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FIELD PROPERTIES OF DIODE STRUCTURES BASED ON SOLID SOLUTION “SILICON-TIN”

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This article presents the results of studies of the conductivity mechanism in pSi-nSi$_{1-\delta}$Sn$_{\delta}$ ($0 \le \delta \le 0.04$) structures based on the Si$_{1-\delta}$Sn$_{\delta}$ solid solution with base n-layer thicknesses W ≈ 20-30 μm. The studied samples were obtained in a single technological cycle using liquid-phase epitaxy on single-crystal p-Si substrates with the (111) orientation. Experimental and computational studies showed that the Poole-Frenkel effect is observed in pSi-nSi$_{1-\delta}$Sn$_{\delta}$ ($0 \le \delta \le 0.04$) structures at room temperature. This circumstance allows the use of high voltage effects on the parameters of various devices based on the solid solution Si$_{1-\delta}$Sn$_{\delta}$. Thus, there is interest in using this effect to convert thermal energy into electrical energy via the thermovoltaic effect. Also, results show the potential of using solid solutions Si$_{1-\delta}$Sn$_{\delta}$ ($0 \le \delta \le 0.04$), grown on silicon substrates, as an active material in thermal energy converters.

Keywords: *Liquid-phase epitaxy; Current-voltage characteristic; Field mechanism; Frenkel coefficient; Activation of charge carriers; Concentration of ionized traps; Thermovoltaic effect*
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INTRODUCTION

Recently, the study of electrophysical processes in semiconductor solid solutions of the A^{IV}B^{IV} type has become increasingly relevant [1]. Analysis of the results of the studies showed that such solid solutions are promising for the creation of lasers, light modulators, photoconverters, and other functional devices [2].

It is known that by changing the zone structure parameters of solid solutions, it is possible to create new, more effective materials for various technological fields with the required combinations of physical characteristics [3-5].

One way to change the band structure of semiconductors is to apply a high voltage to the sample (the Poole-Frenkel effect). The effect is that when sufficiently large electric fields are applied to the semiconductor sample, the activation energy for electrons from the electron energy levels decreases due to the additional energy imparted by the field.

The semiconductor compound Si$_{1-x}$Sn$_x$, belonging to the above-mentioned type A^{IV}B^{IV}, has a number of distinctive properties that allow them to be used in the manufacture of various semiconductor devices [6-8], while the temperature range of their operation depends on the activation energy of charge carriers [9-10]. Thus, it is of interest to study the possibility of changing the activation energy of electrons by the action of electric fields, i.e. the presence of the Poole-Frenkel effect [11-12] and its parameters of solid solutions Si$_{1-\delta}$Sn$_{\delta}$ [13-14]. Based on this, this work is devoted to studying the influence of the base region thickness on the electrical conductivity and on the shape of the potential well-formed near the impurity centers in pSi-nSi$_{1-\delta}$Sn$_{\delta}$ structures.

MATERIALS AND METHODS

Formation of solid solutions of Si$_{1-\delta}$Sn$_{\delta}$. The possibility of forming solid substitution solutions of A^{IV}B^{IV} molecules is determined by their charge states and geometric dimensions, as well as the type of crystal lattices of the components of solid solutions. Academician M.S. Saidov proposed the conditions for the formation of continuous substitution solid solutions in the following form [15-16]

$$\Delta z = \sum_{i=1} z_i^m - \sum_{i=1} z_i^n = 0\,, \tag{1}$$

$$\Delta r = \sum_{i=1} r_i^m - \sum_{i=1} r_i^n \le 0{,}1 \sum_{i=1} r_i^m\,, \tag{2}$$

where z_i^m, z_i^n – valence, r_i^m, r_i^n – covalent radius of the atoms of the solvent m and dissolved n chemical element or elements that form the molecules of the solvent and dissolved compounds, respectively, *i=1, 2, 3, 4.*

When the dissolving and solute elements or molecules are isovalent with each other, they are electrically neutral and condition (1) is fulfilled. It is known that the solubility of an atomic or molecular compound of a dissolved

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component of solid solutions depends on its comparative size with the corresponding size of the solvent. The closer the corresponding sizes of atoms or molecules of the components of solid solutions, the weaker the energy of elastic deformations of the crystal lattice, and the greater the mutual solubility of the solution-forming components, and therefore, the greater the crystalline perfection of solid solutions. When the difference in the sum of the covalent radii of the atoms of the molecules of the solution-forming components is greater than 10%, the formation of solid substitution solutions of these components is insignificant [16].

