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"New Donors" in Czochralski Grown Silicon Annealed at $T \geq 600°C$ under Compressive Stress

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Abstract. Effects of compressive stress on oxygen agglomeration processes in Czochralski grown silicon heat treated at $T= 450^{O}C$, used as a reference temperature, and $T= 600^{O}C$ to $800^{O}C$ are investigated in some detail. Compressive stresses of about $P= 1$ GPa lead to enhanced formation of Thermal Double Donors in materials annealed over a temperature range of $T= 450^{O}C – 600^{O}C$. It has been shown that the formation of thermal donors at $T= 450^{O}C$ under normal conditions and compressive stress is accompanied with loss of substitutional boron. In contrast, the concentration of the shallow acceptor states of substitutional boron in silicon annealed under stress at $T\geq 600^{O}C$ remains constant. An enhancement effect of thermal donor formation is gradually weakened at $T\geq 700^{O}C$. The oxygen diffusivity sensitive to mechanical stress is believed to be responsible for the observed effects in heat-treated silicon.

Introduction

Silicon crystals grown by the Czochralski technique (Cz-Si) are known to be oxygen-rich. The oxygen concentration in as-grown crystals spans the range from $(3\text{-}5)\cdot 10^{17}$ cm^{-3} to slightly above $1\cdot 10^{18}$ cm^{-3}. This oxygen content in Si at room temperature appears to be higher than an equilibrium one by several orders-of-magnitude. Because of this the oxygen impurity atoms are prone to agglomeration in silicon materials subjected to heat treatment, forming various kinds of oxygen aggregates and precipitates. This is widely used in the fabrication of electronic Si-based devices for internal gettering purposes. The early stages of oxygen agglomeration at relatively low temperatures between $T=400^{O}C$ and $T=500^{O}C$ are characterized by formation of small oxygen aggregates not visible by electron microscopy. Most of them are electrically active, being of donor type. Among these thermal donors, one family of double donors, labeled the Thermal Double Donors (TDDs),

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consists of nearly twenty species. Their shallow and deep energy states are placed between E_C – 45 meV < $E_{shallow}$ < E_C – 70 meV and E_C – 100 meV < E_{deep} < E_C – 150 meV, respectively. The TDD family, absolutely dominating among all the thermal donors formed in Cz-Si for $t \leq 100$ hours over the temperature range given above, have been thoroughly investigated by a variety of experimental techniques; see for instance review papers [1-3]. With the increasing temperature of heat treatment the agglomeration and precipitation processes of oxygen in Cz-Si become more and more complicated. Large-scale precipitates and accompanying structural defects like dislocations etc are formed at elevated temperatures, especially at $T \geq 700^{O}C$ [3,4]. Some characteristic changes in these processes take place in the temperature range from $T = 600^{O}C$ to $T = 650^{O}C$. For a long time the thermal donors formed in this range were used to call the "New Donors", thus separating them from the TDD family by their properties and thermal stability [4]. Lately, it has been established that the so-called New Donors are in fact a combination of three families of thermal donors, also including the TDDs [5,6]. Recently, it has been found that the formation of TDDs in Cz-Si annealed at $T = 450^{O}C$ can be greatly enhanced due to compressive stresses of $P \geq 1$GPa [7,8]. Even in Cz-Si materials with low oxygen concentrations of $N_{OXY}^{O} \approx 6 \cdot 10^{17}$ cm^{-3} the enhancement factor in respect to the duration of heat treatment under compressive stress and normal conditions was found to be about six. These observations are believed to be associated with the increasing oxygen diffusivity in Si crystals subjected to compression [7,8]. Recent computer simulations of the oxygen diffusion process in Si under high hydrostatic pressures have also provided support to this suggestion [9]. The aim of the present work is to see how the effect of compressive stress upon thermal donor formation in Cz-Si is changed with the increasing temperature of heat treatment from $T = 450^{O}C$ to $T = 800^{O}C$.

