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Thermal Donors in Silicon Implanted with Rare Earth Impurities

V.V. Emtsev Jr.[1], C.A.J. Ammerlaan[1], B.A. Andreev[2], G.A. Oganesyan[3], D.S. Poloskin[3], E.I. Shek[3] and N.A. Sobolev[3]

[1] Van der Waals-Zeeman Institute, University of Amsterdam, Valckenierstraat 65, NL-1018 XE Amsterdam, The Netherlands

[2] Institute for Physics of Microstructures, Russian Academy of Sciences, RU-603600 Nizhnyi Novgorod GSP-105, Russia

[3] Ioffe Physico-Technical Institute, Russian Academy of Sciences, RU-194021 St.-Petersburg, Russia

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Abstract. Effects of oxygen coimplantation on the formation process of donor centers in silicon implanted with rare earth ions, primarily erbium, are investigated. Three kinds of most important donor centers responsible for the electrical conductivity of implanted layers have been established. The results obtained correlate well with the defect identification made earlier.

Introduction

Some optical properties of erbium impurity ions in silicon, first of all the 1.54 μm photoluminescence band due to the *f-f* intrashell transitions, still give hope of their practical use in optoelectronics. Intense studies of optically active centers in Er implanted Si have been conducted for a long time; see for instance [1-3].

On the other hand, the electrical properties of Er-related centers, especially those determining the electrical conductivity of implanted layers at room and cryogenic temperatures, are also of deep interest. Recently it has been demonstrated [4-6] that three kinds of donor centers in Er doped Si with high oxygen contents, no matter float-zone Si coimplanted with Er and O ions (FZ-Si:Er:O) or Czochralski grown Si solely implanted with Er ions (Cz-Si:Er), are dominant after postimplantation annealing to T=700°C: shallow donors at $\leq E_C-$ 40 meV and deeper donor centers at $\approx E_C-$ 70 meV and $\approx E_C-$ 120 meV; see Fig 1. As is seen from the same figure, this is in contrast to the only kind of dominating deep donor centers at $\approx E_C-$ 200 meV found in FZ-Si:Er.

The shallow donor states in Er implanted Si with high oxygen contents are attributed to oxygen-related thermal donors. The involvement of intrinsic defects in their structures allow to survive these thermal donors even after annealing to T=900°C [6]. Deep donors at $\approx E_C-$ 70 meV and $\approx E_C-$ 120 meV were found to be [ErO]-related complexes, designated as *[ErO]-1* and *[ErO]-2* centers, respectively [5]; see also Fig. 1. The similar deep donor centers with slightly different ionization energies dependent on dopant species make their appearance in Cz-Si implanted with other rare earth impurities (Dy, Ho and Yb) [6].

At elevated temperatures of postimplantation annealing up to T=900°C the shallow thermal donors and *[ErO]-1* centers are still present, though in smaller concentrations. The *[ErO]-2* complexes are transformed to deeper donors at $\approx E_C-$ 140 meV, designated as *[ErO]-3* centers. The latter ones are believed to be somehow involved in the excitation process of the inner *f*-shells of Er ions; see for instance [2].

In the present paper the effects of oxygen coimplantation on the formation of oxygen-related donor centers in Si implanted with rare earth ions, primarily Er ions, are discussed in some detail. Special attention is placed on practically important cases of high doses of Er and O ions.

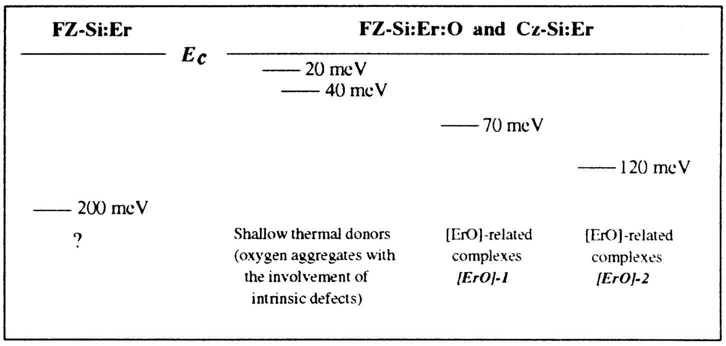

Fig. 1. Donor centers determining the electrical conductivity of FZ-Si and Cz-Si implanted with Er ions and annealed to T=700°C. The donor levels are shown in respect to the conduction band.

