ELSEVIER

Physica B 308–310 (2001) 350–353

PHYSICA B

www.elsevier.com/locate/physb

Shallow donors in silicon coimplanted with rare-earth ions and oxygen

V.V. Emtsev Jr.[a,*], C.A.J. Ammerlaan[a], B.A. Andreev[b], G.A. Oganesyan[c], D.S. Poloskin[c], N.A. Sobolev[c]

[a] Van der Waals–Zeeman Institute, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands
[b] Institute for Physics of Microstructures, Russian Academy of Sciences, 603600 Nizhnyi Novgorod, GSP-105, Russia
[c] Ioffe Physicotechnical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia

Abstract

Formation processes of shallow donors in Czochralski-grown silicon coimplanted with rare-earth ions and oxygen are studied. There is no indication that rare-earth ions are components of the structures of shallow donors. However, intrinsic defects appear to be involved in the formation processes. These oxygen-related thermal donors survive even at $T = 900°C$. They are responsible for the electrical conductivity in the implanted layers at cryogenic temperatures.

Keywords: Silicon; Rare-earth ions; Implantation; Thermal donors

1. Introduction

Earlier [1–3] it has been established that in Czochralski-grown silicon (Cz-Si) implanted with rare-earth (RE) dopants (Dy, Ho, Er and Yb) and annealed to $T = 700°C$ three main kinds of donor centers make their appearance: shallow donors at $\leqslant E_C - 40\,meV$ and deeper donor centers at $\approx E_C - (60-80)\,meV$ and $\approx E_C - (110-140)\,meV$; see Fig 1. All of them were found to be oxygen-related, since their formation takes place only in the presence of oxygen, no matter in Cz-Si implanted with RE ions [1] or float-zone silicon (FZ-Si) coimplanted with RE ions and oxygen [3]. Without oxygen coimplantation in FZ-Si only one kind of dominating donors at $\approx E_C - 200\,meV$ can be detected; see Fig. 1 and Ref. [3]. Besides, a comparative study of various dopants in Cz-Si allowed to conclude that the position of donor centers at $\approx E_C - (60-80)\,meV$ and $\approx E_C - (110-140)\,meV$ are dependent on the chemical nature of RE impurities [1]. This is why these centers have been identified as (RE-oxygen)-related complexes [1–3].

In the present paper, most attention has been paid to the formation of oxygen-related shallow donors responsible for the electrical conductivity of implanted layers at cryogenic temperatures.

2. Experimental

The initial materials were p-type Cz-Si wafers of $\rho \approx 20\,\Omega\,cm$. The oxygen concentration varied over a wide range, from $\approx 2 \times 10^{17}$ to $\approx 1 \times 10^{18}\,cm^{-3}$. In some cases, n-type Si : P epilayers of $\rho \approx 20\,\Omega\,cm$ were grown on low-resisistivity p-type Cz-Si substrates and then implanted with Er ions.

RE ions, mostly Er, were implanted at energies of 1.0–1.2 MeV. The RE implantation dose Φ varied in the range of 5×10^{11}–$1 \times 10^{13}\,cm^{-2}$. In the case of oxygen coimplantation, the energy of oxygen ions was between 0.11 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 $\Phi(RE) \geqslant 5 \times 10^{11}\,cm^{-2}$, the implanted layers of

*Corresponding author. Tel.: +31-20-525-5642; fax: +31-20-525-5788.
E-mail address: emtsev@wins.uva.nl (V.V. Emtsev Jr.).

0921-4526/01/$ - see front matter
PII: S0921-4526(01)00697-4

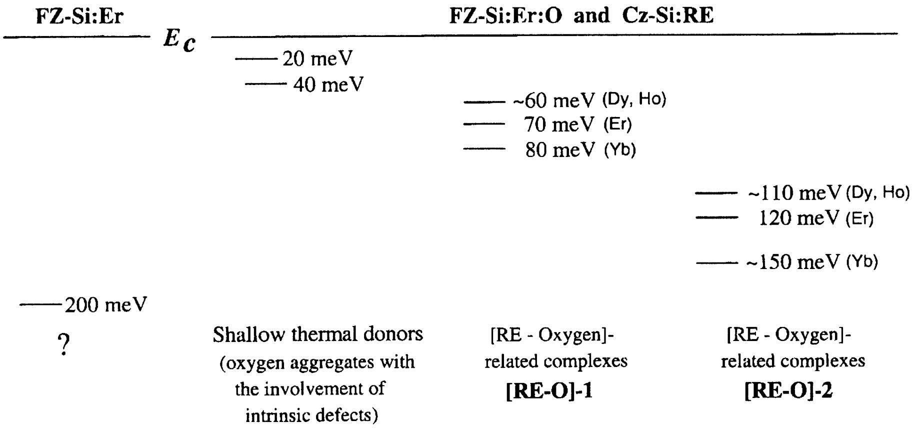

Fig. 1. Donor centers determining the electrical conductivity of FZ-Si and Cz-Si implanted with RE ions and annealed at $T = 700°C$. The donor levels are shown with respect to the conduction band of silicon.

about 0.5 μm in thickness became n-type, even in the initially p-type Cz-Si samples.

