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Physica B 340–342 (2003) 769–772

PHYSICA B

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Stress-induced changes of thermal donor formation in heat-treated Czochralski-grown silicon

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Abstract

Formation processes of oxygen-related thermal donors in Czochralski-grown silicon annealed at $T = 450°C$ under high hydrostatic pressures at $P \geqslant 1$ GPa are studied by means of electrical and optical measurements. As for heat treatment of materials at atmospheric pressure, the formation of thermal double donors (TDDs) takes also place in Czochralski-grown silicon subjected to compressive stresses during heat treatment. However, their formation rate turned out to be much larger than that observed under normal conditions, even in carbon-rich materials. This strongly enhanced formation of thermal donors is believed to be due to increasing diffusivity of oxygen under pressures. In addition to the TDDs, other shallow and deep thermal donors are also making their appearance in silicon heat treated under high pressures.
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PACS: 61.72.Ji; 62.50.+P; 71.55.Cn

Keywords: Silicon; Thermal donors; Compressive stress

1. Introduction

Oxygen aggregation and precipitation processes in Czochralski-grown silicon (Cz–Si) with high oxygen contents become practically important upon annealing at $T \geqslant 400°C$. The early stages of oxygen aggregation take place in a temperature range from $T \approx 400°C$ to 500°C resulting in the appearance of small oxygen aggregates. These oxygen aggregates are double donors labeled thermal double donors (TDDs) in the literature. This dominant family of donor states being closely spaced in two energy ranges of $E_C - 40$ meV $\leqslant E \leqslant E_C - 70$ meV and $E_C - 100$ meV $\leqslant E \leqslant E_C - 160$ meV consists of more than 15 species [1–3]. A vast amount of papers are devoted to experimental and theoretical studies of the TDDs; see reviews [1,4]. Despite this fact the question of how these oxygen aggregates are built and formed are

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doi:10.1016/j.physb.2003.09.118

still open to discussion so far. Calculations of the TDD formation kinetics are usually based on a certain model of the atomic structures of TDDs and a certain model of oxygen diffusion in silicon at low temperatures $T \leqslant 600°C$. This is a difficult problem to be solved because the real formation kinetics of TDDs in Cz–Si crystals is sensitive to many factors such as different heat treatment conditions, effects associated with impurities, first of all oxygen and carbon, and the presence of structural defects; see for instance Ref. [1]. Recently, it was found that oxygen precipitation processes are strongly modified under compressive stresses [5,6]. This is also true for the TDDs starting from hydrostatic pressures at $P \geqslant 1$ GPa [7].

In the present paper, the formation processes of thermal donors in Cz–Si annealed at $T = 450°C$ under compressive stresses are studied in some detail.

2. Experimental

The initial materials were wafers cut from Cz–Si crystals with different contents of oxygen and carbon. Heat treatment was carried out at $T = 450°C$ under normal conditions in a nitrogen ambient or hydrostatic pressures of about 1 GPa in pure argon.

Electrical measurements of charge carrier concentrations in Cz–Si samples, $n, p(T)$, were taken over a temperature range of $T = 20$–300 K making use of the Van der Pauw technique. Experimental curves $n, p(T)$ were analyzed on a basis of the relevant equations of charge balance using the statistics of charge carriers; see for instance Ref. [8]. Infrared absorption and photoconductivity spectra were recorded with the help of a Fourier transform spectrometer of IFS-113v type at cryogenic temperatures. Concentrations of each TDD species can be estimated using the absorption cross sections of the 2p transitions at the neutral $TDDs^0$ [9]. A combination of electrical and optical data allows one to determine the TDD concentrations in a reliable way.

3. Results and discussion

As an illustration, several $n(T)$ curves for the heat-treated Cz–Si:B after $p \to n$ conversion due to formation of thermal donors are plotted in Fig. 1. The formation of shallow and deep donor states of TDDs is clearly seen from Figs. 1 and 2. The distributions of TDDs in the same samples are shown in Fig. 3. The total concentrations of TDDs determined from the electrical and optical data on the samples heat treated at atmospheric pressure are in good agreement, thus confirming that the TDD family is absolutely dominant among the thermal donors formed. Compressive stresses during heat treatment give rise to a large enhancement of the TDD production rate, so one can estimate the enhancement factor by six for the Cz–Si:B shown in Fig. 3; cf. curves 2 and 3 for $t = 60$ h under normal conditions and $t = 10$ h at a hydrostatic pressure of about 1 GPa, respectively. It is interesting to note that the TDD distributions in both cases turned out to be practically the same.

