Solid State Phenomena Vols. 82-84 (2002) pp. 259-264
online at http://www.scientific.net
© (2002) Trans Tech Publications, Switzerland

Impact of Compressive Stress on the Formation of Thermal Donors in Heat-Treated Silicon

V.V. Emtsev[1], A. Misiuk[2], B.A. Andreev[3], V.V. Emtsev Jr.[4], C.A. Londos[5], G.A. Oganesyan[1] and D.S. Poloskin[1]

[1] A.F.Ioffe Physico-Technical Institute, Russian Academy of Sciences, Polytekhnicheskaya st. 26, RU-194021 St.-Petersburg, Russia

[2] Institute of Electron Technology, Al. Lotników 32/46, PL-02-668 Warsaw, Poland

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

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

[5] Solid State Section, Physics Department, University of Athens, Panepistimiopolis, Zografos, GR-157 84 Athens, Greece

Keywords: Compressive Stress, Heat Treatment, Oxygen Aggregation, Silicon, Thermal Donors

Abstract. Formation processes of thermal donors in Czochralski grown silicon with Ge impurity subjected to heat treatment at T=450°C at atmospheric pressure and a high hydrostatic pressure of P=1 GPa are investigated. Ge impurity can suppress the formation of Thermal Double Donors in Cz-Si heat treated under normal conditions. It has been shown that the compressive stress applied during heat treatment to Cz-Si with high concentrations of this isoelectronic impurity gives rise to an enhanced formation of thermal donors. This effect is thought to be associated with increasing oxygen diffusivity under stress. A comparison with the formation processes of thermal donors in conventional Cz-Si heat treated with and without hydrostatic pressure is also drawn.

Introduction

Oxygen impurity atoms in Czochralski grown silicon (Cz-Si) are known to be present in abundance, much above its solubility at room temperature. Because of this oxygen agglomeration processes are greatly enhanced upon heating of Cz-Si. Small oxygen aggregates of different size start forming at high rates at $T\approx$ 450°C. These oxygen clusters have electrically active cores, so the formation of Thermal Double Donors (TDDs) takes place; see for instance [1,2]. This family of oxygen-related thermal donors consists of more than 16 species with their shallow and deep energy states in the ranges of E_C–(40-70) meV and E_C–(100-160) meV, respectively [1-4]. For short heat treatment at around T=450°C the TDD family appears to be a dominant kind of thermal donors formed. The formation rate at the beginning of heat treatment as well as the maximal concentration of TDDs are strongly dependent on impurity concentrations in Cz-Si crystals, first of all that of oxygen [1,2,5,6].
Recently it has been established that high hydrostatic pressure applied to Cz-Si at T=450°C can enhance and modify oxygen aggregation processes [7,8]. As a result, the total concentration of thermal donors formed in Cz-Si at a pressure of $P\approx$ 1 GPa increases by an order-of-magnitude as compared to that formed at atmospheric pressure. Reportedly, the similar effects of compressive

All rights reserved. No part of contents of this paper may be reproduced or transmitted in any form or by any means without the written permission of the publisher: Trans Tech Publications Ltd, Switzerland, www.ttp.net. (ID: 195.134.94.101-17/09/07,11:42:55)

stress are also observed in oxygen-implanted Si layers [9]. In addition, the electrical data showed that the stress leads to strong modifications of oxygen-related thermal donors [7,8]. Under these conditions the TDD family was found to play a subsidiary role.
It has long been known that such isoelectronic impurities as carbon and germanium in Cz-Si if present in high concentrations can strongly suppress the TDD formation [1,10-12]. Pronounced effects of suppression occur at impurity concentrations of $\geq 1\cdot 10^{17}$ cm^{-3} and $\geq 1\cdot 10^{19}$ cm^{-3} for carbon and germanium, respectively.
The purpose of the present work is a comparative study of the formation processes of thermal donors in Cz-Si doped with germanium (Cz-Si:Ge) heat treated under atmospheric pressure and compressive stress. Besides, a comparison of the obtained results to those for conventional Cz-Si heat treated under high hydrostatic pressure is of practical interest.

