**Dependence of high-pressure thermoelectric and mechanical properties of Cz-Si on nitrogen doping and P-T pre-treatment**

Sergey V. Ovsyannikov, Vladimir V. Shchennikov*, Nadezda A. Shaydarova, Vsevolod V. Shchennikov Jr1, Andrzej Misiuk2, Deren Yang3

High Pressure Group, Institute of Metal Physics of Russian Academy of Sciences, Urals Division, 18 S. Kovalevskaya Str., GSP-170, Yekaterinburg 620041, RUSSIA,
* e-mail: vladimir.v@imp.uran.ru

1 Institute of Engineering Sciences of Russian Academy of Sciences, Urals Division, GSP-207,34 S. Komsomolskaya Str, Yekaterinburg 620219, Russia

2 Institute of Electron Technology, Al. Lotnikow 32/46, PL-02-668 Warsaw, Poland

3 State Key Lab of Silicon Materials Science, Zhejiang University, Hangzhou 310027, People’s Republic of China

**Summary**

In the present work the thermoelectric and mechanical (compressibility) properties were studied of Czochralski-grown Si (doped with nitrogen and P-T pre-treated) at high pressure up to 20 GPa. The anomalies were established of the electronic, thermal and mechanical properties related to the phase transitions in Si. The influence of N – doping as well as P-T pre-treatment of samples is discussed on the above properties.

**Introduction**

Nowadays, in substrate manufacturing for advanced microelectronics devices and integrated circuits the silicon wafers cut from single crystalline Si rods are used (Nakai et al 2001). Typically, single crystalline Si rods for microelectronic applications are grown by the Czochralski technique (Cz-Si). Silicon produced by this technique contains residual oxygen mostly in intercite (Oi), which can affect the electronic, mechanical, thermal and other properties. It has been shown that presence of N atoms in Cz-Si results in locking of dislocations and, so, in increasing of mechanical strength. Nitrogen dopant can generate N-O complexes, suppress a creation of defects by increasing of activation energy, and affect an oxygen precipitation under annealing (Nakai et al 2001, Cui et al 2003, Misiuk et al 2004, Orlov et al 2004). Besides, doping with nitrogen in process of Cz-Si growth prevents a creation of grown-in defects (Nakai et al 2001). So, because of the reasons above-mentioned doping with nitrogen is actively applied in growing of large-diameter Cz-Si single crystals (Nakai et al 2001, Cui et al 2003, Misiuk et al 2004, Orlov et al 2004).

To remove the crystal originated particles from surface layer of Cz-Si wafers (Nakai et al 2001), and to reduce the residual oxygen concentration as-grown Cz-Si rods are usually annealed at high temperatures (Nakai et al 2001, Cui et al 2003, Misiuk et al 2004, Orlov et al 2004). At annealing, oxygen admixture transforms in part into electrically active oxygen-containing clusters (thermodonors) as well as into electrically passive spherical precipitates SiO2-x associated with structural defects (Misiuk et al 2004, Shchennikov et al 2003a, 2003b, 2004a, 2004b, Ovsyannikov et al 2004a, 2004b). Pressure medium was reported to enhance the oxygen precipitation process (Misiuk et al 2004). Cz-Si:N contains more oxygen precipitation centres then N-free Cz-Si mostly due to formation of N-O pairs and N2 complexes; that is the main reason why more Oi is removed from Cz-Si:N at annealing (Misiuk et al 2004).

Thermoelectric properties being very sensitivity to peculiarities of crystalline lattice, that is why thermopower data can contribute to understanding of electron structure features of semiconductors (Shchennikov et al 2003a, 2003b, 2004a, 2004b, Ovsyannikov et al 2004a, 2004b). Numerous thermopower studies have been performed on polycrystalline, amorphous, porous Si, and on the Si-based compounds and structures (Nakai et al 2001, Cui et al 2003, Misiuk et al 2004, Orlov et al 2004, Shchennikov et al 2003a, 2003b, 2004a,
2004b, Ovsyannikov et al 2004a, 2004b). Dependence of thermoelectric power especially of high pressure on pre-treatment conditions can supply information on charge carries and defects (Shchennikov et al 2003a).

So, a goal of the present research was to study the influences of both nitrogen doping and high-temperature pre-annealing on the thermoelectric properties and the phase transitions in Cz-Si single crystal substrates at high pressure (0–20) GPa at room temperature conditions.

**Experiment**

The samples of sizes ~ 200×200×20-50 µm were cut from the (111) oriented Czochralski-grown Cz-Si:N substrates (N concentration was \( C_N \leq 5 \times 10^{14} \) cm\(^{-3} \)) (Table 1). The high-pressure thermopower technique used corresponded to one described in (Shchennikov et al 2003a, 2003b, 2004a, 2004b, Ovsyannikov et al 2004a, 2004b).

**Table 1.** The samples' parameters and the results obtained for Cz:Si:N samples.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Pre-treatment conditions</th>
<th>Concentration of ( O_i ) [cm(^{-3} )]</th>
<th>Results obtained in the present work</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( P_t ) of direct S-M [GPa]</td>
</tr>
<tr>
<td>N1</td>
<td>(as-grown)</td>
<td>9×10(^{17} )</td>
<td>10.4</td>
</tr>
<tr>
<td>N2</td>
<td>957</td>
<td>8.3×10(^{17} )</td>
<td>9.4</td>
</tr>
<tr>
<td>N4</td>
<td>1130 Amb.</td>
<td>7×10(^{17} )</td>
<td>8.0</td>
</tr>
<tr>
<td>N5</td>
<td>1130 1 GPa</td>
<td>6.2×10(^{17} )</td>
<td>6.9</td>
</tr>
</tbody>
</table>

The concentrations of charge carriers (electrons) and their mobility at room temperature were as following \( n_e = 5.4 \times 10^{15} \) cm\(^{-3} \) (from Hall coefficient measurements) and 1380 cm\(^2\)/(Vs). The concentrations of residual interstitial oxygen \( O_i \) for all samples are given in Table 1. Some samples were subjected to pre-annealing at high temperatures \( T \) (957 and 1130 °C) at ambient and high gaseous (Ar) pressure conditions (~1 GPa). The above annealing was found to be optimal for oxygen precipitation in Cz-Si:N (Nakai et al 2001, Cui et al 2003). The pre-annealing conditions are summarized in Table 1.