Experimental

Samples were cut from several wafers of Cz-Si, nominally undoped or doped with boron and phosphorus in concentrations of $1 \cdot 10^{14}$ cm^{-3} to $2 \cdot 10^{15}$ cm^{-3}. The initial concentration of oxygen was in the range of $N_{OXY}^{O} = 6 \cdot 10^{17}$ cm^{-3} to $N_{OXY}^{O} = 9 \cdot 10^{17}$ cm^{-3}. The materials investigated were carbon-lean, $N_C < 5 \cdot 10^{16}$ cm^{-3}. Heat treatment under high hydrostatic pressures of about $P = 1$ GPa was carried out in a gas chamber in pure argon. Electrical measurements were carried out by means of a computerized facility making use of the Van der Pauw technique over a wide temperature range from T=20 K to T=300 K. Experimental curves of the charge carrier concentration *versus* reciprocal temperature, n (T), were analyzed on a basis of the relevant equations of charge balance. This makes it possible to separately determine the concentrations of shallow donors and compensating acceptors as well as other electrically active centers with ionization energies less than 0.3 eV. Samples were mostly annealed in pairs, at atmospheric pressure and under compressive stress, making the effect of stress on the formation of thermal donors much more pronounced. To have a look into distributions of Thermal Double Donors over their ionization energies IR absorption and photoconductivity spectra were also recorded at cryogenic temperatures, T< 20 K, in dark and under band gap illumination. In addition, this allows one to observe other majority and minority impurity centers, first of all the shallow ones of boron and phosphorus. Moreover, before taking IR spectra the heat-treated samples were illuminated with band gap light in the course of their cooling from room temperature down to cryogenic temperatures in order to transform all the bistable TDD1 and TDD2 species into the atomic configuration with the two normal donor states indicated above; see for instance [1]. On a basis of the known calibration factors for the electronic transitions at TDDs as well as shallow donor and acceptor centers [10] it is possible to convert the intensities of the relevant absorption lines into concentrations of the centers under consideration.

Results and Discussion

Heat treatment of Cz-Si at T= 450°C under compressive stress. The initial samples were of p-type, doped with boron in concentrations of about N_B= 2·10^{15} cm^{-3}. After a heat treatment step at atmospheric pressure for t= 10 hours the material was still of p-type but the hole concentration was substantially decreased due to an effective compensation of the shallow acceptor states of substitutional boron by TDDs. Conversion of the conductivity type $p \to n$ took place in the Cz-Si heat treated for t= 30 hours under normal conditions. As is seen from Fig. 1, at this stage only the deep donor states of TDDs, partially compensated at T= 0 K , can be found by electrical measurements. Further heat treatment at atmospheric pressure leads to the appearance of the both donor states of TDDs. Under compressive stresses of about P= 1 GPa, the formation of thermal donors at T= 450°C is greatly enhanced, so the electrical properties of samples heat treated under the stress for t= 10 hours are very similar to those of the same material heat treated for t= 120 hours under normal conditions.

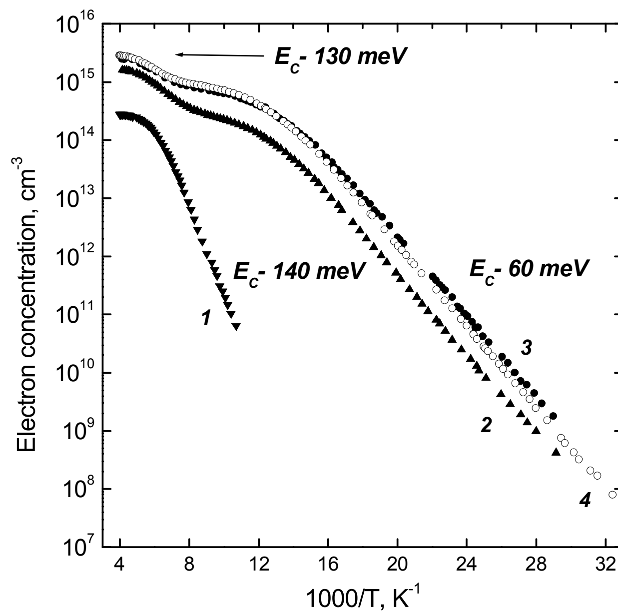

Fig. 1. Charge carrier concentration *vs* reciprocal temperature for the Cz-Si:B after $p \to n$ conversion due to heat treatment at T= 450°C for t= 30 hours (*curve 1*), 60 hours (*curve 2*) and 120 hours (*curve 3*) under hydrostatic pressures of P= 1.12 GPa. Initial oxygen concentration, 6.5·10^{17} cm^{-3}. The effective ionization energies of shallow and deep donor states are indicated.

