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Thermoelectric Properties of Oblique SiGe Whiskers

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The effects of geometric features of *p*-type $Si_{1-x}Ge_x$ (x = 0.01-0.05) whiskers on their thermoelectric properties have been studied. Oblique whiskers of various diameters (10-100 μm) with boron impurity concentration ranging from 10^{17} to 10^{20} cm^{-3} have been studied in the temperature range of 290-390 K. The Seebeck coefficient and resistivity of SiGe whiskers increased, while thermal conductivity decreased with decreasing diameter of crystals. However, the thermoelectric figure of merit of SiGe whiskers remained low, resembling that of bulk pure silicon. The influence of dopant impurities and germanium spatial distribution on the electronic and thermal transport in $Si_{1-x}Ge_x$ whiskers was likely dominant, however, little effect of the geometry was also observed. The engineering of whiskers shape and dimensions (up to 15 % improvement of thermopower in whiskers with certain obliquity), combined with appropriate doping, would likely allow for substantial improvement of their thermoelectric performance even in bulk-like scales.

Keywords: SiGe, Whiskers, Thermoelectric properties, Thermal conductivity, Size effect.

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1. INTRODUCTION

SiGe solid solutions with low germanium content have maximum ratio of charge carriers mobility to phonon thermal conductivity, which is prospective for thermoelectrics [1]. In nanoscale, e.g. in nanowires, the phonon boundary scattering channel occurs due to low dimensionality [2] and the thermal conductivity is substantially reduced [3, 4]. Though bulk SiGe is a high temperature thermoelectric material, the low values of thermal conductivity in crystals with high surface-to-volume ratios allow for gaining high values of thermoelectric properties even at low temperatures. For example, significant suppression of thermal conductivity and, consequently, enhanced figures of merit *ZT* have been observed for silicon nanowires with diameters less than 30 nm and up to 115 nm in [3] and [2, 4] in the temperature ranges of 20-100 K and up to 300 K, respectively. Authors of [4] have concluded that quantifying of surface roughness is crucial for explaining of phonon transport mechanisms and designing of thermoelectric devices. High *ZT* values of 2D silicon nanostructures can be obtained at room temperature via optimization of the doping level and effective surface passivation [5]. Using facile conversion chemistry one can enhance the thermoelectric performance of nanowires [6]. Previously we have reported the studies of temperature behavior of Seebeck coefficient of SiGe whiskers in low temperature range from 4.2 K to above room temperatures [7, 8]. The experimental results revealed a slight difference of thermoelectric parameters of micron-scale SiGe whiskers from those of their bulk counterparts. However, we have not considered the effects of whisker geometry and shape on the thermoelectric properties so far, which could be crucial as mentioned above. We did report certain results for Si, where it was shown that the features of whisker shape could be successfully used for determination of various thermoelectric values as well as for device applications [9, 10], but such investigations were not earlier conducted on SiGe whiskers. The aim of this work is to study a possible influence of SiGe whiskers geometry on their thermoelectric parameters and performance.

2. MEASUREMENTS METHODOLOGY

To adequately assess the thermoelectric efficiency of SiGe whiskers in a certain temperature range one should know their resistivity ρ and coefficients of thermal conductivity κ and thermopower α (Seebeck coefficient). These parameters, in particular, the thermal conductivity, are highly dependent on the composition, degree of solid solution perfection, doping level and dimensionality of crystal. We have developed a setting to measure the electronic and heat transport properties of SiGe whiskers dependent on temperature, composition, size and shape of such virtually one-dimensional crystals (Fig. 1). In this setting oblique $Si_{1-x}Ge_x$ (x = 0.01-0.05) whiskers of various effective cross-sections are suspended like a bridge between two pedestals made of thermally conductive paste (TCP) on the electrically insulating but thermally conductive substrate (e.g. sapphire). With this configuration the 3ω-method [11] was implemented to measure the temperature dependencies of thermal conductivity of whiskers, as in details described elsewhere [12]. Alternating electric current $I_0\sin(\omega t)$ of a certain frequency ω, passed through the whisker (electrodes 1 and 4, Fig. 1), heats the center of the crystal so that a thermal flow from the center to the ends of whisker occurs. One can neglect the heat flux in air in these conditions, because it does not exceed 1 % of the heat accumulated in the dielectric substrate. Adopting certain boundary conditions imposed by the limited sample sizes and geometric value of the current flowing through the sample, the solution of continuity equation can be written as follows [11, 12]:

