

Early stages of oxygen aggregation and thermal donors in silicon annealed under hydrostatic pressure

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Thermal donor formation in Czochralski-grown silicon heat treated at $T = 450^\circ\text{C}$ under hydrostatic pressure is investigated by means of optical and electrical measurements. It has been shown that oxygen agglomeration processes in stressed Cz-Si lead to an enhanced formation of the well-known thermal double donors. This effect is believed to be due to increasing oxygen diffusivity under stress. Some important differences between the formation processes in Cz-Si annealed under normal conditions and high hydrostatic pressure are discussed.

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1. Introduction

Oxygen impurity atoms in Czochralski-grown silicon (Cz-Si) are present in concentrations well above their solubility at $T < 1000^\circ\text{C}$. Because of this they are prone to agglomerate in Cz-Si upon heating. Small oxygen aggregates of different size are formed intensively at $T \approx 450^\circ\text{C}$. They have electrically active cores, so the formation of thermal double donors (TDDs) is observed; see, for instance, the review by Wagner and Hage [1]. This family of oxygen-related thermal donors consists of more than 16 species (TDD1, TDD2 and so on) with their shallow and deep energy states in the ranges of $E_C - (40 \text{ to } 70) \text{ meV}$ and $E_C - (100 \text{ to } 160) \text{ meV}$, respectively [1–3]. At the beginning of heat treatment at around $T = 450^\circ\text{C}$ the TDD family appears to be the principal kind of thermal donors formed. The formation rate and maximal concentration of TDDs are strongly dependent on impurity concentrations in Cz-Si crystals, first of all oxygen and carbon [1, 4, 5].

Recently [6, 7] it has been established that high hydrostatic pressure applied to Cz-Si at $T = 450^\circ\text{C}$ can enhance the oxygen agglomeration processes. As a result, the total concentration of thermal donors formed

in Cz-Si at a pressure of $P \approx 1 \text{ GPa}$ increases by an order-of-magnitude as compared to that formed at atmospheric pressure. Reportedly [8], similar effects of hydrostatic pressure were also observed in oxygen-implanted Si layers annealed at $T = 450^\circ\text{C}$. In addition, the electrical data [6, 7] strongly suggest that the stress leads to modifications of the formation processes of thermal donors. Under these conditions, the well-known TDD family seems not to be a dominant one among other oxygen-related donors. However, the photoconductivity spectra showing the presence of thermal double donors in Cz-Si heat treated under stress [6, 7] could not provide quantitative information on their concentration.

The main purpose of the present work is to study the effects produced by hydrostatic pressure on the TDD formation in Cz-Si with different concentrations of oxygen.

2. Experimental

Several p-type Cz-Si wafers were used. The concentrations of boron were in the range from $1 \times 10^{15} \text{ cm}^{-3}$ to $2 \times 10^{15} \text{ cm}^{-3}$. The compensation ratio was small, less

than 10%. The initial concentrations of oxygen were between $9.5 \times 10^{17} \text{ cm}^{-3}$ and $6.0 \times 10^{17} \text{ cm}^{-3}$ using a conversion factor of $2.45 \times 10^{17} \text{ cm}^{-2}$ for the oxygen absorption band at 1108 cm^{-1} . The carbon concentrations were less than $5 \times 10^{16} \text{ cm}^{-3}$.

Square samples cut from the wafers were annealed at $T = 450^\circ\text{C}$ for $t = 10 \text{ h}$ in pure argon under a hydrostatic pressure of $P = 1.0 \text{ GPa}$ or 1.2 GPa . Some reference samples were heat treated under similar conditions at atmospheric pressure. After heat treatment, a layer of about $50 \mu\text{m}$ was removed from the sample surface by polishing and etching.

Infrared absorption spectra at $T < 6 \text{ K}$ were recorded in the range of $200\text{--}800 \text{ cm}^{-1}$ with the help of an IFS-113V Bruker spectrometer. The resolution was 1 cm^{-1} . Hall effect measurements over the temperature range of 20 K to 300 K were conducted by the Van der Pauw technique. Experimental curves of the charge carrier concentration versus reciprocal temperature, $n(T)$, or $p(T)$, were analyzed on the basis of the relevant equations of charge balance, similar to those used earlier [4, 9].

