Fabrication and photoluminescence properties of erbium doped size-controlled silicon nanocrystals

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Abstract

Er doping of dense arrays of nearly monodisperse Si nanocrystals produced by a new SiO/SiO 2 superlattice approach is presented. This synthesis method is fully compatible with standard Si technology. The prepared samples show a strong increase of Er-related luminescence by a factor of up to 5000 in comparison with Er-doped bulk SiO2 . Photoluminescence (PL) spectra and transients of the undoped and Er-doped size-controlled nanocrystalline Si/SiO 2 superlattices have been comparatively investigated as a function of implantation dose and Si nanocrystal size. It is shown that the energy of the optically excited Si nanocrystals can almost be completely transferred to the Er 3+ ions, resulting in a very strong emission at 1.54 μm. The efficiency of the energy transfer increases for smaller crystal sizes and an increasing overlap between the emission energy of the Si-related luminescence and the absorbing Er 3+ energy levels. For superlattices with nanocrystal sizes of 2 nm a transfer efficiency to the Er 3+ ions is found to be nearly one at room temperature under an excitation with photons of 3.7 eV. This properties of a highly efficient excitation of the Er ions via the Si nanocrystals is in agreement with the Förster mechanism.

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1. Introduction

Erbium is a rare earth element of the group of lanthanides. The different optical transitions in erbium are parity-forbidden. If erbium is incorporated into a solid matrix, it is mostly observed as Er3+ ions. Two different processes occur. The Er3+ levels split up due to the Stark effect and the matrix introduces an odd character into them which makes the transitions weakly allowed. Due to this processes the absorption cross-sections of the Er3+ increases to values of about 10−21 cm2, which is still rather low. The strong interest in Erbium with its luminescence at 1.54 μm is based on the absorption minimum of the silica fibers used in telecommunication technology at the same wavelength. Amplifiers based on erbium doped silica fibers are state of the art in today’s long range optical interconnections [1]. An increased absorption cross-section of the Er3+ levels and a combination with common Si-based technology would be necessary for using erbium in integrated optoelectronics.

Different approaches to combine Er and Si technology were tested. Er implantation into bulk crystalline Si results in a quite high Er luminescence at 5 K. Excitons are formed at erbium-induced defects and transfer their energy to the Er ions by an Auger process [2]. At room temperature the excitons are not localized at the very shadow defect levels anymore, which result in a dissociation of the electron hole pairs and a decrease of the Er3+ luminescence by more than three orders of magnitude. Using co-doping of oxygen or amorphous silicon instead of crystalline Si results in a better but still not sufficient temperature behavior of the Er3+ luminescence [2,3]. One way to overcome these problems is to combine Erbium with Si nanocrystals. After the observation of room temperature photoluminescence (PL) of Si nanocrystals in the so-called porous silicon [4,5], a decade of intense research on the light emission of Si nanocrystals is passed. The origin of the infrared PL and electroluminescence (EL) band is clearly related to Si nanocrystals. For porous silicon, the excitation character of the luminescence signal was...
proven by Calcott et al. [6,14,26]. The EL efficiency of all these bands, however, is in the range of only 1 × 10^{-3}, which is too low for applications. Using the Si nanocrystals as a localization of excitons which can transfer their energy to Er^{3+} ions would overcome both the limitations of Si-based light emission and the very small absorption cross-sections of direct excitation of the Er^{3+} energy levels [7]. The absorption cross-section of the Er^{3+} ions in the vicinity of Si nanocrystals was estimated to be 10^{-16} cm^{2} at an excitation wavelength of 488 nm [8], which corresponds well to the Si nanocrystal absorption cross-section at the same wavelength [9].

