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ERBIUM LUMINESCENCE IN SILICON*

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We report on high resolution photoluminescence investigations of Er-implanted Si and demonstrate the variety of Er centers or complexes with impurities and native Si-defects formed depending on the processing parameters. These centers are shown to differ in the efficiency of excitation transfer as well as high temperature photoluminescence yield. The mechanisms responsible for the photoluminescence quenching at different temperature regimes are discussed.

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1. Introduction

The interest in Er-doped silicon as a potential infrared light source is closely connected with the development of fiber optics communication systems. The transition between the two lowest spin–orbit split levels of the trivalent erbium ion occurs namely at a wavelength about 1.54 μm, which coincides with the minimum loss as well as minimum dispersion of silica based optical fibers [1]. Moreover, in contrast to near band gap lasers based on III–V compounds, the emission wavelength is temperature stable, which is of great importance in terrestrial applications. The ultimate goal is to obtain an Er-activated light source on silicon, which would open the way to fast intra- and inter-chip optical data transfer.

Silicon is a material with the most mature integration processing technology, however, due to its indirect energy gap the probability of optical transitions is very low, which makes it unsuitable for optoelectronic applications. Despite the many attempts to relax the momentum conservation rules for interband transitions, such as zone folding or interface scattering in Si–Ge superlattices, the results are far from satisfactory. The most promising alternative path is, therefore, doping of silicon with luminescent impurities, such as erbium. Such a system is expected to combine the ultra sharp, atomic-like emission originating from intra-4f-shell transitions with the efficient pumping via electrons and holes. It is thus not surprising that the optical activity of Er in Si has achieved a lot of attention recently [2–12].

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2. Er-doping of silicon

One of the main obstacles in obtaining efficient light emission from erbium activated silicon is the difficulty of incorporating a sufficient number of Er ions in a good quality crystal. The very low solubility of Er (estimated to be about 10^{16} cm^{-3} [5]) requires the application of nonequilibrium technologies. Among them, ion implantation, especially for high ion energies (2–5 MeV), seems to be the most promising technique.

Ion implantation is a very convenient method of introducing dopants into silicon. The impurity distribution is well controlled by the choice of the implantation energy and dose. Also the radiation defects in Si (produced at concentrations exceeding that of the dopant by many orders of magnitude) are well characterized and standard annealing techniques have been developed enabling a complete removal of typical postimplantation damage. It turns out, however, that in the case of Er ions radiation defects are unusually stable [3, 11, 12] and higher annealing temperatures are required than those sufficient for implantation with light ions.

Depending on the dose used two annealing procedures have been proposed. For moderate doses, i.e., below the amorphization limit, annealing at 900°C for 30 min. in vacuum or nitrogen flux was found to be the best [3–6]. The highest photoluminescence (PL) yields reported in such prepared samples are obtained for Er peak concentrations around 4×10^{17} cm^{-3} [6]. Higher Er concentrations as well as longer annealing times lead to Er clustering and eventually the formation of optically inactive Er silicide precipitates. The onset of Er precipitation for annealing at 900°C is found to occur for Er peak concentrations exceeding 1.3×10^{18} cm^{-3} [7]. Higher annealing temperatures (even for very low Er doses, corresponding to peak concentrations below 10^{17} cm^{-3}) result in the formation of extended defects, such as end-of-range dislocations, which act as very efficient carrier recombination centers.

If the applied dose is high enough to amorphize the implanted layer it was found best to regrow the layer at a lower temperature (600–620°C), with a duration depending on the layer width, and then apply a so-called rapid thermal anneal (RTA) step for 15–30 s at 900°C to remove the remaining point defects [8]. Without the second annealing step hardly any Er emission can be observed. For Er peak concentrations below 10^{19} cm^{-3} the formation of dislocations can be thus much reduced. The PL yield of such samples, however, is usually lower than in the case of 900°C anneals, despite the greater number of incorporated Er ions in an apparently good quality crystal.