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$$V_{3\omega} = \frac{\sqrt{2} I_0^{\,3} R R' L}{\pi^4 \kappa S}\,, \qquad (1)$$

where I_0 is the current with frequency ω, $V_{3\omega}$ is a voltage with frequency 3ω (third harmonics), R is whisker resistance, R' is a change in resistance with temperature, L is the length of crystal, S is cross-sectional area. Thus, the third harmonics voltage in a tested object inversely depends on its thermal conductivity, and the coefficient κ can be easily derived from the measurements of $V_{3\omega}$ signal developed between electrodes 2 and *3* (Fig. 1).

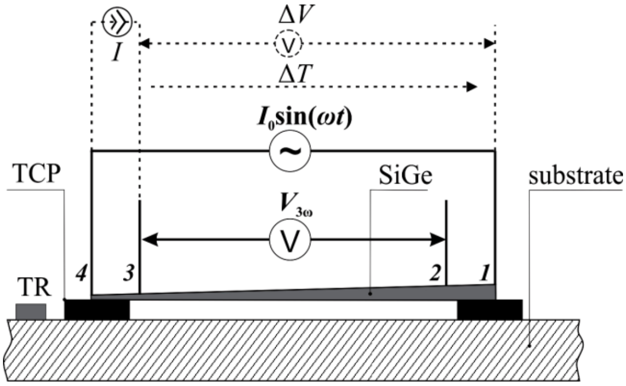

Fig. 1. – Schematic view of the setting for thermal conductivity measurements by 3ω-method (solid lines) and for measurements of Seebeck coefficient (dashed lines) of SiGe whiskers. In the latter case, the part of whisker is heated by current *I*, which is passed between two adjacent electrodes *(*here, 3 and 4), and the thermo-e.m.f. ΔV induced due to temperature difference ΔT is measured between the hot and cold ends (here, 3 and 1, respectively)

The above-described setting has been used also for the measurements of Seebeck coefficient α of oblique p-type $Si_{1-x}Ge_x$ whiskers ($x = 0.01$-0.05) with boron concentrations ranging from 10^{17} cm^{-3} to 10^{20} cm^{-3}. The hot end has been heated by passing a current between two neighboring contacts, which induced the Joule heating of one of the ends, and the temperature was determined from the known $R(T)$ dependencies for studied SiGe whiskers, as described in [8]. Since active direct heating of whisker end was applied and a whisker-to-substrate thermal contact area was negligible in comparison with dimensions of virtually infinite substrate, the temperature gradient ΔT along the crystal could be easily maintained, even though the substrate was thermally conductive. To elucidate the effect of obliquity on thermopower of whiskers, the measurements were performed in such a manner that in one case the thickest part (1-2) was heated and in another – the thinnest one (3-4), as shown in Fig. 1. Resistance of whiskers was determined by a two-probe method, in which the readings obtained upon passing a current in two directions were averaged, and the resistivity was derived accounting for an effective cross-sectional area of oblique crystals. For measurements of temperature dependencies of thermal conductivity, thermopower and resistance the designed setting was placed inside the resistive furnace, and the temperature of the inset was determined by a thermoresistor (*TR*) attached to the substrate.

3. RESULTS AND DISCUSSION

3.1 Temperature Dependencies of Transport Properties of $Si_{1-x}Ge_x$ whiskers

Experimental temperature dependencies of thermal conductivity for SiGe and Si whiskers, measured with 3ω-method, are plotted in Fig. 2. For comparison the model dependencies of lattice component of κ on T are presented, which were calculated according to the relations provided in [13]. The experimental values of thermal conductivity for bulk Si, obtained by Cahill [14], are also appended.

