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Pressure-induced formation of electrically active centres in irradiated silicon: comparison of electron and neutron irradiation

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Abstract

The effect of annealing at 300–500 °C under enhanced hydrostatic pressure (up to 1.2 GPa) in argon ambient on the interstitial oxygen aggregation (thermal donors) in Czochralski-grown silicon subjected to electron and neutron irradiation was investigated by infrared absorption and electrical techniques. Strong pressure- and irradiation-enhanced changes in oxygen concentration, formation of intrinsic p–n-junctions, conversion of conductivity type due to formation of the thermal donors and thermal acceptors were found. A comparison with neutron-irradiated samples is made.

Keywords: Electron and neutron irradiation; Oxygen-related defects; Electrically active defects; Effect of pressure

1. Introduction

Annealing at moderate temperatures (300–700 °C) of silicon irradiated with electrons or neutrons leads to formation of two types of electrically active centres. Shallow thermal acceptors (TAs), belonging to the first type, are created in irradiated silicon after annealing at moderate temperature [1]. The origin of acceptors and the conditions of their formation are debatable. The well-known thermal donors (TDs) represent the second type of electrically active centres. They

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are formed in Czochralski-grown silicon (Cz-Si) only because interstitial oxygen is a component of TDs [2]. It has been established that the TD consist of several TD families, for example the shallow TD family with energy of ionisation $E_c - E_i \leqslant 30$ mev (STDs), and of the family of classical thermal double donors (TDDs) [3]. Irradiation by electrons or neutrons can affect the TD formation. Electron irradiation of silicon leads to the creation of point defects only [4], whereas neutron irradiation results, in addition, in the formation of relatively large defect clusters, known as the disordered regions [4]. Introduction of TAs is expected to be more pronounced in neutron-irradiated silicon in comparison with electron irradiation [1]. It is known that enhanced pressure (HP) of the gas ambient during annealing increases the formation kinetics of the oxygen-related TDs [5]. However, the effect of pressure on the TAs formation kinetics in the electron-irradiated silicon is practically unknown. The aim of the present work is to study and compare the HP effect on the TD and the TA formation in electron- and neutron-irradiated Cz-Si.

2. Experimental

p-Type Cz-Si samples with a hole concentration $p = (6–8) \times 10^{20}\,m^{-3}$ and initial oxygen concentration $[O_i]_o = 8 \times 10^{23}\,m^{-3}$ were used. The concentration of the interstitial oxygen, O_i, was monitored by measuring the well-known absorption band at $1107\,cm^{-1}$, using a calibration coefficient equal to $3.14 \times 10^{23}\,m^{-2}$. The electron irradiation was carried out in sets of pulses of 2.5 MeV energy, at a fluence in the range of 1×10^{14}–$1 \times 10^{17}\,cm^{-2}$. The pulse duration was 400 μs and the current flowing during the pulse was in the range of 0.12–0.14 A. The interval between pulses was varied so that the average sample temperature was kept below 50 °C. Another group of samples was irradiated with 2 MeV fast neutrons at room temperature, at a fluence of $5 \times 10^{16}\,cm^{-2}$. Then the samples were heat treated at temperatures between 300 and 500 °C, at atmospheric and enhanced hydrostatic pressure (HT–HP treatment), in argon ambient, in the HP range of 0.1–1.2 GPa, for times between 45 min and 10 h.

The carrier concentration was monitored by using high-frequency capacity–voltage, *CV*, and resistivity measurements. *CV* measurements were performed with the use of a mercury probe. The probe square was $4.5 \times 10^{-2}\,mm^2$. Following the HP–HT treatment, infrared (IR) absorption measurements with a resolution 4–0.5 cm^{-1} were carried out at 300–11 K over a spectral range of 1500–200 cm^{-1} with the aid of a Brucker IFS 113 v Fourier transform infrared (FTIR) spectrometer.

3. Experimental results and discussion

The relative concentrations of the interstitial oxygen, $[O_i]$ in silicon irradiated and HP treated in the temperature range of 300–325 °C are given in Table 1. Treatment at 300–325 °C of irradiated silicon regularly leads to annealing of the vacancy–oxygen, VO, centre and to the formation of the vacancy–two-oxygen, VO_2, defect. A strong decrease in the concentration of interstitial oxygen in the as-irradiated samples and in the samples annealed at 300–325 °C was found despite the fact that the temperature and time duration of the heat treatment were sufficient for the annealing of the main part of the electrically active defects (see Fig. 1). Fig. 1 presents the *CV* characteristics of electron-irradiated Cz-Si subjected to anneals at atmospheric pressure (AP) and to the HP treatment at 300 325 °C. The *CV* characteristic for the sample irradiated at a fluence of $10^{16}\,cm^{-2}$ is typical for p-type silicon (Fig. 1a, at negative

Table 1
The relative concentration of interstitial oxygen in silicon irradiated by electrons and HP treated at temperature of 300–325 °C