Native Si impurities, in particular oxygen, can also play a considerable role affecting both the Er incorporation as well as the luminescence intensity of Er implanted silicon. In high purity float-zone (FZ) silicon the PL intensity of Er is typically 1–2 orders of magnitude lower than in the Czochralski grown (CZ) material. This is obviously related to the at least 2 orders of magnitude higher oxygen content of CZ silicon (about 10^{18} cm^{-3}) as compared to FZ and led to speculations that the optically active Er centers form complexes with oxygen [6], though high resolution PL investigations show that Er–O complex formation is rather limited [9–11]. On the other hand it is well known that oxygen can getter

nonradiative recombination centers in Si. In particular, the concentration of deep electron trap states observed in Er implanted and heat treated Si by means of deep level transient spectroscopy (DLTS) was found to be reduced upon oxygen coimplantation [11, 12], with a simultaneous increase of both the Er-related and near band edge PL intensities. The gettering effect can be quite considerable, as not only Er but also the Si host emission intensity in Er implanted FZ-Si was found to be dramatically poor, indicating that nonradiative recombination processes dominate [12, 13]. Another effect worth consideration is the oxygen induced expansion and mechanical hardening of the Si lattice, which improve the incorporation of heavy dopants and simultaneously prevent the movement of end of range dislocations formed during heat treatment into the active layer. Additional oxygen codoping was found to improve enormously the crystalline quality of CZ-Si implanted with high Er doses [8]. Both effects have been thoroughly investigated in silicon device technology, as it turned out that float zone silicon, unless specially treated, is unsuitable for planar device processing [13].

3. Optically active Er centers

Due to the narrow band gap of silicon (1.12 eV at room temperature) only transitions from the lowest $^4I_{13/2}$ excited state of Er^{3+} are observed. The transition from the next $^4I_{11/2}$ level occurs already at above band gap energies. The 15-fold degenerate ground state ($^4I_{15/2}$) is weakly split by the crystal field. If Er occupies a substitutional or a tetrahedral interstitial lattice site, the ground state is split into two doublets (Γ_6 and Γ_7) and three quartet (Γ_8) states, so that at low temperatures, when only transitions from the lowest level of the $J = 13/2$ multiplet occur, 5 emission lines should be visible. When the site symmetry is lower the degeneracy of the Γ_8 states is lifted and altogether 8 PL lines may be observed for one site. In high resolution Fourier spectroscopy, however, more than 100 PL lines are visible in a spectral region covering only 100 cm^{-1}, i.e., about 20% of the range where Er emission lines are observed. Obviously a variety of Er centers or complexes with native Si-defects are formed. The intensities of the PL lines belonging to individual centers depend strongly on sample preparation conditions, such as implantation energy, dose, as well as annealing temperature and duration. By a careful adjustment of these parameters it is even possible to "breed" centers of a particular type, as shown in Fig. 1.

The examples chosen show a cubic center with the characteristic 5-fold splitting of the Er ground state (upper trace in Fig. 1a), which has been attributed to an isolated Er ion occupying an interstitial lattice site [9–11]. Such a spectrum can be easily observed in CZ-Si implanted to peak concentrations even exceeding the Er precipitation limit, especially for high energy implants performed at elevated temperatures and annealed subsequently at 900°C. The reported PL spectrum has been recorded for a sample implanted at 300°C with 2 MeV energy to the peak concentration of 3×10^{18} cm^{-3}, however, secondary ion mass spectroscopy (SIMS) investigations suggest that it stems from a low concentration tail of the Er doping profile (see Fig. 2). Cubic centers dominate also in FZ-Si annealed at 900°C implanted with low Er doses ($\leq 5 \times 10^{17}$ cm^{-3}). In contrast, they are hardly found in CZ-Si for similar Er concentrations, unless annealed at lower tempera-

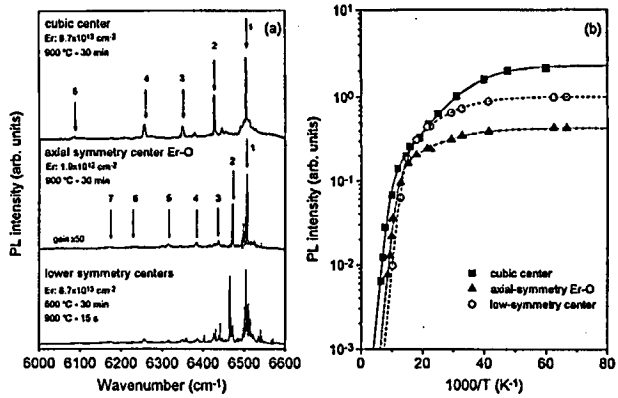

Fig. 1. (a) Spectra of Er implanted into Si at 2 MeV (top and bottom) and 320 keV (middle), the Er dose and the annealing conditions are indicated in the figure. The PL was excited with the 514.5 nm Ar laser line and measured at 10 K. (b) Temperature dependence of the PL intensity for the cubic center from the top spectrum in (a), as well as the axial symmetry Er–O complex and a lower symmetry center (with the main line at 6464 cm^{-1}) measured in the same sample (bottom spectrum in (a)).

