Er-O clustering and its influence on the lattice sites of Er in Si

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Abstract

We present emission channeling experiments on the lattice location of Er in CZ Si single crystals with a well-defined O concentration of $6.5\text{--}6.6 \times 10^{17} \text{ cm}^{-3}$ and 60 keV-implanted Tm+Er doses ranging from $4.3 \times 10^{12} \text{ cm}^{-2}$ to $3.6 \times 10^{13} \text{ cm}^{-2}$. The experimental results are compared to the predictions of a simulator which models the formation of Er_nO_m clusters on the basis of simple diffusion and capture kinetics. We find that our experimental data compare favorably with a scenario where the formation of Er_nO_m defects with one or more O atoms is responsible for removing the Er atoms from their tetrahedral interstitial (T) sites. This suggests that Er does no longer occupy the T site even in simple (ErO) pairs.

Keywords: lattice location, Er in Si, implantation

Introduction

The presence of O is known to increase the luminescence from Er-related centers in Si. It can be regarded as proven that O forms complexes with Er which directly modify the structural, electrical and optical properties of Er [1-15]. However, there is also strong evidence that, possibly apart from ErO complex formation, additional mechanisms exist how O enhances the Er luminescence yield [6, 7]. More knowledge on the composition and microscopic properties of ErO complexes can help to better understand the different mechanisms. Presently, engineering the optimum atomic neighborhood of Er in Si will be helpful in maximizing the luminescence output of Er-based light-emitting devices.

As a first step in order to allow a comparison of possible scenarios of Er_nO_m clustering to experimental data we have developed a simulator that allows to model the interaction of Er and O during high-temperature annealing on the basis of simple diffusion and capture kinetics [14]. Previously we have compared predictions of the simulator to experimental results on the lattice location of radioactive $^{167\text{m}}\text{Er}$, which was determined by means of conversion electron emission channeling [14]. Experimentally, it was found that during annealing at 900°C the interaction of Er and O leads to a removal of Er from near-tetrahedral interstitial (T) lattice sites. In O-rich Czochralski (CZ) Si with a shallow Er profile close to the surface, the time scale for this process is limited by the out-diffusion of O from the bulk of the sample. The remaining fraction of Er on near-T sites therefore shows qualitatively a $1 - C_{\text{Ox}}/(m_{\text{av}}\phi) (D_{\text{Ox}} t)^{1/2}$ behavior, where t is the time of annealing, C_{Ox} and D_{Ox} the concentration and diffusion coefficient of oxygen, ϕ the implanted Er dose, and m_{av} the average number of O atoms needed to remove one Er atom from its T site. However, since the oxygen concentration in our previous CZ Si samples was only known within an order of magnitude, an accurate estimate on the mean number m_{av} of O atoms was difficult. In this contribution we present the results of recent emission channeling experiments in CZ Si single crystals with a well-defined O concentration.

Method

The preparation of 60 keV ^{167}Tm ($t_{1/2}=9.45 \text{ d}$) implanted samples at CERN's ISOLDE facility and the emission channeling lattice location experiments using conversion electrons from $^{167\text{m}}\text{Er}$ ($t_{1/2}=2.28 \text{ s}$) have been described in previous publications [8, 13, 16]. For our recent experiments we used $n\text{-Si:P}$ CZ single crystals ($\langle 111 \rangle$ orientation, $7.3\text{--}12 \text{ }\Omega\text{cm}$) with an oxygen concentration of $6.5\text{--}6.6 \times 10^{17} \text{ cm}^{-3}$. The implanted doses of Er+Tm were $4.3 \times 10^{12} \text{ cm}^{-2}$ (sample A, resulting in a peak concentration of $[\text{Er}+\text{Tm}]_{\text{max}} = 2.0 \times 10^{18} \text{ cm}^{-3}$), $5.7 \times 10^{12} \text{ cm}^{-2}$ (B, $2.7 \times 10^{18} \text{ cm}^{-3}$), $6.8 \times 10^{12} \text{ cm}^{-2}$ (C, $3.2 \times 10^{18} \text{ cm}^{-3}$), $1.2 \times 10^{13} \text{ cm}^{-2}$ (D, $5.7 \times 10^{18} \text{ cm}^{-3}$), $2.3 \times 10^{13} \text{ cm}^{-2}$ (E, $1.1 \times 10^{19} \text{ cm}^{-3}$), and $3.6 \times 10^{13} \text{ cm}^{-2}$ (F, $1.7 \times 10^{19} \text{ cm}^{-3}$). A filament that heats the backside of the Ta sample holder allowed *in-situ* thermal processing in the channeling goniometer at $<10^{-6} \text{ mbar}$. The temperature was measured by two thermocouples attached to the sample holder, and the annealing time given is the time after reaching the setpoint temperature. Due to the temperature gradients between the thermocouples, the sample holder and the sample surface, the temperature uncertainty amounts to $\pm 15^\circ\text{C}$. Quantitative identification of Er atoms on near-T interstitial sites was achieved through fitting the experimental electron emission yields by theoretical channeling patterns calculated for these lattice sites [8, 13, 16].