The sum of the valences of the atoms of the Si_2 and SiSn molecules is equal, and the conditions of electroneutrality (1) are satisfied for them:

$$\Delta z = (z_{Si} + z_{Si}) - (z_{Si} + z_{Sn}) = 0 \tag{3}$$

where z_{Si} and z_{Sn} are the valences of silicon and tin atoms, respectively. The sums of the covalent radius of the atoms of the Si_2 and Sn molecules have close values, then from condition (2) we can obtain:

$$\Delta r = \left|(r_{Si} + r_{Si}) - (r_{Si} + r_{Sn})\right| = \left|2{,}34\,\overset{0}{A} - 2{,}51\,\overset{0}{A}\right| \approx 0{,}073 \cdot (r_{Si} + r_{Si}) < 0{,}1(r_{Si} + r_{Si}) \tag{4}$$

Where r_{Si} and r_{Sn} covalent radius of silicon and tin atoms according to Pauling, respectively [17]. From (4) it is evident that the difference in the sums of the covalent radii of the atoms of the Si_2 and SiSn molecules is about 7.3%, therefore, these components satisfy the condition for the formation of a continuous substitution solid solution presented in [18].

Substitution of Si_2 by a SiSn molecule does not strongly deform the crystal lattice, while the energy of elastic distortions of the crystal lattice will be insignificant and the substitution solid solution in the form of $Si_{1-\delta}Sn_\delta$ is a stable solid phase. The spatial configuration of two stable tetrahedral bonds of the $Si_{1-\delta}Sn_\delta$ solid solution is shown in Fig. 1.

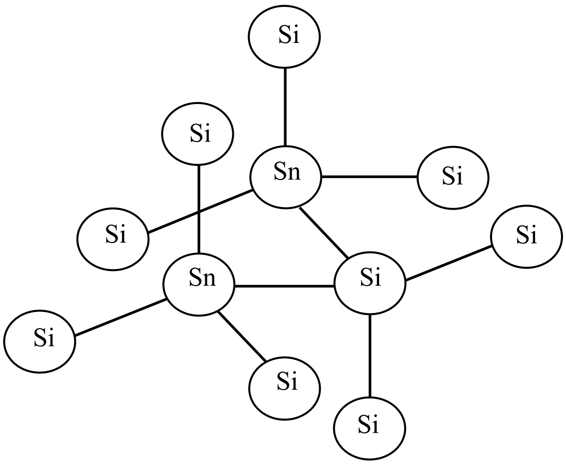

Figure 1. Hypothetical crystal lattice of the solid solution $Si_{1-\delta}Sn_\delta$

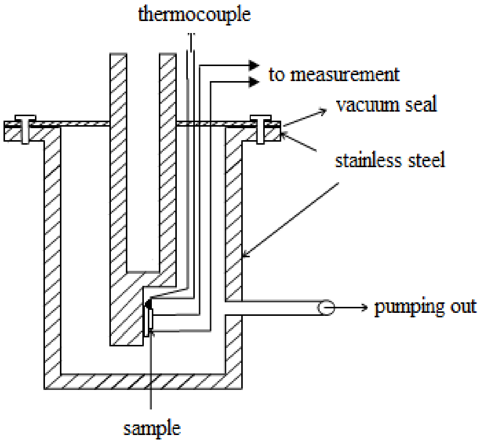

Figure 2. Metal cryostat for taking measurements

Sample preparation and research methods. Solid solutions of $Si_{1-\delta}Sn_\delta$ were grown by liquid-phase epitaxy from a limited volume of tin (Sn) melt solution in a hydrogen atmosphere. Hydrogen was purified by passing through a palladium tube. The film growth process was carried out by forced cooling of the melt solution. Liquid-phase epitaxy was carried out on a vertically positioned quartz reactor with horizontally positioned substrates. To obtain a good interface between the substrate and the epitaxial film, close values of the lattice parameters, thermal expansion coefficients and crystal structure of the substrate and film materials are required [19]. On the other hand, the substrate material must be accessible and well studied. It is known that among elementary semiconductors, silicon and tin are accessible and fairly well studied materials. The linear thermal expansion coefficients of Si and Sn are $4.2 \cdot 10^{-6}$ 1/K [20] and $23.4 \cdot 10^{-6}$ 1/K [21], respectively. Therefore, Si is a suitable material for obtaining a good quality $Si_{1-\delta}Sn_\delta$ solid solution layer.

The elemental chemical compositions of the surface and transverse cleavage of as grown $Si_{1-\delta}Sn_\delta$ solid solution epilayers were studied on a JSM 5910LV X-ray electron probe microanalyzer (JEOL, Japan). It was found that both components are uniformly distributed over the surface, while composition in depth of the film varies within $0 \le \delta \le 0.04$, as in [22].

In addition, it is known that the crystallographic plane with the orientation (111) has two broken bonds, and the plane (100) has one broken bond. Therefore, elementary semiconductors grow well on substrates with the orientation (111), but it is quite difficult to obtain a high-quality film on substrates with the orientation (100) [23]. Therefore, Si washers with the crystallographic orientation (111) and a specific resistance of 1 Ω·cm were used as substrates. The thickness of the film layers varied within 10-40 μm, depending on the growth mode and the thickness of the gap between the substrates. The grown layer thicknesses were determined using a thickness gauge EV-01.

