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The Thermoelectric Effect in a Graded-Gap nSi–pSi$_{1-x}$Ge$_x$ Heterostructure

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Abstract—The thermoelectric effect, i.e., generation of current and voltage under uniform heating, is for the first time observed in a graded-gap Si$_{1-x}$Ge$_x$ ($0 \leqslant x \leqslant 1$) continuous solid solution and an n–Si–p–Si$_{1-x}$Ge$_x$ heterostructure made on its basis. Currents of 0.0025–0.0035 μA and voltages of 0.05–0.3 mV have occurred in the temperature range of 40–250°C.

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In recent years, there have been numerous reports on observing the electromotive force (EMF) during uniform heating of various homogeneous materials: samarium monosulphide [1], zinc oxide ZnO [2], polycrystalline silicon produced by multiple melting of industrial silicon in a solar furnace in the open air [3], and several semiconductors of A$^{\text{III}}$B$^{\text{V}}$ group (GaAs⟨Sn⟩, GaAs⟨Te⟩, GaSb⟨Te⟩, and InP⟨Sn⟩) [4, 5].

The objective of this paper is to report on the observation of the thermoelectric effect in the film of a graded-gap Si$_{1-x}$Ge$_x$ ($0 \leqslant x \leqslant 1$) solid solution and in a p–n heterostructure fabricated from it on a silicon substrate.

The graded-gap Si$_{1-x}$Ge$_x$ ($0 \leqslant x \leqslant 1$) solid solution was grown from a limited volume of a Sn–Si–Ge solution-melt using the liquid-phase epitaxy method on a silicon substrate of n-type conductivity with (111) orientation in the temperature range of 1000–750°C. From the obtained material, samples of 8-mm length and 5-mm thickness were made. These films were single-crystal in character. After that, ohmic contacts were applied to the structures by silver coating. Two contacts with an area of 2 × 1 mm^2 were applied to each solid solution film, and one contact was applied to the substrate. The scheme of the studied n–Si–p(Si)$_{1-x}$(Ge)$_x$ ($0 \leqslant x \leqslant 1$) heterostructure is shown in Fig. 1.

It should be noted that the advantage of the liquid-phase epitaxy method is that it allows one to obtain a material with variable concentration of the second component and, as a consequence, with a variable band gap in a wide range. In particular, this method has allowed a continuous Si$_{1-x}$Ge$_x$ solid solution in which the germanium content varies from $x = 0$ (pure silicon) to $x = 1$ (pure germanium) to be obtained. As a consequence, band gap width $E_g(x)$ strongly depends on the sample length. The measurement results of $E_g(x)$ for the given solid solution acquired by measuring the photoluminescence in a sample cleavage are shown in Fig. 2.

Thus, n–Si–p–Si$_{1-x}$Ge$_x$ heterostructures constructed on the basis of films of a Si$_{1-x}$Ge$_x$ solid solution with a strong band gap variability have been subjected to uniform heating in vacuum. The presence of ohmic contacts (see Fig. 1) allows one to perform measurements directly on the solid solution film, as well as on the heterostructure. The studies have shown that, even at a minor increase of temperature, the samples generate currents and voltages detectable by the equipment connected either between the two ohmic

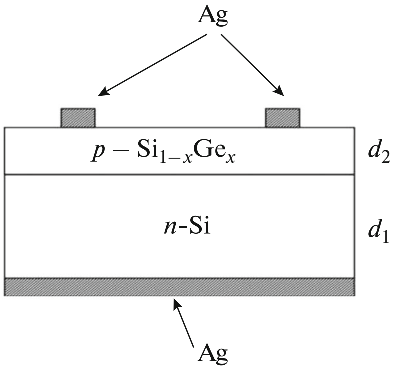

Fig. 1. Scheme of the studied n–Si–p–Si$_{1-x}$Ge$_x$ ($0 \leqslant x \leqslant 1$) heterostructure, $d_1 = 400$ μm, $d_2 = 90$ μm.

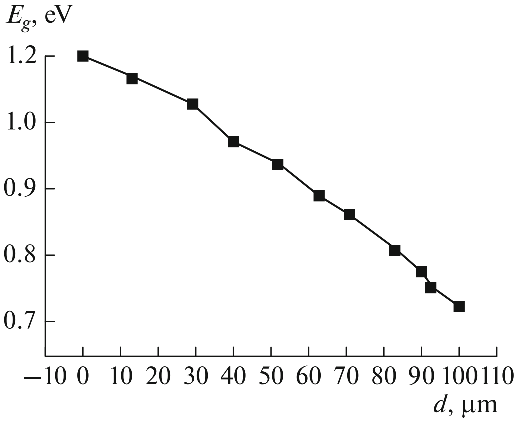

Fig. 2. Dependence of the $Si_{1-x}Ge_x$ band-gap width on the sample length.