Experimental

As starting materials we used p-type Cz-Si wafers of $\rho \approx 20$ Ohm·cm. The initial oxygen concentrations were over a wide range, from $\approx 2 \cdot 10^{17}$ cm^{-3} to $\approx 1 \cdot 10^{18}$ cm^{-3}. In some cases n-type Si epilayers of $\rho \approx 20$ Ohm·cm were grown on low-resistivity p-type Cz-Si substrates and then implanted with Er ions.

Rare earth ions, mostly Er ions, were introduced by means of ion implantation at energies of 1.0 MeV to 1.2 MeV. The rare earth implantation dose Φ varied in the range of $5 \cdot 10^{11}$ cm^{-2} to $1 \cdot 10^{13}$ cm^{-2}. In the case of oxygen coimplantation the energy of oxygen ions was between 0.11 MeV and 0.18 MeV. The implanted samples were annealed at T=700°C for 30 min in a chlorine containing ambient. The radiation damage is mostly recovered at this annealing stage. At implantation doses $\Phi(\mathrm{RE}) \geq 5 \cdot 10^{11}$ cm^{-2}, the implanted layers of about 0.5 μm in thickness became n-type, even in the initially p-type Cz-Si samples. Under our experimental conditions the peak concentration of RE impurities at a maximal dose of $\Phi(\mathrm{RE}) = 1 \cdot 10^{13}$ cm^{-2} was about $3 \cdot 10^{17}$ cm^{-3}.

Electrical measurements of the electron concentration in implanted layers against temperature, *n (T)*, were taken with the help of the Van der Pauw technique over the temperature range from $T \approx 20$ K to $T \approx 300$ K. Analysis of the *n (T)* curves was carried out on the basis of the equations of charge balance [7,8]. Photoconductivity spectra of implanted layers at cryogenic temperatures were recorded in the range of 200 cm^{-1} to 800 cm^{-1} with the aid of an IFS-113V Bruker spectrometer. The resolution was 1 cm^{-1}.

Some implanted samples were subjected to 0.9 MeV electron irradiation at room temperature to produce A-centers (oxygen-vacancy complexes) for partial compensation of shallow donor states.

Results and Discussion

As an illustration, in Fig. 2 three *n(T)* curves are displayed for the FZ-Si epilayers coimplanted with Er and O ions. The Er dose was fixed at $\Phi(Er)=1\cdot10^{13}$ cm^{-2}, whereas the dose of oxygen coimplant was varied between $\Phi(Er)=5\cdot10^{13}$ cm^{-2} and $\Phi(Er)=5\cdot10^{14}$ cm^{-2}. In Fig. 3 the fragments of the same curves at 77 K$\leq T\leq$ 300 K are shown on an expanded scale.
Our analysis of all the *n(T)* curves revealed some interesting features of the donor formation processes in Er implanted layers.

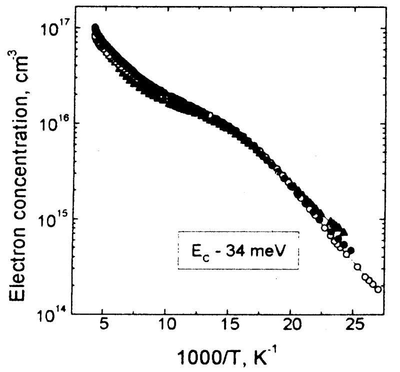

Fig. 2. Electron concentration against reverse temperature in the Fz-Si coimplanted with Er and O ions and annealed at T=700°C. Dose $\Phi(Er)=1\cdot10^{13}$ cm^{-2}. Dose $\Phi(O)=5\cdot10^{13}$ cm^{-2} (open circles), $1\cdot10^{14}$ cm^{-2} (solid circles) and $5\cdot10^{14}$ cm^{-2} (solid triangles). Concentration of shallow donors (open circles), $2.8\cdot10^{16}$ cm^{-3}.

