right| = \frac{1}{\left|\frac{\partial}{\partial k}\omega(k)\right|} \qquad (3)$$

in which $(\omega(k))^{-1}$ indicates the inverse function of $\omega(k)$. The divergence ∇_k is replaced by the partial derivative to k, because $\omega(k)$ is known only along three directions.

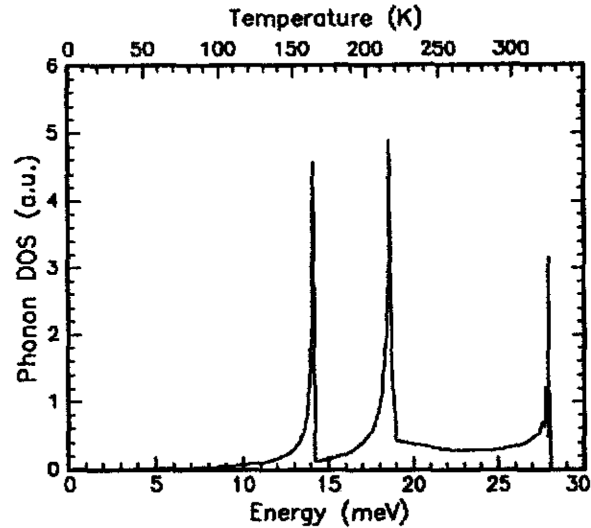

***Figure 2:** The calculated estimate of the phonon density of states in crystal silicon. The estimate consist of three peaks at energies of 14, 18 and 27 meV.*

The integral in eq. (2) is evaluated by multiplication of the result for all branches with k^2. This factor of k^2 indicates that the number of k values on a sphere with radius k increases with k^2. This results in four phonon density of states for four different branches. In fact there are six branches, two in every direction. In the (110) direction there is no degeneration, in the (111) and (100) direction there is a two-fold degeneration. These six contributions should be added to yield the estimate of the phonon density of states.

Figure 2. shows the calculated estimate of the phonon density of states. The bottom axis shows the energy in meV of the phonons, the top axis shows the corresponding temperate according to kT, which gives an idea of relevant temperatures. As seen from the figure the density of states consists of three peaks at energies of 14, 18 and 27 meV.

These energies are of the same order as the observed activation energy of 1-10 meV for the Er^{3+} luminescence quenching at low temperatures. This indicates that the luminescence quenching at low temperatures can be attributed to a single phonon assisted process. The measured activation energies of 75 and 135 meV for the lifetime and luminescence quenching however indicate that multiple phonons are involved. It should be noted that when impurities or defects are introduced in the Si, they give rise to so called local modes. These local modes will have different energies than these calculated above. Whether such modes are important fir the Er^{3+} luminescence quenching may be studied by systematically varying the local environment of the Er.

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