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Oxygen agglomeration and formation of oxygen-related thermal donors in heat-treated silicon

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The characteristic features of production processes of thermal donors in Czochralski grown silicon heat treated at T=450°C under hydrostatic pressures of about 1 GPa are studied. Two families of oxygen-related donors are formed under compressive stress. The first one is the well-known thermal double donors whose production rate is increased by a factor of five as compared with that observed at atmospheric pressure. Along with them, new thermal donors with similar energy states are also produced. This family was found to be a dominant contributor to the thermal donors formed under compressive stress. The features of formation processes of both kinds of thermal donors are briefly discussed.

1 Introduction

Czochralski-grown silicon (Cz-Si) wafers widely used in the fabrication of electronic devices usually contain oxygen impurity atoms in abundance, about $8\cdot10^{17}$ cm^{-3} [1,2]. Oxygen precipitates and large-scale structural defects formed due to heat treatment of Cz-Si are effective traps of metallic impurities and intrinsic defects. These gettering properties of such oxygen-related defects are of keen interest in the defect engineering in silicon materials.

The first formation stage of small oxygen aggregates known as Thermal Double Donors (TDDs) spans a temperature interval between T = 400°C and T = 500°C. This dominant family of thermal donors consists of nearly twenty species of shallow and deep donor states between E_C – 45 meV and E_C – 70 meV, and between E_C – 110 meV and E_C – 150 meV, respectively (the values are given with the respect to the conduction band). They have been studied most extensively by various techniques; see review papers [1,2]. Recently it has been established that the application of compressive stress during heat treatment of Cz-Si at T = 450°C leads to strong modifications of oxygen agglomeration processes, where other shallow and deep thermal donors are also produced. Consequently, the TDD family is not the main contributor to the thermal donors formed any longer [3,4].

In the present work the contributions of different families of thermal donors in Cz-Si heat treated at T= 450°C under high hydrostatic pressures up to P = 1.2 GPa are investigated. Taking into account that the initial

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oxygen content in Cz-Si is an important factor affecting the oxygen aggregation processes we used Cz-Si wafers with oxygen concentrations above and below a critical one of about $7 \cdot 10^{17}$ cm^{-3}; see for instance [5].

2 Experimental

Several wafers of carbon-lean Cz-Si doped with boron in concentrations of about $2 \cdot 10^{15}$ cm^{-3} were cut. The initial oxygen concentrations $N_{oxy}{}^{0}$ in samples were $6.0 \cdot 10^{17}$ cm^{-3} and $9.5 \cdot 10^{17}$ cm^{-3}, i.e. below and higher than a critical value. The classical regimes of heat treatment at $T = 450$°C for $t = 2$ hours to 10 hours were used under a hydrostatic pressure of 1.2 GPa in pure argon. The temperature region around $T = 450$°C at atmospheric pressure is known to be appropriate for the most effective production of TDDs. IR absorption and photoconductivity spectra at $T < 6$ K were recorded using a IFS-113V Bruker spectrometer. The resolution was 1 cm^{-1}. To reveal all TDD species, including those displaying the negative U-properties, is possible if the cooling of heat-treated samples is performed under bandgap illumination [1]. Similar bandgap illumination was also used in optical measurements at $T \leq 6$ K for the appearance of energy states of compensating centers. Hall effect measurements in the temperature range of 20 - 300 K were made using the Van der Pauw technique. Electrical data were analyzed employing the relevant equations of charge balance; see for instance [6].

3 Results and discussion

For illustration purposes Fig. 1a and Fig. 1b show some plots of electron concentration against reciprocal temperature for the Cz-Si samples heat-treated under compressive stress at both ends of the time interval studied. A comprehensive analysis of such *n(T)* curves allows one to estimate the total concentrations and effective ionization energies of shallow and deep centers. As seen in Fig. 1a, only deep donor states at $E_C - 115$ meV in the Cz-Si with lesser oxygen contents can be detected by Hall effect measurements if the heat treatment is short, $t \leq 3$ h. However, even in this case the presence of shallow donor states compensated by boron can be demonstrated by means of optical measurements under bandgap illumination; see Fig. 2.

