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The Thermovoltaic Effect in Variband Solid Solution $Si_{1-x}Ge_x$ $(0 \leq x \leq 1)$

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Abstract—The thermovoltaic effect in films of variband solid solution $Si_{1-x}Ge_x$ $(0 \leq x \leq 1)$ has been observed for the first time. The samples comprised *n*-Si–*p*-$Si_{1-x}Ge_x$ $(0 \leq x \leq 1)$ heterostructures grown by liquid phase epitaxy. An electromotive force within 0.05–0.3 mV and a current of 0.0025–0.0035 μA appeared on heating samples in a temperature range from 40 to 250°C.

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The phenomenon of electromotive force (emf) appearing in homogeneously heated materials based on samarium monosulfide (SmS) is among the most interesting discoveries in recent decades [1–5]. Recently, Pronin et al. [6] reported on the observation of analogous thermo emf in homogeneously heated zinc oxide (ZnO) doped nonuniformly with mixed-valence impurities. Similar effects in quite different materials have been recent observed at the Physicotechnical Institute (Tashkent). Previously, we have reported [7–9] on the appearance of emf and current in homogeneously heated samples with simple ohmic contacts, which were made of polycrystalline silicon obtained by multiple remelting of technical-grade silicon in air in a solar furnace. An analogous phenomenon, whereby the emf and current appeared in homogeneously heated samples with simple ohmic contacts, was observed in Czochralski grown $A^{III}B^{V}$ semiconductors possessing *n*-type conductivity [10, 11]. As has been correctly pointed out [6], this phenomenon is of interest for developing some fields of technical physics, in particular, for creating sensors and memristors.

This Letter presents the results of observation of the thermovoltaic effect in films of $Si_{1-x}Ge_x$ variband solid solution $(0 \leq x \leq 1)$.

Epitaxial layers of variband solid solution $Si_{1-x}Ge_x$ $(0 \leq x \leq 1)$ were grown by liquid phase epitaxy from Sn–Si–Ge solution melt confined between *n*-type silicon substrates with ⟨111⟩ and ⟨100⟩ orientations in a temperature interval of 1000–750°C. The samples were cut to lateral dimensions 8 × 8 mm and a thickness of about 5 mm. Solid solution layers grown on ⟨111⟩-oriented substrates had a single-crystalline structure, while the films grown on 100-oriented substrates were polycrystalline. Ohmic contacts to the samples were formed by depositing silver in the form of 2×1 mm^2 contact pads on each solid solution film. Schematic diagram of a sample is shown in the inset to Fig. 1a. The thickness of *n*-Si substrate was d_1 = 400 μm, and the variband film thickness was d_2 = 90 μm. The thermovoltaic effect was studied on samples homogeneously heated in vacuum.

The investigation showed that even a small increase in the temperature of samples leads to the generation of currents and voltages, which can be measured between the two ohmic contacts situated on the surface of variband solid solution. The results of measurements are presented in Figs. 1a and 1b. As can be seen from Figs. 1a and 1b, variband films of $Si_{1-x}Ge_x$ $(0 \leq x \leq 1)$ generate the emf and current irrespective of the Si substrate orientation ⟨111⟩ or ⟨100⟩, but the effect is more pronounced in the samples grown on Si⟨111⟩ substrates.

To confirm that the observed effect is related entirely to the variband films of $Si_{1-x}Ge_x$, we have measured their current–voltage (*I*–*U*) characteristics in the same temperature interval. As can be seen from the results of these measurements presented in Fig. 2, the *I*–*U* curves of films on both substrates exhibit an ohmic character and remain virtually unchanged in the temperature interval studied.

