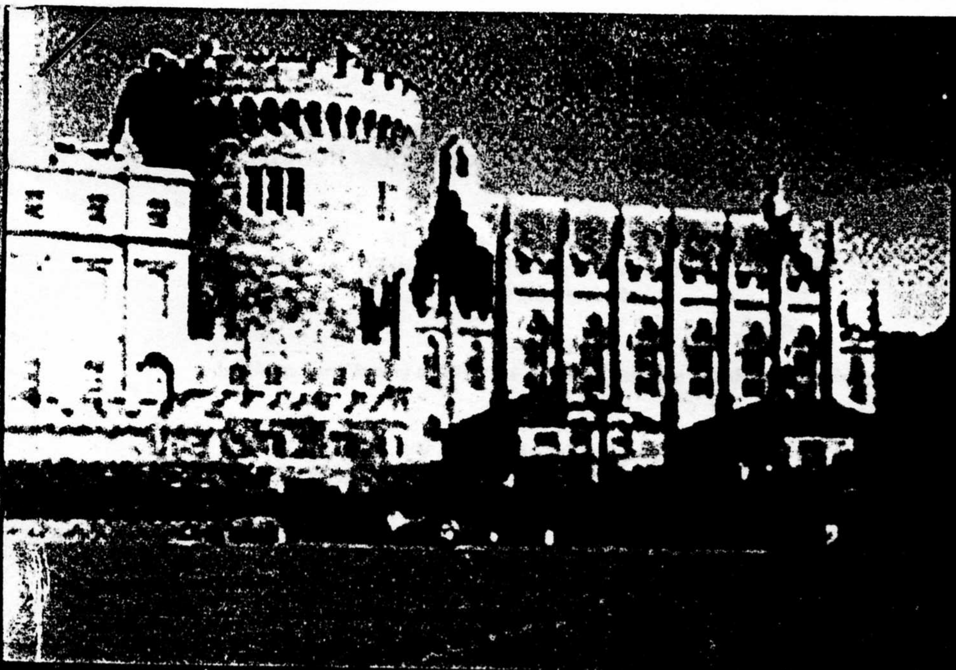
25



Conference Pre-Prints

3rd International Conference on

MATERIALS FOR MICROELECTRONICS

Dublin Castle, Republic of Ireland

IOM Communications

LECTRON
EVICES
OCIETY

Institute of Physics

16-17 | 10 | 2000

EARLY STAGES OF OXYGEN AGGREGATION AND THERMAL DONORS IN SILICON ANNEALED UNDER HYDROSTATIC PRESSURE

VV Emtsev Jr and CAJ Ammerlaan
Van der Waals-Zeeman Institute, University of Amsterdam
The Netherlands

BA Andreev
Institute for Physics of Microstructures, Russian Academy of Sciences
Russia

VV Emtsev and GA Oganesyan
Ioffe Physicotechnical Institute, Russian Academy of Sciences
Russia

A Misiuk
Institute of Electron Technology
Poland

CA Londos
Physics Department
University of Athens
Greece

ABSTRACT

Thermal donor formation in Czochralski grown silicon heat treated at T=450°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 ≈ 450°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°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°C can enhance and modify oxygen aggregation processes; Emtsev et al (6,7). As a result, the total concentration of thermal donors formed in Cz-Si at a pressure of $P\approx 1$ 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; Neustroev et al (8). In addition, the electrical data showed that the stress leads to strong modifications of oxygen-related thermal donors; Emtsev 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 $1.34\cdot10^{15}$ cm^{-3} and $1.78\cdot10^{15}$ 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 $9.5\cdot10^{17}$ cm^{-3} and $6.0\cdot10^{17}$ cm^{-3}, respectively. The carbon concentrations in both wafers were less than $5\cdot10^{16}$ cm^{-3}. One wafer was cut from a n-type Cz-Si ingot. The concentration of phosphorus was $2.0\cdot10^{14}$ cm^{-3}. The compensation ratio was 15 percent. The initial concentrations of oxygen and carbon were $7.0\cdot10^{17}$ cm^{-3} and $9.0\cdot10^{16}$ cm^{-3}, respectively.

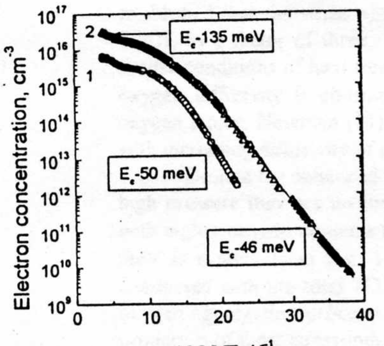
Samples cut from the wafers were annealed at T=450°C for up to 10 hours in pure argon under a hydrostatic pressure of P= 1.2 GPa. After the heat treatment, a layer of about 50 µm was removed from the sample surface by polishing and etching.