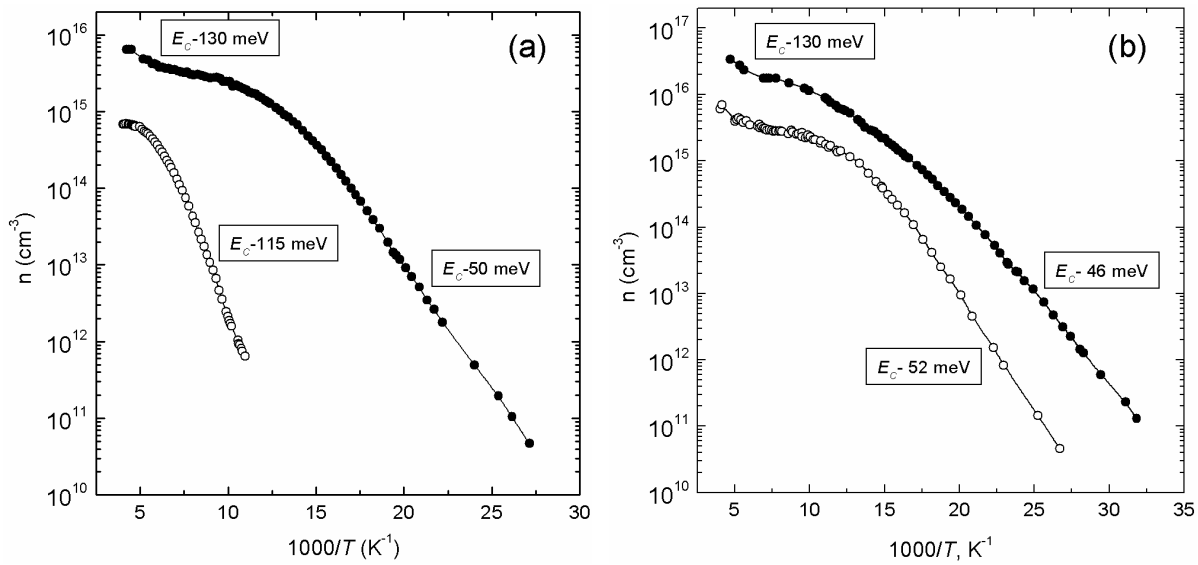

Fig. 1 Electron concentration *versus* reciprocal temperature in the Cz-Si heat treated at $T = 450$°C for $t = 2$ h (open circles) and $t = 10$ h (solid circles) under a hydrostatic pressure of $P = 1.2$ GPa. Initial oxygen concentration $N_{oxy}{}^{0}$: (***a***) $6.0 \cdot 10^{17}$ cm^{-3} and (***b***) $9.5 \cdot 10^{17}$ 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}.

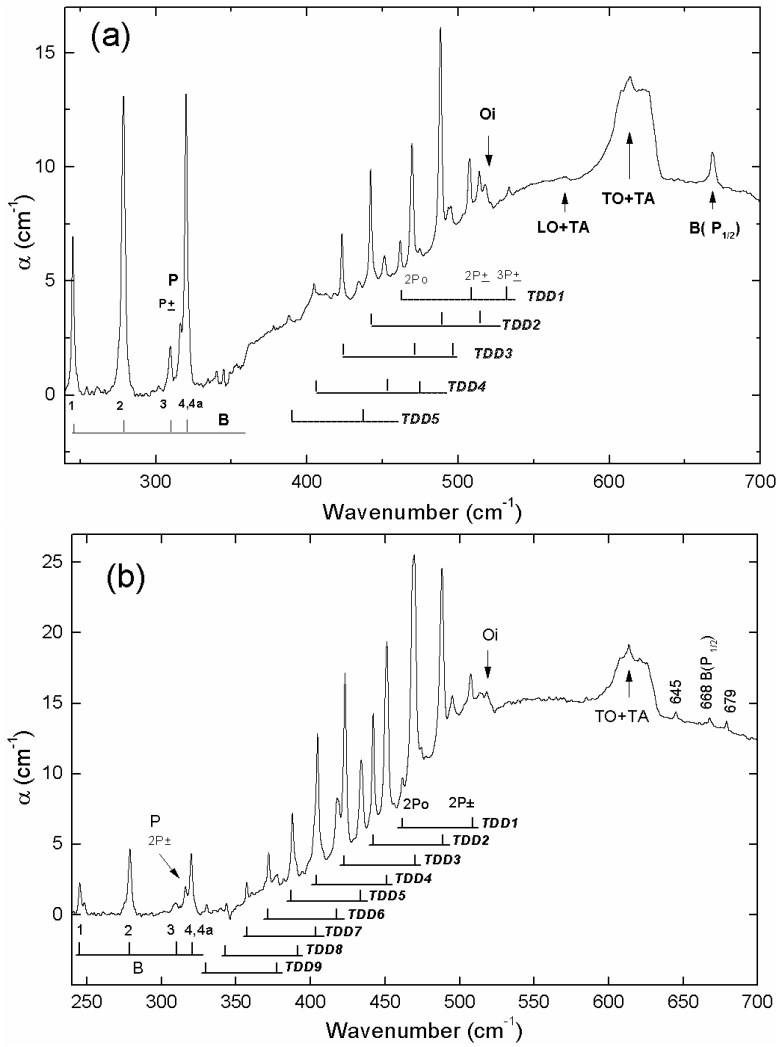

Fig. 2 IR absorption spectra for the Cz-Si heat treated at T = 450°C for (***a***) t = 2 h and (***b***) 10 h, under a hydrostatic pressure of P = 1.2 GPa. Initial oxygen concentration $N_{oxy}^{\ 0}$ = $6.0 \cdot 10^{17}$ cm^{-3}. Before measurements the samples were cooled down to T < 6K under bandgap illumination. The spectra were also recorded under bandgap illumination. The known 2p-transitions of the neutral TDD species are given. Some identified transitions of the shallow centers of P and B are also shown.

