Micro-characterisation of Si wafers by high-pressure thermopower technique

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Abstract

In the present work a set of Czochralski-grown silicon wafers (Cz–Si) differently pre-treated (annealed at high temperatures in pressure medium, doped with nitrogen, implanted with high-energy hydrogen ions) has been characterised by high-pressure thermopower \( S \) technique in the phase transitions region \((0–20 \text{ GPa})\). The shifts were observed in pressure of semiconductor–metal phase transition \( P_t \) determined from the \( S(P) \) under pre-treatments. For the first time, correlation dependence has been established between high-pressure thermoelectric properties on the one hand and concentration of residual interstitial oxygen \( c_{O} \) (which is always present in Cz–Si) on the other hand. The dependence exhibited a maximum of \( P_t \) near \( c_{O}/9 \times 10^{17} \text{ cm}^{-3} \).

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1. Introduction

Characterisation of Si wafers is important for micro-electronics and advanced micro-opto-electro-mechanical systems (MOEMS) technologies [1]. Single crystalline Si wafers are usually grown by the Czochralski (Cz) technique. Czochralski-grown silicon (Cz–Si) contains interstitial oxygen which is redistributed at annealing both into electrically active oxygen containing clusters and also into electrically passive precipitates associated with structural defects [2–4]. The first high-pressure thermopower \( S \) studies of silicon [5–8] have revealed a sensitivity of \( S \) value to the oxygen-related defects in Cz–Si. Thus, a pressure of semiconductor–metal (S–M) phase transition (from spherelite to \( \beta \)-Sn lattice) was established to depend essentially on oxygen states [6,7]. Also, the oxygen-related defects influence at whole \( S(P) \) dependence.

So, a purpose of the present work was a comparative characterisation of micro-samples of Si wafers that suffered different pre-treatments (\( P–T \) treatment; doping with N; implanted with H\textsuperscript{+}) (Tables 1–3), by thermoelectric measurements in the pressure region \( 0–20 \text{ GPa} \), where Si crystallizes into diamond-like (initial), and by three high-pressure modifications, body-centred tetragonal (\( \beta \)-Sn), body-centred orthorhombic (\( \text{Imma} \)) and simple hexagonal (\( sh \)) lattices [9].
Values of pressure were estimated with 10% uncertainty from a “stress–pressure” calibration curve obtained with assistance of known phase transitions in Bi, ZnS, GaP, etc. [10]. The high-pressure set-up [11] made it possible to measure simultaneously several parameters: applied force, sample’s contraction, anvils’ temperatures, thermal difference $\Delta T$ along a sample, and electrical signal from a sample [6,11]. A thermal difference was produced by heating of the anvils. The synthetic conducting diamond anvils served as a heater and a cooler in the $S$ measurements [10]. Both before and after high-pressure treatment, the crystal state of wafers were controlled by emission $L_{2-3}$ X-ray measurements using spectrometer with the high space ($\Delta l$~5 $\mu$m) and energy ($\Delta E$~0.4 eV) resolutions. Deconvolution of X-ray radiation into the spectrum was performed with assistance of diffraction grid with 2 m radius of curvature, 600 lines/mm. Accelerating voltage of the X-ray lamp anode was 8 kV with a current of 1000–1200 nA. The parameters of the Si wafers taken for characterisation are summarised in Tables 1–3.

### 3. Results and discussion

The $S(P)$ dependencies for p- and n-type wafers looked rather similar (Fig. 1). The drop in the absolute value of $S$ observed for all the Cz–Si samples (Fig. 1) was related to the S–M transition. For high-pressure phases of all 3 sets of Si wafers, holes conductivity has been established (Fig. 1). $S(P)$ dependencies for p-type wafers exhibited a minimum near 7–11 GPa, then $S$ value increased up to $\sim 13$–14 GPa, and decreased after $\sim 15$–16 GPa for majority of the samples (Fig. 1); the last two features were observed also for the n-type wafers (Fig. 1). Whereas, $S$ value at all high-pressure metallic phases were close ($S \approx 8 \pm 3$ $\mu$V/K), the sign of $dS/dP$ twice inverted (Fig. 1). So, we related these changes in $dS/dP$ to the phase transformations known in an interval of $P \approx 9$–16 GPa [9,12–18] (Fig. 1). Unlike the thermopower, value of electrical resistance $R$ and its pressure coefficient (not shown) had no appreciable peculiarities which might be related to the transitions.

The $P$–$T$ pre-treatment resulted in a change of both concentration and type of charge carriers because of formation of thermodonors [19,20] (Table 1); that led to a variation of $S(P)$ dependencies (Fig. 1a). However, above the semiconductor–metal phase transition point, the behaviour of $S(P)$ dependencies of p- and n- samples were rather similar (Fig. 1).

Doping with nitrogen during the process of Cz–Si growth prevents creation of grown-in defects [21] and results in an increase of mechanical strength. V-Group element N is a donor for Si that explained the negative sign of thermopower for the Si:N samples (Table 2, Fig. 1b). Doping with nitrogen (sample N1) (Table 2, Fig. 1b) resulted in a shift of S–M transition to higher magnitude of pressure in comparison with undoped Cz–Si (Table 1, Fig. 1a). Similar shifts to higher pressures were observed also for the return transitions in the sample N1 (not

### 2. Experiment

A quasi-hydrostatic pressure $P$ was produced in the anvil-type chambers [6,10,11]. The samples for investigation were cut from the Si wafers in the form of plates with sizes $\sim 200 \times 200 \times 20$–50 $\mu$m and were placed into a hole $\sim 250$ $\mu$m in diameter drilled in the centre of a catlinite container (which served as a pressure-transmitting medium). In case of wafers implanted with $H^+$ ions, the samples were cut from the implanted surface and contained both thin ($\sim 0.5$ $\mu$m) $H^+$-rich layers and crystalline Si. See Tables 1–3 for details on the samples.