Experimental

Two wafers of Cz-Si doped with germanium were used. The initial materials were n-type. The concentration of phosphorus was about $1\cdot 10^{15}$ cm^{-3}. The initial concentrations of oxygen in both wafers was about $7\cdot 10^{17}$ cm^{-3} using a conversion factor of $2.45\cdot 10^{17}$ cm^{-2} for the oxygen absorption band at 1108 cm^{-1}. The germanium concentrations in these wafers were about (1 to 2)$\cdot 10^{19}$ cm^{-3} and $5\cdot 10^{19}$ cm^{-3}.
Three wafers of conventional carbon-lean p-Cz-Si doped were also used for comparison purposes. The concentration of boron was about $2\cdot 10^{15}$ cm^{-3}. The initial concentration of oxygen was between $6.0\cdot 10^{17}$ cm^{-3} and $9.5\cdot 10^{17}$ cm^{-3}.
Square samples of 7x7x1 mm^{-3} were cut from these wafers. The electrical contacts in the Van der Pauw geometry were applied to samples. Samples were annealed at T=450°C for t=10 hours in pure argon under a hydrostatic pressure of $P\approx 1$ GPa. For comparison some reference samples were annealed under similar conditions at atmospheric pressure. After heat treatment a layer of about 50μm were removed from sample surface by polishing and etching
Hall effect measurements over the temperature range of 20 K-300 K were conducted by means of the Van der Pauw technique. Experimental curves of charge carrier concentration *vs* reciprocal temperature, $n(T)$ or $p(T)$, were analyzed on the basis of the relevant electroneutrality equations. Infrared absorption spectra at T<6 K were recorded in the range of 200-800 cm^{-1} with the help of an IFS-113V Bruker spectrometer. The resolution was 1 cm^{-1}.

Results and Discussion

In Fig. 1 and Fig. 2 some $n(T)$ curves are shown for the initial and heat treated Cz-Si:Ge samples with higher Ge concentrations. It is known that the TDD formation in Cz-Si:Ge is retarded [10-12], despite the fact that in the presence of germanium the oxygen diffusivity increases [12,13]. However, the TDDs are still a dominant family of thermal donors. Our data on the Cz-Si:Ge heat treated under atmospheric pressure are consistent with this conclusion. Actually, the initial formation rate of thermal donors was estimated to be about $3\cdot 10^{13}$ $cm^{-3}\cdot h^{-1}$. Without germanium the TDD formation rate in Cz-Si with similar oxygen contents is larger by a factor of two. The heat treatment of the same material for t=10 hours under a pressure of P=1 GPa results in a strong enhancement of the thermal donor formation. This is evident if one compares the $n(T)$ curves for two samples annealed for t=10 hours at atmospheric pressure and under compressive stress; see Fig. 2. The electron concentration at room temperature is increased by a factor of four for the Cz-Si heat treated under stress. As is seen from the same figure, under such conditions of annealing the electron concentration

at room temperature turned out to be even larger that that after annealing of the same material for t=120 hours at atmospheric pressure.

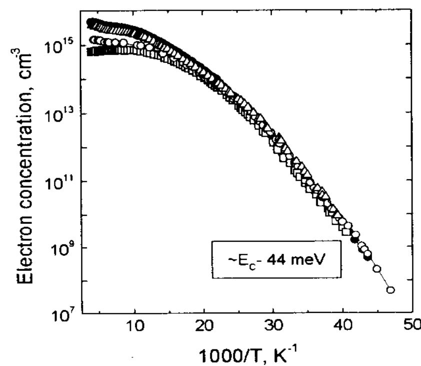


Fig. 1. Electron concentration *versus* reciprocal temperature in the Cz-Si:Ge (N_{Ge}=5·10^{19} cm^{-3}) heat treated at T=450°C for t=10 hours (open and black circles) and 120 hours (open triangles) under atmospheric pressure (open circles and triangles) and a hydrostatic pressure of P=1 GPa (black circles). For comparison the $n(T)$ curve for the Cz-Si:Ge in the initial state is also shown (open squares). Activation energies of donor centers are given.

