Oxygen and erbium related donor centers in Czochralski grown silicon implanted with erbium

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Hall effect measurements were conducted on Czochralski grown silicon after implantation of erbium and two step annealing at 700°C and 900°C. At the first step the formation of oxygen-related shallow donors at $E_c - 20 \ldots 40$ meV as well as erbium-related donor centers at $\approx E_c - 70$ meV and $\approx E_c - 120$ meV is observed. Along with the same oxygen-related shallow thermal donors and donor centers at $\approx E_c - 70$ meV, other donor centers at $\approx E_c - 150$ meV are formed following the 900°C anneal, instead of those at $\approx E_c - 120$ meV. The new donor states are of keen interest because of their possible involvement in the photoluminescence process. The obtained results for erbium-implanted silicon are compared to some fragmentary DLTS data available in current literature on the donors with ionization energies less than 0.2 eV.

Studies of erbium impurity in silicon aim to produce the impurity-related centers with a strong luminescence band at $1.54\,\mu$m. To realize this goal is possible by investigating electrical and optical properties of Er-related centers. Implantation of Er is widely used for the doping of Si. Postimplantation annealing of Si : Er at $T \geqslant 600$°C is needed to remove the radiation damage and activate Er-related centers. In Si implanted with Er, many deep centers with activation energies larger than ≈ 0.2 eV have been studied by means of DLTS most extensively; see for instance [1–3]. In contrast, the information available in current literature about shallow donor centers is meager [1]. The purpose of this communication is to present electrical data on these centers responsible for the electron conductivity of Si : Er at cryogenic and room temperatures.

Wafers of carbon-lean Czochralski-grown silicon (*Cz*-Si) with high oxygen contents ($\approx 10^{18}$ cm^{-3}) were used; the conversion factor for the well-known absorption band of oxygen at 1108 cm^{-1} was taken according to ASTM F 121-83 ($2.45 \cdot 10^{17}$ cm^{-2}). The boron concentration in the starting materials of *p*-type was in the range from $3 \cdot 10^{14}$ cm^{-3} to $2 \cdot 10^{15}$ cm^{-3}. Er ions at 1.2 MeV were implanted in Si at doses Φ(Er) ranged from 10^{11} cm^{-2} to 10^{13} cm^{-2}, i.e. beyond the onset of amorphization of the implanted layers. In some cases, the oxygen concentration in the samples subjected to Er implantation was increased by co-implantation of oxygen ions at 0.17 MeV. The implantation dose of oxygen was always an order-of-magnitude higher than that of the erbium, i.e. $\Phi(\mathrm{O}) = 10\Phi(\mathrm{Er})$. All samples were then annealed in two successive steps at 700°C and 900°C for 30 min in a chlorine containing ambient. Electrical measurements were taken after each annealing step. Most of the radiation damage due to ion implantation is removed at the first step. The annealing at $T = 900$°C is used for the formation of the well-known centers with light emission at $\approx 1.54\,\mu$m; see for instance [4]. This two-step annealing makes possible observing most pronounced modifications of donor centers in the temperature range of current interest. After the first annealing step the Er-implanted layers of about $0.5\,\mu$m became *n*-type with the exception of those at $\Phi(\mathrm{Er}) = 10^{11}$ cm^{-2}. Under our experimental conditions, the Er peak concentration was $3 \cdot 10^{17}$ cm^{-3} at a largest dose of $\Phi(\mathrm{Er}) = 10^{13}$ cm^{-2}. Electrical measurements of the concentration of free electrons in the implanted layers *vs* temperature, $n(T)$, were conducted by means of the Van der Pauw technique over the temperature range from $T = 20$ K to $T = 300$ K. Analysis of the $n(T)$ curves was carried out on the basis of the relevant electroneutrality equations.

Annealing of *Cz*-Si : Er at $T = 700$°C

At $\Phi(\mathrm{Er}) = 10^{11}$ cm^{-2} the Er-implanted layers remain *p*-type, even for the nominally undoped *Cz*-Si. It allows us to estimate the total concentration of shallow donors, being less than $3 \cdot 10^{14}$ cm^{-3} at this low dose. Starting from $\Phi(\mathrm{Er}) = 5 \cdot 10^{11}$ cm^{-2} the donor concentration due to the Er implantation is well in excess to overcompensate the boron acceptors available in the starting materials; see Fig. 1. Analysis of the $n(T)$ curves for Φ(Er) ranged from $5 \cdot 10^{11}$ cm^{-2} to 10^{13} cm^{-2} permitted us to separate and identify three kinds of donors with activation energies less than 0.2 eV.