Electrical measurements of the electron concentration in implanted layers versus temperature, $n(T)$, were taken by means of the Van der Pauw technique over the temperature range from $T \approx 20-300$ K. Analysis of $n(T)$ curves was carried out on the basis of the corresponding equations of charge balance [4,5]. Photoconductivity spectra of several implanted layers at cryogenic temperatures were recorded in the range of 200–800 cm^{-1} with the aid of an IFS-113 V Bruker spectrometer. The resolution was 1 cm^{-1}.

In some cases, 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.

3. Results and discussion

By way of example, in Fig. 2, three $n(T)$ curves are shown for the FZ-Si epilayers coimplanted with Er and O ions. The Er dose was fixed at a maximum, $\Phi(\mathrm{Er}) = 1 \times 10^{13}$ cm^{-2}, whereas the dose of oxygen coimplant varied between $\Phi(\mathrm{O}) = 5 \times 10^{13}$ and 5×10^{14} cm^{-2}.

Analysis of all the $n(T)$ curves revealed some interesting features of the donor formation processes in Er implanted layers.

First, at $\Phi(\mathrm{Er}) \leqslant 5 \times 10^{12}$ cm^{-2} the concentration of shallow thermal donors in Cz-Si:Er with high oxygen concentrations (about 1×10^{18} cm^{-3}) varies directly with the Er implantation dose. This observation is consistent with our earlier conclusion [3] that the intrinsic defects produced by Er ions play a key role as nucleation sites of oxygen aggregates (shallow thermal donors). In this way, the shallow thermal donors are substantially stabilized as compared to those usually formed during oxygen precipitation processes in conventional Cz-Si at $T = 700°C$: cf. also [6–8]. The shallow thermal donors in Cz-Si:RE survive even after annealing to $T = 900°C$ [1,2]. At $\Phi(\mathrm{Er}) > 5 \times 10^{12}$ cm^{-2} there is a pronounced trend towards saturation of the concentration of shallow donors in Cz-Si:Er.

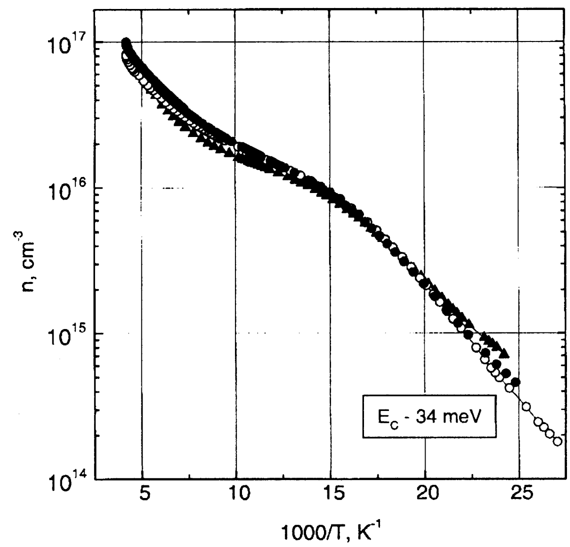

Fig. 2. Electron concentration against reverse temperature in the Fz-Si coimplanted with Er and O ions and annealed at $T = 700°C$. Dose $\Phi(\mathrm{Er}) = 1 \times 10^{13}$ cm^{-2}. Dose $\Phi(\mathrm{O}) = 5\times 10^{13}$ cm^{-2} (open circles), 1×10^{14} (solid circles) and 5×10^{14} cm^{-2} (solid triangles). Concentration of shallow donors (open circles), 2.8×10^{16} cm^{-3}.

Second, as would be expected, the damage produced by oxygen ions turned out to be not so important for the formation of shallow thermal donors. Actually, the total concentration of shallow donors is close to 3×10^{16} cm^{-3} at $\Phi(\mathrm{O}) = 5 \times 10^{13}$ and 1×10^{14} cm^{-2}, whereas at $\Phi(\mathrm{O}) = 5 \times 10^{14}$ cm^{-2} it even drops by 20%; see also Fig. 3. This slight decrease may be due to increasing formation rate of electrically inactive oxygen precipitates in oxygen-rich samples.