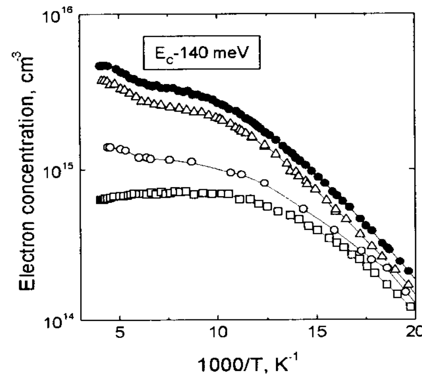
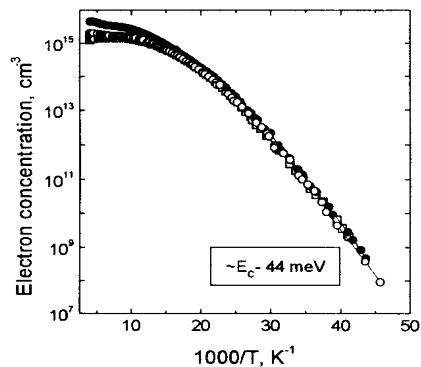


Fig. 2. Fragments of the $n(T)$ curves shown in Fig. 1.

With decreasing germanium concentration one could expect that the suppression effect of thermal donor formation should weaken. In Fig. 3 and Fig. 4 we show some $n(T)$ curves for the Cz-Si with a smaller concentration of Ge. The observed effects of heat treatment, no matter with or without stress, are very similar to those described above. No marked difference between the two materials has been seen. IR measurements revealed that this can be due to different concentrations of carbon. In contrast to the carbon-lean Cz-Si:Ge with N_{Ge}≈5·10^{19} cm^{-3}, the lightly Ge doped Cz-Si was found to be carbon-rich, the carbon concentration being about 1·10^{17} cm^{-3}. As already stated above, both isolelectronic impurities produce the similar suppression effect on the thermal donor formation.

According to [11], the mechanism of TDD suppression in Cz-Si doped with germanium is mainly associated with decreasing capture radius of diffusing oxygen atoms by nucleation centers, the precursors of forming TDDs. Both factors mentioned, increasing oxygen diffusivity and decreasing capture radius, are thought to be due to internal stress produced in Cz-Si:Ge by the large isoelectronic impurity atoms. In our case the high pressure applied to Cz-Si:Ge during heat treatment is believed to strongly enhance the oxygen diffusivity, thus changing the contributions of the factors considered as well as the rate of quasichemical reactions.

The impact of compressive stress on oxygen agglomeration processes in Cz-Si is very much more pronounced in conventional Cz-Si doped with boron. By way of example, in Fig. 5 we show some $n(T)$ curves for the Cz-Si:B annealed at T=450°C for t=10 hours under the stress. As a result of this heat treatment the initially p-type Cz-Si samples were converted to n-type, even for the Cz-Si with lesser oxygen contents. This effect is profound, since the electron concentrations at room



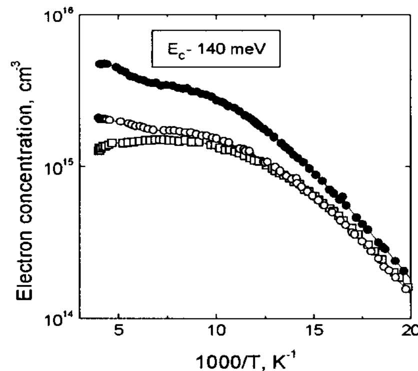


Fig. 3. Electron concentration *versus* reciprocal temperature in the Cz-Si:Ge ($N_{Ge} \approx 2 \cdot 10^{19}$ cm^{-3}) heat treated at T=450°C for t=10 hours (open and black circles) and 120 hours (open triangles) under atmospheric pressure (open circles and triangles) and a hydrostatic pressure of P=1 GPa (black circles). For comparison the $n(T)$ curve for the Cz-Si:Ge in the initial state is also shown (open squares). Activation energies of donor centers are given.

Fig. 4. Fragments of the $n(T)$ curves shown in Fig. 3.

temperature are between $3 \cdot 10^{15}$ cm^{-3} and $7 \cdot 10^{14}$ cm^{-3} in the samples with rather different oxygen contents.