Variband semiconductors are materials with varying bandgap width $E_g(x)$ dependent on the sample thickness. Structures based on these semiconductors have been studied since the 1980s. In particular, original investigations have been performed on GaAs–AlGaAs heterojunctions at the Ioffe Physical Technical Institute (St. Petersburg) under guidance of Nobel

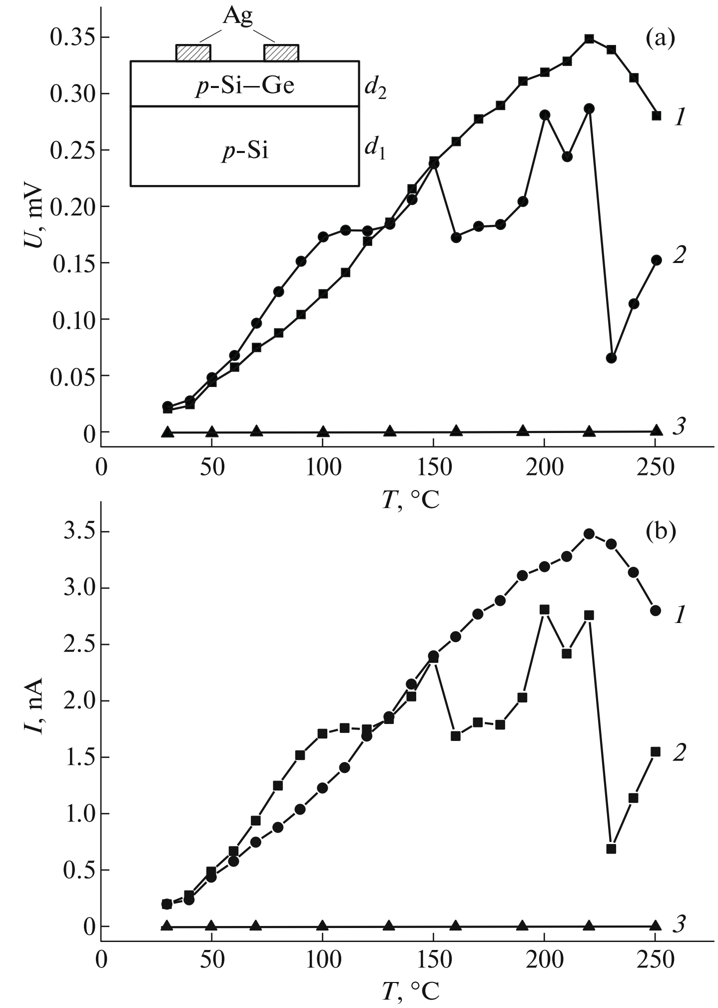

Fig. 1. Temperature dependence of the (a) voltage and (b) current appearing between simple ohmic contacts on p-$Si_{1-x}Ge_x$ ($0 \leq x \leq 1$) variband films grown on n-Si substrates with (*1*) ⟨111⟩ and (*2*) ⟨100⟩ orientation in comparison to (*3*) analogous temperature dependences for standard single-crystalline silicon film. The inset to (b) shows schematic diagram of a sample studied.

Prize winner Zh. Alferov [12]. The method of liquid phase epitaxy used in the present work allows $A^{III}B^{V}$ semiconductors to be grown with varying concentration of the second element and, hence, bandgap width varying in a broad interval. In particular, this method allowed us to grow continuous solid solution $Si_{1-x}Ge_x$ in which the content of germanium changed from $x = 0$ (pure silicon) to $x = 1$ (pure germanium). Accordingly, bandgap width $E_g(x)$ of this material also strongly depends on the thickness.

Figure 3 shows the results of E_g determination for $Si_{1-x}Ge_x$ solid solution film by data of photoluminescence measurements on the transverse cleavage of a sample. As can be seen from this plot, the bandgap width in a film (with a thickness of ~90 μm) strongly varies on the passage from silicon ($E_g \approx 1.12$ eV) to germanium ($E_g \approx 0.74$ eV). Evidently, the initial equilibrium carrier concentration can change within several orders of magnitude. Computer processing of the obtained curve shows that $E_g(x)$ function is nonlinear and can be well described by the following relation:

$$E = E_0 - Ae^{R_0 x}, \quad (1)$$

where $E_0 = 1.479$ eV, $A = 0.377$ eV, and $R_0 = 0.007$.