Electron fluence	Treatment	$[O_i]/[O_i]_o$
$1 \times 10^{16}\,cm^{-2}$	As irradiated	1
	300 °C, 1.1 GPa, 45 min	0.92
	325 °C, 1.1 GPa, 45 min	0.69
$1 \times 10^{17}\,cm^{-2}$	As irradiated	1
	300 °C, 1.1 GPa, 45 min	0.70
	325 °C, 1.1 GPa, 45 min	0.79

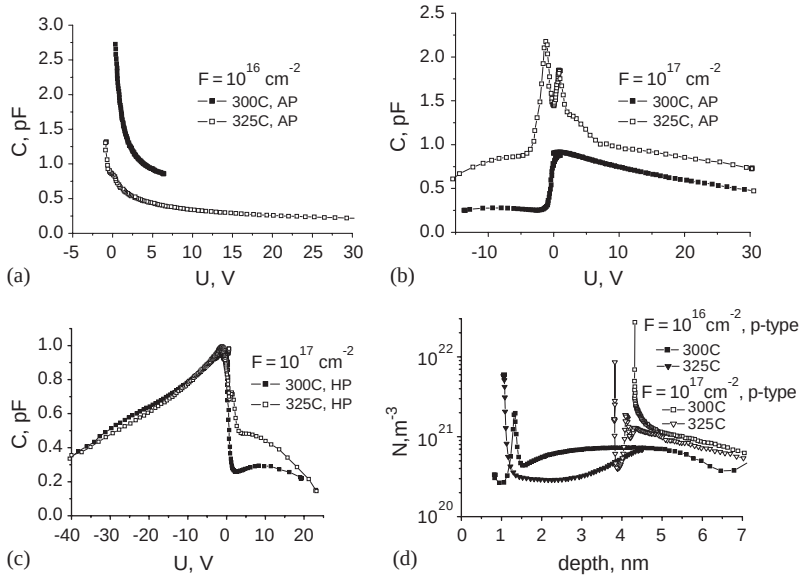

Fig. 1. Capacity–voltage characteristics (a–c) and carrier profiles (d) of electron-irradiated samples annealed at 300 and 325 °C for 45 min at different pressures. Values of electron fluence (F) are given in the figures. AP means atmospheric pressure while HP = 1.1 GPa.

voltage C is strongly increased). Formation of the intrinsic p–n junction(s) is revealed in the samples subjected to an electron fluence of $10^{17}\,cm^{-2}$ (Fig. 1b and c). The p–n junctions are formed both after annealing at AP and HP, but the carrier concentration in the p-type silicon was practically unchanged after such treatment (Fig. 1d).

Annealing at 450 °C leads to the inhomogeneous formation of the TDs and TAs at atmospheric pressure. The domains with p- and n-type conductivity are revealed in the samples irradiated with a high electron fluence of 10^{16}–$10^{17}\,cm^{-2}$ (Fig. 2). The presence of p-type domains and the increase in the hole concentration within domains as a function of annealing time are suggested to be related to the generation of the defect-related TAs. Formation of the domains with p- and n-type conductivity is correlated with a non-uniform distribution of oxygen. TAs are suggested to be electrically active complexes of TD-like oxygen aggregates with radiation defect(s).

Utilisation of the enhanced pressure during heat treatments causes uniform distribution of the carrier concentration in the crystal. Fig. 3 presents the donor concentration in silicon irradiated with

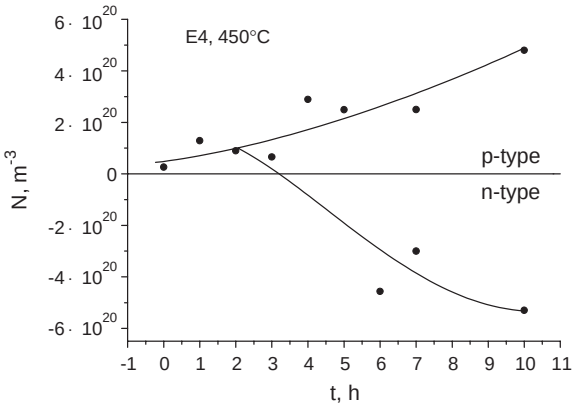

Fig. 2. Carrier concentrations as a function of annealing time obtained from CV measurements for p-type and n-type domains in the sample irradiated with $F = 1 \times 10^{17}\,cm^{-2}$ and annealed at 450 °C.

electrons and treated at 450 °C for 10 h, as a function of pressure. Electron fluence was the parameter. For the samples annealed at atmospheric pressure only domains with TDs were taken into consideration in Fig. 3.

An increase in the TD formation rate with pressure occurs in the non-irradiated crystals. Preliminary irradiation leads to the higher electron concentration at low pressure and to the lower electron concentration in the case of high pressure ~1 GPa. The decrease in the electron concentration after HP treatment of electron-irradiated samples is most likely connected with the simultaneous presence of TAs and TDs, but, in this case, both TAs and TDs have uniform distributions in the crystal. The difference between the electron concentrations in the non-irradiated and the irradiated samples is caused by the introduction of TAs. The TA concentration for the irradiated sample treated at HP of ~1 GPa is estimated from Fig. 3 to be equal or larger than $(1–1.5) \times 10^{21}\,cm^{-3}$.