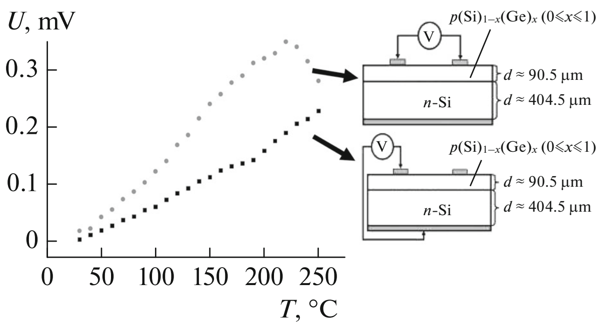

Fig. 3. Temperature dependence of voltage generated in the graded-gap p–$Si_{1-x}Ge_x$ $(0 \leqslant x \leqslant 1)$ film with simple ohmic contacts on an n–Si substrate with (111) orientation (curve *1*) and in the n–Si–p–$Si_{1-x}Ge_x$ heterostructure (curve *2*).

contacts on the surface of the graded-gap solid solution, or between the surface contact and the substrate contact (Figs. 3, 4).

As can be seen from Figs. 3 and 4, the graded-gap $Si_{1-x}Ge_x$ $(0 \leqslant x \leqslant 1)$ films and n–Si–p–$Si_{1-x}Ge_x$ heterostructures on their basis generate current and voltage. It is interesting that, in a large temperature range (40–200°C), both current and voltage values will be higher in the film than in the heterostructure, starting to decrease in the film at 200°C, but continuing to increase in the heterostructure (see curves *1* and *2* in Figs. 3, 4).

To verify that only the graded-gap $Si_{1-x}Ge_x$ film is responsible for this effect, we have measured the current-voltage characteristics of both the film (Fig. 5) and heterostructure (Fig. 6) in the same temperature range.

As can be seen from Fig. 5, the current-voltage characteristic of the p–Si_xGe_{1-x} solid solution film is ohmic in character and practically does not change within the studied range of temperatures. At the same time, as Fig. 6 shows, the n–Si–p–Si_xGe_{1-x} heterostructure has rectifying properties and its current-voltage characteristic changes with temperature. The performed experiments indicate the possibility of EMF (voltage) and current generation under a uniform temperature heating of graded-gap Si_xGe_{1-x} solid solution films with simple ohmic contacts. The observed effect is, to some extent, similar to thermovoltaic effects observed previously in samarium sulphide SmS [1] and zinc oxide [2], but there is one substantial difference. In the aforementioned materials, only the voltage is generated; in our case, both voltage and current are. For this reason, this effect can be called thermoelectric. It is a completely new phenomenon, so it is not possible to provide its theoretical treatment immediately. However, some suggestions can be made. As is shown in Fig. 2, in the studied films of up to 90-μm length, the band gap width E_g varies greatly, starting from silicon ($E_g \approx 1.12$ eV) and ending with germanium ($E_g \approx 0.8$ eV). Apparently, the initial equilibrium concentration can change by several orders of magnitude. Thus, in the studied graded-gap structure, an inhomogeneous distribution of original equilibrium carriers is realized, which makes it similar, to some extent, to zinc oxide inhomogeneously doped with mixed valence impurities. However, in the n–Si–p–Si_xGe_{1-x} $(0 \leqslant x \leqslant 1)$ structure, this inhomogeneity is realized through the dependence of the band-gap width on the sample length. During heating of the system, the electron concentration will be increasing inhomogeneously. At the silicon-dominated end, the concentration will be higher than at the germanium end. As a result, occurrence of Dember's EMF is possible, similarly to that observed in [4, 5] for $A^{III}B^{V}$ n-semiconductors, which, in turn, leads to generation of

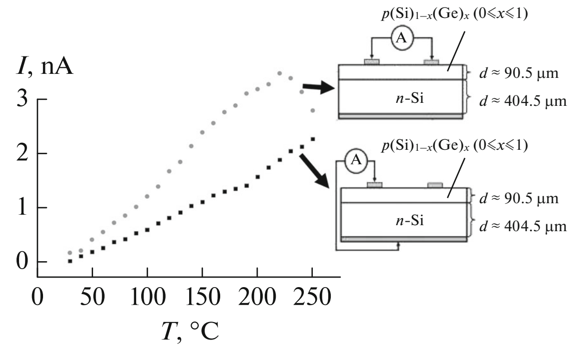

Fig. 4. Temperature dependence of current generated in the graded-gap p–$Si_{1-x}Ge_x$ $(0 \leqslant x \leqslant 1)$ film with simple ohmic contacts on an n–Si substrate with (111) orientation (curve *1*) and in the n–Si–p–Si $_{1-x}Ge_x$ heterostructure (curve *2*).