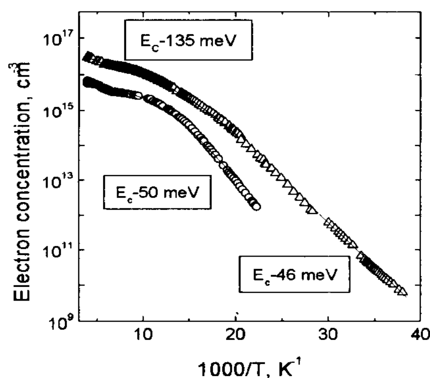


Fig. 5. Electron concentration *vs* reciprocal temperature in two Cz-Si samples annealed at T=450°C for t=10 hours under a hydrostatic pressure of P=1.2 GPa. The initial concentrations of oxygen are $6.0 \cdot 10^{17}$ cm^{-3} (open circles) and $9.5 \cdot 10^{17}$ cm^{-3} (open triangles).

Under normal conditions, such strong effects due to heat treatment at T=450°C could be observed only for t>40 hours. The next question one has to address to is the nature of thermal donors formed.

First of all, the presence of TDDs has been detected by means of IR spectroscopy. The absolute concentration of each identified species can be estimated using the optical cross-sections of the $2p_0$ transitions of the neutral TDDs [14]. On this basis it has been established that the stress applied leads to a substantial increase in the total concentration of TDDs, by a factor of three, as compared with the concentration of all TDDs formed under similar conditions of heat treatment without stress. As can be seen from Fig. 6, the heat treatment for t=10 hrs at high hydrostatic pressure yields the same results as the heat treatment for t=60 hrs at atmospheric pressure. The TDD distributions are very similar in both cases. This strongly suggests that the governing factor should be the same for the TDD formation processes in Cz-Si annealed under atmospheric and high hydrostatic pressure. In many models the oxygen diffusivity is considered as a decisive factor in the sequential agglomeration of oxygen atoms leading to the appearance of TDDs; see for instance review [2]. Therefore, the enhanced TDD formation can be associated with increasing diffusivity of oxygen under compressive stress. In this connection, it is important to point out that the local vibrational modes of isolated

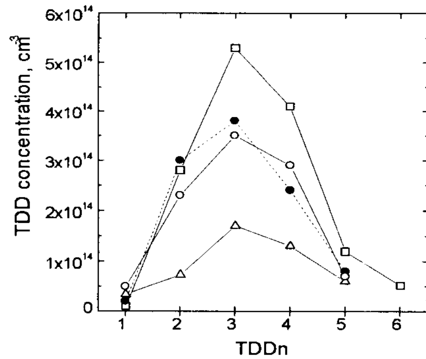


Fig. 6. Distributions of Double Thermal Donors in the Cz-Si annealed at T=450°C for t=30 hours (open triangles), t=60 hours (open circles), and t=120 hours (open squares) at atmospheric pressure and for t=10 hours (black circles) under a hydrostatic pressure of P=1.0 GPa. The initial concentration of oxygen is $6.5 \cdot 10^{17}$ cm^{-3}.

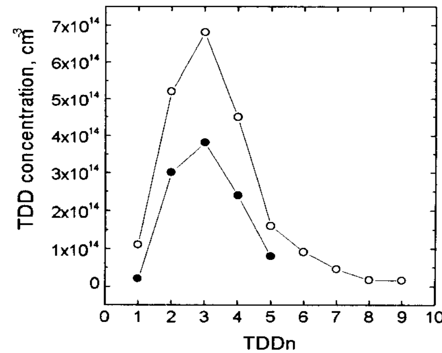


Fig. 7. Distributions of Double Thermal Donors in the Cz-Si annealed at T=450°C for t=10 hours under a hydrostatic pressure of P=1.0 GPa (black circles) and P=1.2 GPa (open circles). The initial concentrations of oxygen are $6.5 \cdot 10^{17}$ cm^{-3} (black circles) and $6.0 \cdot 10^{17}$ cm^{-3} (open circles).

oxygen atoms and staggered oxygen dimers, both kinds of diffusing units in Si upon heating, were calculated to be markedly changed with hydrostatic pressure at $P \geq 1$ GPa [15]. Figure 7 displays another interesting feature. An increase of pressure by 20 per cent doubled the total concentration of TDDs. Therefore, the oxygen diffusivity in Si should be rather sensitive to pressure above 1 GPa.