Let us now consider the results for the neutron-irradiated samples. The carrier concentration n, the oxygen concentration $[O_i]$, and the phosphorous concentration P, obtained from resistivity and IR absorption measurements are presented in Table 2. In the IR absorption spectra, taken over a spectral region of 250–550 cm^{-1} at 11 K, the sharp lines related to the TDDs are observed in the samples heat treated at 450 °C. The total concentration of TDDs, estimated from the absorption data, are given in Table 2. The excess in electron concentration above the phosphorous concentration in the initial sample is most likely connected with the presence of STDs. The STD concentration in the initial samples is equal to $3.2 \times 10^{20}\,m^{-3}$. The decrease in phosphorous and oxygen concentrations in the neutron-irradiated samples is caused by the formation of complexes with radiation-produced vacancies. The carrier concentration in this sample was lower than the total of the phosphorous and TDDs concentrations ($9.56 \times 10^{20}\,m^{-3}$). As seen from Table 2, the high concentration of TDDs ($27.0 \times 10^{20}\,m^{-3}$) and of STDs ($52.8 \times 10^{20}\,m^{-3}$) is introduced in the HT–HP treated non-irradiated sample. It is, therefore, concluded that the production of TDDs in neutron-irradiated Cz-Si during HP–HT treatment at 450 °C is strongly reduced. This effect can be caused by the formation of TAs. The TA concentration in this case would be equal or higher than $6 \times 10^{20}\,m^{-3}$. This value (if compared with the corresponding values for electron–irradiated samples) is found to be lower than expected [1].

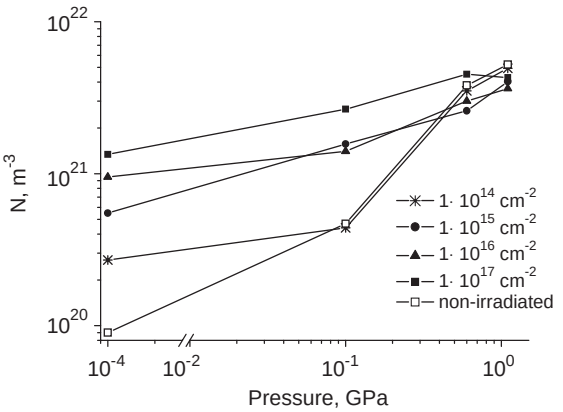

Fig. 3. Donor concentration in silicon irradiated with electrons and treated at 450 °C for 10 h as a function of the pressure. Electron fluences are given in the figure.

4. Conclusions

A non-uniform distribution of the TAs and TDs was found in silicon heat treated at 320 °C under AP and HP. A non-uniform distribution of the TAs and TDs was observed in silicon heat treated at 450 °C under AP and a uniform distribution of the TAs and TDs was found in silicon treated at

Table 2
Basic parameters of studied samples: parameters of the treatments, carrier concentration obtained from resistivity measurements, n, phosphorous (P) and interstitial oxygen concentrations ([Oi]) and TDDs concentration calculated from the FTIR data, N_{TDD}

Sample: n^o irradiation + treatment, temperature/time/pressure	n (m^{-3})	P (m^{-3})	$[O_i]$, (m^{-3})	N_{TDD}, (m^{-3})
Initial	8.2×10^{20}	5.0×10^{204}	8.5×10^{22}	—
n^o + 450 °C/10 h/1 GPa	2.4×10^{20}	3.7×10^{20}	7.7×10^{22}	5.86×10^{20}
450 °C/10 h/1 GPa	84.8×10^{20}	5.0×10^{20}	8.6×10^{22}	27.0×10^{20}

HP. The TA concentration for the electron-irradiated sample treated at HP of ~1 GPa is estimated to be equal or larger than $(1–1.5) \times 10^{21}\,m^{-3}$. The TA concentration in the case of neutron irradiation is equal or higher than $6 \times 10^{20}\,m^{-3}$.

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References

[1] Antonova IV, Stas VF, Neustroev EP, Popov VP, Smirnov LS. Thermal acceptors in irradiated silicon. Semiconductors 2000;34:155–60.
[2] Borhgesi A, Pivac B, Sassella A, Stella A. Oxygen precipitation in silicon. J Appl Phys 1995;77:4169–244.
[3] Emtsev VV, Oganesyan GA, Schmalz K. New donors in heat-treated Cz-Si, their components and formation kinetics. Solid State Phenom 1996;47–48:259–66.
[4] Smirnov LS, Novosibirsk, editors. Radiation technology for semiconductors. 1980. p. 292 (in Russian).
[5] Misuk A, Jung W. The effect of pressure on the concentration of thermal donors in Czochralski grown silicon. Phys Stat Sol B 1996;198:565–8.