A comparison between optical and electrical data reveals some characteristic features of the thermal donor production. First of all, it has been shown that the concentration of the shallow acceptor states of substitutional boron B_S is substantially decreased in the course of heat treatment of Cz-Si under normal conditions as well as compressive stresses of about P= 1 GPa; see Fig. 2*a*. The loss of substitutional boron atoms in Cz-Si heat treated at atmospheric pressure can be approximated by an exponential law of first order, i. e. $N(B_S) = N^{init}(B_S) \exp(-t/\tau) + N_0(B_S)$ where t is the annealing duration in hours, τ =46 hours, $N^{init}(B_S)$= 1.23·10^{15} cm^{-3} and $N_0(B_S)$= 4.14·10^{14} cm^{-3} are the initial and ultimate boron concentrations, respectively. Figure 2*a* also demonstrates that the loss of substitutional boron in heat-treated Cz-Si is greatly enhanced under high hydrostatic pressures, thus pointing out to a close relation of this process with the oxygen aggregation upon annealing. A very much pronounced decrease in the concentration of the boron acceptor states can be explained by the well-known Watkins reaction [11] taking place in electron-irradiated Si when mobile self-interstitials Si_I are trapped at substitutional boron atoms B_S leading to the appearance of interstitial boron atoms: $Si_I + B_S \to [Si\text{-}B]_I$. In the case of irradiation of silicon with fast electrons the self-

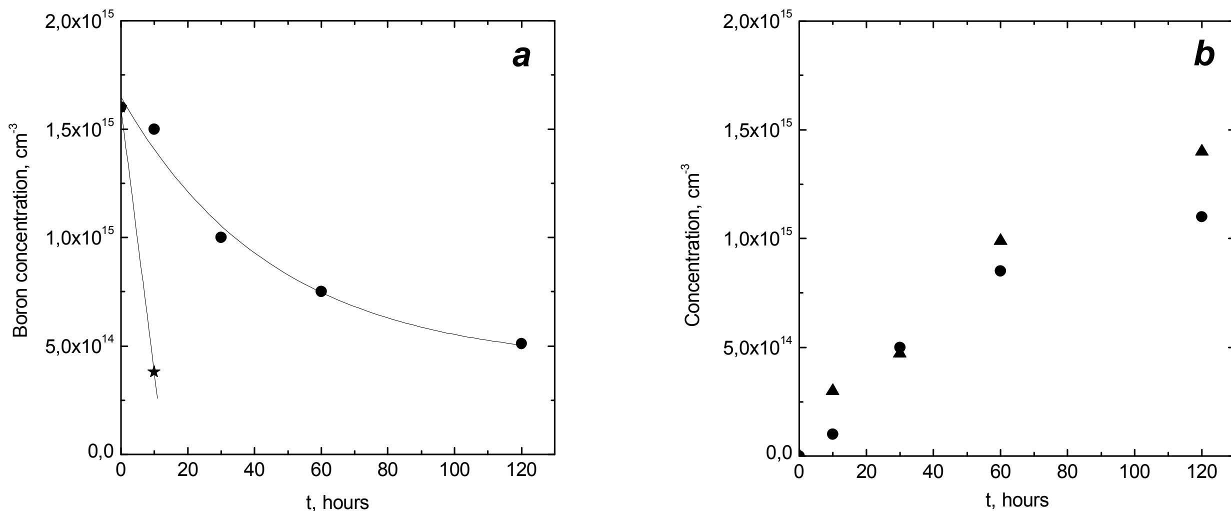

Fig. 2. (*a*) Loss of substitutional boron in the Cz-Si:B heat treated at T= 450°C as a function of the annealing time at atmospheric pressure (*circles)* and under hydrostatic pressures of P= 1.2 GPa (*stars*). Points, experimental; curves, calculated. Initial oxygen concentration, $6.5\cdot10^{17}$ cm^{-3}. *(b)* Changes in the concentrations of substitutional boron (*circles*) and Thermal Double Donors (*triangles*) for the Cz-Si:B heat treated at T= 450°C as a function of the annealing time at atmospheric pressure. Initial oxygen concentration, $6.5\cdot10^{17}$ cm^{-3}.