**Results and discussions**

The \( S (P) \) dependencies obtained for the First and Second cycles of \( P \) increasing are presented at Fig.1 V Group element N is a donor for Si, that explained a negative sign of thermopower for all Cz-Si:N samples (Fig.1, Table 1). The Cz-Si:N samples underwent the semiconductor-metal (S-M) phase transition within \( P_t \sim 6.9-10.4 \) GPa range accompanying by the \( \sim 30-40 \) time decrease in \( S \) (Fig.1) as well as by the inversion of its sign (Fig.1a, insert). The S-M phase transition corresponds to the structural transformation from the initial diamond-like to the body-centred tetragonal lattice (\( \beta \)-Sn) (Shchennikov et al 2003a, 2003b, 2004a, 2004b, Ovsyannikov et al 2004a, 2004b). While, during the return transitions into the rhombohedral phase Si-XII (\( \rho 8 \)) near 9-11.5 GPa and into the Si-III (\( bc8 \)) phase with body-centred cubic structure near 2-3.5 GPa the thermopower kept a positive value (not shown at Figs).

Doping with nitrogen (sample \( N1 \)) resulted in a shifting the S-M transition to higher magnitude of pressure in comparison with undoped Cz-Si (Shchennikov et al 2003a, 2003b, 2004a, 2004b, Ovsyannikov et al 2004a, 2004b).

The \( P_t \) shifts may be explained by an effect of increasing of the mechanical strength and hardening of Cz-Si substrates grown under doping with N (Nakai et al 2001, Cui et al 2003, 2003b, 2004a, 2004b, Ovsyannikov et al 2004a, 2004b).
Misiuk et al 2004, Orlov et al 2004, Brinkevich et al 1999) The shift of S(P) curves at the First cycle of P increasing (Fig.1) may be induced by the different thermal pre-treatment conditions.

Fig. 1. The dependencies of thermoelectric power (Seebeck coefficient) S on pressure P for nitrogen-doped Cz-Si for consequent First (a) and Second (b) cycles of P increasing measured at T=293 K. (a) At the insert an enlarged fragment is shown of a part of S(P) near the n-p inversion; the arrow points the phase transition (as an example) for N5 sample. (b) At the insert the dependencies are shown of thermoelectric voltage U on thermal difference ∆T for N5 sample for the First cycle at different pressures (given in GPa at the plot).
Annealing at high temperatures resulted in a non-monotonic decrease of the concentration of residual interstitial oxygen $c_O$ in Cz-Si (Nakai et al 2001, Shchennikov et al 2003a, 2003b, 2004a, 2004b, Ovsyannikov et al 2004a, 2004b, Brinkevich et al 1999). The pressurised environment led to an additional decrease in $c_O$ value (Table 1). The data of S-M phase transition pressure $P_t$ versus $c_O$ for several groups of Cz-Si measured including ones doped with N are summarised at Fig. 2. The dependence has maximum at $c_O \sim 9 \times 10^{17}$ cm$^{-3}$. Basing on this correlation one can conclude that S-M $P_t$ in Cz-Si may be varied in a range of pressures $\sim$ (7–11) GPa. Influence of other factors such as doping and annealing on and is included via $c_O$. Probably, the maximum of $P_t$ ($c_O$) is related to low concentration of nucleation sites for phase transitions (Tolbert et al 1996).

**Fig.2.** The dependence of S-M phase transition pressure ($P_t$) on concentration of residual interstitial oxygen ($c_O$) for Cz-Si at $T=293$ K. The points were taken from the thermopower experiments: A – the data for Cz-Si:N from the present work, B and C – our data for undoped Cz-Si from Ovsyannikov et al 2004a, 2004b, Shchennikov et al 2004b and Shchennikov et al 2003a, 2003b, 2004a, respectively. The line is a fitting curve.

The typical contraction of the Cz-Si:N sample thickness is given at the Fig.3. One can see the contraction curve as well as behaviour of thermal gradient along a sample reflect the structural phase transformations in Si under the pressurisation detected by thermopower dependence on pressure (Fig.1 and (Ovsyannikov et al 2004a)).
Fig.3. The dependencies of contraction of Si:N single crystal (N1) under pressure at $T=293$ K. At the insert the thermal gradient is shown. The linear slopes of both dependencies were deducted (eliminated).

Within the high-pressure metal phase a thermopower behaviour of Cz-Si:N was similar to one for undoped $n$-type Cz-Si (produced by 10 hours annealing at 450 °C from as-grown $p$-type Cz-Si) (Shchennikov et al 2004b, Ovsyannikov et al 2004a, 2004b). But for high-pressure metal phases as well as for rhomboedral Si-XII (below ~ 9 GPa) and body-centred cubic Si-III phase (metastable below 2 GPa) the thermopower’s sign became positive both for Cz-Si:N (present paper) and for N-free Cz-Si (Shchennikov et al 2004b, Ovsyannikov et al 2004a, 2004b) indicating an essential change of binding type in the lattices.

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