The influence of oxygen on the lattice sites of rare earths in silicon

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Abstract

We have used conversion electron emission channeling to investigate the lattice sites of ^{167m}Er following implantation of the radioactive isotope ^{167}Tm into CZ Si and FZ Si at varying doses (6×10^{12} - $5 \times 10^{13} \text{ cm}^{-2}$). In all cases isothermal annealing at 900°C caused Er to leave its preferred near-tetrahedral sites in favour of random lattice sites, but this process occurred by orders of magnitude faster in CZ Si. Furthermore, in CZ Si the incorporation of Er on random lattice sites was fastest in samples implanted with low doses of Tm+Er. We compare our experimental results to a simple numerical model which accounts for the diffusion of Er and O and the formation of Er_nO_m complexes. On the basis of this model, our experimental data indicate that only a few (probably between 1 and 2) O atoms are required in order to remove an Er atom from its tetrahedral site.

keywords: Si, Er, lattice location, Er diffusion, Er-O interaction

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1. Introduction

The beneficial influence of oxygen on the luminescence properties of erbium in Si has been known for a couple of years [1]. Good optical activation of Er may be obtained, e.g., by Er implantation into O-rich Si (CZ Si or O co-doped Si) followed by annealing at high temperatures (900 - 1000°C). Extended X-ray absorption fine structure (EXAFS) experiments [2,3] have shown that this procedure results in the majority of Er within Er_2O_3 -like surroundings, while Er implantation into oxygen-lean FZ Si produces an ErSi_2 -like neighbourhood. On the other hand, transmission electron microscopy (TEM) has revealed the formation of precipitates in both Er implanted CZ and FZ Si annealed at 900°C [4]. While the exact mechanisms of how O enhances the luminescence yield of Er are still a matter of debate, the binding of O to Er can be regarded as well-proven. As a complementary technique to EXAFS and TEM we use conversion electron emission channeling from the radioactive nucleus ^{167m}Er in order to characterize the structural properties of Er in Si [5-9]. While EXAFS investigates the immediate neighbourhood of the Er atoms and TEM visualizes the crystalline quality on a nanoscale, emission channeling measures the position of the Er nucleus with respect to the lattice of a single crystal.

2. Experimental results

In order to introduce ^{167m}Er into Si, we implant the radioactive isotope ^{167}Tm ($t_{1/2}=9.25 \text{ d}$) which decays into ^{167m}Er ($t_{1/2}=2.28 \text{ s}$). In this case the thermal processing always affects a mixture of Tm and Er but lattice localization is uniquely done on Er. The chemical similarity of both rare earth elements, however, should allow us to draw conclusions on the behaviour of Er in Si as such. Still it should be kept in mind that if in the following we speak of Er concentrations, Er doses, Er_n complexes etc. this actually refers to a mixture of Tm and Er.

Following implantation of ^{167}Tm with doses from 6×10^{12} to $5 \times 10^{13} \text{ cm}^{-2}$ and annealing at 600°C , we find the majority of ^{167m}Er on near-tetrahedral interstitial (T) sites in both FZ and CZ Si [5,6]. For FZ Si, *in-situ* measurements at 900°C give direct evidence that ^{167m}Er even resides on these sites at that temperature [7]. Fig. 1 shows the fractions of ^{167m}Er remaining on near-T sites as a function of isothermal annealing time at 900°C for 4 FZ and 4 CZ Si samples implanted with different doses of ^{167}Tm [8], divided by the near-T fractions measured following annealing at 600°C (which were usually between 0.8 and 1). This normalization has been chosen in order to account for Er which is still (or already) in disordered surroundings following the recrystallization of the samples at 600°C . It is obvious that the near-T fractions in CZ Si decrease rapidly but only prolonged annealing of the order of hours is able to reduce them in FZ material. Furthermore, in CZ Si the rate of decrease is anti-correlated with the implanted dose, i.e. the stability on near-T sites is higher for samples implanted with a higher dose of Er. In FZ the trend is not so obvious. While so far this behaviour could only be qualitatively explained by the preferential formation of disordered rare earth silicide precipitates in FZ Si (e.g.