interstitials are produced as a result of dissociation of Frenkel pairs as primary defects. In our case of heat-treated Cz-Si, self-interstitials may come from the growing oxygen aggregates. Actually, the formation of oxygen aggregates is always associated with strains between them and the silicon matrix due to a considerable mismatch between the silicon oxide and silicon lattices. These strains can be reduced by emitting self-interstitials from the aggregate interface. Another important conclusion is that the Thermal Double Donors, most likely consisting of up to few tens of impurity oxygen atoms, are really produced self-interstitials. In actual fact, there is a striking correlation between the total concentration of TDDs and the observed loss of B_S in heat-treated materials, no matter under normal conditions or compressive stress; see Fig. 2*b*. This provides conclusive evidence that both processes are interdependent. At present it is not clear why the formation processes of TDDs is saturated at prolonged heat treatment. It may be due to a competitive equilibrium between direct and reverse reactions in the chain scheme of their formation; see for instance [12]. Of course, loss of substitutional boron in heat-treated Cz-Si must be taken into account in analysis of the electrical properties of materials after annealing, especially when the concentration of thermal donors is derived from conductivity data. It should be mentioned that a loss of B_S was observed previously in [13] by means of local mode spectroscopy in heavily doped materials with high oxygen concentrations. Because of this a direct comparison of the kinetics of oxygen agglomeration and loss of B_S in such materials for very long anneals, starting from $t \approx 100$ hours and up to 2400 hours, appears to be complicated.

Heat treatment of Cz-Si at T= 600°C to 800°C under compressive stress. In contrast to the oxygen agglomeration processes in Cz-Si at T= 450°C taking place just from the beginning of heat treatment, anneals of Cz-Si at T= 600°C under normal conditions display a latent period in the formation of thermal donors, when changes in the electrical properties of annealed materials are little if any. In Cz-Si materials with $N_{OXY}^{O} \approx 8\cdot10^{17}$ cm^{-3} this period is about $t \approx 20$ hours [5,6].

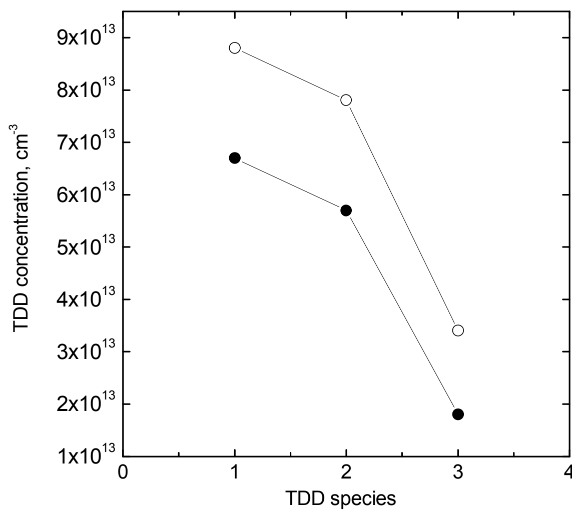

Fig. 3. Distributions of Thermal Double Donors in the Cz-Si:B heat treated at *T*= 600°C for *t*= 10 hours under hydrostatic pressures of *P*= 1.2 GPa. Initial oxygen concentration, 9.5·10^{17} cm^{-3} (*open circles*) and 6.0·10^{17} cm^{-3} (*black circles*).