Despite the enhanced formation of Thermal Double Donors in Cz-Si heat treated under high pressure they are no longer most important among other donor centers. In the samples with higher oxygen contents the presence of new thermal donors at E_C–46 meV and E_C–135 meV is evident from Fig. 5. Their concentrations were found to about $2 \cdot 10^{16}$ cm^{-3}. This has to be compared with the total TDD concentration of about $3 \cdot 10^{15}$ cm^{-3}. Therefore, one can conclude that the oxygen aggregation processes are strongly modified under the applied stress.

Summary

The formation processes of thermal donors in Ge doped Cz-Si annealed at T=450°C under atmospheric and high pressure have been studied. Under normal conditions of heat treatment this isoelectronic impurity if present in large concentrations can retard markedly these processes. Heat treatment of Cz-Si:Ge at T=450°C under compressive stress leads in a strong enhancement of the thermal donor formation. It has also been demonstrated that the oxygen agglomeration processes in conventional Cz-Si can be enhanced greatly under hydrostatic pressure $P \geq 1$ GPa applied during heat treatment at T=450°C. It is thought that in all cases the enhancement effect observed is mainly due to increasing oxygen diffusivity in silicon subjected to compressive stress.

References

[1] P.Wagner and J.Hage: Appl. Phys. Vol. **A49** (1989), p. 123.

[2] R.C.Newman: J. Phys.: Condens. Matter Vol. **12** (2000), p. 335.

[3] W.Götz, G.Pensl and W.Zulehner: Phys. Rev. Vol. **B46** (1992), p. 4312.

[4] B.J.H. Liesert, T.Gregorkiewicz and C.A.J.Ammerlaan: Mater. Sci. Forum Vol **83-87** (1992), 404.

[5] P.Gaworzewski and K.Schmalz: Phys. St. Sol. (a) Vol. **55** (1979), p. 699.

[6] P.Gaworzewski and K.Schmalz: Phys. St. Sol. (a) Vol. **58** (1980), K223.

[7] V.V.Emtsev, B.A.Andreev, A.Misiuk and K.Schmalz: NATO ASI Series (3.High Technology) Vol. **17** (1996), 345.

[8] V.V.Emtsev, B.A.Andreev, A.Misiuk, W.Jung and K.Schmalz: Appl. Phys. Lett., Vol. **71** (1997), p. 264.

[9] E.L.Neustroev, I.V.Antonova, V.P.Popov, D.V.Kilanov and A.Misiuk: Fiz. Tekh. Poluprovodn. [Semiconductors (AIP)] Vol. **33** (1999)], p. 1153.

[10] Yu. M. Babitskii, N.I. Gorbacheva, P.M. Grinshtein, M.A. Il'in, V.P. Kuznetsov, M.G. Mil'vidskii and B.M. Turovskii: Fiz. Tekh. Poluprovodn. [Sov. Phys. Semicond. (AIP)] Vol. **22** (1988), p. 307.

[11] D.I. Brinkevich, V.P. Markevich, L.I. Murin and V.V. Petrov: Fiz. Tekh. Poluprovodn. [Sov. Phys. Semicond. (AIP)] Vol. **26** (1992), p. 682.

[12] V. M. Babich, V.P. Baran, K.I. Zotov, V.L. Kiritsa and V.B. Koval'chuk: Fiz. Tekh. Poluprovodn. [Semiconductors (AIP)] Vol. **29** (1995), p. 58.

[13] A.K. Tipping, R.C. Newman, D.C. Newton and J.H. Tucker: *Mater. Sci. Forum* Vol. **10-12** (1986), p. 887.

[14] P.Wagner: MRS Symp. Proc. Vol. **59** (1986), p. 125.

[15] J. Coutinho, R. Jones, P.R. Briddon and S. Öberg: Phys. Rev. Vol. **B62** (2000), p. 10824.