ABSTRACT
Thermal donor formation in Czochralski grown silicon heat treated at $T=450^\circ C$ under a hydrostatic pressure of $P=1.2$ GPa are investigated by means of optical and electrical measurements. It has been shown that the applied stress leads to an enhanced formation of the well-known Thermal Double Donors. However, this way of thermal donor formation plays only a subsidiary role, in contrast to what is observed in Czochralski grown silicon heat treated under normal conditions. Stress-induced modifications of oxygen aggregation lead to the appearance of new donor centers.

INTRODUCTION
Oxygen impurity atoms in Czochralski grown silicon (Cz-Si) are present in concentrations much above its solubility at room temperature. Because of this they are prone to aggregate upon heating of Cz-Si. Small oxygen aggregates of different size start forming intensively at $T \approx 450^\circ C$. The clusters are electrically active, so the formation of Thermal Double Donors (TDDs) is observed; see for instance Wagner and Hage (1). 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 Wagner and Hage (1), Götz et al (2), Liesert et al (3). At the beginning of heat treatment at around $T=450^\circ C$ the TDD family appears to be a principal kind of thermal donors formed. The formation rate and maximal concentration of TDDs is strongly dependent on impurity concentrations in materials, first of all those of oxygen and carbon; Wagner and Hage (1), Gaworzewski and Schmalz.
(4,5). Carbon if present in high contents can suppress the TDD formation completely, Wagner and Hage (1).

Recently it has been established that high hydrostatic pressure applied to Cz-Si at
\( T=450^\circ C \) can enhance and modify oxygen aggregation processes, Emtev et al (6,7). As a
result, the total concentration of thermal donors formed in Cz-Si at a pressure of \( P=1 \) GPa
increases by an order-of-magnitude as compared to that formed at atmospheric pressure.
Reportedly, similar effects of pressure are also observed in oxygen-implanted Si layers,
Neustroe et al (8). In addition, the electrical data showed that the stress leads to strong
modifications of oxygen-related thermal donors, Emtev et al (6,7). Under these conditions
the well-known TDD family is not a principal one.

The present work deals with the effects produced by hydrostatic pressure on the
formation of thermal donors in Cz-Si with different concentrations of oxygen and carbon.

EXPERIMENTAL

Two wafers labelled S and E were cut from the seed and end portions of the same p-type Cz-Si
ingot. The concentrations of boron were \( 1.34 \times 10^{15} \) cm\(^{-2} \) and \( 1.78 \times 10^{15} \) cm\(^{-3} \) in the S and E
wafers, respectively. The compensation ratio was small, between 3 and 5 per cent. The initial
concentrations of oxygen in the S and E wafers were \( 9.5 \times 10^{17} \) cm\(^{-3} \) and \( 6.0 \times 10^{17} \) cm\(^{-3} \),
respectively. The carbon concentrations in both wafers were less than \( 5 \times 10^{16} \) cm\(^{-3} \). One wafer
was cut from a n-type Cz-Si ingot. The concentration of phosphorus was \( 3.0 \times 10^{14} \) cm\(^{-3} \). The
compensation ratio was 15 percent. The initial concentrations of oxygen and carbon were
\( 7.0 \times 10^{18} \) cm\(^{-3} \) and \( 9.0 \times 10^{18} \) cm\(^{-3} \), respectively.

Samples cut from the wafers were annealed at \( T=450^\circ C \) for up to 10 hours in pure
argon under a hydrostatic pressure of \( P=1.2 \) GPa. After the heat treatment, a layer of about 50
\( \mu m \) was removed from the sample surface by polishing and etching.

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\(^{-1} \). Hall effect
measurements over the temperature range of 50-300 K were conducted with the help of the
Van der Pauw technique. Experimental curves of the charge carrier concentration vs reciprocal
temperature, \( n(T) \) or \( p(T) \), were analyzed on the basis of the relevant electroneutrality
equations, similar to those used earlier; Gaworzezowski and Smalz (4), Emtev et al (9).

RESULTS AND DISCUSSIONS

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 and Fig. 2 we show some \( n(T) \) curves
for the p- and n-type Cz-Si annealed at \( T=450^\circ C \) for \( t=10 \) hours under the stress. As a result
of the heat treatment the initially p-type Cz-Si samples were converted to n-type, even for
short duration. This effect is profound, since the electron concentrations at room temperature
are about \( 4 \times 10^{15} \) cm\(^{-3} \) and \( 7 \times 10^{14} \) cm\(^{-3} \) in the samples from the seed and end portions of the
crystal, respectively. Under normal conditions, such strong effects due to heat treatment at
\( T=450^\circ C \) could be observed only for \( t=40 \) hours, based on the well documented information in
the literature; Gaworzezowski and Smalz (4), Wagner (10). The next question one has to
address is the nature of thermal donors formed.

First of all, the presence of TDDs can be detected by means of IR spectroscopy; see
Fig. 3. The absolute concentration of each identified species can be estimated using the optical

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Fig. 1. Electron concentration vs reciprocal temperature in two Cz-Si samples heat treated at $T_1=450^\circ C$ for $t=10$ hours under a hydrostatic pressure of $P=1.2$ GPa. The initial concentration of oxygen is $6.0 \times 10^{17}$ cm$^{-3}$ (curve 1) and $9.5 \times 10^{17}$ cm$^{-3}$ (curve 2).

Fig. 2. Electron concentration vs reciprocal temperature in the n-Si before heat treatment (curve 1), after heat treatment at 450$^\circ$C for 10 hours at atmospheric pressure (curve 2) and hydrostatic pressure of 1 GPa (curve 3). Initial oxygen concentration, $7 \times 10^{17}$ cm$^{-3}$.

Fig. 3. Infrared absorption spectrum for one of the Cz-Si samples heat treated at $T_1=450^\circ$C for $t=10$ hours under a hydrostatic pressure of $P=1.2$ GPa. The initial concentration of oxygen is $6.0 \times 10^{17}$ cm$^{-3}$. Before measurements the sample was cooled down to $T<6$ 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.

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cross-sections of the 2p\textsubscript{3} transitions of the neutral TDDs; Wagner (10). 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. In many models of the TDD formation the oxygen diffusivity is considered as a governing factor in the sequential agglomeration of oxygen atoms, Newman (11). In such a case, the enhanced TDD formation can be associated with increasing diffusivity of oxygen under stress.

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. 1. Their concentrations were found to be close to $2 \times 10^{16}$ cm\(^{-3}\). Compared with the total TDD concentration of about $3 \times 10^{17}$ cm\(^{-3}\) one can conclude that the oxygen aggregation processes are strongly modified under the applied stress. The nature and properties of these stress-induced thermal donors need further detailed investigations.

In the case of n-type Cz-Si with high concentrations of carbon a hydrostatic pressure of 1 GPa does not produce strong effects on the TDD formation, in contrast to carbon-lean materials; see above. Interestingly, the formation of new thermal donors at $E_c$ = -50 meV and $E_c$ = -130 meV under stress turned out to be insensitive to the presence of carbon.

In conclusion, the enhanced formation of Thermal Double Donors in Cz-Si heat treated at $T$=450°C at a hydrostatic pressure of $P=1.2$ GPa is observed. This effect is thought to be associated with increasing diffusivity of oxygen under stress. Along with these centers, new kinds of thermal donors with shallow and deep energy states are also formed. Their concentrations can exceed that of the TDD family by an order-of-magnitude. In contrast to the TDDs, the formation of new thermal donors appears to be practically independent of carbon concentrations.

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