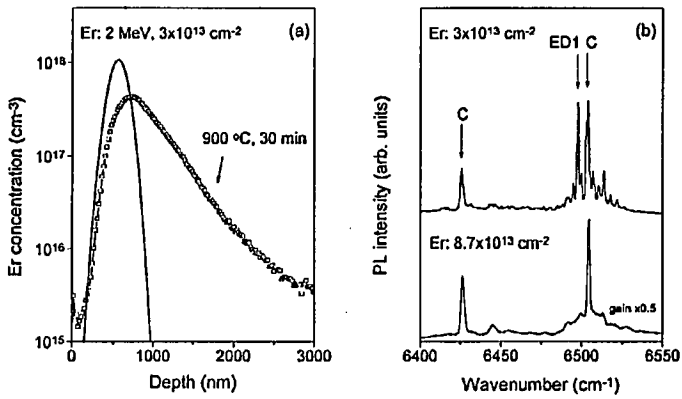

Fig. 2. (a) Calculated (solid line) and measured (after annealing at 900°C for 30 min) Er profiles for the implantation energy and dose indicated in the figure. (b) High energy region of the Er PL spectra measured in the sample from (a) — upper trace, and a sample with 3 times higher Er implant dose but prepared in the same way. The Er peak concentrations are indicated in the figure. Cubic lines are labeled C, ED1 denotes a characteristic Er complex with an implantation defect.

tures (600–800°C). The middle trace shows the spectrum of an axial symmetry center with 7 out of 8 expected PL lines, which occurs exclusively in oxygen rich (CZ) material and dominates the PL for Er peak concentrations smaller than 5×10^{17} cm^{-3}. The center has been assigned to an Er–O complex [9–11]. At annealing temperatures above 900°C the complex dissociates [11]. The bottom trace

shows a typical spectrum of many low symmetry Er complexes, usually found in samples implanted with high Er doses and annealed in two stages. (Apart from the different annealing procedure applied for the samples yielding the top and bottom PL spectra in Fig. 1a the samples themselves and their preparation are identical.) Centers of that kind can be also found for low Er concentrations when the samples are either annealed above 900°C or coimplanted with light elements, e.g. N or O [9–11]. Evidently, Er forms complexes with a variety of radiation and heat treatment induced lattice defects. The identification of the various Er centers is described in detail elsewhere [11].

The understanding and controlling of the processes leading to the formation of particular Er centers are of great importance for obtaining efficient room temperature emission from Er doped silicon. Various Er centers turn out to exhibit quite different PL quenching behavior with increasing temperature even if they occur in the same sample. Figure 1b shows the temperature dependence of the PL intensities of the characteristic features of the three types of spectra presented in Fig. 1a. The other lines identified as belonging to the same center behave in the same way within the experimental accuracy: their intensity is scaled only by a factor which depends neither on temperature nor on the pump power. It can be seen that the cubic center is the strongest luminescent center in the whole temperature regime. Among the lower symmetry centers the axial Er–O complex is seen to dominate at elevated temperatures despite the fact that its concentration (and hence the low temperature PL intensity, since the radiative lifetimes of the various centers are practically the same) is lower than that of the other optically active centers present in the sample. Obviously, the centers differ in their efficiency of capturing the excitation from the Si host and converting it into the intra-4*f*-shell radiative emission. The underlying physical mechanisms will be discussed in the following section.

One of the reasons for the different efficiencies of Er centers found in the same sample is the spatially inhomogeneous impurity distribution, particularly after heat treatment, which explains also the apparent paradox that the concentration of isolated, cubic Er ions increases with increasing implant dose. Figure 2a shows the erbium concentration profile calculated for the ion energy of 2 MeV and implant dose of 3×10^{13} cm^{-2} (solid line) as compared to the distribution profile measured after annealing at 900°C with SIMS. It is evident that the cubic PL emission originates from Er ions diffused deep into the Si wafer, whereas low symmetry Er centers occur mainly in a spatial region with a greater Er concentration and, simultaneously, a greater number of nonradiative recombination centers generated by implantation. The PL spectrum measured in this sample is shown in the upper trace of Fig. 2b. The cubic transitions are labeled "C", whereas the dominant PL line stemming from an Er complex with an implantation defect is labeled "ED1". When the Er dose is increased by a factor of 3 (lower trace in Fig. 2b) in the highly Er doped part of the sample optically inactive Er clusters and precipitates are formed, whereas the concentration of Er centers diffused into the undamaged part of the sample can even grow.