ErSi₂) and rare earth oxide precipitates in CZ Si (e.g. Er₂O₃), we have now developed a model on the basis of simple diffusion and capture kinetics of Er and O, which allows us to compare possible scenarios to the experimental data.

3. Model for Er_n and Er_nO_m cluster formation

We consider the formation of Er_n and Er_nO_m clusters by a diffusion-limited process, i.e. reaction rates which are given by the following expressions:

The diffusion coefficient D_{Ox} of oxygen is known to be $D_{\text{Ox}} = 0.13 \text{ cm}^2 \text{ s}^{-1} \times \exp(-2.53 \text{ eV}/kT)$. This has been established from the outdiffusion of O at temperatures above 700°C [10,11]. We do not consider the formation of O₂ dimers and higher-order O_m clusters, since these are unstable at 900°C [12]. The diffusion coefficient of Er at 900°C is around $D_{\text{Er}} \approx 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ [13]. Note that this is about three orders of magnitude lower than D_{Ox} at 900°C, which is $1.8 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$. We assume that all Er_n and Er_nO_m clusters are immobile. The capture radii, which are not very sensitive parameters in our scheme, were roughly estimated from the mean volume of the defects by $R_{\text{Er}(n)\text{Ox}(m)} = b (n+m)^{1/3}$, with $b = 2.35 \text{ Å}$ being the typical binding length in Si.

The coupled diffusion and capture equations for Er and O are then solved by the finite differences method using the fully explicit "forward-time centered space" (FTCS) approach, as outlined in Ref. [14]. For that purpose the concentrations $C_{\text{Er}(n)\text{Ox}(m)}$ of all desired Er- and O-containing defects are updated within finite time intervals Δt and depth intervals Δx . In addition to the rate of reactions (1a) to (1e), diffusional motion then causes changes in the Er and O concentrations according to

$$C(x, t+\Delta t) = C(x, t) + [C(x+\Delta x, t) + C(x-\Delta x, t) - 2C(x, t)] D\Delta t / (\Delta x)^2 \quad (2).$$

The boundary conditions at the surface can be freely chosen, e.g., as impermeable wall or perfect sink. The FTCS approach is easy to program and results in stable solutions if the time interval Δt is chosen so that the mean diffusion width $(2D\Delta t)^{1/2}$ is smaller than the bin width Δx [14]. We used $\Delta x = 10 \text{ Å}$ and hence time steps of $\Delta t = 2 \text{ ms}$ were adequate to properly describe both O and Er diffusion, while simulations considering only Er diffusion could be done with time steps of 1 s and are much faster. As starting point we used Gaussian depth profiles of Er at $x_0=336 \text{ Å}$ (FWHM 195 Å) resulting from 60 keV ion implantation, while initially constant O concentrations of 10^{16} cm^{-3} in FZ and 10^{18} cm^{-3} in CZ Si were assumed.

Let us first have a look at the FZ case. If we neglect completely any interactions of Er and consider the surface as a perfect sink, the dashed line in Fig. 1(a) shows the fraction of Er remaining in the bulk of the sample. In the emission channeling experiments we would then observe a somewhat steeper descent of this curve since the broadening of the Er profile would also increase the dechanneling of the emitted conversion electrons. This scenario is of course independent from the Er dose. On the other hand, let us assume that Er forms stable and immobile Er_n clusters. Then the two solid lines in Fig. 1(a) represent the Er fractions remaining outside the clusters for the highest ($2.4 \times 10^{19} \text{ cm}^{-3}$) and lowest ($2.7 \times 10^{18} \text{ cm}^{-3}$) Er peak concentrations, respectively. Note that both for the highest and lowest dose this process would result in approximately 63% of Er in Er₂, 25% in Er₃, 6% in Er₄ and only 2% in higher order clusters. Our experimental results therefore show that either these clusters are not formed at all or that Er still occupies the near-T sites within the clusters. In the latter case, a possible scenario would be that the small clusters dissolve again on time scales around 1000-10000 s, resulting in the formation of larger clusters and finally precipitation. Due to the variety of parameters required to describe this phenomenon (results are quite sensitive to the life time of the various Er_n clusters, which are unknown) we consider it useless to follow it with our computational approach. We conclude that in the case of FZ Si, it is not obvious whether we have simple out-diffusion of Er or initially formed small Er_n clusters. More experimental data with different Er doses and implantation depths and also knowledge of the final Er depth profiles would help to clarify this point.