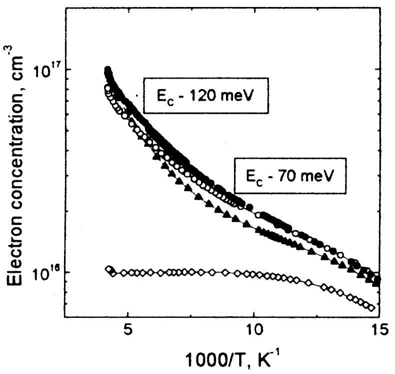

Fig. 3. Fragments of the *n(T)* curves shown in the Fig. 2. For comparison purposes, the electron concentration against reverse temperature in the same FZ-Si implanted solely with O ions at $\Phi(O)=5\cdot10^{14}$ cm^{-2} and annealed at T=700°C is also given (open diamonds). Concentration of *[ErO]-1* centers (open circles), $2.5\cdot10^{16}$ cm^{-3}. Concentration of *[ErO]-2* centers (open circles), $1.0\cdot10^{17}$ cm^{-3}.

First, the concentration of shallow thermal donors in Cz-Si with high oxygen concentrations, about $1\cdot10^{18}$ cm^{-3}, turned out be nearly proportional to the Er implantation dose at $\Phi(Er)\leq5\cdot10^{12}$ cm^{-2}. This observation correlates well with our earlier conclusion [6] that the intrinsic defects produced by Er ions play a leading role as nucleation sites of oxygen aggregates (shallow thermal donors). In this way the shallow thermal donors are stabilized as compared to those usually formed during oxygen precipitation processes in conventional Cz-Si at T=700°C: cf [9] and [10]. However, their concentration tends to saturate at $\Phi(Er)>5\cdot10^{12}$ cm^{-2}. The damage produced by oxygen ions is not so important for the formation of shallow thermal donors. In actual fact, the total concentration of shallow donors is close to $3\cdot10^{16}$ cm^{-3} at $\Phi(O)=5\cdot10^{13}$ cm^{-2} and $1\cdot10^{14}$ cm^{-2}, whereas at $\Phi(O)=5\cdot10^{14}$ cm^{-2} it even drops by 20 per cent. This slight decrease may be associated with increasing formation rate of electrically inactive oxygen precipitates in oxygen-rich samples.
It is instructive to compare the formation processes of donors in FZ-Si:Er:O and FZ-Si:O; see Fig. 3. From this figure, the key role of Er ions in the formation of donor states at $\approx E_C-$ 70 meV and $\approx E_C-$ 120 meV is evident, thus confirming their nature as [ErO]-related complexes. (It should be remind that in FZ-Si:Er, i e without oxygen, these centers are lacking [6]). The enhanced production of

shallow thermal donors in Er implanted layers is also clearly seen. This observation is consistent with the conclusion concerning the involvement of intrinsic defects in oxygen agglomeration processes. What is more, the shape of the *n(T)* curve for the FZ-Si:O in Fig. 3 is characteristic for the ionization of one kind of shallow thermal donors, similar to those formed in FZ-Si:Er:O.

Second, the shallow thermal donors under discussion, like similar donor species formed during heat treatment of conventional Cz-Si at T<700°C, are distributed over their ionization energies from ≈40 meV to ≈25 meV, the gravity center being placed at ≈40 meV. This is evident from the analysis of low-temperature portions of *n(T)* curves whose slope changes over the interval given above with increasing Er dose. To prove this model is possible by partial compensation of shallow donors due to deep acceptors, e g vacancy-oxygen complexes (A-centers at $\approx E_C-$ 170 meV [11]) formed in Er implanted Si layers as a result of fast electron irradiation. By way of illustration, in Fig. 4 the compensation effect of electron irradiation on the shallow thermal donors in Cz-Si:Er:O is demonstrated. Moreover, the quantitative analysis showed that the distribution of these donors as well as the concentrations of Er-related deep donor centers do not change noticeably after irradiation, so the whole *n(T)* curves can be satisfactory described by changing the concentration of A-centers only; see Fig. 4.

Third, our photoconductivity measurements on Ho-implanted layers revealed the presence of Double

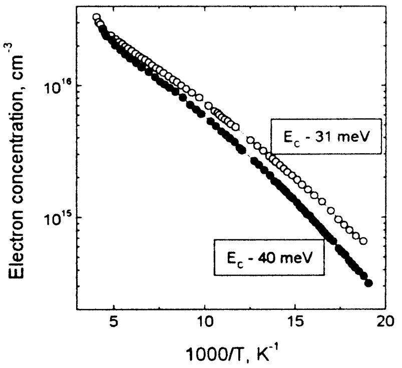

Fig. 4. Electron concentration against reverse temperature in the Cz-Si:Er before (open circles) and after fast electron irradiation (solid circles). Dose Φ(Er)=$1\cdot10^{13}$ cm^{-2}. Postimplantation annealing was performed at T=700°C. After the implantation and annealing the Er-doped layer was irradiated with 0.9 MeV electrons at a dose $1\cdot10^{17}$ cm^{-2}.