4. Energy transfer and PL quenching

The questions how the energy is transferred from the host crystal to the $4f$ shell of Er and what are the processes responsible for the rapid decay of the luminescence intensity with increasing temperature are so far only tentatively answered. It is generally accepted that localization of excitons or non-equilibrium carriers is involved in the energy transfer process [14]. In the first step, the incident photon is absorbed, generating an electron–hole pair. For photon energies in the visible spectral range (such as the green Ar ion laser line typically used for Er excitation) the absorption occurs via an allowed, direct interband transition and is extremely efficient. At low temperatures and low excitation densities the thermalized carriers form long living excitons, since due to the indirect band gap of Si exciton recombination requires the participation of a wave vector conserving phonon. Such excitons can transport near band edge excitation energy over macroscopic distances [15], much wider than the shallow Er-containing surface layers. These excitons can be trapped at or close to an Er containing defect. In the next step, the exciton recombines nonradiatively transferring the necessary energy for the intra-$4f$ transition from the $J = 15/2$ ground state to the excited $J = 13/2$ state. Finally the Er ion recombines radiatively. The reverse process, i.e., nonradiative recombination of the Er ion with energy transfer back to the exciton is highly improbable as it requires multiphonon absorption to account for the 300 meV energy mismatch between the near band edge and Er emissions. In the absence of other recombination centers competing with Er in the capture of the host excitation the quantum efficiency of the Er PL would be 100%.

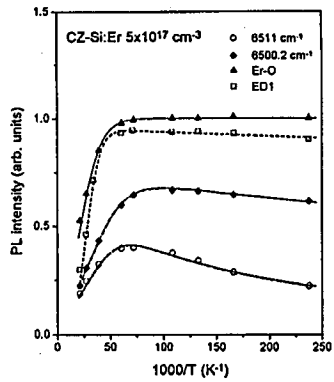

Fig. 3. Temperature dependence of the PL intensities of 4 different Er centers measured in a sample implanted with 3.2×10^{12} cm^{-2} Er at 320 keV.

The temperature quenching of the Er PL intensity seen in Fig. 1b can be understood in the following way. Below 20 K all excitons either generated within or diffusing into the Er-layer are firmly bound close to the Er centers and have sufficient time to transfer their energy. For thin, near surface Er doped layers, as shown in Fig. 3, the PL intensity of some centers, the less efficient ones in exciton trapping, is even observed to increase with increasing temperature in this

regime, since the excitons (which are generated within the absorption length of about 1 μm at the applied pump wavelength) are easily trapped by other crystal imperfections [15], such as neutral donors or acceptors, before they reach Er ions. At slightly elevated temperatures they can be thermally released from centers with low binding energies and migrate more efficiently towards the doped layer. We observe a PL intensity increase activated with an energy typical for P or B exciton binding (5 or 4.2 meV, respectively) accompanied by a simultaneous increase of free exciton emission.

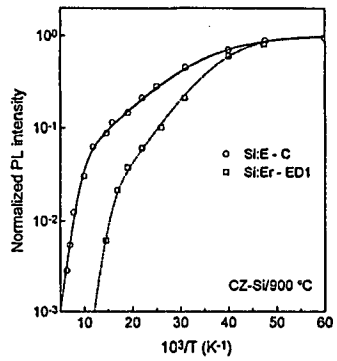

Fig. 4. Temperature dependence of the normalized PL intensities of the cubic and ED1 Er centers measured in a sample implanted with 3×10^{13} cm^{-2} Er at 2 MeV, the SIMS profile of this sample is shown in Fig. 2a.

At intermediate temperatures, typically in the range of 20 to 100 K, the PL decays with an activation energy varying between 5 and 15 meV, depending only on the type of Er center but not on the sample investigated. This deactivation energy is ascribed to the thermal ionization of excitons bound at or near the Er center, which increases the probability of exciton decay at other recombination centers, distant from the optically active Er ion. This process can account for more than an order of magnitude decrease in the Er PL intensity at 100 K, depending on the sample preparation conditions and the center investigated. For illustration, in Fig. 4 the temperature dependence of the normalized PL intensities for the cubic and ED1 centers from Fig. 2 is shown. It turns out that many of the nonradiative recombination defects responsible for locking the excitation away from the luminescent Er centers are introduced by implantation and annealing, as evidenced by deep level transient spectroscopy (DLTS). Even for extremely low Er implant doses (10^{12} cm^{-2}) a variety of deep electron trap levels has been observed after annealing [11, 12]. Though the concentration profiles of those defects coincide with the as-implanted Er profile and Er evidently enters into such defects, a comparison of their annealing curves with those of the luminescent Er centers excludes the possibility that electrically and optically active Er centers are in any way related to each other. In contrast, the deep defects act as very efficient nonradiative recombination centers as the intensities of both the near band edge and Er related

emissions reach a maximum for the annealing temperature of 900°C, when the total defect concentration approaches minimum. Three of the deep levels observed, with apparent enthalpies (the capture coefficient was too big for direct determination) of 0.15, 0.6 and 0.8 eV remain, however, stable up to annealing temperatures of 1000°C and might be involved in the parasitic recombination channels.