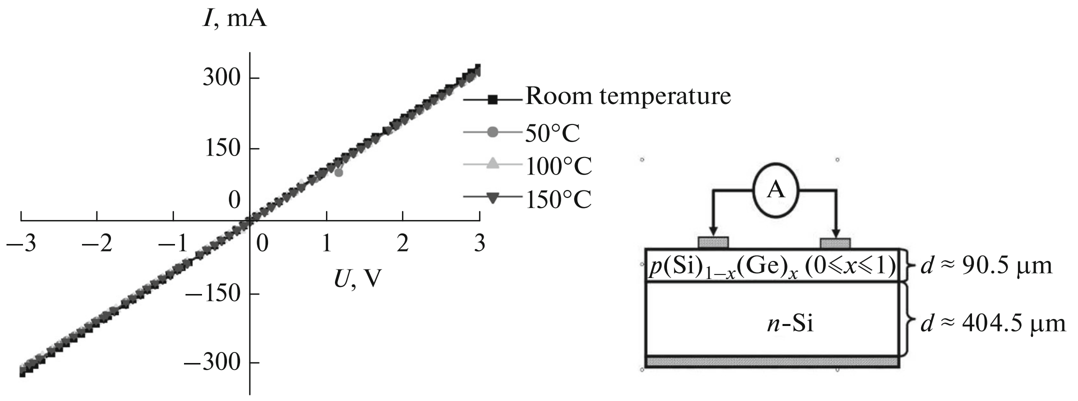

Fig. 5. Current-voltage characteristic of the $Si_{1-x}Ge_x$ $(0 \leqslant x \leqslant 1)$ film.

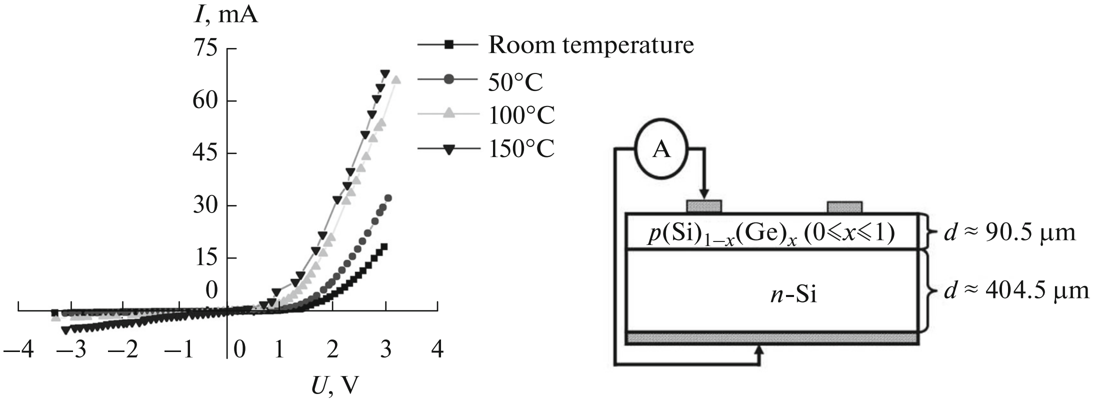

Fig. 6. Current-voltage characteristic of the *n*–Si–*p*–$Si_{1-x}Ge_x$ $(0 \leqslant x \leqslant 1)$ heterostructure.

current that is synergetic in nature. Of course, these model approximations require further detailed development.

In conclusion, we would like to emphasize that we are here talking about studying the properties of a completely new material, $Si_{1-x}Ge_x$ silicon-germanium solid solution with a continuous change of composition along the sample length from x to 1, i.e., with pure silicon ($x = 1$) at the beginning and pure germanium ($x = 0$) at the end. Such a material possesses properties that distinguish it from both silicon and germanium in particular, a different optical range, which is very important for photoelectric conversion. Additionally, the effective use of the thermoelectric effect discovered in this material, i.e., a correctly selected combination of thermo- and photoeffects (with combined influence of temperature and light), should lead to improvement of the usual photoelectric characteristics.

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