Thermal Donors (TDDs); see Fig 5. Their concentration is roughly estimated to be about 10^{15} cm^{-3}. This family of thermal donor states at $\approx E_C-$ 70 meV and $\approx E_C-$ 140 meV makes its appearance in conventional Cz-Si during heat treatment at T≤500°C; see for instance review paper [12]. They are known to be unstable above T=600°C. After annealing of Ho implanted layers to T=700°C one could expect to detect the presence of TDDs in trace concentrations only, about 10^{13} cm^{-3}. At present we are conducting similar photoconductivity measurements on Er implanted layers in the hope to estimate the TDD concentration in reference to that of phosphorus.

Let's turn now to the [ErO]-related complexes. With increasing dose of Er ions the concentrations of *[ErO]-1* and *[ErO]-2* centers, averaged over a set of Cz-Si:Er samples, increase nearly proportional to Φ(Er). The oxygen coimplantation at Φ(O)=$5\cdot10^{13}$ cm^{-2} and $1\cdot10^{14}$ cm^{-2} produces little effects on the concentrations of *[ErO]-1* centers in the layers implanted at Φ(Er)= $1\cdot10^{13}$ cm^{-2}; see also Fig. 3. With further increase in the oxygen coimplantation dose the concentration of *[ErO]-1* centers drops noticeably. This effect can be seen in Fig. 3 in the temperature range where the strong ionization of *[ErO]-1* centers takes place, at around 1000/T=7.5. In contrast, the concentration of *[ErO]-2* centers increases by a factor of two over the dose range of $5\cdot10^{13}$ cm^{-2}≤Φ(O)≤$5\cdot10^{14}$ cm^{-2}. The

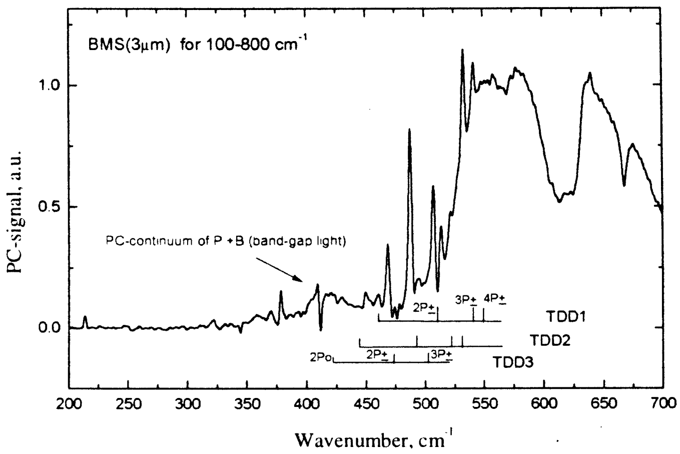

Fig. 5. Photoconductivity spectrum in the Cz-Si:Dy. Dose $\Phi(Dy)=1\cdot10^{13}$ cm^{-2}. Postimplantation annealing was performed at T=700°C. The spectrum was recorded at T≈30 K under bandgap illumination. Three species of Thermal Double Donors are identified.

underlying defect reactions leading to such different behavior should await their microscopic identification.

Summary

The information gained in the present work provides additional strong support for our earlier identification of donor centers in Si implanted with rare earth impurities, first of all erbium.
The formation kinetics of shallow thermal donors as well as [ErO]-related donor centers is studied. The contribution of each kind of the above-mentioned donors with ionization energies less than 0.15 eV to the electrical conductivity of Er implanted layers has been established.
Previously it was shown by DLTS on Er implanted Cz-Si [2] that the contribution of deep centers with activation energies larger than 0.14 eV to the electrical conductivity of implanted layers is insignificant. In this way the general picture of main electrically active centers associated with implantation of rare earth ions in Si is emerged.

Acknowledgments

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