Optical properties of isoelectronic centers in crystalline silicon

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Appendix A

Specific Aspects of Er Excitation Across the Bulk of a Si Wafer

A.1 Introduction

It is known that emission from Er ions implanted into a silicon wafer can be excited by an Ar laser pointed at the non-implanted side of the sample. In such a configuration, energy has to be transferred across the entire thickness of the sample (300-500 μm), which exceeds by 2 orders of magnitude absorption depth of a 514.5 nm line of an Ar ion laser. This effect is commonly ascribed to diffusion of excitons across the bulk of the Si wafer, and its appearance has been taken as evidence for participation of excitons in the energy transfer between Si host and Er\(^{3+}\) ions. In our earlier work we have shown that under illumination of the non-implanted side the energy transfer process leads to a delay in the onset of Er PL signal, whose magnitude depends on the excitation power. This effect is illustrated in Fig. A.1. As can be seen, for experiments conducted at low temperatures (\(T = 4.2\) K), delay times of an order of ms are measured. According to a simple diffusion model, the diffusion related delay time \(\Delta t\) between the exciton generation in the sub-surface region of the sample and its arrival at depth \(s\) is given by \(\Delta t = s^2/4D\). For a reasonable parameter value of \(D = 90\) cm\(^2\)s\(^{-1}\) [126], the time delay due to diffusion for the distance of \(s \approx 350\) μm is about 3.5 μs which is 2 orders of magnitude faster than observed in the experiment.

Having excluded exciton diffusion across the silicon wafer as a possible reason for the long delay time observed in appearance of PL signal, we have considered charge accumulation at Si/Si:Er interface as an alternative mechanism. Indeed, it is generally accepted [127] that erbium implantation into oxygen-rich silicon leads to the formation of donor centers with ionization energies in the 0.1-0.25 eV range and concentration comparable to that of Er ions. For a sample prepared from
p-type Si, a p-n junction should occur in equilibrium at the boundary with the Er-implanted layer. The excitons arriving at the p-n junction will therefore experience the electric field related to the depletion layer formation. In this field, whose value can reach $10^4$ V/cm, the excitons will be divided into electrons and holes. These will gradually accumulate at a junction lowering the potential. Excitons will start to appear in the Er-doped layer and excite Er only after the depletion region has been removed due to charge compensation. According to this scenario, the effect of p–n junction on exciton diffusion could be influenced by biasing the junction. We confirmed this hypothesis by showing that the actual value of the delay time can be tuned by a bias voltage applied to the junction.

### A.2 Experimental details

The experimental configuration for this purpose is illustrated in Fig. A.2a. It allowed for an easy change between excitation of either the implanted side or the backside of the sample, while a DC voltage (-10 V to +10 V) could be applied by electrical contacts on both surfaces. In both excitation modes PL was collected from the Er-implanted side. The experiments were performed in a closed cycle cryostat in the temperature range between $T \approx 15$ K and $T = 150$ K. An on-off modulated (25 Hz) argon laser operating at $\lambda = 514.5$ nm was used as an excitation source. The emerging PL signal was monitored with a high sensitivity germanium detector (Edinburgh Instruments). Time-resolved measurements of erbium were carried out using a digital oscilloscope (Tektronics TDS 3000) in combination with an InP/InGaAs nitrogen-cooled photomultiplier tube Hamamatsu R5509-72. In this configuration, the experimentally measured system response time was 250 μs.

The investigation was conducted for a low-energy (300 keV, $3 \times 10^{12}$ cm$^{-2}$ dose) Er-implanted oxygen-rich p-type (B-doped) Cz-Si wafer of approximately 350 μm thickness. The sample was also co-implanted with oxygen (40 keV, $3 \times 10^{13}$ cm$^{-2}$ dose) and annealed at 900 °C in a nitrogen atmosphere for 30 minutes.

### A.3 Effect of electrical bias on PL delay time

In the initial measurement we have checked that the spectral shape of the Er-related emission was not influenced by experimental conditions, i.e., by the illumination mode (front/back side of the sample) and applied bias. Subsequently, we looked at the effect of biasing voltage on the delay time. For the purpose of this experiment contacts were made with silver paste on the opposing faces of the sample, which was then placed in the low-temperature experimental set-up allowing
A.3. Effect of electrical bias on PL delay time

Figure A.1: Time dependence of the intensity of Er-related PL under implanted and non-implanted side excitation. The laser pulse is also shown. In the inset, the delay time observed for the non-implanted side excitation is plotted as a function of (inverse) laser power.

For measurements in the two illumination configurations (Fig. A.2a). In addition, DC voltage from a stabilized power supply could now be applied, providing electric field across the thickness of the sample. The results, depicted in Fig. A.2b, clearly show that the delay time can be tuned by the applied voltage increasing upon reverse bias and shortening upon forward bias [128]. Following our interpretation, under conditions of reverse bias the delay time can be increased as the depletion region increases; the delay time can be brought down to zero under forward bias which reduces the depletion region to a level at which excitons diffusing towards the Er-implanted layer are no longer destroyed. The effect is very similar to the delay time reduction upon increase of excitation density (Fig. A.1(b)).