The donor states of the first kind are shallow, with ionization energies less than 50 meV. They are very similar to the oxygen-related shallow donors formed in *Cz*-Si [5] and *Cz*-Si doped with Mg [6] during heat treatment at $T \geqslant 600$°C–700°C. In both cases [5,6] these small oxygen aggregates in *Cz*-Si are distributed over the ionization energy interval from ≈ 20 meV to ≈ 40 meV, the maximum of their distribution always being placed at around 40 meV. It has been found that a simplified model of two donor levels at $E_1 \leqslant E_c - 30$ meV and $E_2 \approx E_c - 40$ meV used in calculations of $n(T)$ curves can be a reasonable substitute for the real donor distribution. This is just the case for *Cz*-Si : Er, too. For all the samples studied in this work, the

calculated $n(T)$ curves fit the experimental ones at $T \leqslant 80\,\mathrm{K}$ using a similar two-level model; see for instance Fig. 1. This invites us to conclude that the nature of the shallow donors in *Cz*-Si : Er is akin to the nature of oxygen-related shallow donors in *Cz*-Si, originating from oxygen aggregation at high temperatures [5,6]. However, there are some distinctions in their behavior in the implanted layers, because the formation of oxygen-related donors takes place in the presence of implantation-induced native defects in sizable concentrations. These defects can serve as nucleation sites for oxygen atoms. In actual fact, the total concentration of shallow donors turned out to be dose-dependent; see Fig. 2. The involvement of native defects in oxygen aggregation appears to contribute to higher thermal stability of the shallow donors as well as their larger production rate as compared to those formed under the "pure" heat treatment conditions; cf [5] and present work. The question of whether a fraction of the Er atoms, perhaps in complex form, may be included in the electrically active core of shallow donors at $E_c - (20 \div 40)$ meV is still open.

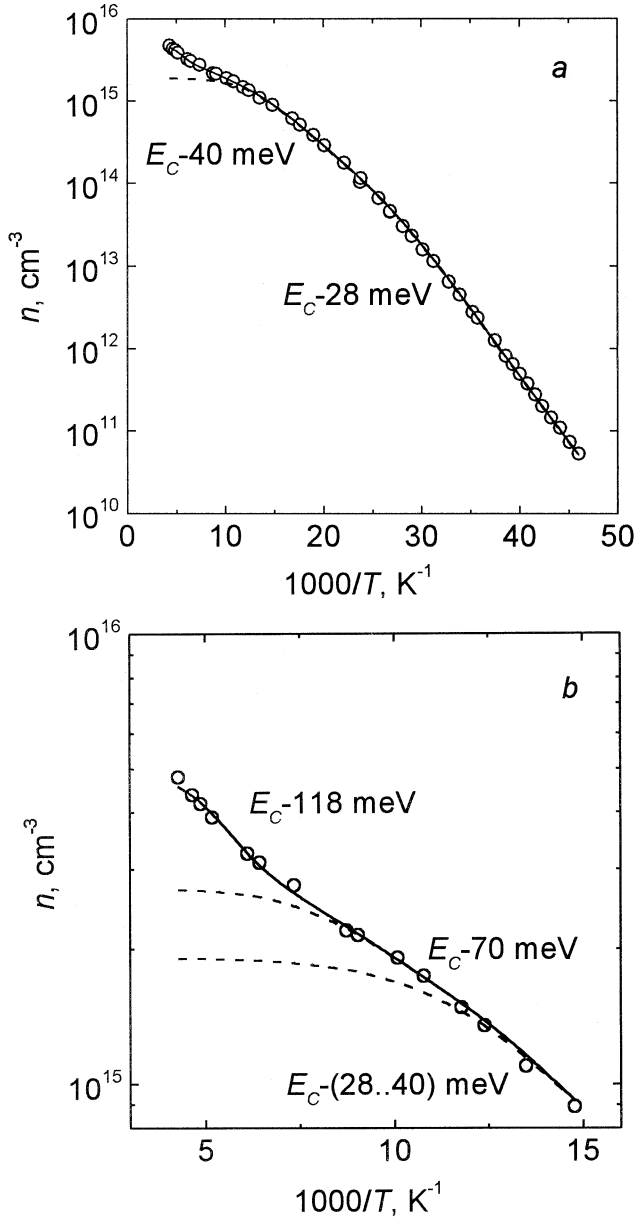

Figure 1. Electron concentration *vs* reciprocal temperature for *Cz*-Si implanted with Er and annealed at $T_{\mathrm{ann}} = 700^{\circ}\mathrm{C}$. $\Phi(\mathrm{Er}) = 5 \cdot 10^{11}\,\mathrm{cm}^{-2}$. Points, experimental; curves, calculated. The $n(T)$ curve at $T \geqslant 70\,\mathrm{K}$ is shown on the expanded scale in figure *b*. Contributions of the donor centers at the saturation plateau are given by dashed lines.

