MECHANISM OF ACCEPTOR IMPURITY INITIATION IN THE p-TiCoSb INTERMETALLIC SEMICONDUCTOR HEAVILY DOPED WITH A V DONOR IMPURITY. 2. ELECTROKINETIC STUDIES

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The temperature and concentration dependences of the resistivity and the thermopower coefficient of the intermetallic p-TiCoSb semiconductor heavily doped with a V donor impurity have been studied within the impurity concentration range $N_D^{\mathrm{V}} = 9.5 \times 10^{19} \div 1.9 \times 10^{21}$ cm^{-3} and the temperature interval $T = 80 \div 380$ K. A conductivity transition of the insulator–metal–insulator type, which is caused by a change in the relative arrangement of the Fermi level and the percolation level in the conduction band, has been found; the latter phenomenon occurs owing to a change of the compensation degree in the semiconductor and runs following the mechanism that was established in our previous work.

1. Introduction

In this work, we report the results of the second part of our researches dealing with the influence of considerable concentrations of the donor V impurity (the impurity concentration $N_D^{\mathrm{V}} = 9.5 \times 10^{19} \div 1.9 \times 10^{21}$ cm^{-3}) on the variation of electrokinetic characteristics of the intermetallic semiconductor p-TiCoSb. The results obtained confirm the existence of the mechanism of the simultaneous generation of defects of the acceptor nature in a crystal, which was revealed in work [1].

For instance, the X-ray diffraction studies of $Ti_{1-x}V_xCoSb$ indicate different occupation degrees of the crystallographic positions of Co and Ti atoms. It turned out that the crystalline structure of the TiCoSb compound, which is an undoped semiconductor, is defective; in particular, only 95.8 and 93.3% of the crystallographic positions of Co and Ti atoms, respectively, are occupied. Free atomic positions are vacancies, which is equivalent to the introduction of defects of the acceptor nature into the semiconductor. Therefore, a TiCoSb specimen undoped with V atoms contains about 10^{20} defects of the acceptor nature in cm^3, which makes the initial specimen to be a heavily doped semiconductor. Doping p-TiCoSb with the donor admixture of V in a significant concentration affects substantially the occupation degrees of the crystallographic positions of Co and (Ti,V) atoms [1].

In work [2], it was shown that the approaches applied to the description of conventional and heavily doped semiconductors differ drastically. In the last case, an electron is considered to be not in the periodic field of a crystal, but in a stochastic field induced by impurities. At low temperatures, a doped crystalline semiconductor is a disordered system that resembles amorphous systems; and the the electrostatic interaction between various charged defects, the arrangement of which has a statistical and fluctuation character, substantially influences the band structure of a semiconductor and is accompanied by the fluctuation of the potential relief and by the modulation of continuous-energy bands (Fig. 1).

The calculation of the electron density distribution [1] showed that the doping of p-TiCoSb with the donor V impurity and a simultaneous generation of compensating defects of the acceptor nature do not result in a

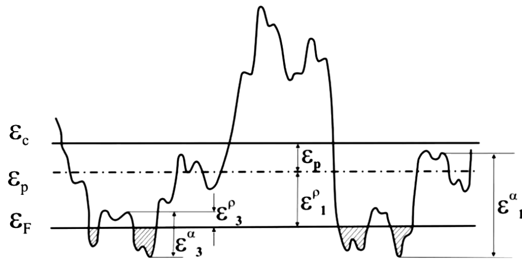

Fig. 1. Energy diagram of heavily doped and compensated semiconductors: the solid curve represents the distortion of the conduction band, the upper solid line (ε_c) marks the bottom energy of the conduction band in the absence of impurity-induced potential, the lower solid line ($\varepsilon_{\rm F}$) marks the Fermi level, and the dash-dotted line (ε_p) marks the percolation level. The hatched regions are occupied by electrons

monotonous drift of the Fermi level ($\varepsilon_{\rm F}$) towards the conduction band, as it happens in the case of the doping of p-TiCoSb with the donor Ni or Cu impurities [3, 4].

Hence, the doping of the intermetallic p-TiCoSb semiconductor with the donor V impurity is accompanied by a variation of the compensation degree, which, in its turn, should bring about to a change in the relative position of the Fermi level and the percolation level in the conduction band, as well as to a change of mechanisms of electroconductivity. In this work, we present examples of such changes.

The temperature dependences of the resistivity ρ and the thermopower coefficient α of p-TiCoSb (see Fig. 2) were studied at doping the latter with the donor V impurity and the formation of a solid $\mathrm{Ti}_{1-x}\mathrm{V}_x\mathrm{CoSb}$ solution (the impurity concentration $N_D^{\rm V}$ varied from 9.5×10^{19} cm^{-3} at $x = 0.005$ to 1.9×10^{21} cm^{-3} at $x = 0.10$). The technique of specimen fabrication, the regimes of homogenizing annealing, and the procedures of ρ- and α-measurements with respect to copper in the temperature range $T = 80 \div 380$ K were expounded in work [1].