A nearly temperature-independent luminescence signal was found due to the increased binding energy of the localized excitons compared to bulk silicon [2]. This system allowed the fabrication of silicon-based LEDs with an efficiency of 10% [10]. However, the mechanism of the energy transfer between the Si nanocrystals and the Er^{3+} ions is still under discussion. The overlap of the luminescence signal of the Si nanocrystals in the range of 1.3–1.8 eV with the 4I and 4F levels of the Er^{3+} ions indicates a possible resonant energy transfer (RET). In [12] it was shown that at least part of the process is resonantly. Dips in the Si luminescence spectra were shown which correlate energetically with the absorbing Er^{3+} energy levels. Transfer times for this energy transfer increase with the size of the Si nanocrystals from 11 to 115 μs. There are still a number of reports with controversy results. In [11] it is reported that the lifetime of the Si nanocrystals remains constant after Er implantation, where in [8,12] a decrease of the lifetime with increasing Er concentration is reported. Also, the number of Er ions pumped by one Si nanocrystal is controversially discussed. In [11] this number is supposed as unity, while in [13] the maximum number of pumped Er^{3+} ions was estimated to be the ratio of Si nanocrystal lifetime to Er lifetime.

For a detailed characterization of this energy transfer process and an effective energy transfer from Si nanocrystals to Er^{3+} ions an independent control of Si nanocrystal size and density would be necessary. The conventional methods like producing porous Si by electrochemical etching of a crystalline Si wafer using HF [15], ion implantation of Si into high quality SiO_{2} films [16,17], or the growth of non-stoichiometric oxide (SiO_{2}) films by different methods like CVD [18], co-sputtering [19] or reactive evaporation [20], does not satisfy the described need of a size control of the Si nanocrystals.

Recently we developed a new synthesis method based on a SiO_{2}/SiO_{2} superlattice approach [22]. In this method the phase separation of the SiO_{2} layers is combined with a size control of the Si nanocrystals by the SiO_{2} layer thickness. By the stoichiometry of the SiO_{2} layers an additional control over the Si nanocrystal density is possible. This approach for Si nanocrystal synthesis is ideal for characterizing the Si nanocrystal size dependence of the energy transfer to the Er^{3+} ions. In this way, a dense package of monodispersed crystals could be synthesized providing excitons of proper energy for an optimal transfer to the Er ions.

2. Förster transfer

For such and similar systems at least four different processes of a resonant energy transfer between a “donor” and an “acceptor”, how the emitter and the absorber in these processes are called, are possible. The resonant energy transfer, often called Förster process, the re-absorption, a transfer due to the formation of complexes, and the energy transfer due to collisions [23]. The last mentioned process requires a transport of the donor and the acceptor and is only found in liquids or gases. The transfer due to the formation of complexes requires a molecular contact between donor and acceptor. In the case of re-absorption, a photon emitted by the donor is absorbed by the acceptor. The observed decrease of the excitonic Si nanocrystal lifetime and the nearly unchanged spectra of the Si and Er systems indicate a Förster process as the basic mechanism of the energy transfer.

A Förster process can be understood as a dipole–dipole interaction between an excited donor and an acceptor. The theory of this process was developed by Förster in 1948 [24]. Here, a short summary of this mechanism is given, which is helpful for understanding of the shown experimental data. Using the simple classical view of an electrical field represented by the oscillating dipole (donor) the field can be developed for $r$ (distance from the donor) up to the $r^{-3}$ term. This term represents the Förster transfer. In the near field, for small $r$, the electric field is dominated by the Förster term where for larger $r$ the field follows a $r^{-4}$ dependence. The near field represents a sphere of a radius $0.1 \times b$ with:

$$b = \frac{\lambda}{2 \pi n}$$

(1)