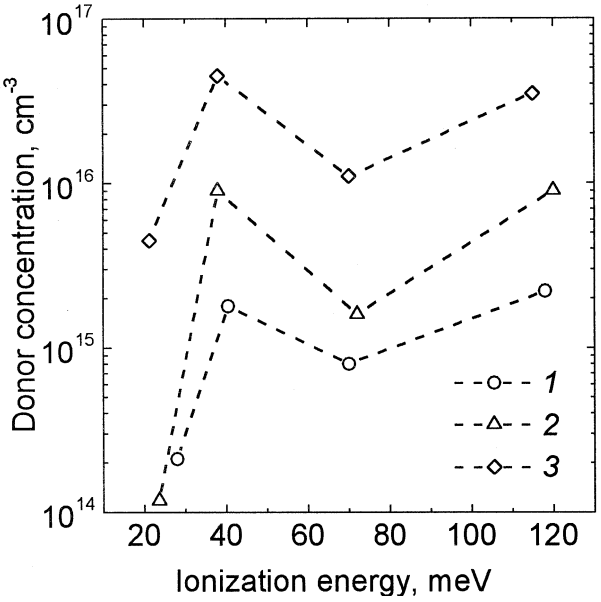

Figure 2. Donor concentrations *vs* ionization energies for *Cz*-Si implanted with Er and annealed at $T_{\mathrm{ann}} = 700^{\circ}\mathrm{C}$. Implantation dose $\Phi(\mathrm{Er})$, $10^{11}\,\mathrm{cm}^{-2}$: *1* — 5, *2* — 10, *3* — 100; implantation dose $\Phi(\mathrm{O})$, cm^{-2} : *1, 2* — 0, *3* — 10^{14}. Dashed lines are shown as a eye's guide only.

The donor centers of the second kind are well characterized by a single ionization energy of 70 ± 2 meV (Fig. 1). Their concentration was found to be dependent on the Er dose; see Fig. 2. Our claim that these donor centers are Er-related has been substantiated by the observation that the doping of the same material with Ho and Yb gives rise to the appearance of other donor centers at $\approx E_c - 60$ meV and $\approx E_c - 80$ meV, respectively [7]. As in the case of *Cz*-Si : Er, the oxygen aggregation at $T = 700^{\circ}\mathrm{C}$ also takes place in *Cz*-Si : Dy, Ho, and Yb and the formation of oxygen-related shallow donor states with ionization energies less than 50 meV is observed [7].

Besides the donors of two kinds given above, additional donor centers at $E_c - (118 \pm 5)$ meV have been found in *Cz*-Si : Er; see Fig. 1. Based on the Fermi level position most reliable estimations of their concentration can be made for the samples implanted at $\Phi(\mathrm{Er}) \leqslant 10^{12}\,\mathrm{cm}^{-2}$. At larger doses such estimates are less accurate in energies and concentrations. Again, the position of similar donor states in *Cz*-Si : Ho and *Cz*-Si : Yb is different by $\Delta \geqslant 15$ meV [7] in respect to that in *Cz*-Si : Er. Consequently, these donor centers appear to be impurity-related.

So far, DLTS measurements on *Cz*-Si : Er have provided some detailed information only for centers with activation energies greater than 0.15 eV [3].

Annealing of *Cz*-Si : Er at $T = 900^\circ$C

At elevated temperatures of the postimplantation annealing some pronounced changes in the donor formation occur; see Fig. 3 and Fig. 4. First, though the formation of shallow donor states at $E_c - (20 \div 40)$ meV is also observed, they are formed in appreciable concentrations at heavier doses $\Phi(\mathrm{Er}) \geqslant 10^{12}\,\mathrm{cm}^{-2}$ as compared to *Cz*-Si : Er after the 700°C anneal; cf Fig. 1 and Fig. 3. Second, we couldn't detect the presence of donor states at $\approx E_c - 120$ meV. Instead, new donor states at $E_c - (145 \pm 5)$ meV are developed in *Cz*-Si : Er annealed at $T = 900^\circ$C (Fig. 3). As is seen from Fig. 2 and 5, the concentration of these new donor states is comparable to that of donors at $\approx E_c - 120$ meV formed at $T = 700^\circ$C. This is a marked characteristics of the erbium impurity, because similar donor centers at $E_c - 105$ meV in *Cz*-Si : Dy and *Cz*-Si : Ho were found to be stable at $T = 700^\circ$C and $T = 900^\circ$C [7].