Optical spectra permit one to identify each species of the TDD family and determine its absolute concentration using the optical cross-sections of the $2p_0$-transitions of the neutral TDDs [7]. As an example, Fig. 2a and Fig. 2b show two IR absorption spectra taken on the Cz-Si with subcritical concentrations of oxygen. It is evident that the identification of the higher numbered species of TDDs available in concentrations much less than $1 \cdot 10^{14}$ cm^{-3} presents no serious difficulties. The absolute contributions of TDDs to the thermal donors produced under compressive stress are given in Fig. 3.

Let us first discuss the influence of hydrostatic pressure upon the TDD production. The enhancement effect of mechanical stress is much more pronounced in Cz-Si with low oxygen contents. In fact, the production rate of TDDs in Cz-Si with $N_{oxy}^{\ 0}$ of about $6.0 \cdot 10^{17}$ cm^{-3} under similar heat treatment conditions at atmospheric pressure is close to $6 \cdot 10^{13}$ cm^{-3} h^{-1}; in this connection see also [7]. It increases by a factor of five, up to $3.2 \cdot 10^{14}$ cm^{-3} h^{-1}, if high hydrostatic pressure is applied to Cz-Si during heat treatment. It should be mentioned that this value is even much larger than the production rate of TDDs in Cz-Si with high oxygen contents heat treated under normal conditions; cf $1.6 \cdot 10^{14}$ cm^{-3} h^{-1} in the Cz-Si with $N_{oxy}^{\ 0} = 1.1 \cdot 10^{18}$ cm^{-3} in [8].

Another important feature of the formation process of TDDs under stress is that their production rate at the beginning of heat treatment increases linearly with the initial oxygen concentration; cf $3.2 \cdot 10^{14}$ cm^{-3} h^{-1} in the Cz-Si with $N_{oxy}^{\ 0} = 6.0 \cdot 10^{17}$ cm^{-3} and $4.9 \cdot 10^{14}$ cm^{-3} h^{-1} in the Cz-Si with $N_{oxy}^{\ o} = 9.5 \cdot 10^{17}$ cm^{-3} . This is in a sharp contrast to what has been observed in Cz-Si annealed at atmospheric pressure. In the last case the initial

production rate is dependent on the fourth power of the oxygen concentration; see for instance [1,7]. The formation kinetics of TDDs under normal conditions varies directly with the duration of heat treatment, up to t = 20 h. Thereafter it deviates gradually from linearity, approaching a saturation plateau for 100 h ≤ t ≤ 200 h [8,9]. This is not true for Cz-Si heat treated under compressive stress where the kinetics becomes nonlinear for $t \geq 4$ h. As a result, the production rate of TDDs for t = 10 h is only a half of that observed just in the beginning of heat treatment.