where $\lambda$ is the wavelength of the donor luminescence, and $n$ represents the refractive index of the matrix material (SiO_{2}). For a wavelength of 600–1000 nm and a refractive index of 1.4–1.6 we can estimate $b$ to be below 100 nm. That means, the Förster zone represents a sphere with a radius of 10 nm around the donor, i.e. the Si nanocrystals. Acceptors (i.e. Er^{3+} ions) within this range will be a potential partner for the Förster transfer. In addition, for achieving a Förster transfer between a donor and an acceptor the following conditions should be fulfilled. The donor and acceptor should have strong transitions in the ultraviolet to near infrared, there should be a spectral overlap between the donor and acceptor states and the distance between the donor and acceptor is below the Förster zone. A simplified energy diagram of the transfer process is shown in Fig. 1. This diagram neglects the resonant character of the energy transfer but illustrates the kinetics of the processes clearly. The transfer efficiency $E_T$ for the energy transfer is given by the percentage of all absorbed photons which go nonradiatively from the donor to the acceptor:

$$E_T = \frac{k_T}{k_T + k_{4I} + k_{4F}}$$

(2)
acceptor ($\tau_D$, $\kappa_k$) the excited states. The symbol $k$ represents the donor and $A$ the acceptor. The star indicates the presence of the acceptor ($\tau_A$) and under the presence of an acceptor ($\tau_{DA}$) the transfer efficiency can be determined by:

$$E_T = 1 - \frac{\tau_{DA}}{\tau_D}$$

using:

$$\tau_D = \frac{1}{k_D + k_{DA}}$$

and

$$\tau_{DA} = \frac{1}{k_A + k_D + k_{DA}}$$

A further useful parameter is the so-called Förster distance $R_0$, where the transfer probability is 50% of all possible processes, which means an equal decay rate for processes within the nanocrystal system and for the transfer to the acceptor: $k_T = k_D + k_{DA}$. The transfer efficiency can then be expressed as:

$$E_T = \frac{R_0^6}{R_0^6 + r^6}$$

and $R_0$ scales with:

$$R_0^6 \propto \frac{\kappa_D \kappa_A}{n^3}$$

$k$ represents the orientation of the donor-acceptor dipole, $Q_0$ the quantum efficiency of the donor, $J$ the overlapping integral of the donor emission and acceptor absorption spectra, and $n$ is the refractive index of the matrix. For a fixed $k$ and $n$ the transfer efficiency $E_T$ increases with increasing quantum efficiency of the donor (i.e., nanocrystal) and with increasing overlap of the respective states.

3. Experimental details

The samples were prepared by reactive evaporation of SiO powder using a conventional thermal evaporation system which enables the use of 4 in. wafers. The substrates temperature was 100 °C. The material used for evaporation was a conventional SiO powder (Balzers, 99.9%) which was either evaporated under vacuum or by using additional oxygen gas ($1 \times 10^{-4}$ mbar) for SiO$_2$ deposition. A shutter enabled the fast interruption of the process. The used growth rate was 12 nm min$^{-1}$. In this way a superlattice structure can be prepared by alternatively depositing SiO or SiO$_2$ layers. The thickness of the SiO layers varied between 2 and 6 nm (depending on the sample). For the SiO$_2$ barrier layers a thickness of 4 nm was used. Usually, 30–45 periods were prepared. Sample rotation enabled a homogeneity below 10% over the whole wafer. For crystallization the samples were annealed for 1 h at 1100 °C under N$_2$ atmosphere.

The size of the Si nanocrystals were determined by the SiO layer thickness [22]. After crystallization the samples were implanted with Erbium using an implantation energy of 300 keV. After implantation the samples were annealed at 900 °C under argon atmosphere. For comparison, a 200 nm thick SiO$_2$ layer was implanted and annealed under the same conditions.

Two sets of samples will be discussed here. The first set (set A) is based on one sample wafer with 45 periods of 4 nm thick SiO layers and 4 nm thick SiO$_2$ layers. Different pieces of the sample were implanted with various Er doses ranging from $1 \times 10^{14}$ to $5 \times 10^{15}$ cm$^{-2}$. The time of the second annealing after implantation was 5 min. The second set (set B) contains samples of 30 periods of different SiO layer thickness (varied from 2 to 6 nm) which were implanted with an Er dose of $2 \times 10^{15}$ cm$^{-2}$. This sample set was annealed for 1 h under Ar atmosphere after implantation.