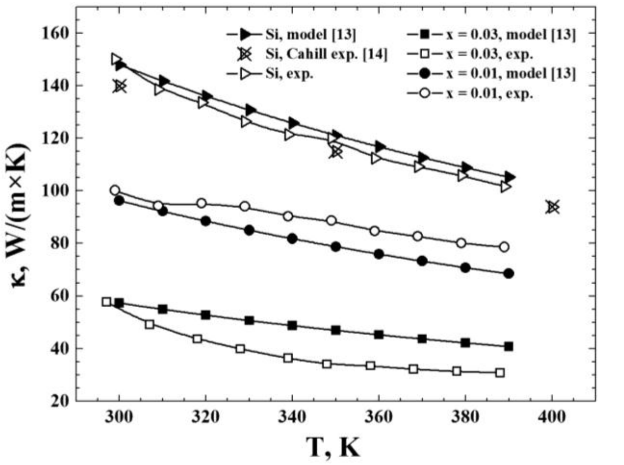

Fig. 2. – Thermal conductivity κ of pure Si and $Si_{1-x}Ge_x$ *p*-type whiskers of the 50 µm effective diameter with dopant concentration N_A of 6×10^{18} cm^{-3} (Si, $\rho_{300K} = 10$ mΩ × cm, triangles), 5×10^{18} cm^{-3} ($x = 0.01$, $\rho_{300K} = 20$ mΩ × cm, circles) and 3×10^{18} cm^{-3} ($x = 0.03$, $\rho_{300K} = 25$ mΩ × cm, squares). Solid symbols represent the calculated lattice components (κ_L) of thermal conductivity, according to the model provided in [13]. Crossed triangles display the experimental data for pure silicon, obtained by Cahill [14]

Noteworthy, the several tens micrometer scale whiskers should rather be considered as bulk materials with properties resembling those of massive objects: one should expect the occurrence of size effects at scales below 1 µm. As seen in Fig. 2, the measured values of total thermal conductivity κ_{tot} for Si whisker fit well with both modeled and experimental data for bulk material from the literature. Likewise, the total thermal conductivity of SiGe whiskers decreases with increasing of germanium content and the initial (room temperature) values as well as temperature dependencies agree with those expected from the model. As the charge carriers' concentration was relatively low, the contribution of their transport in total thermal conductivity can be neglected, and the experimental curves could be fairly compared with only phonon theoretical component of the latter. A little bit higher values of κ_{tot} for $x = 0.01$ samples might indicate that the actual content of germanium was slightly lower. Meanwhile, a substantial difference has been observed for $Si_{0.97}Ge_{0.03}$ whiskers, the total κ of which was significantly lower even than the expected lattice component and the character of its dependence on temperature deviated from the model. Despite the obvious effect of Ge content, one can assume also the influence of dimensions and shape of the crystal on the behavior of its thermal conductivity. On the other hand, the observed difference may be a consequence of irregular distribution of either Ge atoms or doping impurities.

The measured values of Seebeck coefficient changed from 80 to 750 μV/K at room temperature depending on the impurity concentration in whiskers. The maximum values of α were inherent for whiskers with least carrier concentration of the order of 10^{17} cm^{-3} (ρ_{300K} = 60 mΩ × cm). For SiGe whiskers doped to concentration of ~ 10^{18} cm^{-3} the Seebeck coefficient rised from 430-440 to 580-600 μV/K in the temperature range of 300-390 K (Fig. 3). Due to still high values of thermal conductivity the thermoelectric figure-of-merit *ZT* of these samples remained quite low, i.e. comparable with that of bulk silicon. At higher doping levels, i.e. ~ 10^{19} cm^{-3} (ρ_{300K} = 6-9 mΩ × cm), the Seebeck coefficient of SiGe whiskers weakly depended on temperature, and the minimum values of α (80-90 μV/K at room temperature) were observed for whiskers with up to (0.5-1) × 10^{20} cm^{-3} impurities (ρ_{300K} = 2 mΩ × cm).

