Thermal energy converters based on granular silicon

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Abstract. The use of granular silicon (GS) makes it possible to create a system like “electronic crystal-phonon glass” and reduce the cost of materials. With GS from silicon slurry, it is possible to obtain values of the Zeebeck coefficient of ~500 μV/deg and to reduce the thermal conductivity by 7-9 times as compared to single-crystal silicon. The GS high conductivity is proposed to be achieved by resonant tunneling of current carriers through a nanosized SiO\textsubscript{2} layer covering the GS particles.

1. Introduction
One of the possible solutions of the problem of increasing the thermoelectric Q-factor Z for thermal energy converters (TEC) is based on creation of an “electronic crystal-phonon glass” (EC-PG) system [1, 2], which can be realized with application of expensive nanotechnologies. Another problem in this field of technology, namely search for new materials for TEC to replace expensive ones containing rare-earth elements, is far from being solved. In our opinion, a possible solution may be the use of different modifications of polycrystalline silicon as thermoelectric materials. Because of small value of the Zeebeck coefficient α and the high values of thermal conductivity γ the single crystals are not suitable for this purpose [3].

It was shown that high concentration of deep impurities both in crystalline silicon doped by ion implantation and in polycrystalline one having much higher dopant solubility, makes it possible to increase α by 2 times and reduce γ due to the thermovoltaic effect [4] which causes charge carrier generation via absorption of subband photons by deep impurity levels.

2. Experimental Techniques
For the thermovoltaic effect to manifest itself, an optimal, in our opinion, device has been studied. TEC body was made of silicon powder with particle sizes from 1 to 30 μm and a doping level of more than 10\textsuperscript{18}cm\textsuperscript{-3}. The powder made by grinding the single crystalline plates of KES-0.01 quality was neither sintered, no melted. Its particles were simply brought into contact with each other under some force, which ensures preservation of a nanosized SiO\textsubscript{2} layer covering surface of the particles in oxygen atmosphere. It is easy to see that such a material is a two-component system similar to the desired EC-PG for which the thermoelectrical Q-factor is written as:

\[ Z_{\text{eff}} = \frac{\alpha^2_{\text{Si}} \gamma_{\text{SiO}_2}}{\gamma_{\text{SiO}_2}} \]

where \( \alpha_{\text{Si}} \) is the silicon particle Zeebeck coefficient regulated by the particle size, defectiveness of their surface and level of deep impurity doping; \( \gamma_{\text{SiO}_2} \) is the thermal conductivity of silicon dioxide.
which is much less than that of silicon: $\sigma_{SiO_2}$ is the oxide conductivity. The latest parameter should be maximally increased to obtain high $Z$.

The experiments were performed with TEC made of a ceramic pipe of 12 mm in length and 2 mm in inner diameter containing the above-described working body of 6 mm in length. The following parameters were measured: open circuit voltage $U_{cc}$, short circuit current $I_{sc}$, sample resistance, as well as their dependences on temperature $T$ and pressure applied to the body. The Zeebeck coefficient $\alpha$ and heat conductivity $\gamma$ were also estimated using standard techniques.

Note, that mechanical compressing of the working body strongly influences contact between GS particles.

3. Results and Discussion

Fig. 1 shows impact of the pressure on the measured parameters for temperature 400K. As seen, $U_{cc}$ is almost independent of pressure, whereas $I_{sc}$, on the contrary, greatly depends on it, at least within the range of 20-200 MPa.

![Figure 1](image.png)

**Figure 1.** Dependences of open circuit voltage $U_{cc}$ and short circuit current $I_{sc}$ on pressure applied to the TEC body measured at the same temperature gradient.

Figure 2 illustrates the effect of outer pressure within the range of 0-250 MPa on resistivity of the working body of the same TEC observed at 300 K. As seen, the GS resistivity decreases with raise in pressure in a rather complicated way. Up to 50 MPa it drops very sharply, by four orders of a magnitude from $\sim 10^5$ Ohm·cm to $\sim 10$ Ohm·cm. At higher pressure, shown in the Figure inset, a quasi-linear decrease of $\rho$ with the coefficient of 0.05 Ohm·cm/MPa is observed up to $\sim 100$-120 MPa, and then $\rho$ changes more slowly with the coefficient of 0.009 Ohm·cm/MPa.
Figure 2. Typical dependence of resistivity of the TEC working body made from GS on pressure for temperature 400 K. A quasi-linear change in \( \rho \) is shown in the inset in enlarged scale.

It should be noted that even for the largest pressure values ~250 MPa, the powder resistivity determined in direct measurements at 300 K turned out to be ~100 times greater than that of material from which the powder was made. This directly indicates that \( \rho \) value is defined by resistance of both the silicon powder particles and the nanoscale layers \( \text{SiO}_2 \); the oxide layers actually determine the total resistance and then, according to the expression (1), the thermoelectric Q-factor \( Z \) of the material.

For most used thermoelectric alloys such as the BiTe, PbTe, SiGe, the specific thermo-emf (the Zeebeck coefficient) \( \alpha \), considered as one of the main parameters of a thermoelectric material, has the value of ~200-400 mV/K. For single crystalline silicon \( \alpha \) is only ~44 mV/K at 300 K, and for this reason it is not considered as a promising material for TEC manufacturing. For GS the quantity \( \alpha \) estimated from \( U_{xx} \) measurements at 310-360 K [5] is higher than that of conventional thermoelectric materials and has the value of ~500 mV/deg.