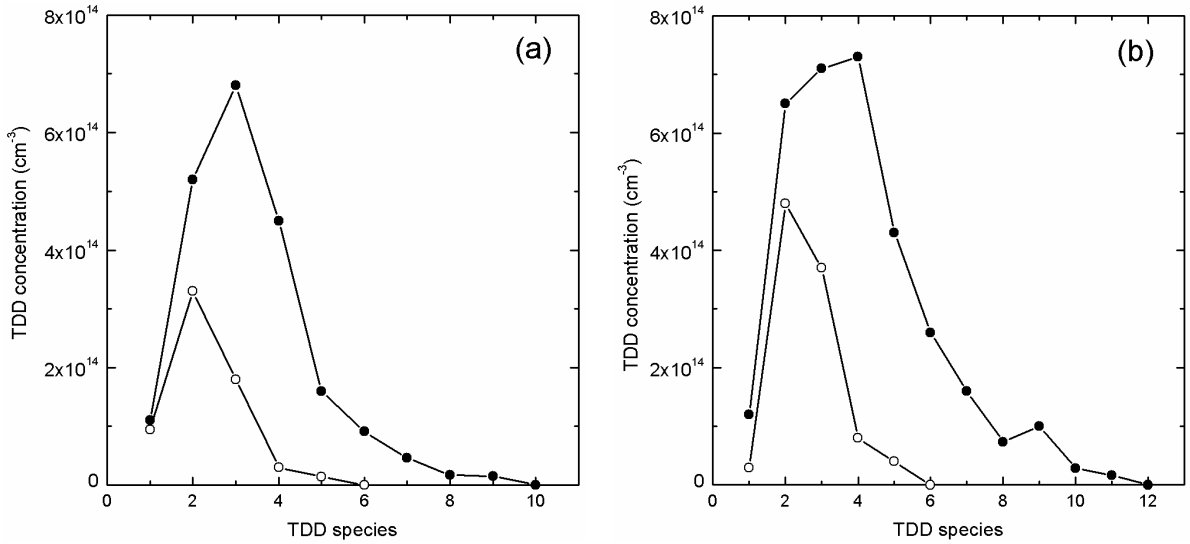

Fig. 3 TDD distributions in the heat-treated Cz-Si with different initial oxygen concentrations $N_{oxy}{}^{0}$: (**a**) 6.0·10^{17}cm^{-3} and (**b**) 9.5·10^{17}cm^{-3}. Heat treatment at T = 450ºC for t = 2 h (open circles) and 10 h (solid circles) under a hydrostatic pressure P = 1.2 GPa.

It is well known that the TDD family is a dominant kind of oxygen-related thermal donors formed during heat treatment of Cz-Si at T = 450°C for t ≤ 200 h under normal conditions. Contrary to this situation, the application of compressive stress to Cz-Si during the heat treatment leads to some strong modifications of oxygen aggregation processes. A combined analysis of the optical and electrical data showed that the fraction of TDDs formed under pressure is about one-third and one-fifth of the total concentration of thermal donors in the Cz-Si with low and high oxygen concentrations, respectively; cf Fig. 1a and 1b with Fig. 3. As is evident from Fig. 1a and 1b, there are a lot of other thermal donors whose shallow and deep energy states are located practically in the same ranges as those of the TDDs; see above. However, no sharp spectral lines associated with new shallow donor states can be seen in the IR absorption spectra, though their presence in Cz-Si annealed under stress is readily detected by electrical measurements. Further investigations are needed to gain a deep insight into the nature of these centers. Two characteristic features of their formation kinetics are of special interest. First, the production rate of these thermal donors was found to be very high, of about 2·10^{15} cm^{-3} h^{-1} in the Cz-Si with $N_{oxy}{}^{0}$ = 9.5·10^{17} cm^{-3} in comparison with the maximal production rate of TDDs under normal conditions, where it is smaller by an order of magnitude (see above). Second, their total concentration increases directly with the duration of heat treatment of Cz-Si with high oxygen contents under pressure. However, the formation kinetics reveals pronounced nonlinearity in materials with low oxygen concentrations.

4 Conclusions

The effects of high hydrostatic pressure upon oxygen agglomeration processes in Cz-Si heat-treated in a classical way at T=450°C have been studied in some detail. The formation of thermal double donors under compressive stress is greatly enhanced. Moreover, their formation kinetics is markedly changed as compared to

that observed at atmospheric pressure. Particularly, it should be pointed out that the initial production rate of TDDs varies proportional to the oxygen concentration, in contrast to the forth power law under normal conditions being well documented in the literature. However, despite the enhanced formation of TDDs under high hydrostatic pressure they do play a second role among other thermal donors formed. The properties of new donor centers seem to be puzzling taking into consideration that these thermal donors appear to be similar to the TDDs in some respects. The extremely high rates of their production put them in the forefront of future investigations.

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References

[1] P. Wagner, J. Hage, Appl. Phys. A **49,** 123 (1989).
[2] A Borghesi, B. Pivac, A. Sassella, A. Stella, J. Appl. Phys. **77**, 4169 (1995).
[3] V. V. Emtsev, B. A. Andreev, A. Misiuk, W. Jung, K. Schmalz, Appl. Phys. Lett. **71**, 264 (1997).
[4] V. V. Emtsev Jr., C. A. J. Ammerlaan, B. A. Andreev, V. V. Emtsev, G. A. Oganesyan, A. Misiuk, C. A. Londos, J. Mater. Sci.: Mater. in Electronics **12** (2001) 223.
[5] V.V. Emtsev, G.A. Oganesyan, K. Schmalz, Semiconductors **27,** 856 (1993).
[6] Yu. N. Daluda, V. V. Emtsev, P. D. Kervalishvili, V. I. Petrov, K. Schmalz, Sov. Phys. Semicond. **21,** 778 (1987).
[7] P. Wagner, in: Oxygen, Carbon, Hydrogen and Nitrogen in Crystalline Silicon, eds J.C. Mikkelsen Jr., S.J. Pearton, J. W. Corbett, S. J. Pennycook, MRS Symp. Proc., vol. **59**, MRS, Pittsburgh, Pennsylvania, 1986, p.125.
[8] P. Gaworzewski, K. Schmalz, Phys. Stat. Sol. (a) **55,** 699 (1979).
[9] P. Gaworzewski, K. Schmalz, Phys. Stat. Sol. (a) **58,** K223 (1980).