2. Electrokinetic Researches of $\mathrm{Ti}_{1-x}\mathrm{V}_x\mathrm{CoSb}$

The temperature dependences $\ln\rho(1/T)$ and $\alpha(1/T)$ for the p-TiCoSb compound are typical of doped semiconductors. Both high- and low-temperature activation sections can be distinguished in them. The availability of those sections evidences the existence of activation mechanisms of electroconductivity of at least two types. These are the activation of electrons from the Fermi level onto the percolation level in the conduction band (the activation energy ε_1^ρ) [2] and the electron hopping [5] over the states with energies close to the Fermi level (the activation energy ε_3^ρ) (small-scale fluctuations of the conduction band are isolated).

For the specimens, whose $\ln\rho(1/T)$- and $\alpha(1/T)$-dependences contained activation sections, we, making use of the Mott relation [6]

$$\alpha = \frac{2\pi^2}{3}\frac{k_{\rm B}^2 T}{e}\frac{\partial \ln n(\varepsilon_{\rm F})}{\partial E}$$

for the thermopower coefficient, evaluated the activation energies ε_1^ρ, ε_1^α, ε_3^ρ, and ε_3^α (see the Table). The obtained values agree with the results obtained in the framework of an approach proposed in work [7] for the description of fluctuation parameters (Fig. 1): the amplitude of large-scale fluctuations ε_1^α and the average depth of small-scale fluctuations ε_3^α (a fine structure). In such a case, knowing the activation energy for hopping conductivity ε_3^ρ makes it possible to determine the filling degree of the potential well of small-scale fluctuations by the electron gas.

The fact that the thermopower coefficient α for p-TiCoSb changes its sign at $T \approx 95$ K indirectly testifies that the concentrations of ionized acceptors and donors are close to each other, i.e. the compensation degree is high. It follows from the Table that, of all studied specimens, the undoped p-TiCoSb one is characterized by the largest ε_1^ρ-value. In accordance with the results of work [8], the Fermi level is located in the middle of the energy gap in heavily doped and completely compensated semiconductors, which means that the activation energy from the Fermi level onto the percolation one is the highest.

As follows from Fig. 2, the doping of p-TiCoSb to the concentrations of donor V impurity that are least accessible in experiment ($x = 0.005$) is accompanied by the overcompensation of the semiconductor conductivity from the hole to the electron type. The magnitude of electroconductivity increases at that, and the conductivity transition insulator–metal is implemented.

Concentration and energy characteristics of $\mathrm{Ti}_{1-x}\mathrm{V}_x\mathrm{CoSb}$

x	$N_D^{\rm V}$, cm^{-3}	ε_1^ρ, meV	ε_1^α, meV	ε_3^ρ, meV	ε_3^α, meV
0	0	106.1	196.2	5.2	10.67
0.005	9.5×10^{19}	–	12.9	–	0.3
0.01	1.9×10^{20}	10.4	43.6	–	0.2
0.02	3.8×10^{20}	6.4	34.1	–	0.3
0.03	5.7×10^{20}	27.1	53.3	3.1	1.4
0.04	7.6×10^{20}	22.1	51.6	0.3	0.4
0.06	$1.1\ 10^{21}$	20.0	50.2	1.6	1.7
0.08	1.5×10^{21}	17.4	42.1	1.5	1.8
0.1	1.9×10^{21}	15.2	46.2	0.8	2.6