To conduct the studies, pSi-n$Si_{1-\delta}Sn_{\delta}$ structures were fabricated by growing a solid solution of $Si_{1-\delta}Sn_{\delta}$ with n-type conductivity and a resistivity of $\rho \approx 0.8$ Ω·cm. When measuring the current-voltage characteristics, samples with a thickness of 10-40 μm of the epitaxial layer of the solid solution were used. Ohmic current-collecting contacts, solid on the back side and quadrangular with an area of 9 mm^2 on the side of the epitaxial layer, were created by vacuum deposition of silver, at a pressure of ~ $1.33 \cdot 10^{-3}$ Pa. The current-voltage characteristics of the pSi-n $Si_{1-\delta}Sn_{\delta}$ heterostructures were measured in the dark at different values of the thickness of the $Si_{1-x}Sn_{x}$ epitaxial layer in the forward and reverse directions of the current at bias voltages from -3 to +5 V. For this, the samples were mechanically tightly fixed to a metal cryostat, which was evacuated to a residual pressure of ~ 0.133 Pa (Fig. 2).

As a voltage source we used the B5-11 power supply. The voltage across the sample was measured with the VK7-9 volt-ohmmeter, and the current through the semiconductor structure was measured with the combined device Sh-300. The VK7-9 voltmeter was connected directly to the sample terminal and only in this case we were able to correctly measure the voltage on the sample, since during the measurement a redistribution of the voltage supplied to the circuit between the sample and the divider may occur.

RESULTS AND DISCUSSION

Figure 3 shows the current-voltage characteristics of pSi-n $Si_{1-\delta}Sn_{\delta}$ structures with different thicknesses of the $Si_{1-\delta}Sn_{\delta}$ solid solution at room temperature (293 K). From Fig. 3 it is evident that the dependence of the magnitude of the direct current on the applied voltage, for all values of the $Si_{1-\delta}Sn_{\delta}$ thickness, is nonlinear. The magnitude of the current through pSi-n$Si_{1-\delta}Sn_{\delta}$ increases and changes by 1-2 orders of magnitude, i.e. the I-V characteristic has a diode character. The following 2 sections are revealed on the current-voltage characteristic: 1 - ohmic $(I \propto U)$ and 2 - the region of sharp current growth $(I \propto U^m,\ m > 1)$. It is evident that the transient voltages from the ohmic region to the sharp current growth decrease as thickness decreases. This proves the presence of the Poole-Frenkel effect in the studied samples.

According to the Poole-Frenkel theory, which explains the Poole-Frenkel effect, the growth of the field dependence of conductivity is represented as [12, 24]

$$\sigma = \sigma_0 \exp(\beta \sqrt{E}), \tag{5}$$

here β - is the Frenkel coefficient and it is determined by the slope of the dependence $\ln \sigma = f(\sqrt{E})$.

Fig. 4 shows the calculated dependences of electrical conductivity at room temperature in coordinates $\ln \sigma = f(\sqrt{E})$ for the region of sharp current growth in the I-V characteristics of the pSi-n$Si_{1-\delta}Sn_{\delta}$ structure, with a base region thickness of d = 20 μm. From the graphical data, the values of the Frenkel coefficient were determined, which amounted to $\approx 8.7 \cdot 10^{-2} (cm/V)^{1/2}$.

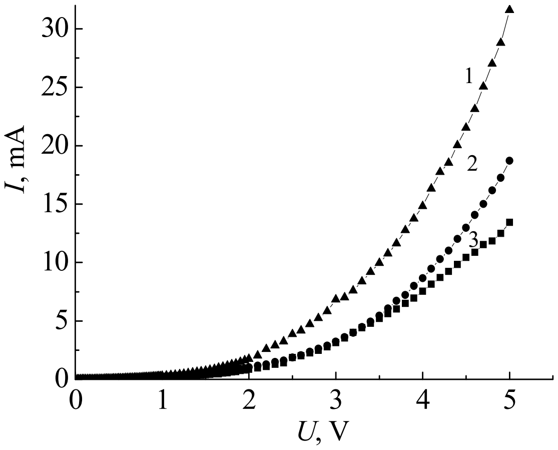

Figure 3. Forward currents of dark I-V characteristics pSi-n$Si_{1-\delta}Sn_{\delta}$ structures at T=293 K. Sample thickness, μm: 1 - 20, 2 - 25, 3 – 30