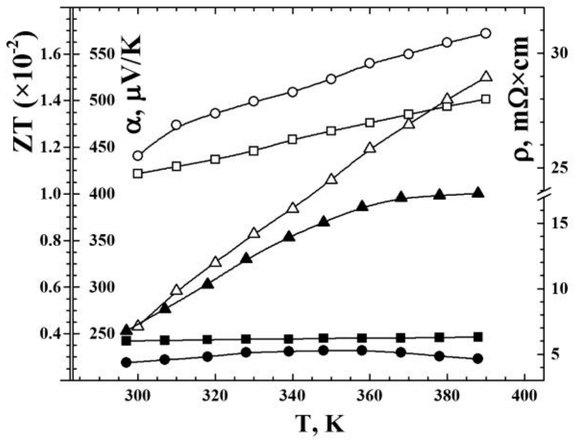

Fig. 3. – Temperature dependencies of thermopower (α, circles), resistivity (ρ, squares) and figure-of-merit (*ZT*, triangles) for $Si_{0.97}Ge_{0.03}$ whiskers (effective diameter of 50 μm) with acceptor concentrations of 3 × 10^{18} cm^{-3} (ρ_{300K} = 25 mΩ × cm, open symbols) and 2.5 × 10^{19} cm^{-3} (ρ_{300K} = 6 mΩ × cm, solid symbols). Experimental data for thermal conductivity from Fig. 2 were used to calculate *ZT*

Comparing the temperature dependencies for *ZT* of samples with different acceptor concentrations, one can infer about much stronger impact of the charge carriers on the figure-of-merit of SiGe than of the thermal conductivity for whiskers with lower doping levels. Such boron doped whisker display temperature rise of Seebeck coefficient in the range of 300-400 K, with a slope and magnitude of $\alpha(T)$ dependent on impurity concentration. Atoms of boron are known to create the shallow acceptor levels in the band gap of SiGe with ionization energy of 42 meV. At room temperature these levels for heavily doped whiskers are completely ionized. That is why the character of $\alpha(T)$ dependencies in the measured temperature range corresponds to a weak change of Fermi level position in the band structure of whiskers at temperature rise.

3.2 Geometry Effects on Thermoelectric Properties of $Si_{1-x}Ge_x$ Whiskers

Let us now consider the effects of $Si_{1-x}Ge_x$ whiskers' geometry on their thermoelectric properties. For this purpose we have studied the Seebeck coefficient and resistivity dependencies on size and obliquity of whiskers. In order to evaluate the dependence of figure-of-merit for our micron-scale SiGe whiskers on their dimensions, we estimated the size dependencies of thermal conductivity basing on the calculated results for $Si_{0.8}Ge_{0.2}$ nanowires reported in [15].

The resistivity rapidly scaled up with diminishing of effective diameter of whiskers below 50 μm (Fig. 4). For the Seebeck coefficient the rapid scaling down was inherent for straight whiskers with diameters above 50 μm. Further we have studied the effect of obliquity on the Seebeck coefficient of $Si_{0.97}Ge_{0.03}$ whiskers with various acceptor concentrations (various resistivities). The results of these studies are combined in Table 1, where the obliquity factor $k = \Delta d/2\Delta l$, i.e. the change of whisker diameter along its length, is introduced. We measured the Seebeck coefficient of whiskers with different diameters of their ends. Interestingly, upon heating of thicker end of whiskers the measured value of Seebeck coefficient was substantially greater when compared to that obtained upon heating of thinner end. These relative changes of Seebeck coefficient at constant temperature gradient of ΔT = 80 °C and at room temperature of the cold end are presented in Table 1. For such oblique whiskers the Seebeck coefficient almost linearly increased with increasing resistivity and diminishing thickness (Fig. 4).

Table 1 – Relative change of Seebeck coefficient (at temperature gradient ΔT = 80 °C) versus resistivity and obliquity of $Si_{1-x}Ge_x$ (x = 0.03) whiskers

№	ρ	Δl	Δd	$k = \Delta d/2\Delta l$	$\Delta U/U_c$
	mΩ×cm	mm	μm	× 10^{-3}	%
1	60	13,4	40	1.50	14.1
2	30	14,5	40	1.39	11.3
3	30	6,5	22	1.74	9.6
4	2	5,6	31	2.81	5.1
5	2	4,85	29	2.98	4.6
6	8	12,2	45	1.85	4.6

In general, we observed that obliquity impact (positive sign of $\Delta U/U_c$ parameter) was weak but more significant when thicker end of whisker was heated. The dependence of thermopower on the obliquity value k for different whisker sets, however, was not clear. Apparently, the doping level of whiskers played a decisive role: from Table 1 it is obvious that greater impact on the relative change of thermopower was likely caused not by the relative size of crystals but their resistivity.