Selected samples were characterized by transmission electron microscopy using a CM20F or a JEM-4010 electron microscope. The cross-section samples were prepared in the usual way including final Ar ion milling. Imaging the superlattice structures as deposited and after annealing was realized applying the Fresnel defocus method at medium magnifications. A HeCd laser with power density below 0.5 mW cm$^{-2}$ was used for the cw PL-measurements and a N$_2$ laser for the time resolved measurements. The luminescence was detected either by a CCD camera for the visible range, or by a Germanium detector EL-L (Edinburgh Instruments) for the infrared luminescence. All spectra were corrected for spectral response of the measurement system. Additionally, transients of Er-related PL under pulsed laser excitation were measured by InGaAs photodiodes with preamplifiers processing time resolutions of 0.5 ms, 1 s and 0.2 s. PL transients in the spectral range of 2.2–1.2 eV were recorded by a photomultiplier PMT928 (Hamamatsu).

4. Results

After annealing of the amorphous SiO/SiO$_2$ superlattices the Si nanocrystals are arranged in layers and separated by a thin barrier oxide, as can be seen in the TEM image in Fig. 2. The process and the different stages of phase separation are already discussed elsewhere [21]. The PL of the
Fig. 2. TEM image of the sample of sample set A (4 nm SiO layer thickness) after crystallization. The darker areas represent the Si nanocrystals which are separated by oxide.

nanocrystals can be tuned from 1.29 to 1.7 eV by adjusting the Si nanocrystal size by the SiO layer thickness [22]. The luminescence is clearly assigned to exciton recombination. This could be shown by resonant excitation spectroscopy where steps with the expected energies for momentum conserving phonons for an electron–hole recombination in Si were visible. An increasing recombination probability, increasing exchange energy splitting and an increasing binding energy of the excitons with decreasing Si nanocrystal size clearly prove the excitonic character of the luminescence signal [25]. Nonradiative recombination channels due to surface states play only a minor role in this samples due to the good surface passivation of the nanocrystals by the surrounding oxide.

Fig. 3 shows the influence of an increasing Er dose on the luminescence of the Si nanocrystals for the sample set A (4 nm SiO layer thickness). The peak position of the nc–Si luminescence was around 860 nm and does not change for increasing Er dose. The Si nanocrystal luminescence intensity decreases continuously with increasing Er dose. For Er doses above $2 \times 10^{15} \text{cm}^{-2}$ the nc–Si–PL vanishes completely. Simultaneously, the Er luminescence (Fig. 4) increases with increasing Er dose and saturates for Er doses above $2 \times 10^{15} \text{cm}^{-2}$.

Fig. 5 summarizes the results for the integrated PL intensity from Figs. 3 and 4 and compares it with an equally doped SiO$_2$ layer. As can be seen here, the Er luminescence is enhanced up to 4 orders of magnitude with the presence of nanocrystals compared to the doped oxide. The Er dose of $2 \times 10^{15} \text{cm}^{-2}$, where the Er luminescence saturates in the presence of the nanocrystals, corresponds to an Er to Si nanocrystal ratio of about 40 assuming a Si nanocrystal density of $10^{19} \text{cm}^{-3}$ estimated by TEM images (see Fig. 2). For the SiO$_2$ layer a higher dose ($1 \times 10^{16} \text{cm}^{-2}$) is needed for a saturation of the Er-related PL signal. Also at this very high doses the PL intensity is still at least a factor of 10 reduced, compared to the Er-doped Si nanostructures. These results are a strong evidence for the very effective Si–Er energy transfer.

Fig. 4. Er luminescence signal for different implantation doses on sample set A.
A decrease of the Si nanocrystal lifetime for the same emission energy with increasing Er dose was observed (see Fig. 6). The lifetimes of the nc-Si measured at 100 K were determined for different emission energies at sample set A using a stretched exponential fit. Neglecting the influence of beam damage, the efficiency of the energy transfer from Si nanocrystals to the Er$^{3+}$ ions can be estimated by Eq. (3) (see Fig. 7).

