Effect of hydrogen implantation on semiconductor–metal transition and high-pressure thermopower in Si

Sergey V. Ovsyannikov, Vladimir V. Shchennikov, Irina V. Antonova, Vsevolod V. Shchennikov Jr., Yuri S. Ponosov

Abstract

In the present work Czochralski-grown silicon single crystals were investigated implanted with different doses of H+ ions. The Si wafers were characterized by the Raman scattering technique. Thermoelectric power was studied in a pressure range of 0–20 GPa of p-type Si single crystal wafers containing a thin hydrogenated layer consisting of amorphous Si, nanocrystalline Si and H-rich Si layers. In the region of the pressure-induced phase transition from the initial semiconductor diamond-like into the metal β-Sn lattice, a lowering of thermopower values was noticed in comparison with ones of p-Si.

Keywords: Si; High pressure; Thermoelectric power (Seebeck coefficient); Phase transitions; Raman scattering

1. Introduction

Crystalline and amorphous Si are the basic materials for solid state electronics and optoelectronic technologies [1–4]. Layers of amorphous hydrogenated silicon produced at the surface of Si wafers by ion-plasma deposition or low-energy ion implantation [4] are promising for different technological applications. Thus, the study of electro-physical properties of Si:H/p-Si heterostructures formed by H+ implantation is important for the development of manufacture technologies of modern electronic devices [5].

The high-pressure thermopower S method is known to determine the type and concentration of charge carriers in microsamples as well as the changes in electron structure [6–10]. In the present work the high-pressure thermopower technique has been applied for the investigation of Si wafers with a hydrogenated layer in the 0–20 GPa pressure P range. The Raman scattering technique was used for the characterisation of the surface layer of Si wafer. Hydrogenated [11] and porous Si [12,13] layers typically exhibit negative values of S indicating dominant electronic conductivity, so their influence on the thermoelectric properties of p-type Si wafers would be expected to be essential.

2. Experiment

The Si wafers were grown by the Czochralski technique with (1 0 0) orientation. The implantation was carried out from a pulse source of ions with energy of 3–23 keV. The doses ranged from $2 \times 10^{16}$ to $3 \times 10^{17}$ cm$^{-2}$. A sample of 200 μm x 200 μm x 40 μm was cut with the help of an ultrasonic setup from a surface layer of a Si wafer as well as from a substrate. The samples cut from the surface contained a thin ~0.3 μm hydrogenated layer [4,5]. The surface of the wafers was characterized by Raman scattering (Fig. 1). The spectra were studied both for parallel $Z(X)Z$ and cross $Z(X)Y$ polarisations under excitation with the 514.5 nm line of an Ar-laser of 5 mW power. In this case the penetration depth of light in Si was comparable with thickness of the layer. Thus, a scattering light was collected both from the hydrogenated layer and from crystalline Si (c-Si).
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The measurements of thermolectric power $S$, electrical resistance $R$ and plunger displacement $\Delta P$ (characterising a thickness contraction of a sample) under high pressure $P$ were performed in an automated setup with synthetic diamond anvils supported by external pressure [6–10,14–23]. The thermolectric properties were determined at room temperature in the direction perpendicular to the layers by using the technique developed in Ref. [6]. The lithographic stone gasket was used as a pressure-transmitting medium [6]. Diamond is the best material for heat sink due to the highest value of thermal conductivity $\lambda_0$, that explains the usage of synthetic diamond anvils in our technique as a heater and a cooler for the creation of temperature difference $\Delta T$ across a sample, as well as electrical outputs to a sample [6,15–23]. Temperature difference $\Delta T$ was measured in the fixed points of the anvils by means of the thermocouples. The equation of thermal diffusion was solved by the finite difference method for numerous points of every element of the high pressure apparatus [24,16–18]. A temperature distribution in the anvils was calculated under variation in a wide range of both sample sizes and its thermal conductivity $0 < \lambda < \lambda_0$ [24,16–18]; the data obtained were used in determination of $\Delta T$ along a sample [6,16–24]. The $S$ measurements were carried out both at stationary conditions at constant density of a thermal flow $q$, and at non-stationary thermal regime [16–23]. The errors in measurements of $R$ and $S$ were estimated to be $\sim 5\%$ and $20\%$, respectively [6,16–24]. The $S(P)$ data gathered by the above technique for a list of materials [25] showed a good agreement with the ones obtained at hydrostatic pressure up to 2–9 GPa. Its hardly possible to reconcile wide pressure interval with high accuracy and high efficiency of $S(P)$ measurements. To solve this problem one can use a combine method (parallel studies at ultrahigh quasi-hydrostatic and moderate hydrostatic pressures) as it was suggested in Refs. [16–19].

The alternative technique of the thermopower measurements up to 25 GPa developed in Ref. [26] implies a creation of temperature gradient perpendicular to diamond anvils axis, and is used at present mainly in obtaining of temperature dependence of $S$ at fixed pressures [27–29]. In the modern version of this technique, the thermal gradient is created by laser heating (instead of electrical heating) but pressure range is usually limited by 10–12 GPa [30], where the apparatus with the large-volume compressible capsule with liquid media is preferable [31].