The mathematical simulator which models the diffusion of Er and O and the formation of Er_n and Er_nO_m clusters has been described in Ref. [14]. The starting situation is a Gaussian depth profile of 60

keV implanted Er (mean depth 336 Å, FWHM 195 Å) and a constant O profile. Both Er and O are allowed to diffuse at 900°C, and, assuming that they interact with each other within certain capture radii which we derive from the mean volume of the defects, a set of coupled differential equations determines the concentrations $C_{Er(n)O(m)}$ of Er_nO_m complexes. These equations are solved by the method of finite differences. This means that the concentrations $C_{Er(n)O(m)}$ of all desired Er- and O-containing clusters are updated within finite time intervals Δt and depth intervals Δx . The diffusion coefficients of erbium ($D_{Er} \approx 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ at 900°C) [2] and oxygen [$D_{Ox} = 0.13 \text{ cm}^2 \text{ s}^{-1} \times \exp(-2.53\text{eV}/kT)$, corresponding to $1.8 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ at 900°C] [17] are taken from the literature. All complexes are assumed to be thermally stable and immobile. However, formation of O_2 dimers and oxygen precipitation are neglected since the dimers are unstable at 900°C, and O precipitation occurs at this temperature only on time scales of the order of 100 h [17].

Results

Figure 1 shows the normalized fraction of Er remaining on near-T sites as a function of isothermal annealing time at 900°C for all 6 CZ Si samples investigated in the present study. The qualitative behavior with respect to the implanted Er dose is similar to the data we have published in Refs. [13, 14], the removal of Er from near-T sites being fastest in low-dose implanted samples. The solid lines in Fig. 1 display the calculated fraction of free Er plus Er within Er_n clusters, i.e. all Er atoms remaining outside $Er_nO_{m \geq 1}$ complexes, while the dotted lines show the calculated fraction of free Er plus Er within Er_n and $Er_{n \geq 1}O_1$ clusters, i.e. all Er outside $Er_nO_{m \geq 2}$ clusters. As can be seen, the assumption that all Er within $Er_nO_{m \geq 1}$ clusters is removed from near-T sites agrees well with the experimental data for all implanted Er doses and annealing times, except for the initial 30 and 60 s anneal steps. While this may indicate that initially not all O is bound to Er, it is highly probable that during these relatively short annealing periods the implanted Si surface may not have fully reached 900°C. On the other hand, the scenario which considers only Er within $Er_nO_{m \geq 2}$ clusters as being off the T sites (dotted lines) is clearly not in accordance with the experimental data.

Fig. 1. The data points are the fractions of ^{167m}Er atoms which are left on near-T sites in CZ Si as a function of isothermal annealing time at 900°C, observed by emission channeling experiments in samples with an oxygen concentration of $6.5\text{--}6.6 \times 10^{17} \text{ cm}^{-3}$. Solid lines: fractions of Er remaining outside $Er_nO_{m \geq 1}$ clusters calculated for four different Er+Tm peak concentrations according to the model described in the text; dashed lines: the same for all Er remaining outside $Er_nO_{m \geq 2}$ clusters.