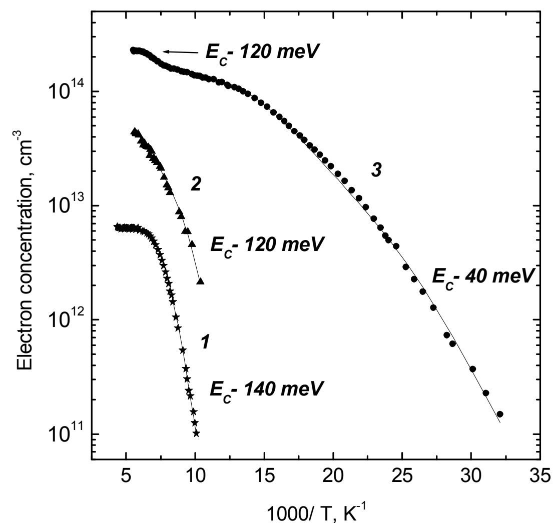

Fig. 4. Charge carrier concentration *vs* reciprocal temperature for the nominally undoped Cz-Si of n-type in the initial state (*curve 1*), after heat treatment at *T*= 650°C for *t*= 1 hour (*curve 2*) and *t*= 10 hours (*curve 3*) under compressive stresses of *P*= 1.06 GPa (*curve 3*). Initial oxygen concentration, 9.0·10^{17} cm^{-3}. The effective ionization energies of shallow

Contrary to the earlier belief that the TDD family in Cz-Si is unstable and cannot be formed at *T*= 600°C [3], these thermal donors make their appearance in noticeable concentrations of a few 10^{14} cm^{-3} in materials annealed at this temperature for $t \geq 60$ hours [5,6]. For prolonged annealing the TDD concentration runs closely into 10^{15} cm^{-3}. The situation is markedly changed during heat treatment of Cz-Si under high hydrostatic pressures of $P \approx$ 1 GPa. The formation of TDDs in concentrations of (1-2)·10^{14} cm^{-3} has already been observed in Cz-Si after a short heat treatment step at *T*= 600°C for *t* = 10 hours; see Fig. 3. In other words, the latent period in their formation is getting much shorter. It is also interesting to note that the formation rate of TDDs in Cz-Si materials at *T*= 450°C and *T*= 600°C under compressive stresses of *P*=1 GPa was found to be proportional to the initial oxygen content, though being different by an order-of-magnitude. The concentration of substitutional boron in Cz-Si annealed at *T*= 600°C, no matter under normal conditions or compressive stresses, does not change markedly. It means that other sinks for self-interstitials become important, resulting in the production of extended structural defects visible by electron microscopy, among them rodlike defects, dislocations etc [3]. With the increasing temperature of heat treatment of Cz-Si at atmospheric pressure, the fraction of TDDs in the "New Donors" is rapidly dropped, so after an annealing step at *T*= 700°C they can be present only in trace concentrations [6]. From Fig. 4 it is evident that the application of compressive stresses to materials subjected to high-temperature annealing also enhances the production of thermal donors at *T*= 650°C. However, the enhancement effect of high hydrostatic pressures at elevated temperatures $T \geq$ 700°C is faded away. As a result, the thermal donor production in Cz-Si annealed at *T*= 800°C under compressive stresses is barely detected, resembling the situation observed under normal conditions.

Conclusions

The influence of compressive stress on the early stages of oxygen agglomeration in Czochralski grown silicon subjected to heat treatment at T= 450°C was investigated in some detail. New information on the production of thermal donors has been gained. It has been demonstrated that the formation of Thermal Double Donors is accompanied by the loss of boron atoms at substitutional sites in a 1:1 correspondence. This implies a close relation between two processes via emitting self-interstitials from the growing oxygen aggregates. These mobile intrinsic defects are trapped by substitutional boron giving rise to the appearance of interstitial boron atoms. This effect takes place in materials annealed at T= 450°C under normal conditions. It was also found that the both processes in Cz-Si heat treated under high hydrostatic pressures of P= 1 GPa are enhanced at least by a factor of six on the time scale. With the increasing temperature of heat treatment under compressive stresses the formation of Thermal Double Donors in Cz-Si at T= 600°C to 650°C is also running faster, though at markedly reduced rates as compared to those observed at T= 450°C. The enhancement effect of compression becomes extinct at T= 800°C. This behaviour correlates reasonably well with the calculated oxygen diffusivity in silicon annealed under high hydrostatic pressures [9].

Acknowledgments

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