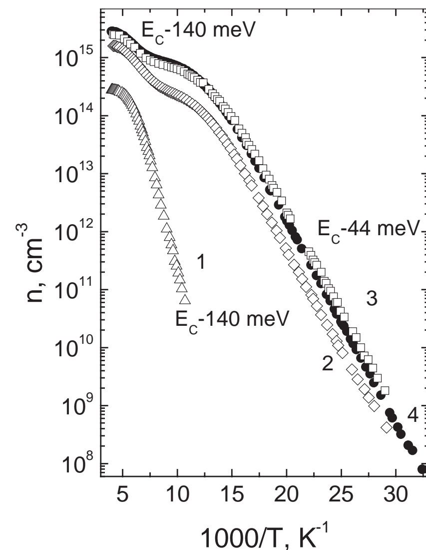

Fig. 1. Electron concentration versus reciprocal temperature in the Cz–Si:B heat treated at $T = 450°C$ for $t = 30$ (curve 1), 60 (curve 2), and 120 h (curve 3) at atmospheric pressure and at $T = 450°C$ for $t = 10$ h (curve 4) under a hydrostatic pressure of $P = 1.12$ GPa. Initial oxygen concentration, $N^0_{OXY} = 6.5 \times 10^{17}$ cm^{-3}. The effective activation energies of thermal donors are given. The initial material was p-type, with boron concentrations in the low 10^{15} cm^{-3}.

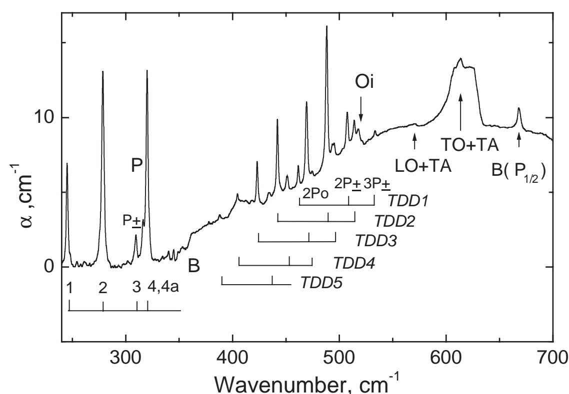

Fig. 2. IR absorption spectra for the Cz–Si:B heat treated at $T = 450°C$ for $t = 10\,h$ under a hydrostatic pressure of $P = 1.20\,GPa$. Initial oxygen concentration, $N^0_{OXY} = 6.0 \times 10^{17}\,cm^{-3}$. Before measurements the sample was cooled down to $T < 6\,K$ under band gap illumination. The spectrum was also recorded under band gap illumination. The known 2p transitions of the neutral TDD species are given. Some identified transitions at the shallow centers of P and B are also shown.

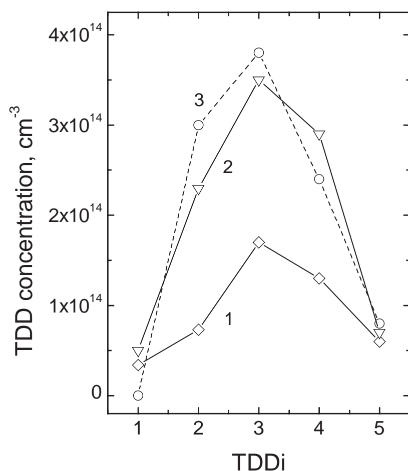

Fig. 3. TDD distributions in the Cz–Si:B heat-treated at $T = 450°C$ for $t = 30$ (curve 1) and 60 h (curve 2) at atmospheric pressure and at $T = 450°C$ for $t = 10\,h$ (curve 3) at a hydrostatic pressure of 1.12 GPa. Initial oxygen concentration, $N^0_{OXY} = 6.5 \times 10^{17}\,cm^{-3}$.

This fact permits one to conclude that the increasing diffusivity of oxygen under compressive stresses is responsible for the enhancement effect discussed.