In fact the biggest changes of thermopower (up to 15 %) were found in crystals with the highest resistivity of 60 mΩ × cm, while their characteristic obliqueness was the lowest (1.50 × 10^{-3}). Instead, the sample with the greatest obliquity of 2.98 × 10^{-3} but with the lowest resistivity of 2 mΩ × cm had rather small relative change in thermopower – only 5 %. Nevertheless, comparing the samples with same resistivities (2 and 30 mΩ × cm), one can still infer a little effect of whisker shape on the change of Seebeck coefficient as more prominent as lower is the carriers' concentration. Similarly to the case of temperature dependence of Seebeck coefficient (Fig. 3), for heavily doped samples the shape effect seems to be negligible. For lightly doped samples with concentration of about 10^{18} cm^{-3} the amount of thermally generated charge carriers rapidly increases upon heating, but constrained in crystals of smaller dimensions they are subjected to increased boundary scattering (rapid increase of resistivity in crystals below 50 μm), and the saturation of Seebeck effect occurs in thinner whiskers (Fig. 4, top). The onset of boundary scattering with diminishing diameter of a crystal is confirmed by the dimensional dependence of thermal conductivity of $Si_{0.97}Ge_{0.03}$ whiskers. As it can be seen from Fig. 4 (bottom), κ is almost independent on the whisker thickness above 40 μm, and the thermal conductivity starts to decrease for thinner whiskers. However, contrary to the expected improvement, the figure-of-merit ZT decreased with whisker diameter, which is a consequence of drastic increase in resistivity. For the thickest studied samples the ZT at room temperature still remained very low – only 6.4×10^{-3}.

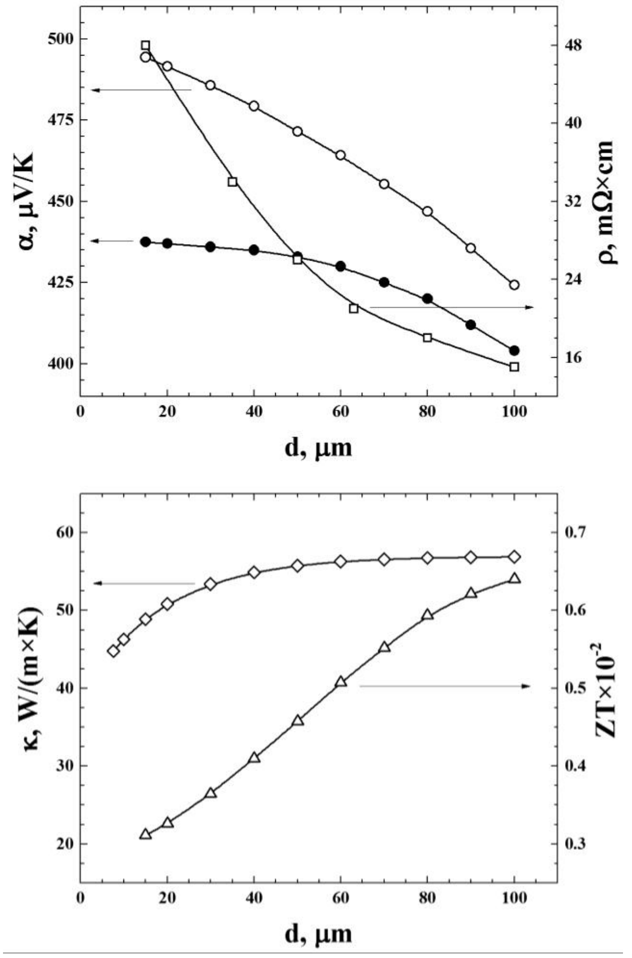

Fig. 4. – Changes of Seebeck coefficient α and resistivity ρ (top) and of thermal conductivity κ and ZT (bottom) with effective diameter of oblique $Si_{0.97}Ge_{0.03}$ ($N_A = 3 \times 10^{18}$ cm^{-3}) at 300 K. Diameter dependence of thermal conductivity has been estimated basing on the data from [15]. Solid circles represent the diameter dependence of Seebeck coefficient for straight (non-oblique) whiskers