3. Results and discussion

The Raman spectra of the samples are presented at Fig. 1 for $Z(XX)\overline{Z}$ polarisation. The spectra exhibited the characteristic features both of amorphous (a-Si) and hydrogenated silicon (Si–H) ($\sim 160$–170, $\sim 300$, $\sim 470$, $\sim 620$–630, $\sim 790$–800, $\sim 950$ cm$^{-1}$) [32,33] and of c-Si (520 cm$^{-1}$). One may notice the increase of the peak intensities related to both a-Si and Si–H with the dose of H$^+$ implantation, while the increase of the c-Si line at 520 cm$^{-1}$ was also observed (Fig. 1, insert). Thus, in Ref. [32] the structures of some LO and LA lines were found to become weaker as the hydrogen concentration increased. This may be a reason for the non-monotonic dependence of Raman spectra on implantation, and in particular, of lowering of Raman intensities for sample H2 in comparison with the H1 one (Table 1, Fig. 1). Similar Raman spectra (but without second order 2LO phonon peak near 800 cm$^{-1}$) were established for the thin hydrogenated samples of Si [32]. An increase of H$^+$ implantation dose created the porous and amorphous Si layers responsible for the growth of the Raman peaks on the one hand, but on the other hand an increase of the amount of Si–H under implantation was able to reduce their intensities.

The pressure dependencies of $S$ (Fig. 2) reflected the phase transitions in Si at $\sim 8$, $\sim 12$ and $\sim 16$ GPa into B-Sn, orthorhombic and simple hexagonal lattices, respectively [9,34]. The $S(P)$ dependencies for both samples looked similarly (Fig. 2, samples H1 and H2 are not shown). A difference between the samples cut from a surface and from a volume of the wafers was seen in a region of the first transition (Fig. 2a). The lowering of the thermopower value was likely due to the presence of a hydrogenated Si layer always having n-type conductivity [11–13]. By the same reasons a break at the $S(P)$ dependencies in a region of the first transition shifted to lower pressures (Fig. 2a).

Under decompression the anomalies of $S(P)$ (Fig. 2b) were observed (not shown) related to the known transitions into Si-XII (below 9 GPa) and Si-III phase (below $\sim 3$ GPa). The last phase (Si-III) is stable at ambient conditions and is p-type semimetal.

Table 1
Parameters of Si wafers implanted with H$^+$ ions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dose of H$^+$ implantation (cm$^{-2}$)</th>
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<tbody>
<tr>
<td>H1</td>
<td>$2 \times 10^{16}$</td>
</tr>
<tr>
<td>H2</td>
<td>$1.6 \times 10^{17}$</td>
</tr>
<tr>
<td>H3*</td>
<td>$2 \times 10^{17}$</td>
</tr>
<tr>
<td>H4</td>
<td>$3 \times 10^{17}$</td>
</tr>
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* The wafer was additionally annealed at 500°C for 30 min.
An observed decrease of the thermopower after ultrahigh pressure treatment was related to a formation of the amorphous phase besides the metastable Si-III one. The presence of amorphous and nanoporous Si was concluded from the shift of the typical Raman peaks to the less wave numbers (Fig. 1, left insert). At the subsequent cycles of pressurization the phase transitions were observed already from the Si-III phase (Fig. 2, insert).

It is interesting to note that the phase transitions were seen also at the dependencies of plunger displacement (including both a contraction of sample thickness Δx, and the elastic deformations of the high-pressure setup, and the lithographic stone gasket) as well as at ΔT(P) curves (at permanent density of typical Raman peaks to the less wave numbers (Fig. 1, left insert). At the subsequent cycles of pressurization the phase transitions were observed already from the Si-III phase (Fig. 2, insert).

![Fig. 2. Thermopower S of Si samples (see Table 1) as a function of pressure P of at T=293 K: (a) at pressure range of 0–20 GPa and (b) in the phase transitions region into β-Sn, orthorhombic and simple hexagonal lattices. The dashed rectangles point the phase transitions regions established by the structural measurements [34]. (a) At the insert the dependencies are given of thermoelectric voltage U on thermal difference ΔT along a sample (substrate of H3) both for the first cycle of pressurisation [(1) P∼0.25 GPa, S=161 μV/K (determined from the linear slope); (2) P∼0.35, S=307 μV/K; (3) P=18.7 GPa, S=9.5 μV/K], and for the second one [(4) P∼0.38 GPa, S=11.7 μV/K]. (b) The insert shows S(P) curves for the second cycle of pressurisation.

![Fig. 3. Pressure dependencies of sample contraction Δx(a), and the temperature difference ΔT(b) for H4 sample (the large linear contributions were subtracted to reveal anomalies related to transitions, so magnitudes near “y”-axis are relative). The peculiarities are seen at P~10 and 16–17 GPa where the phase transitions happen (Fig. 2b). At the inserts the whole Δx(P) and ΔT(P) dependencies are shown.]
thermal flow $q$, the $\Delta T$ is proportional to $q(\Delta x/\lambda)$, where $\lambda$ the thermal conductivity) (Fig. 3).

Thus, $H^+$ implantation might result in two effects: (i) lowering of the thermopower value in a vicinity of the phase transitions due to a contribution of H-rich layers of n-type, and (ii) possible shift of the semiconductor--metal transition pressure to lower values because of formation of nanoporous and amorphous Si [1].

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References