While the amount of O in FZ Si is so small that even ErO pair formation plays only a minor role, the situation is different in CZ Si. Due to the high Er peak concentrations, following an initial transient of ErO pairing the Er profile is practically depleted from most of its free O. Further O can then only be supplied by long-range diffusion from the bulk of the sample, i.e. we encounter O out-diffusion with the Er profile acting as a nearly perfect sink. A lower limit for the time t_{sat} in order to saturate a sheet density ϕ_{Er} of implanted Er atoms with m O atoms per Er atom can then be estimated by

$$t_{\text{sat}} > [(\phi_{\text{Er}} m / C_{\text{Ox}}) - x_0]^2 / D_{\text{Ox}} \quad (3).$$

Note that this simple estimate is not sensitive to the details of the Er-Er interaction, and hence does not depend on the possible formation and stability of, e.g., Er_2 , Er_3 etc. The solid and dashed lines in Fig. 1(b) show the calculated fractions of Er atoms which remain outside of $\text{Er}_n\text{O}_{m \geq 1}$ and $\text{Er}_n\text{O}_{m \geq n}$ complexes, respectively, for the four different Er peak concentrations. We have considered $n=1,2,3,4$ and $m=1,2,3,\dots,24$ but with the restriction $m \leq 6n$ (this allows at maximum 6 O atoms to be bound to one Er atom). If Er occupies different lattice sites within the various Er_nO_m clusters, once a variety of such clusters has formed it is very likely that this results in a more or less isotropic electron emission yield, which we would identify with Er on random lattice sites. Indeed, if we compare the calculated curves to the experimental fraction of Er atoms remaining on near-T sites, we see that most data points lie between or close to the lines for $m \geq 1$ and $m \geq n$. However, it is clear that we cannot derive exactly how many O atoms are required in order to remove Er from its tetrahedral site without knowing the exact O concentration of the samples. This is due to the fact that we calculate similar curves assuming an O concentration of, e.g., $2 \times 10^{18} \text{ cm}^{-3}$ instead of $1 \times 10^{18} \text{ cm}^{-3}$ and tracing the fraction of Er atoms within defects with $m \geq 2$ or $m \geq 2n$. Note that the simple estimate in eq. (3) also illustrates this behaviour since t_{sat} only depends on the ratio m/C_{Ox} . However, typical O concentrations in CZ Si are $1\text{--}2 \times 10^{18} \text{ cm}^{-3}$, and we therefore conclude that a small number of O atoms, most likely between one and two, is sufficient to remove an Er atom from its tetrahedral lattice site.

4. Conclusions

The amount of Er remaining on near-tetrahedral interstitial sites as a function of annealing time at 900°C shows pronounced differences between FZ and CZ Si. A simple numerical model has been presented in order to describe the reaction kinetics of diffusing O and Er. According to this model several scenarios have been compared to the experimental data. From this comparison we draw the following conclusions.

In the case of FZ Si we can not yet distinguish between the two possibilities that

- a) initially Er_n ($n = 2,3,4$) clusters are formed where Er still occupies near-T sites, and that these small clusters dissolve on the time scale of hours, resulting in the formation of larger clusters and precipitation; or that
- b) Er_n clusters have such a low probability of formation that we simply observe out-diffusion of Er to the surface.