The simulations confirm that the cluster distributions depend strongly on the processing conditions. In order to illustrate different scenarios, Fig. 2 displays calculated fractions of Er_nO_m clusters for three different sample treatments. For instance, annealing of the high-dose implanted sample F for 1800 s should favor mainly Er-rich clusters [Fig. 2(a)]. On the other hand, a short 120 s anneal of sample B

should produce mainly O-rich clusters but still leave a relatively high amount (23%) of isolated Er [Fig. 2(c)]. An intermediate situation is suggested for typical processing conditions which are used to optimize the luminescence output of Er implanted CZ Si, such as described in Ref. [12] (2 MeV implantation, $[Er]_{\max} = 3.5 \times 10^{18} \text{ cm}^{-3}$, $[O] = 1.8 \times 10^{18} \text{ cm}^{-3}$, 900°C for 1800 s). The simulator indicates 75% of Er bound in clusters with O, 19% in pure Er clusters and only 6% of free Er [Fig. 2(b)]. If we do not allow for Er_n cluster formation, as would be the case if these small clusters were unstable, 13% of Er would remain isolated.

Fig. 2. Calculated distribution of Er_nO_m clusters for three different processing conditions using the model described in the text.

Note that we have in all cases assumed that at maximum 6 O atoms can be bound to one Er atom. The high amount of Er within Er_1O_6 clusters reflects this boundary condition. From theoretical considerations it has been suggested that Er_1O_6 defects with Er on a hexagonal (H) site with respect to the Si lattice are particularly stable. In order to check whether such defects are produced in substantial amounts, we have annealed sample B for a total of 2000 s at 900°C , which should result in the formation of Er_nO_m complexes with an O/Er ratio of 5.9. However, we only obtained flat electron emission patterns and thus did not find any indication for a preferred lattice site of Er.

Discussion

The results presented above have shown that the onset of O diffusion is of vital importance in producing complexes of Er and O. Concerning the Er lattice location following implantation and annealing, the emission channeling experiments with ^{167m}Er suggest three main structural stages, which are distinguished by the amount of remaining lattice damage and the possibilities for Er_nO_m complex formation. In the following we will discuss these three stages in comparison with the results of other techniques which have investigated Er implanted Si samples.

a) The as-implanted state of Er. This situation is characterized by isolated Er atoms in defect-rich surroundings. For the lowest doses used in our studies ($4\text{--}6 \times 10^{12} \text{ cm}^{-2}$ at 60 keV) we found already about 70% of Er close to tetrahedral interstitial sites (T) [13], with a mean displacement of $0.42 \text{ \AA}$ from the T site. As already remarked before [8, 13, 16], the displacement of $0.42 \text{ \AA}$ can also be interpreted as a mixture of several sites in the range 0 to $\approx 0.6 \text{ \AA}$ from the T sites. Tetrahedral interstitial sites have also been predicted by theory to be the most stable sites for isolated Er in Si [11, 18, 19]. With increasing dose the observable near-T fraction decreases due to accumulation of damage. No difference is found between oxygen-rich CZ Si ($[O] \approx 10^{17}\text{--}10^{18} \text{ cm}^{-3}$) and oxygen-lean float zone (FZ) Si ($[O] \approx 10^{15}\text{--}10^{16} \text{ cm}^{-3}$). This is also indicated by extended X-ray absorption fine structure (EXAFS)

experiments on Er and O co-implanted samples. Even following 30 min of annealing at 450°C, the surroundings of Er were still dominated by 6 ± 2 nearest neighbor (NN) Si atoms [9]. Due to the remaining implantation damage, which forms efficient recombination centers for electrons and holes, luminescence from as-implanted samples is weak.