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 20-300 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; Gaworzewski anf Schmalz (4), Emtsev 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°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 $4\cdot10^{15}$ cm^{-3} and $7\cdot10^{14}$ 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°C could be observed only for t> 40 hours, based on the well documented information in the literature; Gaworzewski and Schmalz (4), Wagner (10). The next question one has to address to 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



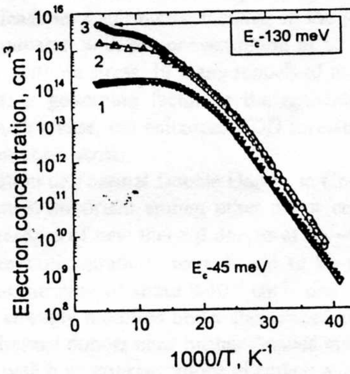


Fig. 1. Electron concentration *vs* reciprocal temperature in two Cz-Si samples heat treated at T=450°C for t=10 hours under a hydrostatic pressure of P=1.2 GPa. The initial concentrations of oxygen is $6.0 \cdot 10^{17}$ cm^{-3} (curve 1) and $9.5 \cdot 10^{17}$ cm^{-3} (curve 2).

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

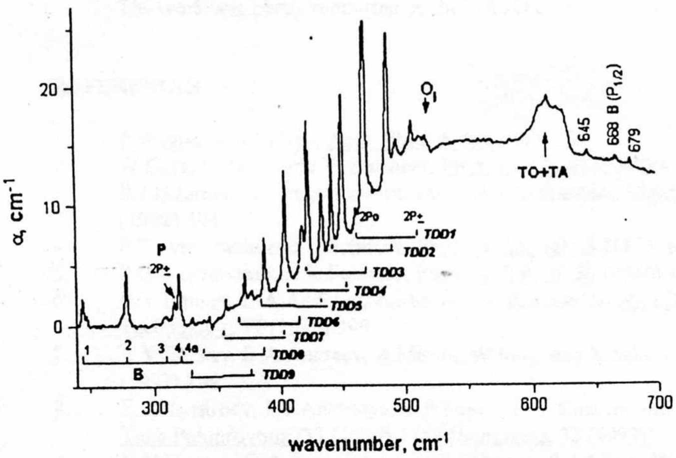


Fig. 3. Infrared absorption spectrum for one of the Cz-Si samples heat treated at T=450°C for t=10 hours under a hydrostatic pressure of P=1.2 GPa. The initial concentrations of oxygen is $6.0 \cdot 10^{17}$ cm^{-3}. Before measurements the sample was cooled down to T<6 K under bandgap illumination.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

cross-sections of the $2p_0$ 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 $2 \cdot 10^{16}$ cm^{-3}. Compared with the total TDD concentration of about $3 \cdot 10^{15}$ 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 $\approx E_C$–50 meV and $\approx E_C$–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.

The work was partly supported by the NATO project SA (HTECH CRG 974588).

REFERENCES

1. P.Wagner and J.Hage, Appl. Phys. A 49 (1989) 123
2. W.Götz, G.Pensl, and W.Zulehner, Phys. Rev. B 46 (1992) 4312
3. B.J.H.Liesert, T.Gregorkiewicz, and C.A.J.Ammerlaan, Mater. Sci. Forum 83-87 (1992) 404
4. P.Gaworzewski and K.Schmalz, Phys. St. Sol. (a) 55 (1979) 699
5. P.Gaworzewski and K.Schmalz, Phys. St. Sol. (a) 58 (1980) K223
6. V.V.Emtsev, B.A.Andreev, A.Misiuk, and K.Schmalz, NATO ASI Series (3.High Technology) 17 (1996) 345
7. V.V.Emtsev, B.A.Andreev, A.Misiuk, W.Jung, and K.Schmalz, Appl. Phys. Lett., 71 (1997) 264
8. E.L.Neustroev, I.V.Antonova, V.P.Popov, D.V.Kilanov, and A.Misiuk, Fiz. Tekh.Poluprovodn. 33 (1999) 1153 [Semicond. 33 (1999)].
9. V.V.Emtsev, G.A.Oganesyan, and K.Schmalz, Solid State Phenomena 47-48 (1996) 259
10. P.Wagner, MRS Symp. Proc. 59 (1986) 125
11. R.C.Newman, NATO ASI Series (3. High Technology) 17 (1996) 19