In contrast to little importance of oxygen ions as a damaging factor, the contribution of heavy Er ions to the production of intrinsic defects being involved in the formation of shallow donor centers can be characterized in a quantitative way. Really, analysis of the curves $n(T)$ shown in Figs. 2 and 3 points to the fact that the production of oxygen-related shallow thermal donors in FZ-Si : Er : O versus FZ-Si : O is enhanced by three times. This observation agrees well with the conclusion concerning the involvement of intrinsic defects in the oxygen agglomeration processes. As seen from Fig. 3, only one kind of shallow thermal donors, similar to those formed in FZ-Si : Er : O, is also produced in FZ-Si : O, thus demonstrating the involvement of Er ions in the formation of deeper donor centers at $\approx E_C - 70$ and 120 meV.

Third, the shallow thermal donors considered, like similar donor species formed during heat treatment of conventional Cz-Si at $T < 700°C$ [6], are distributed over their ionization energies from ≈ 40 to ≈ 25 meV, the gravity center being placed at ≈ 40 meV. This is evident from the analysis of the low-temperature portions of $n(T)$ curves whose slopes change over the interval given above with increasing Er dose. It is possible to prove this model in another way by partial compensation of the shallow donors due to deep acceptors, e.g. vacancy-oxygen complexes (so-called A-centers at $\approx E_C -$ 170 meV [9]) produced in Cz-Si : Er layers subjected to fast-electron irradiation. A compensation effect of shallow thermal donors due to A-centers in electron irradiated Cz-Si : Er : O is shown in Fig. 4. What is more, 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 for electron irradiated layers can be described in a satisfactory way by changing the concentration of A-centers only; see Fig. 4.

Fourth, our photoconductivity measurements on Dy-implanted layers revealed the presence of Thermal Double Donors (TDDs); see Fig. 5. Their concentration is roughly estimated to be about 10^{15} cm^{-3}. This family of thermal donor states at $\approx E_C - 70$ and $\approx E_C - 140$ meV usually makes its appearance in conventional Cz-Si during heat treatment at $T \leqslant 500°C$; see for instance review paper [10]. They are known to be unstable above $T = 600°C$. After annealing of the Dy implanted layers to $T = 700°C$ one could expect to detect the presence of TDDs in trace concentrations only, about 10^{13} cm^{-3}.

4. Conclusions

The information gained in the present work provides additional strong support for our earlier identification of oxygen-related shallow thermal donors in Si implanted

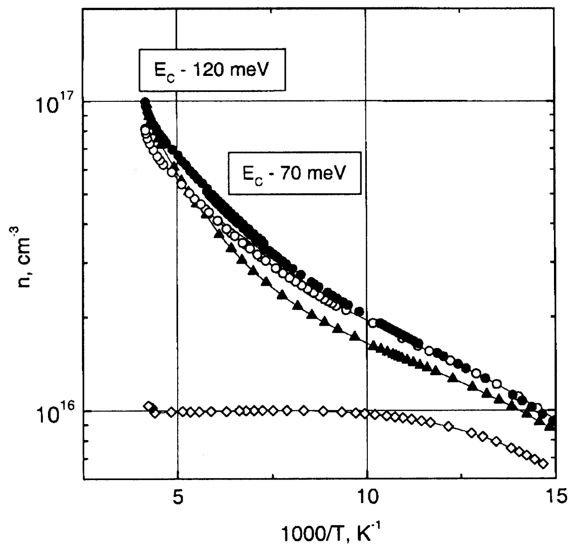

Fig. 3. Fragments of the $n(T)$ curves shown in the Fig. 2. For comparison purposes, the electron concentration against reverse temperature in the same FZ-Si implanted solely with O ions at $\Phi(O) = 5 \times 10^{14}$ cm^{-2} and annealed at $T = 700°C$ is also given (open diamonds). Concentration of [ErO]-1 centers (open circles), 2.5×10^{16} cm^{-3}. Concentration of [ErO]-2 centers (open circles), 1.0×10^{17} cm^{-3}.