In order to evaluate quantitatively if the junction effect can account for the observed delay we have to estimate the time necessary to compensate the change in the depleted region. The width of the depletion region is controlled by boron doping, and at low temperatures is given by:

\[ W \approx \sqrt{\frac{\varepsilon (E_g - (E_D + E_B)/2)}{2\pi e^2 N_B}}, \]  

(A.1)

where \( E_g \) is the energy gap, \( E_D \) and \( E_B \) are the binding energies of the Er-related donors and boron acceptors, respectively, \( e \) is the electron charge, and \( \varepsilon \) is the
dielectric constant of silicon. The calculated depletion region of about 1 μm is situated predominantly in the p-type layer. The negative charge \((-N_B W)\) is accumulated in the depletion region of the p-type layer, and the same positive charge \((+N_D W_D = N_B W)\) is in the n-type layer. \(N_B\) and \(N_D\) are the concentration of boron and Er-related donor center, respectively.

The time \(\delta t\) which is needed for the destruction of the p-n junction can be found from the equation:

\[
\int_0^{\delta t} dt j_{ex}(s, t) = N_B W, \tag{A.2}
\]

where \(j_{ex}(s, t)\) is the exciton density flux. This can be obtained if consider the case of excitation by a green laser (515.4 nm) pointed at the wafer side opposite to the Er-implanted layer. In that case the relevant parameters are as follows: photon energy \(h\nu = 2.4\) eV, absorption coefficient \(\alpha = 10^4\) cm\(^{-1}\), and pumping intensity \(I = 3 \times 10^{16}\) cm\(^{-2}\)s\(^{-1}\) for 0.4 mW. At low temperatures, for such a pumping-level
excitonic recombination dominates, and practically all created electron-hole pairs transform into excitons. As a result we have an exciton source \( S(x, t) \) near the surface (at \( x = 0 \)):

\[
\frac{\partial N_{ex}}{\partial t} = D \frac{\partial^2 N_{ex}}{\partial x^2} - \frac{N_{ex}}{\tau_{ex}} + \alpha I g(t) \exp(-\alpha x). \tag{A.3}
\]

for a continuous pumping:

\[
\frac{\partial N_{ex}}{\partial x} = 0 \quad \text{at} \quad x = 0.
\]

From that we can get the exciton density flux \( J_{ex}(x, t) = -D \partial N_{ex}/\partial x \) at \( x = s \gg \alpha^{-1} \) and for \( t < t_0 \) \([129, 130]\):

\[
J_{ex}(s, t) = \frac{I}{\sqrt{\pi}} \int_0^{t/\Delta t} dz \frac{1}{z^{3/2}} \exp \left[ -\left( \frac{1}{z} + \frac{s^2}{4L^2z} \right) \right]. \tag{A.4}
\]

Here \( N_{ex}, D, \) and \( \tau_{ex} \) are the exciton concentration, diffusion coefficient, and the exciton lifetime, respectively, and \( g(t) \) describes the temporal evolution of the pump: \( g(t) = 1 \) for \( t = t_0 \), and \( g(t) = 0 \) for \( t > t_0 \), where the excitation laser is switched off at \( t = t_0 \). We introduce parameter \( \Delta t = s^2/4D \) and the diffusion length of the excitons \( L = \sqrt{D\tau_{ex}} \). As mentioned above, the parameter \( \Delta t \) determines the diffusion-related time delay, i.e. the time necessary for an exciton to arrive at distance \( s \) due to diffusion.

Assuming the fast diffusion process we can use the equilibrium formula for finding the delay time \( \delta t \):

\[
\delta t \frac{\sqrt{\pi}}{2\sqrt{2}} \exp(-s/L) = N_B W. \tag{A.5}
\]

From here the diffusion length \( L \) can be estimated. With the experimentally obtained value of the delay time \( \delta t \) in the millisecond range, we get \( L \approx 60 \mu \text{m} \). Such a diffusion length corresponds to an exciton lifetime of \( \tau_{ex} \approx 0.4 \mu \text{s} \). Therefore we conclude that the presence of the p-n junction can lead to the observed delay time. Also we note that from Eq. A.5 we get \( \delta t \sim 1/I \), which is also supported by experiment - see Fig. A.1(b).