Clearly, an increasing transfer efficiency with higher emission energies, i.e. smaller crystal sizes, can be observed. The efficiency is higher for higher Er doses. For emission energies of the Si nanocrystals above 1.85 eV the transfer efficiency reaches for both doses a value of ≈ 1. Because in this calculations the beam damage was neglected the calculated values for the transfer efficiency are only a qualitative measure and the given values are only an upper limit of the real efficiencies.

PL and time dependent PL measurements on sample set B (SiO layer thickness between 2 and 6 nm) were done to demonstrate the influence of nanocrystal size on the Er-related luminescence signal. Er luminescence, luminescence line shape, and lifetime of the samples are presented in Fig. 8 for three different nanocrystal sizes. The luminescence intensity increases with decreasing SiO layer thickness, i.e. decreasing size of the nanocrystals. The inset (a) shows the normalized spectra and demonstrates the increase of the full width at half maximum from 17 to 23 meV with increasing nanocrystal size. The inset (b) represents the time decay of the Er signal which are close to a single exponential decay. The respective lifetimes are 2.5 ms for 6 nm thick SiO layers and 3.4 ms for 2 nm SiO layers.

In Fig. 9 the Er luminescence intensity is normalized by the difference between the Si-PL intensity with and without Er doping and is shown as a function of the emission energy of the Si-PL signal. This ratio gives again a qualitative measure for the energy transfer efficiency. Such approximations are used in [27] for similar systems. The vertical lines denote the Er$^{3+}$ energy levels. The energy error bars represent the FWHM of the Si luminescence peak of the sample. The described ratio increases as the overlap between...
the Si luminescence and the Er energy levels increases. For roughly the same overlap, a higher transfer efficiency is observed for higher emission energies of the Si nanocrystals. The reached values of about 1 indicates a very efficient energy transfer even if the given values only give a qualitative measure of the real efficiencies.

5. Discussion

The Si nanocrystals prepared with the described new method of SiO/SiO2 superlattices are nearly monodisperse. Size distributions with half width half maximum (HWHM) of up to 0.2 nm could be shown [28]. The method allows to synthesize very high densities of nanocrystals (10^{12}cm^{-2}) even for nanocrystal sizes below 2 nm. The missing defect luminescence, which is seen in Si implanted oxides around 750 nm, is a further hint for the outstanding quality of the prepared films. The Er spectra seen in Fig. 4 show a main peak at 1535 nm and a satellite peak at 1551 nm. The spectra correspond to the ^4I_{13/2} → ^4I_{15/2} transition of the Er^{3+} ions in SiO2. The PL peak is broadened by Stark splitting which is typically for Er implanted oxides. The increasing FWHM of the Er spectra for larger nanocrystal sizes seen in Fig. 8 might be caused by larger fluctuations of the electronic function near the Er ions and hence an increased Stark splitting and broadening.

The observed high luminescence intensities of the Er^{3+} ions was shown. An increasing transfer efficiency with increasing spectral overlap of the emission energy of the Si nanocrystals and the absorbing Er^{3+} energy levels and with increasing quantum efficiency of Si nanocrystals was observed. All experimental data are in agreement with a resonant energy transfer due to a Förster process. The observed high luminescence intensities of the Er^{3+} ions can only be explained if one Si nanocrystal excited more than one Er ion in the surrounded matrix.

6. Conclusions

A very efficient energy transfer from dense arrays of Si nanocrystals to Er^{3+} ions was shown. An increasing transfer efficiency with increasing spectral overlap of the emission energy of the Si nanocrystals and the absorbing Er^{3+} energy levels and with increasing quantum efficiency of Si nanocrystals was observed. All experimental data are in agreement with a resonant energy transfer due to a Förster process. The observed high luminescence intensities of the Er^{3+} ions can only be explained if one Si nanocrystal excited more than one Er ion in the surrounded matrix.

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