Above 100 K, the PL intensity decays rapidly with a sample dependent deactivation energy of 60–150 meV, which seems, however, to be the same for all Er centers within one sample. This quenching regime is highly efficient owing, first of all, to the reduced efficiency of energy transfer from the host to Er because of the thermal dissociation of Si excitons (the free exciton binding energy is 14.5 meV). Moreover, the increased concentration of free carriers can affect not only the efficiency of nonradiative recombination at deep levels but also activate new parasitic recombination paths. Since the deactivation energy does not depend on the kind of luminescent Er center, obviously a common recombination channel is activated related, e.g., to a level controlling the carrier concentration. As the Er luminescence decay is accompanied by a decrease of the Er lifetime, nonradiative recombination processes within Er centers are also involved. One of the mechanisms which could be responsible for high temperature PL quenching is Auger-type energy transfer from Er to free carriers [16].

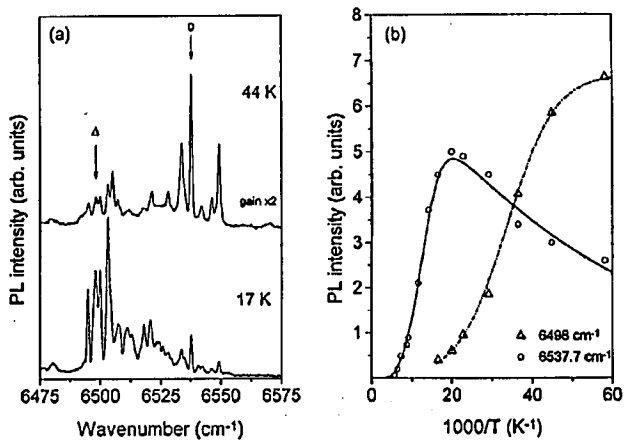

Fig. 5. (a) PL spectra of a sample heavily codoped with oxygen and (b) the temperature dependence of the PL intensity of the features marked with arrows in (a).

In addition to the above-discussed Er excitation by means of energy transfer from shallowly bound excitons an excitation mechanism involving free carriers is also observed. However, such a mechanism is only active for specific Er centers generated in heavily O-codoped silicon. Those centers emit at slightly higher energies than the typical Er centers in Si and are probably related to Er containing SiO_2 precipitates or to Er decorated dislocations. As shown in Fig. 5 the PL intensity of such centers increases with temperature reaching maximum about 60 K, when the intensity of the ED1 center (6498 cm^{-1}) practically disappears. This

behavior correlates with thermal dissociation of excitons. The excitation energy is probably transferred from a deep defect state (e.g., dislocation) trapping a carrier and recombining with a free carrier.

5. Summary and outlook

The results reported above demonstrate the complexity of problems encountered in optimizing the photoluminescence yield of Er doped silicon. Many of them are directly related to the nonequilibrium doping techniques applied, which are nevertheless necessary in order to overcome the low solubility limit of erbium in silicon. Obviously, apart from the variety of optically active Er centers and complexes with native Si defects (produced both during implantation and subsequent heat treatment) erbium can also form electrically active complexes with residual radiation defects which act as efficient nonradiative recombination centers and limit the excitation efficiency of Er PL at increased temperatures. Though the low temperature PL efficiency of Si : Er is quite satisfactory, before any practical (i.e. room temperature) applications can be considered the problem of parasitic recombination channels has to be solved. One of the possibilities is to passivate the competing recombination centers by codoping with, e.g., oxygen, keeping in mind, however, that depending on the processing procedure O can also produce a number of undesirable defects. Another possibility worth investigation is codoping of silicon with impurities capable of exciton binding via short-range potentials. Such excitons are much more deeply bound than those on neutral donors and acceptors in silicon and less liable to Auger recombination. Excitation transfer to Er could be hence more efficient and less affected by the presence of recombination shunts if the latter could not be entirely avoided.

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