### Tables

#### Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>$P$–$T$ pre-treatment</th>
<th>Concentration of interstitial oxygen ($10^17$)</th>
<th>Type of charge carriers</th>
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<tr>
<td>I</td>
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<td>11</td>
<td>p</td>
</tr>
<tr>
<td>D1</td>
<td>450 0.0001 10</td>
<td>10.3</td>
<td>n</td>
</tr>
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<td>450 0.1 10</td>
<td>8.9</td>
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</tr>
<tr>
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<tr>
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<td>10.2</td>
<td>p</td>
</tr>
<tr>
<td>B1</td>
<td>600 0.0001 10</td>
<td>10.7</td>
<td>p</td>
</tr>
<tr>
<td>B3</td>
<td>600 0.6 10</td>
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<td>p</td>
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<td>10.2</td>
<td>p</td>
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<tr>
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<td>650 1.5 10</td>
<td>8.2</td>
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<td>N1</td>
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<td>9</td>
<td>n</td>
</tr>
<tr>
<td>N2</td>
<td>957 amb 5</td>
<td>8.3</td>
<td>n</td>
</tr>
<tr>
<td>N4</td>
<td>1130 amb 5</td>
<td>7</td>
<td>n</td>
</tr>
<tr>
<td>N5</td>
<td>1130 1.0 5</td>
<td>6.2</td>
<td>n</td>
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#### Table 3

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<th>No.</th>
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<td>H3</td>
<td>$2 \times 10^{17}$</td>
<td>500</td>
</tr>
<tr>
<td>H4</td>
<td>$3 \times 10^{17}$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$H$^+$-rich surface layer was of n-type, but a sample containing a thin H$^+$-layer and p-type c-Si wafer was of p-type.
shown). Apparently, $P_t$ shifts may be explained by the effect of increase of mechanical strength and hardening of Cz–Si wafers grown under doping with $N_{21–24}$; increase of microhardness value has been noted for the crystals grown in N$_2$ atmosphere in comparison with the ones grown by the ‘‘typical’’ Czochralski technique—in Ar environment [25]). The shift of $S(P)$ curves (Fig. 1b) may be induced by the different thermal pre-treatment conditions (Table 2).

The p-Si samples containing a thin hydrogenated layer (Table 3) exhibited a decrease of $S$ value in the vicinity of S–M transition (Fig. 1c). Hydrogen implantation is known to result in a formation of nanoporous and amorphous Si [26–29], which exhibits n-type conductivity and influence on phase transitions [30]. So, $S$ lowering likely is related to an appearance of n-type conductivity in the layer [26].

Through the range of Si wafers (Tables 1, 2) one may find a correlation between variations observed in values of pressures of semiconductor–metal phase transitions $P_t$ on the one hand and concentrations of residual interstitial oxygen $c_O$ which are related to the structural defects on the other hand (Fig. 2). The dependence (Fig. 2) exhibited a maximum of $P_t \approx 10.4–11$ GPa near $c_O \approx 9 \times 10^{17}$ cm$^{-3}$. Influence of other factors such as doping and annealing on $P_t$ and thermopower may be analysed via changing $c_O$. Probably, the maximum of $P_t(c_O)$ is related to low concentration of nucleation sites for phase transitions, as

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Fig. 1. The large-scale dependences of thermoelectric powers $S$ of Czochralski-grown Si wafers on pressure $P$ at $T = 293$ K: (a) Si wafers after $P$–$T$ pre-treatment (Table 1); (b) Si wafers doped with nitrogen (Table 2), the arrow shows S–M transition; (c) Si wafers implanted with H$^+$ ions (for comparison $S(P)$ curves for corresponding substrates without H$^+$-layer are given) (Table 3). At the inserts the corresponding general view of $S(P)$ curves are given.

Fig. 2. Dependence of S–M phase transition pressure ($P_t$) on concentration of residual interstitial oxygen ($c_O$) for Cz–Si at $T = 293$ K. $P_t$ were established from $S(P)$ curves (Fig. 1) for Si wafers: A—Table 1, B—Table 2, C—from the Refs. [6–8]. The line is a fitting curve.
it has been offered for explanation of a high value (21 GPa) of $S$–M $P_T$ observed for the Si nanocrystallites coated with SiO$_2$ layer [31].

The emission $L_{2\,3}$ X-ray spectra exhibited 3 peaks related to the three maxima of density of states in valence band [7,8]. The $L_{2\,3}$ spectrum appears due to transition of electrons from 3s- and 3d-levels to vacancies of 2p- one [7,8]. The smoothing of peaks in a high-energy region allowed us to suppose the presence of amorphous phase (a-Si) after $P_T$ treatment up to 22 GPa, but the spectrum essentially is different from the a-Si one (Fig. 3). Whereas we established earlier under $P_T$ treatment up to 16 GPa the spectrum transformed to a-Si [7,8] due to fluctuations of both bond angles and bond lengths.

4. Conclusion

Thus, in the present work for the first time Si wafers were characterised by high-pressure thermoelectric power measurements. The study has revealed differences in $S(P)$ behaviour of wafers to be related to pre-treatment ($P$–$T$ annealing, doping, implantation). The correlation dependence has been established for the first time between $P_T$ determined from $S(P)$ on the one hand and $c_O$ on the other hand. The dependence exhibited a maximum of $P_T$ near $c_O \sim 9 \times 10^{17}$ cm$^{-3}$.

Acknowledgements

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References