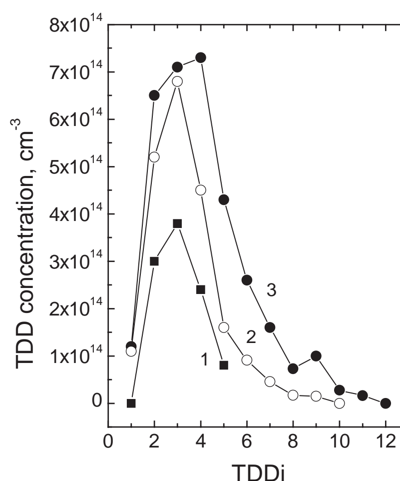

Fig. 4. TDD distributions in the Cz–Si:B heat treated at $T = 450°C$ for $t = 10\,h$ under a hydrostatic pressure of $P = 1.12$ (curve 1) and 1.20 GPa (curves 2 and 3). Initial oxygen concentrations: $N^0_{OXY} = 6.5 \times 10^{17}$ (curve 1), 6.0×10^{17} (curve 2), and $9.5 \times 10^{17}\,cm^{-3}$ (curve 3).

According to Ref. [7], the enhanced formation of thermal donors at $T = 450°C$ under hydrostatic pressures features 'a threshold' at about $P = 0.9\,GPa$, with no enhancement effect at lower pressures. As is seen in Fig. 4, a relatively small increase in compressive stresses above $P = 1\,GPa$ leads to a marked increase in the concentrations of all TDD species; cf. curves 1 and 2. By way of example, the total concentration of TDDs is increased by a factor of two if the pressure is increased by about 10%.

With increasing concentration of oxygen in initial Cz–Si samples the shape of TDD distributions is changed; cf. curves 2 and 3 in Fig. 4. The peak being placed on TDD2, TDD3 and TDD4 becomes broader than that in heat-treated Cz–Si with low oxygen contents. In a sharp contrast to the well-known relationship between the production rate of the higher numbered TDDi ($i \geqslant 3$ [1]) at the early stages of heat treatment at $T = 450°C$ under normal conditions and the initial oxygen concentration $[dN_{TDD}/dt] \propto [N^0_{OXY}]^4$, it has been established that under compressive stresses the power is reduced nearly to unity, i.e. the production rate appears to be proportional to N^0_{OXY}.

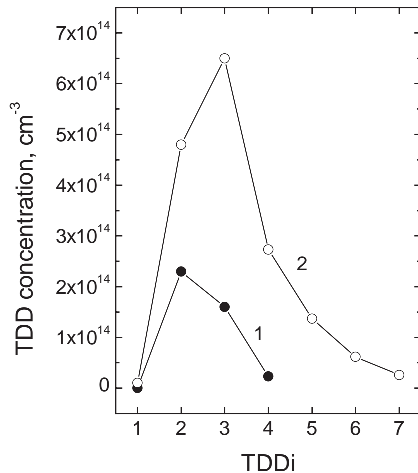

Fig. 5. TDD distributions in Cz–Si:C:P heat-treated at $T = 450°C$ for $t = 10$ h at atmospheric pressure (curve 1) and at a hydrostatic pressure of 1.13 GPa (curve 2). Initial oxygen and carbon concentrations, $N^0_{OXY} = 7.0 \times 10^{17}$ and $N^0_C = 9.0 \times 10^{16}$ cm^{-3}.

The enhancement effect of compressive stress on the TDD formation processes in Cz–Si can be observed even in carbon-rich materials. It is well known that in the presence of this isoelectronic impurity, the production rate of TDDs slows down if the carbon concentration in Cz–Si is $N_C \geqslant 1 \times 10^{17}$ cm^{-3}; see review [1]. By way of illustration, in Fig. 5 the TDD distributions are plotted for the carbon-rich Cz–Si heat treated under normal conditions and compressive stresses. Again, the TDD formation is enhanced by a factor of four in the latter case. Certainly, a single mechanism of increasing diffusivity of oxygen under pressures underlies the observed effects. A threshold behavior of the enhanced formation of TDDs at $P \geqslant 1$ GPa points to some strong changes in the oxygen diffusivity above this pressure. There may be some changes in the configuration of diffusing entities as calculated in Ref. [10]. Another plausible explanation for the increasing diffusivity of oxygen at $P \geqslant 1$ GPa has also been offered in Ref. [11].

4. Conclusions

In the present work, some characteristic features of the formation of TDDs in Czochralski-grown silicon annealed at $T = 450°C$ under high hydrostatic pressures have been established. An enhanced formation of these thermal donors was observed in materials with low and high concentrations of oxygen as well as in carbon-rich crystals. There is evidence that the increasing diffusivity of oxygen atoms under compressive stresses is responsible for this effect. Together with the TDDs, the formation of other thermal donors with shallow and deep energy states also takes place in materials annealed under high pressures.

Acknowledgements

The authors are indebted to INTAS for the financial support (grant INTAS–01-0468).

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