In the case of CZ Si, however, the fraction of Er which is removed from near-T sites is clearly correlated to the amount of O which can be delivered by the bulk of the sample during the time of annealing. Our experimental data can be well understood assuming that only a few (probably between 1 and 2) O atoms are required in order to remove an Er atom from its tetrahedral site. More accurate information on the number of O atoms should be accessible by studying samples with a well-characterized O concentration.

References

- [1] J. Michel, J.L. Benton, R.F. Ferrante, D.C. Jacobson, D.J. Eaglesham, E.A. Fitzgerald, Y.H. Xie, J.M. Poate and L.C. Kimerling, *J. Appl. Phys.* 70 (1991) 2672.
- [2] D.L. Adler, D.C. Jacobson, D.J. Eaglesham, M.A. Marcus, J.L. Benton, J.M. Poate and P.H. Citrin, *Appl. Phys. Lett.* 61 (1993) 2181.
- [3] A. Terrasi, G. Franzo, S. Coffa, F. Priolo, F. D'Acapito and S. Mobilio, *Appl. Phys. Lett.* 70 (1997) 1712.
- [4] D.J. Eaglesham, J. Michel, E.A. Fitzgerald, D.C. Jacobson, J.M. Poate, J.L. Benton, A. Polman, Y.H. Xie and L.C. Kimerling, *Appl. Phys. Lett.* 58 (1991) 2797.
- [5] U. Wahl, A. Vantomme, J. De Wachter, R. Moons, G. Langouche, J.G. Marques, J.G. Correia, and the ISOLDE collaboration, *Phys. Rev. Lett.* 79 (1997) 2069.
- [6] U. Wahl, J.G. Correia, J. De Wachter, G. Langouche, J.G. Marques, R. Moons, A. Vantomme, and the ISOLDE collaboration, *Mat. Res. Soc. Symp. Proc.* 469 (1997).
- [7] U. Wahl, J.G. Correia, G. Langouche, J.G. Marques, A. Vantomme, and the ISOLDE collaboration, *Mat. Sci. Forum* 258-263 (1997) 1503-1508.
- [8] U. Wahl, J.G. Correia, G. Langouche, A. Vantomme, and the ISOLDE collaboration, *Mat. Res. Soc. Symp. Proc.* 486 (1998), in print.
- [9] U. Wahl, J.G. Correia, S. Cardoso, J.G. Marques, A. Vantomme, G. Langouche and the ISOLDE collaboration, *Nucl. Instr. Meth. B* 136-138 (1998) 744.
- [10] J.C. Mikkelsen, *Mat. Res. Soc. Symp. Proc.* 59 (1986) 19.
- [11] Landolt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology*, Vol. 22b, edited by M. Schulz (Springer, Berlin, 1989).
- [12] T. Hallberg, J.L. Lindström, L.I. Murin and V.P. Markevich, *Mat. Sci. For.* 258-263 (1997) 361.
- [13] F.Y.G. Ren, J. Michel, Q. Sun-Paduano, B. Zheng, H. Kitagawa, D. C. Jacobson, J. M. Poate and L. C. Kimerling, *Mat. Res. Soc. Symp. Proc.* 301 (1993) 87.

[14] W.H. Press, B.P. Flannery, S.A. Teukolsky and W.T. Vetterling, Numerical Recipes (Cambridge University Press, Cambridge, 1986).

Fig. 1: The single data points are the fractions of $^{167\text{m}}\text{Er}$ atoms which are left on near-T sites in Si as a function of isothermal annealing time at 900°C, observed by emission channeling experiments.

(a) FZ samples. Dashed line: maximum possible surface loss for the case of freely diffusing Er; solid lines: fractions of Er remaining outside Er_n clusters for the highest and lowest implantation dose according to the model described in the text.

(b) CZ Si. Solid lines: fractions of Er remaining outside $\text{Er}_n \text{O}_{m \geq 1}$ clusters calculated for the four different Tm+Er peak concentrations according to the model described in the text; dashed lines: the same for $\text{Er}_n \text{O}_{m \geq n}$ clusters.