On the other hand, the observed peculiarities may be related with the spatial inhomogeneity of dopant impurity distribution or germanium content along the whisker, which is a typical consequence of unstable conditions of whiskers' growth via the vapor-liquid-solid mechanism upon chemical vapor deposition [16]. At the initial stages the velocity of crystal growth is maximum, the growth is tempestuous and non-equilibrium, so that big amounts of impurity atoms are captured, while their spatial distribution is highly non-uniform. As the growth proceeds, its velocity decreases and the conditions approach equilibrium, the amount of incorporated impurity decreases, so that the resistivity of crystal increases. Finally, with increasing diameter of the crystal's "foot" and exhausting of gold (growth initiator) content in Si-Au eutectic droplet at the tip of the growing whisker, the growth velocity turns to zero and the process stops. As a result, needle-like oblique whiskers with gradient of impurity concentration are obtained. Obviously, in thinner crystals the statistical (or in other words, effective; also the compensation by Au impurities must be accounted) charge carriers concentration would be lower, and the Seebeck coefficient and resistivity would increase. Thus, in bulk-like micron-scale SiGe whiskers the changes of thermoelectric parameters are likely not immediately connected with size or shape effects, and the latter indirectly influence the peculiarities of charge and heat transport due to imposed growth and doping conditions upon whiskers' synthesis process, although thermal conductivity tends to rapidly decrease with the effective diameter of whisker. Unfortunately, we were unable to clearly state the obliquity effect on the thermal transport in SiGe whiskers; however, the deviation of temperature dependence of thermal conductivity from the model (Fig. 2) may testify, in particular, the morphology contribution in the suppression of total thermal conductivity of $Si_{1-x}Ge_x$ whiskers.

Taking into account the results of the above-described studies of temperature, dimension and shape dependent thermoelectric parameters of SiGe whiskers, upon engineering of high-performance thermoelectric converters on their basis, one should reach an appropriate compromise between the proper energy band structure and geometric features of crystals. In particular, scaling down of whisker thickness beyond micrometer, development of proper length-to-diameter configuration and adjustment of Ge content for minimization of thermal conductivity of whisker, while maintaining considerably high mobility of charge carriers, would be required for enhancement of thermoelectric performance of such one-dimensional crystals.

4. CONCLUSIONS

We have performed the study of the effect of dimensions and obliquity of $Si_{1-x}Ge_x$ ($x = 0.01$-0.05) whiskers on their thermoelectric properties. As expected from the model, the thermal conductivity of SiGe whiskers decreased with increasing germanium content. The dimensional effect on thermal conductivity was not evident for crystals thicker than 40-50 μm, below this diameter the lattice thermal conductivity significantly decreased and the obliquity likely caused not only the suppression of the value but also the change of the character of $\kappa(T)$ dependence. In contrast, obliquity had little effect on the charge transport properties of SiGe whiskers, though resistivity and Seebeck coefficient increased with diminishing of their diameters. Apparently, the doping level and impurity and Ge spatial distribution rather than crystals' dimensionality and shape played a dominant role in altering of electrical conductivity and Seebeck coefficient of whiskers, which was especially prominent for lower boron concentrations (~ 10^{18} cm^{-3}). As a result, the thermoelectric figure-of-merit of heavily doped samples saturated with increasing temperature, while for samples with concentrations of the order of 10^{18} cm^{-3} it constantly rised, reaching $ZT \sim 0.015$ at 400 K. However, the obtained values of ZT were still unexpectedly low, resembling that of bulk Si. Moreover, instead of expected improvement, the ZT gradually decreased with whisker diameters due to drastic rise in resistivity that overwhelmed both the improvement of Seebeck coefficient and suppression of thermal conductivity. Therefore, an appropriate engineering of electronic transport properties combined with scaling down to diameters beyond micrometer would be required for successful application of low germanium content $Si_{1-x}Ge_x$ whiskers in thermoelectric converters, in particular, in microgenerators or sensors of thermal values.

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