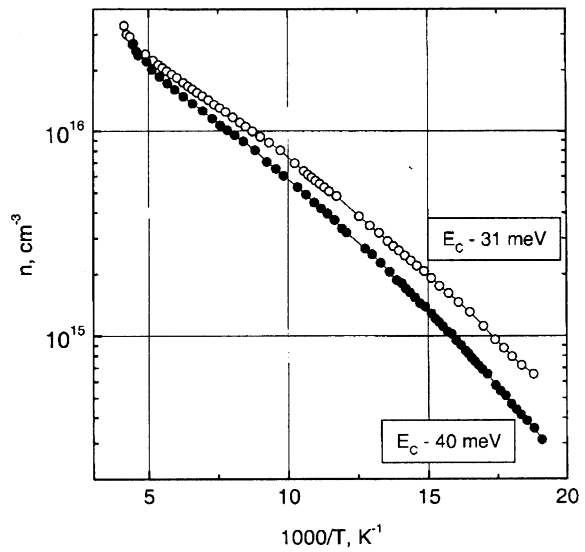

Fig. 4. Electron concentration against reverse temperature in the Cz-Si : Er before (open circles) and after fast electron irradiation (solid circles). Dose $\Phi(Er) = 1 \times 10^{13}$ cm^{-2}. Post-implantation annealing was performed at $T = 700°C$. After the implantation and annealing the Er-doped layer was irradiated with 0.9 MeV electrons at a dose 1×10^{17} cm^{-2}.

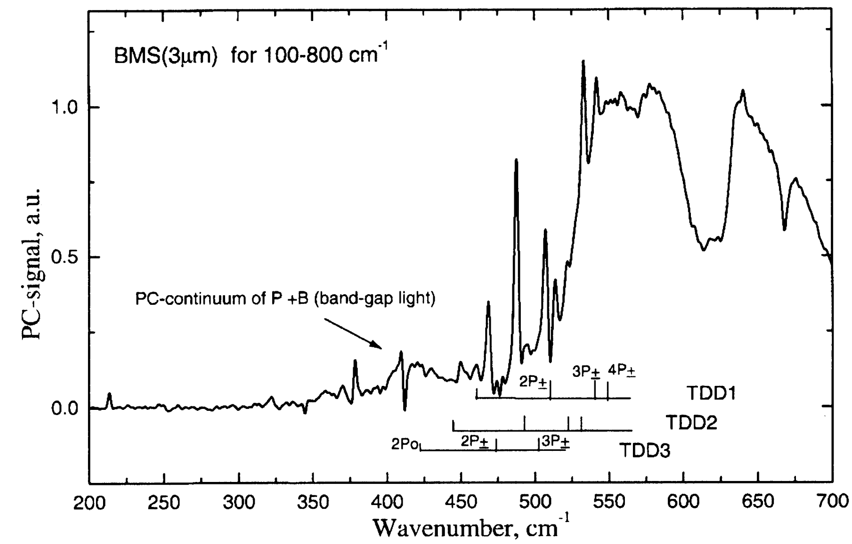

Fig. 5. Photoconductivity spectrum in the Cz-Si:Dy. Dose $\Phi(Dy) = 1 \times 10^{13}\,cm^{-2}$. Postimplantation annealing was performed at $T = 700°C$. The spectrum was recorded at $T \approx 30\,K$ under bandgap illumination. Three species of Thermal Double Donors are identified.

with RE impurities, first of all erbium. These shallow thermal donors are responsible for the electrical conductivity in implanted layers at cryogenic temperatures. The contribution of intrinsic defects produced by heavy RE ions to the formation of shallow donor centers has been studied in detail. The intrinsic defects serve as nucleation sites of growing oxygen aggregates.

Acknowledgements

The work was partly supported by INTAS (grant 99-018-72).

References

[1] V.V. Emtsev, V.V. Emtsev Jr., D.S. Poloskin, E.I. Shek, N.A. Sobolev, J. Lumin. 80 (1999) 391.

[2] V.V. Emtsev Jr., D.S. Poloskin, E.I. Shek, N.A. Sobolev, L.C. Kimerling, Mater. Sci. Eng. B81 (2001) 74.

[3] V.V. Emtsev, V.V. Emtsev Jr., D.S. Poloskin, E.I. Shek, N.A. Sobolev, J. Michel, L.C. Kimerling, Solid State Phenom. 69–70 (1999) 365.

[4] J.S. Blakemore, Semiconductor Statistics, Pergamon Press, New York, 1962.

[5] H.J. Hoffmann, H. Nakayama, T. Nishino, Y. Hamakawa, Appl. Phys. A 33 (1984) 47.

[6] V.V. Emtsev, G.A. Oganesyan, K. Schmalz, Solid State Phenom. 47–48 (1996) 259.

[7] V.V. Emtsev, D.S. Poloskin, N.A. Sobolev, E.I. Shek, Fiz. Tekh. Poluprovodn. 28 (1994) 1084.

[8] V.V. Emtsev, D.S. Poloskin, N.A. Sobolev, E.I. Shek, Semiconductors (AIP) 28 (1994) 624.

[9] G.D. Watkins, J.W. Corbett, Phys. Rev. 121 (1961) 1001.

[10] P. Wagner, J. Hage, Appl. Phys. A49 (1989) 123.