Unfortunately, some yet incomplete DLTS data on centers with activation energies less than ≈ 0.15 eV are available for Si : Er in [1–3]. In Si : Er after implantation and annealing at $T = 900^\circ$C the appearance of centers with an activation energy of about 0.15 eV has been observed by means of DLTS; see for instance [1–3]. Generally, this activation energy estimated on the basis of data recorded under non-equilibrium conditions cannot be considered as the true ionization energy of these centers at equilibrium [1].

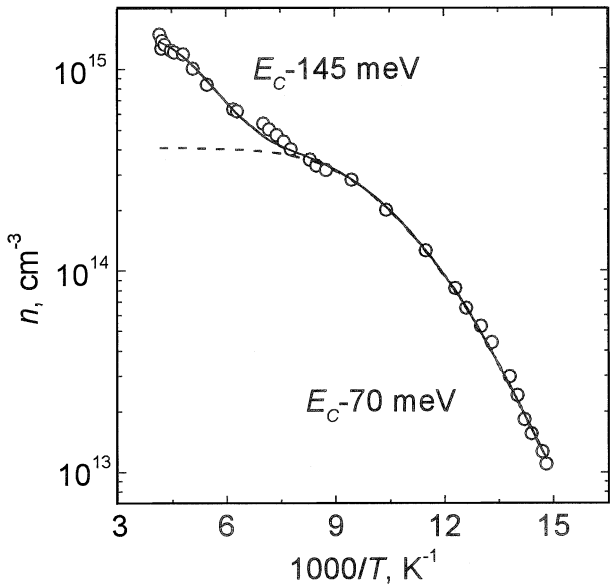

Figure 3. Electron concentration *vs* reciprocal temperature for *Cz*-Si implanted with Er and annealed at $T_{\mathrm{ann}} = 900^\circ$C. $\Phi(\mathrm{Er}) = 5 \cdot 10^{11}\,\mathrm{cm}^{-2}$. Points, experimental; curves, calculated. The contribution of donor centers at $E \approx E_c - 70$ meV at the saturation plateau is shown by dashed line.