3. Results and discussion

The effects of high hydrostatic pressure on the thermal donor formation are very pronounced in all the samples studied. By way of example, in Fig. 1 we show two $n(T)$ curves for the p-Cz-Si annealed at $T = 450^\circ\text{C}$ for $t = 10 \text{ h}$ under the stress. As a result of the heat treatment the initially p-type Cz-Si samples were converted to n-type. This effect is profound, since the electron concentration at room temperature is larger than $5 \times 10^{14} \text{ cm}^{-3}$, even in the samples with low concentrations of oxygen. Under the same heat treatment conditions at atmospheric pressure, the reference samples clearly showed p-type conductivity. The thermal donors formed consist of different kinds of shallow and deep centers [6, 7]. In the present paper we discuss the formation processes of thermal double donors only.

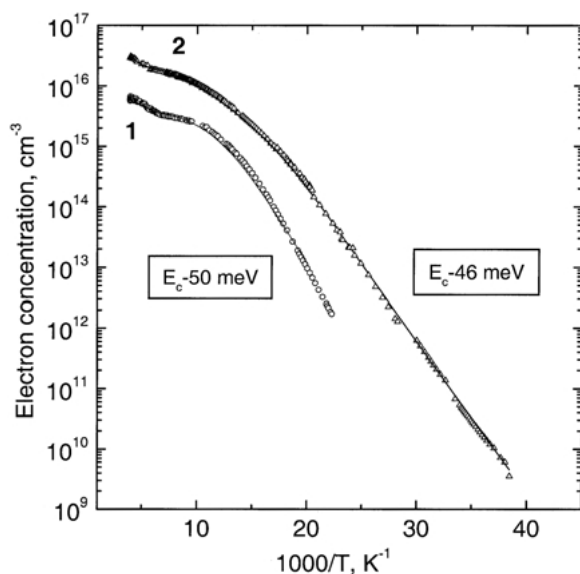


Figure 1 Electron concentration versus reciprocal temperature in two Cz-Si samples annealed at $T = 450^\circ\text{C}$ for $t = 10 \text{ h}$ under a hydrostatic pressure of $P = 1.2 \text{ GPa}$. The initial concentrations of oxygen are $6.0 \times 10^{17} \text{ cm}^{-3}$ (curve 1) and $9.5 \times 10^{17} \text{ cm}^{-3}$ (curve 2).

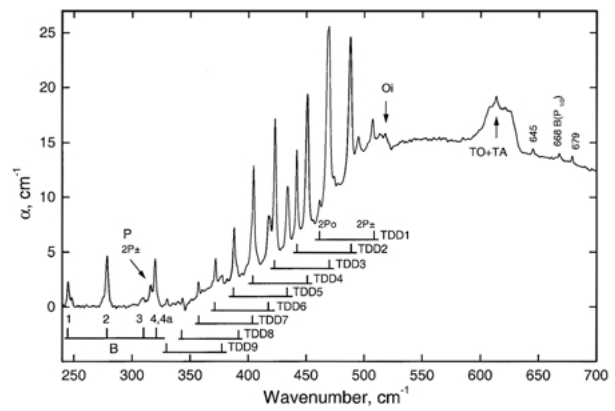


Figure 2 Infrared absorption spectrum for one of the Cz-Si samples annealed at $T = 450^\circ\text{C}$ for $t = 10 \text{ h}$ under a hydrostatic pressure of $P = 1.2 \text{ GPa}$. The initial concentration of oxygen is $6.0 \times 10^{17} \text{ cm}^{-3}$. Before measurements the sample was cooled down to $T < 6 \text{ K}$ under bandgap illumination. The spectrum was 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.

The presence of thermal double donors in heat-treated samples can be detected by means of IR spectroscopy; see Fig. 2. The absolute concentration of each identified species can be estimated using the optical cross-sections of the $2p_0$ transitions of the neutral TDDs [10]. On this basis it has been established that the stress applied to Cz-Si during heat treatment leads to a substantial increase in the concentration of TDDs. In fact, judging from the TDD distributions given in Fig. 3 one can conclude that the heat treatment for $t = 10 \text{ h}$ at high hydrostatic pressure yields the same results as the heat treatment for $t = 60 \text{ h}$ 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 governing factor in the sequential agglomeration of oxygen atoms leading to the appearance of TDDs; see,