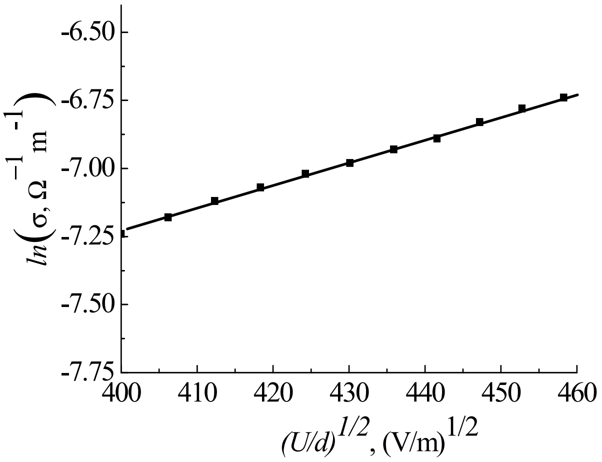

Figure 4. Dependence of electrical conductivity on the electric field, at T=293 K for pSi-n$Si_{1-\delta}Sn_{\delta}$ structures

It is known that by determining the critical value of the electric field corresponding to the beginning of the nonlinear dependence of electrical conductivity on the applied voltage, according to the expression [12]

$$N_t = \left(\frac{2e}{kT\beta} \sqrt{E_{cr}} \right)^3 \tag{6}$$

It is possible to determine the concentration of defects (N_t) responsible for the conductivity of the pSi-n Si$_{1-\delta}$Sn$_\delta$ structure.

Based on the values of the critical electric field E_{cr} , at which Ohm's law is violated, the concentrations of ionized centers in the studied structures were determined using formula (6). Based on data from experiments conducted on different samples (with a thickness of d = 20 ÷ 30 μm), the average trap concentration of ~2,4·10^{14} cm^{-3} was obtained.

CONCLUSIONS

Thus, pSi-nSi$_{1-\delta}$Sn$_\delta$ ($0 \le \delta \le 0.04$) structures with base n-layer thicknesses W ≈ 20-30 μm were manufactured in a single technological cycle by the liquid-phase epitaxy method on single-crystal p-Si substrates with the (111) orientation. The study of the conductivity mechanism in pSi-nSi$_{1-\delta}$Sn$_\delta$ structures based on the solid solution Si$_{1-\delta}$Sn$_\delta$ obtained by liquid-phase epitaxial was carried out. Based on the analysis of the dependence $\ln\sigma = f(\sqrt{E})$, the value of the Frenkel coefficient β was determined and it was established that the nonlinearity of the current-voltage characteristics of these structures is due to the Poole-Frenkel effect. The concentration of ionized centers (traps), the values N_t of which strongly depend on the field effect, was also estimated.

The experimental and calculated results allow us to conclude that in our experiments at room temperature in pSi-nSi$_{1-\delta}$Sn$_\delta$ ($0 \le \delta \le 0.04$) structures, the Poole-Frenkel effect is observed. The presence of this effect in the solid solution Si$_{1-\delta}$Sn$_\delta$ allows us to apply high-voltage effects to the parameters of various devices based on this semiconductor [25]. The most realistic application of the Poole-Frenkel effect in converters of thermal energy into electrical energy together with the thermovoltaic effect seems to be [4, 26-29].

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ПОЛЬОВІ ВЛАСТИВОСТІ ДІОДНИХ СТРУКТУР НА ОСНОВІ ТВЕРДОГО РОЗЧИНУ "КРЕМНІЙ-ОЛОВО"

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У цій статті представлено результати досліджень механізму провідності в структурах pSi-nSi$_{1-\delta}$Sn$_\delta$ ($0 \leq \delta \leq 0{,}04$) на основі твердого розчину Si$_{1-\delta}$Sn$_\delta$ з базовою товщиною n-шарів W ≈ 20-30 мкм. Досліджувані зразки були отримані в одному технологічному циклі методом рідкофазної епітаксії на монокристалічних підкладках p-Si з орієнтацією (111). Результати експериментальних та обчислювальних досліджень показали, що ефект Пула-Френкеля спостерігається в структурах pSi-nSi$_{1-\delta}$Sn$_\delta$ ($0 \leq \delta \leq 0{,}04$) за кімнатної температури. Ця обставина дозволяє використовувати вплив високої напруги на параметри різних пристроїв на основі твердого розчину Si$_{1-\delta}$Sn$_\delta$. Таким чином, існує інтерес до використання цього ефекту в перетворенні теплової енергії в електричну на основі термовольтаїчного ефекту. Також отримані результати показують потенціал використання твердих розчинів Si$_{1-\delta}$Sn$_\delta$ ($0 \leq \delta \leq 0{,}04$), вирощених на кремнієвих підкладках, як активного матеріалу в перетворювачах теплової енергії.

Ключові слова: *рідкофазна епітаксія; вольт-амперна характеристика; польовий механізм; коефіцієнт Френкеля; активація носіїв заряду; концентрація іонізованих пасток; термоелектричний ефект*