Thus, the obtained $Si_{1-x}Ge_x$ ($0 \leq x \leq 1$) solid solution films exhibit a thermovoltaic effect similar to that reported in [1–5], according to which thermo emf and current appear in homogeneously heated samples with ohmic contacts on the film surface. Understanding the nature of this phenomenon requires additional investigation. However, similarity of the results obtained in this work to those reported in [1–5] suggests that the technological process of $Si_{1-x}Ge_x$ ($0 \leq x \leq 1$) solid solution growth is accompanied by the formation of a small gradient of acceptor impurity centers, which makes this system analogous to samarium

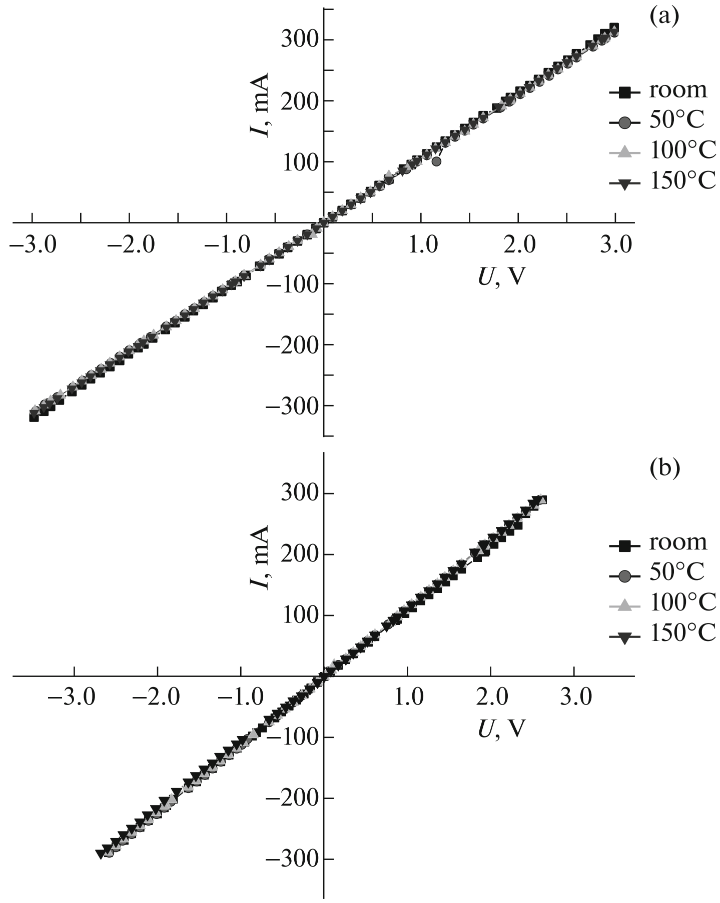

Fig. 2. Current–voltage (I–U) characteristics of p-Si_xGe_{1-x} variband films on n-Si substrates with (a) ⟨111⟩ and (b) ⟨100⟩ orientations.

sulfide (SmS) containing a region of excess samarium content ($Sm_{1.04}S$). Of course, these model notions are only based on analogy and require further detailed investigation.

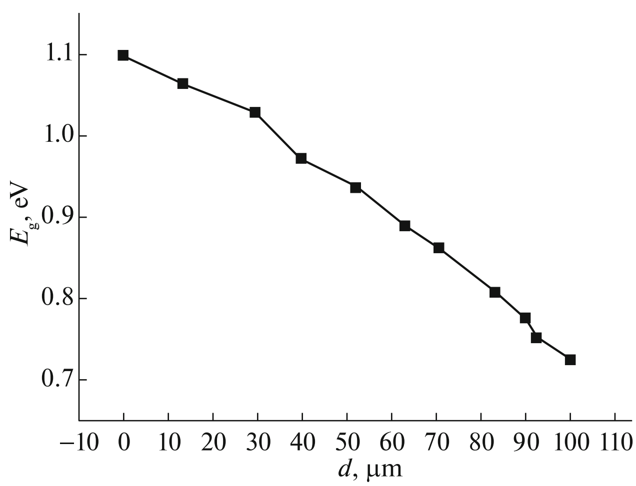

Fig. 3. Plot of bandgap width E_g vs. thickness d of variband continuous solid solution Si_xGe_{1-x} ($0 \le x \le 1$) by data of photoluminescence measurements.

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