Thermal conductivity \( \lambda \) is also one of the major parameters of thermoelectric materials. One of the ways to increase their Q-factor \( Z \) is based on decrease of \( \lambda \), for example, by creating a material like the above mentioned “EC-PG” system. For GS with the particle size of 1-30 microns in the temperature range of 300-400 K the experimentally obtained \( \lambda \) value is within the range from 15.3 to 16.7 W/m·K, which is by ~9 times lower than that of single-crystal silicon [6].

Summing up we conclude that, the key problem for \( Z \) enhancement in GS is to increase the conductivity of the nanoscale \( \text{SiO}_2 \) layers, i.e. to increase the probability of charge transfer through the oxide film. For its solution, we propose to create conducting islands from, for example, \( \text{SnO}_2 \) on the surface of the GS particles, which could play the role of something like a platform for charge transfer [7].

Another way is to create in the band gap of silicon dioxide the energy levels adjacent to the conduction band of GS particles and satisfying a number of the conditions required to organize resonant tunneling of charge carriers like the Gamow tunnel [8]. That should lead to increase in the conductivity of the \( \text{SiO}_2 \) layer.

A technological solution of this rather complicated engineering problem is to develop the methods of creating resonance levels by GS irradiation or a technology of nanoscale \( \text{SiO}_2 \) film implantation with impurities giving color centers in silicon oxide like cobalt, molybdenum, lead, etc. or doping with alkali metals, as well as the technologies of doping an initial material for GS production rather than GS itself [9].

Along with the promising studies to fundamentally increase the energy parameters of GS TEC, it is now advisable to produce TEC from available GS. Powders obtained by grinding silicon materials with the same [10] as well as different [11] types of conductivity can be used with addition of technical silicon powders containing impurities, like Fe, giving deep energy levels.
Technical solutions based on the simultaneous use of heat and outer pressure to produce electricity are of great interest. A sketch of such a device (converter) is presented in Fig. 3(a) together with its characteristics under heating in Figure 3 (b). As seen from the figures, this converter, placed at the boundary of two media with different pressures \(P_{1,2}\) and temperatures \(T_{1,2}\), can successfully operate.

![Figure 3.](image)

**Figure 3.** a) A section of GS TEC operating at the boundary of two media separated by a heat-insulating wall with different temperatures \(T_2>T_1\) and \(P_2>P_1\).

1 – the working body made of GS; 2 – dielectric housing, 3 – fixed electrode; 4 – movable electrode connected with bellows 5 which is placed in a medium with higher pressure \(P_2\) and transmit the compression force to the working body 1; 6 – dividing wall. The arrows indicate the heat supply to the TEC.

b) The typical dependences of current density of GS TEC on temperature \(T_2\) for different pressures \(P_2\).

Development of the TEC production is very attractive because these devices can operate under extreme operating conditions, including open space, the surface of celestial bodies, such as Venus, at which high temperature, pressure and radiation level are distinguished.

The following data can be cited as an example.

If TEC from GS is placed in liquid nitrogen (T~77K) the current and voltage with signs opposite to those observed during heating arise. Both parameters are 10 times less than those measured under heating, for example, up to a temperature of 500 K and they are associated exclusively with the thermoelectric emf of the cooled metal-silicon contact. The abnormally high values of the specific thermoelectric emf and, accordingly \(U_{xx}\) and \(I_{sc}\), under heating are due to the combined thermoelectric and thermovoltaic effects.

Under irradiation of the GS TEC sample by high power laser light (398 W/cm\(^2\), \(\lambda = 1064\) nm) the current density of 357 mA/cm\(^2\) and the voltage of 350 mV are obtained. The device detects the impulses supplied to it and does not fail.

Comparison of the results of GS TEC measurements before and after irradiation by \(^{60}\)Co quanta with the dose \(10^9\) rad, which is destructive for all types and kinds of semiconductor devices, has not revealed any changes in the parameters of the thermal energy converter.
4. Conclusions
The studies of electrophysical properties of powder silicon and TEC produced from it have demonstrated the following.

(i) Under heating of the TEC samples the voltage $U_{xx}$ and the current $I_{sc}$ arise.

(ii) Under GS heating within the temperature range 300-500 K the value of $U_{xx}$ is independent of pressure of powder compression, at least over the range of 20-200 MPa. At the same time, it strongly depends on temperature gradient and weakly on average temperature of the sample. The current $I_{sc}$, on the contrary, depends on a magnitude of outer pressure, on an absolute value of temperature gradient, and on a temperature distribution along the sample length.

(iii) The pioneering measurements of the GS samples made from monocrystalline silicon powder of KES 0.01 quality within the temperature range 300-350 K, have demonstrated that the Zeebeck coefficient $\alpha$ of ~500 $\mu$V/K is more than 10 times greater than that for single crystal silicon. The thermal conductivity of ~16 W/m·K is 9 times less than that for single crystalline silicon, is 4-5 times less than that for the samples sintered from silicon powder, and approaches the values characteristic for porous silicon.

(iv) GS PTE can operate under some extreme conditions, including high temperature, pressure and radiation level.

(v) It is reasonable to master the GS-based TEC manufacturing in view of the low cost of the raw materials and a number of useful properties of GS.

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