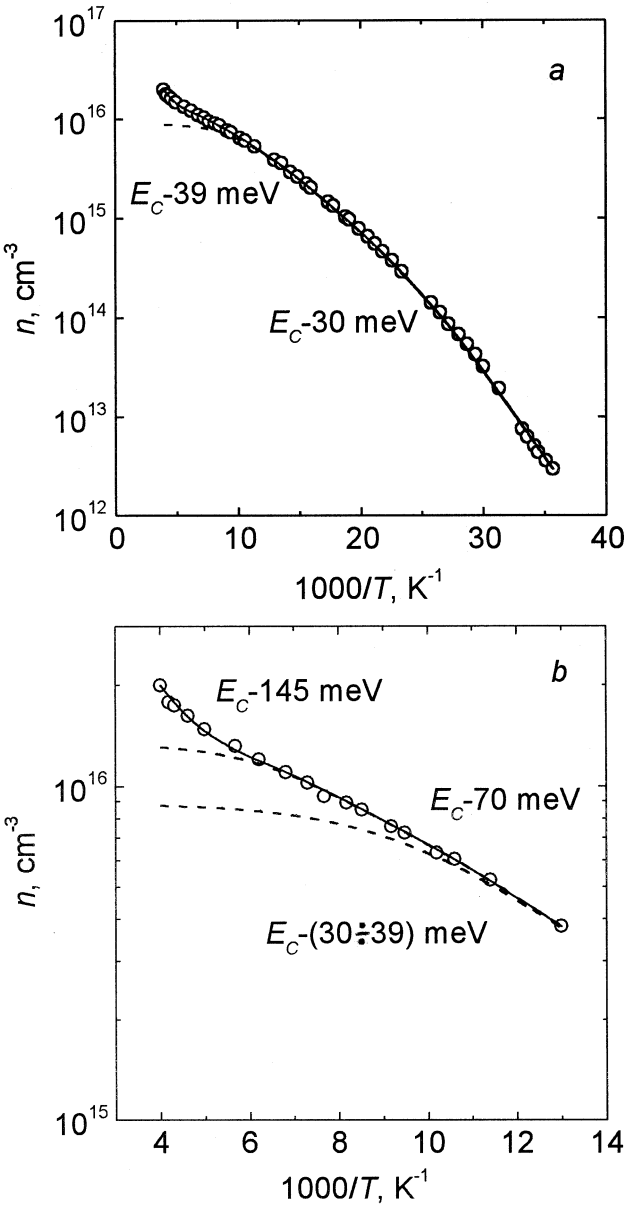

Figure 4. Electron concentration *vs* reciprocal temperature for *Cz*-Si implanted with Er and annealed at $T_{\mathrm{ann}} = 900^\circ$C. $\Phi(\mathrm{Er}) = 10^{12}\,\mathrm{cm}^{-2}$. Points, experimental; curves, calculated. The $n(T)$ curve at $T \geqslant 70$ K is shown on the expanded scale in figure *b*. Contributions of the donor centers at the saturation plateau are given by dashed lines.

Therefore, it is still an open question whether one deals with the same centers while carrying out DLTS and Hall effect measurements. According to [2,3], the centers with an activation energy of 0.15 eV are formed in noticeable concentrations only in Si subjected to coimplantation with erbium and oxygen. Reportedly, in *Cz*-Si : Er without coimplantation of oxygen they are not formed at all [2] or barely observable [3]. Under our experimental conditions, the formation of donor centers at $E_c - (145 \pm 5)$ meV was readily detectable in all cases, independent of whether coimplantation of oxygen in *Cz*-Si was used or not; see Fig. 5.

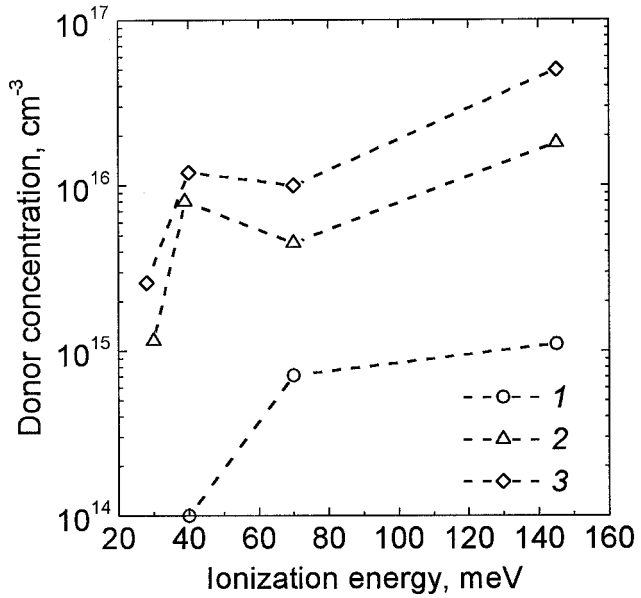

Figure 5. Donor concentrations *vs* ionization energies for *Cz*-Si implanted with Er and annealed at $T_{ann} = 900^\circ$C. Implantation dose Φ(Er), 10^{11} cm^{-2}: *1* — 5, *2* — 10, *3* — 100; implantation dose Φ(O), cm^{-2}: *1*,*2* — 0, *3* — 10^{14}. The sample implanted at $\Phi(\mathrm{Er}) = 10^{13}$ cm^{-2} and $\Phi(\mathrm{O}) = 10^{14}$ cm^{-2} was cut from another *Cz*-Si wafer with low oxygen concentrations (about $2 \cdot 10^{17}$ cm^{-2}). Dashed lines are shown as a eye's guide only.

In a recent paper [8] the nonradiative decay of the excited Er^{3+} ions in *Cz*-Si:P:Er at very low temperatures, at $T \leqslant 30$ K for the most part, is discussed in terms of the Auger impurity process with the energy transfer to free electrons; see also [9]. In the temperature range of interest, free electrons are claimed to be released from shallow donor centers at $\approx E_c - 20$ meV [8]. However, these donor states were found to be present in a small fraction of the total concentration of shallow donors; see Fig. 5. Taking into account a more realistic donor distribution one can estimate that in the *Cz*-Si:P:Er studied in [8] the free electron concentration at $T \leqslant 30$ K may be much less than a critical one of about $7 \cdot 10^{14}$ cm^{-3}. Therefore, there is a need to put this possible channel of Er deexcitation under closer scrutiny.

In summary, three kinds of donor centers are formed in *Cz*-Si after implantation of erbium and subsequent annealing at $T = 700^\circ$C and 900°C. Shallow energy states at $E_c - (20 \div 40)$ meV are attributed to oxygen-related donors. Donor centers at $\approx E_c - 70$ meV and $\approx E_c - 120$ meV appear to be Er-related. The latter ones are annealed out at $T = 900^\circ$C. Instead of them, new donor centers at $\approx E_c - 150$ meV are observed.

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