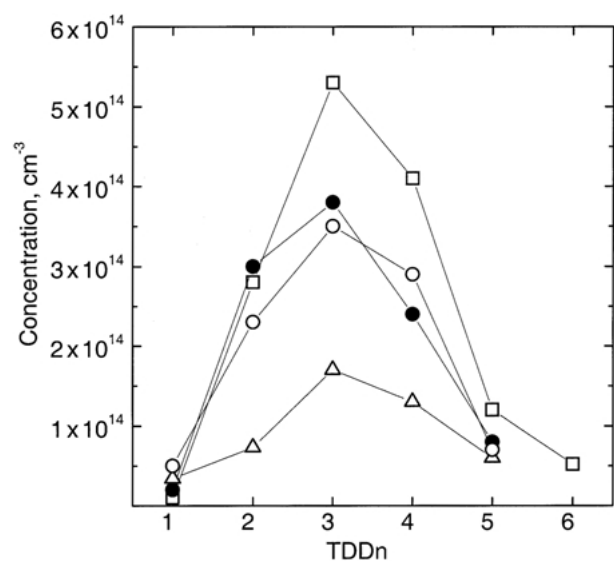


Figure 3 Distributions of double thermal donors in Cz-Si annealed at $T = 450^\circ\text{C}$ for $t = 30 \text{ h}$ (Δ), $t = 60 \text{ h}$ (\circ), and $t = 120 \text{ h}$ (\square) at atmospheric pressure and for $t = 10 \text{ h}$ (\bullet) under a hydrostatic pressure of $P = 1.0 \text{ GPa}$. The initial concentration of oxygen is $6.5 \times 10^{17} \text{ cm}^{-3}$.

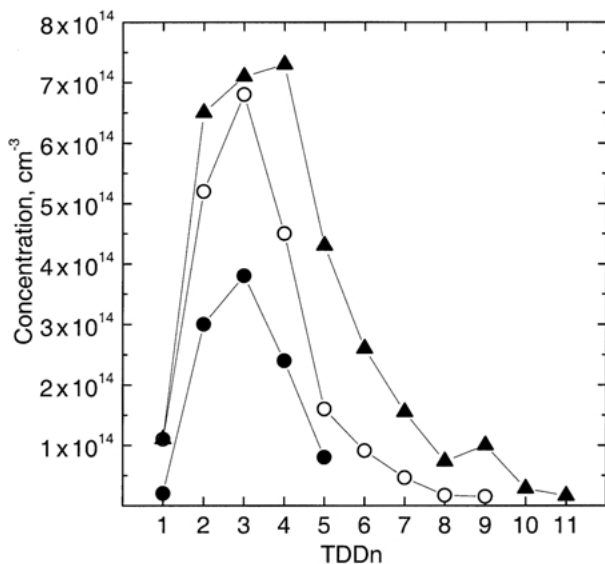


Figure 4 Distributions of double thermal donors in the Cz-Si annealed at $T=450^\circ\text{C}$ for $t=10\text{ h}$ under a hydrostatic pressure of $P=1.0\text{ GPa}$ (●) and $P=1.2\text{ GPa}$ (○ and ▲). The initial concentrations of oxygen are $6.5 \times 10^{17}\text{ cm}^{-3}$ (●), $6.0 \times 10^{17}\text{ cm}^{-3}$ (○), and $9.5 \times 10^{17}\text{ cm}^{-3}$ (▲).

for instance, the review by Newman [11]. In such a case, the enhanced TDD formation can be associated with increasing diffusivity of oxygen under stress. It is interesting to note in this connection that the local vibrational modes of isolated 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 $P \geq 1\text{ GPa}$ [12]. In fact, a pronounced enhancement of oxygen agglomeration under pressure starts at about 0.8 GPa [7]. Fig. 4 displays another prominent feature. An increase of pressure by 20% doubled the total concentration of TDDs. Therefore, the oxygen diffusivity in Si should be rather sensitive to pressure above 1 GPa . From the same figure it is evident that the shape of TDD distributions is dependent on the initial oxygen concentration in heat-treated Cz-Si. Computer analysis of the kinetics curves requires separate investigation.

In conclusion, it has been established that the oxygen agglomeration processes in Czochralski-grown silicon leading to the appearance of thermal double donors depend markedly on the hydrostatic pressure $P \geq 1\text{ GPa}$ applied during heat treatment at $T=450^\circ\text{C}$. It is thought that the enhancement effect observed is due to increasing oxygen diffusivity in silicon under stress. As in the case

of heat treatment of Cz-Si at atmospheric pressure, the TDD distribution obtained under stress is strongly dependent on the initial oxygen concentration. However, it appears that the shapes of TDD distributions in stressed Cz-Si with high oxygen contents differ noticeably from those observed in Cz-Si heat treated under normal conditions; compare [1] to the present work. It may mean that in addition to the oxygen diffusivity other factors operative in the formation processes should also be taken into consideration. The initial formation rate of TDDs in Cz-Si annealed under high hydrostatic pressure was found to be roughly proportional to the initial oxygen concentration. This hints at some peculiarities of the agglomeration processes, since under normal conditions the initial rate of thermal donor formation at $T=450^\circ\text{C}$ is known to be nearly proportional to the fourth power of the oxygen concentration; see, for instance, the review by Newman [11].

Acknowledgments

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