### A.4 Excitation cross section of erbium in silicon

At low temperatures, the most probable excitation mechanism of Er\(^{3+}\) ions in crystalline silicon under optical pumping is by exciton recombination. In the case
Figure A.3: Intensity of Er-related PL under implanted (diamonds) and nonimplanted (triangles) side excitation as a function of pumping photon flux (Ar laser excitation). Solid lines are fitting curves to Eq. A.13.

of band-to-band absorption in the matrix free excitons are formed. Neutral (at low temperatures) donors introduced by erbium and/or erbium-oxygen complexes easily capture them. Excitation of an erbium ion occurs via an Auger recombination of excitons in which the recombination energy is transferred by Coulomb interaction to an electron of 4f shell of the erbium ion. Alternatively the Auger process could take place at collisions of free excitons with donors associated with erbium ions. The presence of a donor electron facilitates the energy conservation in the Auger process.

In order to describe the excitation process, we consider first the rate equations governing concentrations of free electrons and holes. We note that at low temperatures nonradiative recombination via deep centers is suppressed, and the recombination via shallow donor and acceptor centers is negligible. Though the capture cross section of electrons and holes by shallow Coulomb centers is sufficiently large, the interimpurity recombination rate is low, and shallow centers are instantly filled by charge carriers blocking this recombination channel. For this reason binding of free carriers into free excitons dominates at low temperatures and at fairly high pumping levels. Under these conditions rate equations for
A.4. Excitation cross section of erbium in silicon

electrons and holes will have the form
\[ \frac{dn}{dt} = \frac{dp}{dt} = \alpha \Phi - \gamma np \] (A.6)

where \( \Phi \) is the flux of pumping photons, and \( \alpha \) absorption coefficient of silicon, \( n \) and \( p \) are the concentrations of nonequilibrium electrons and holes, respectively, and \( \gamma \) is the coefficient of the exciton binding process. The rate equation for free excitons can be written as follows:
\[ \frac{dn_{ex}}{dt} = \gamma np - \frac{n_{ex}}{\tau_{ex}}. \] (A.7)

where \( \tau_{ex} \) is the exciton lifetime.

We assume that the exciton lifetime is controlled mainly by nonradiative Auger processes associated with neutral Er-related donors or other impurities,
\[ \frac{1}{\tau_{ex}} \approx c_{im}N_{im} + c_{Er}N_{Er} + c_A(N_{Er}^* - N_{Er}) . \] (A.8)

where \( N_{Er} \) is a total concentration of optically active erbium, \( N_{Er}^* \) is the concentration of excited erbium, \( N_{im} \) is the concentration of other impurities, \( c_{im} \), \( c_{Er} \), and \( c_A \) are the capture coefficients of free excitons by impurities (including also optically nonactive erbium), erbium-related donor centers without erbium excitation and with erbium excitation, respectively. In Eq. A.8 we took into account possible saturation of excited erbium, which leads to blocking of Er excitation process.

The rate equation, which describes excitation of erbium ions, has the form
\[ \frac{dN_{Er}^*}{dt} = c_A n_{ex}(N_{Er} - N_{Er}^*) - \frac{N_{Er}^*}{\tau} . \] (A.9)

where \( \tau \) is the lifetime of erbium in the excited state.

In order to analyze the rate equations A.6 – A.9. we shall separate our physical system into two subsystems. One of them (fast) has the relaxation times of all the processes involved not exceeding several microseconds: capture of free excitons by donors induced by erbium or some other impurities. The other one (slow) is characterized by time constant larger by two orders of magnitude: the lifetime of erbium ions in the excited state. Therefore we can regard the “fast” subsystem to be in a quasistationary state and get
\[ n_{ex} = \alpha \Phi \tau_{ex}. \] (A.10)

In this approximation, the rate equation has the form:
\[ \frac{dN_{Er}^*}{dt} = \sigma_{eff} \Phi(N_{Er} - N_{Er}^*) - \frac{N_{Er}^*}{\tau} . \] (A.11)
where we have introduced the effective cross section of erbium excitation \( \sigma_{eff} \) [131]:

\[
\sigma_{eff} = \alpha c_A \tau_{ex}.
\]

(A.12)

The excitation cross section can be obtained from the experimental power dependence of erbium luminescence intensity. From the stationary solution of Eq. A.11 the dependence of erbium luminescence intensity on photon flux should depend on the excitation cross section \( \sigma \):

\[
I_{Er} \propto \frac{N_{Er}^{*}}{\tau_{rad}} = \frac{\sigma_{eff} \Phi}{1 + \sigma_{eff} \tau_{rad}} N_{Er}.
\]

(A.13)

One can expect that the excitation cross section from the non-implanted side excitation is less effective due to the \( p - n \) junction effect and the diffusion of excitons in the silicon. Indeed, Fig. A.3 shows the power dependence of of Er luminescence under excitation from implanted and non-implanted side. Taking the lifetime of erbium to be \( \tau_{Er} = 1.3 \) ms for both configurations we have obtained \( \sigma_{eff} = (1 - 3) \times 10^{-15} \) and \( \sigma_{eff} = (6 - 8) \times 10^{-16} \) cm\(^{-2}\) for the implanted and non-implanted side excitations, respectively.