b) Recrystallization at 600-700°C. At these temperatures the implantation damage recovers to a large extent, resulting in more or less 80-100% of Er on near-T sites. The fact that we observe no difference between CZ and FZ Si [8, 13] is in agreement with the low O and Er mobilities at 600°C and the small O/Er ratio of 0.02-1 in our CZ samples. Substantial formation of Er_nO_m complexes does not take place, and we suggest that in both CZ and FZ Si at low Er concentrations mainly isolated Er exists, however, in an environment where not all defects have been removed. It has been reported that the photoluminescence (PL) of FZ and CZ samples annealed at 600°C showed similar intensity [1, 7] and even in the case of CZ Si annealed at 700°C was dominated by Er centers of cubic symmetry and a number of centers with lower than axial symmetry [7]. The cubic centers were attributed to isolated Er on T sites, while the low-symmetry Er-centers were ascribed to complexes with implantation-induced defects [7]. Exceptions are samples co-implanted with high doses of Er and even higher doses of O (O/Er $\approx$ 10 or greater). In these samples Er_nO_m clusters can already form during solid phase epitaxial regrowth, especially if the crystals have been amorphized during implantation [5]. This is due to the increased mobility of Er at the crystalline-amorphous interface. EXAFS analyses of FZ Si co-implanted with 10^{19} Er cm $^{-3}$ and 10^{20} O cm $^{-3}$ have observed 3 ± 2 NN Si and 4.4 ± 0.6 NN O atoms following recrystallization of the amorphized samples at 620°C for 3 h [9]. Electron paramagnetic resonance (EPR) of the same samples revealed several signals of trigonal and monoclinic symmetry, which were attributed to complexes including Er and O [15].

c) High temperature annealing. At 900°C the diffusivity of Er is moderate while that of O is high. We believe that in CZ Si the high-temperature annealing results in a mixture of various Er_nO_m clusters with Er on different lattice sites. Since emission channeling can not resolve such a mixture of sites, we simply observe random sites. Although we have some indication that in the case of FZ Si the disappearance of near-T Er is due to Er out-diffusion to the surface, occurring on a time scale of hours, the underlying processes are not yet fully understood. A key question, to be answered by future studies, is whether small Er_n clusters are actually formed, and which lattice sites Er might occupy in these complexes.

CZ Si samples implanted with Er resulting in O/Er ratios around 1 generally show an increase of the Er luminescence following annealing for not too long time periods (30 s -30 min) at 900°C. Usually the luminescence in such samples is still dominated by the cubic Er centers, while at the same time additional non-cubic, axial-symmetric Er centers increase in concentration [4, 7, 10, 12, 15]. The axial-symmetric Er centers are ascribed to ErO complexes [7]. In our opinion, the fact that the cubic PL signal increases in the presence of O, too, does not contradict our observation that Er is removed from T sites by reacting with one or more O atoms. It rather points out that there are additional mechanisms for O to enhance the Er luminescence, which are not due to the formation of optically active Er_nO_m centers. One such mechanism, which has already been suggested in the literature, is O passivation of Er-implantation-related recombination levels [6, 7]. This additional role of O is also evidenced by the fact that the Si near-band-edge luminescence, which is not directly related to Er, was found to increase in the presence of oxygen [5, 7].

A direct proof that Er acts as an efficient O getter comes from the EXAFS analyses of CZ Si which was implanted with 5×10^{17} Er cm $^{-3}$ and annealed at 927°C for 30 min [3], and from EXAFS of amorphized FZ Si co-implanted with 10^{19} Er cm $^{-3}$ and 10^{20} O cm $^{-3}$ and annealed at 900°C for 30 s [9]. Under these conditions the Er neighborhood was characterized by 6 NN O atoms, and 5.1 ± 0.5 NN O atoms, respectively.

Following prolonged annealing at 900°C, e.g., for 60 h, especially with high O concentrations (O/Er $\approx$ 10), the Er PL spectra lose their sharp line features, giving way to a broad band luminescence at 1.54 μm , which was attributed to large ErO clusters [4].

Conclusions

In summary, we have shown that in CZ Si the fraction of Er which is removed from near-T sites shows a good correlation with the amount of O that can be delivered by the bulk of the wafers during the time of annealing. One O atom per Er_nO_m cluster is sufficient to remove Er from near-T sites. The structural properties which characterize the three different stages of Er-implanted Si samples (as-implanted, recrystallized, and high-temperature-annealed) have been discussed.

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