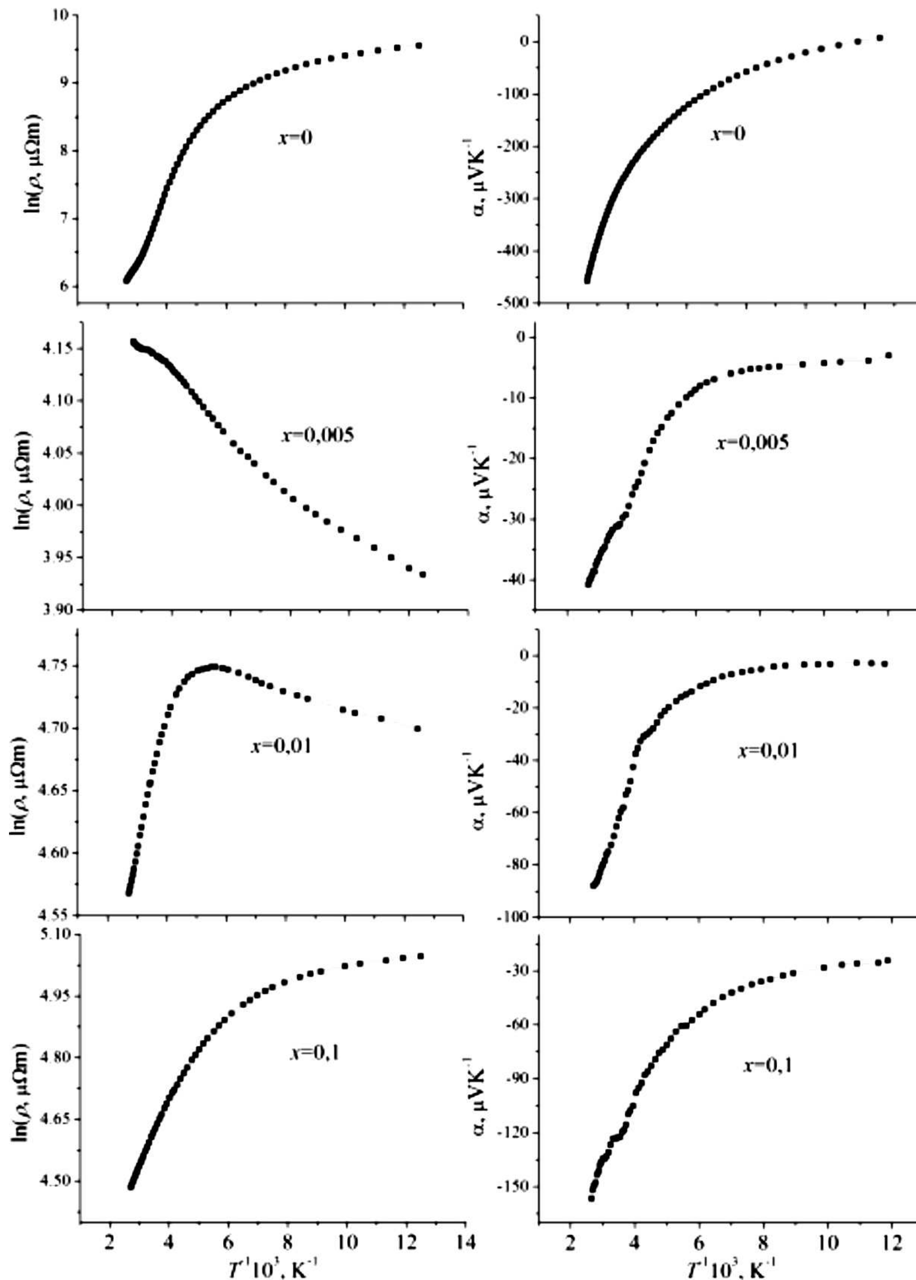

Fig. 2. Temperature dependences of the resistivity ρ and the thermopower coefficient α of $\mathrm{Ti}_{1-x}\mathrm{V}_x\mathrm{CoSb}$

The latter is the Anderson transition [6], because there are no activation sections in the dependence $\ln\rho(1/T)$, and the thermopower coefficient changes its sign from positive to negative at $T = 80$ K. Such a behavior of the resistivity is clear, being associated with the intersection of the percolation level in the conduction band by the Fermi level (there is no high-temperature activation section in the dependence $\ln\rho(1/T)$), as well as with the filling of small-scale modulations of the conduction band by the majority charge carriers [2,5]. However, the shape of $\ln\rho(1/T)$-dependences at higher concentrations of the donor V impurity is the most interesting.

One could have predicted *a priori* that the increase of the donor impurity concentration in the semiconductor now characterized by the electron-type conductivity would not change the metallic character

of the dependences $\ln\rho(1/T)$, which was observed for a $Ti_{1-x}V_xCoSb$ specimen with $x = 0.005$. However, as follows from Fig. 2, such a doping of the intermetallic semiconductor gives rise to the elimination of metallic conductivity and the emergence of – first – the high-temperature activation sections (at $x = 0.01$ and 0.02) and – then, at $x \geq 0.03$ – the low-temperature ones in the $\ln\rho(1/T)$-dependences. Elimination of metallic conductivity in a semiconductor of the electron conductivity type is possible only provided that an acceptor impurity is introduced into the specimen [2]. However, we introduced just the donor V impurity into *p*-TiCoSb.

It is impossible to understand and explain the behavior of $\ln\rho(1/T)$-dependences at $x \geq 0.01$ without taking into account the results of structural researches – and, as a consequence, without knowing the distribution of the electron density in $Ti_{1-x}V_xCoSb$ – which were reported in our previous work [1]. It is the mechanism of synchronous emergence of compensating defects of the acceptor nature at an increase of the impurity V concentration in the crystal that provides the semiconducting character of $\rho(1/T)$-dependences in the studied concentration range, i.e. to $N_D^V = 1.9 \times 10^{21}$ cm^{-3}.

Overcompensation of the *p*-TiCoSb semiconductor and metallization of its conductivity, when the V impurity with the concentration that is the least accessible in experiment is introduced, testify that the activation energy ε_1^ρ changes from the Fermi energy to the energy of the percolation level in the continuous energy band (see the Table). In the undoped *p*-TiCoSb, the activation energy $\varepsilon_1^\rho(x = 0) = 106.1$ meV; at the same time, $\varepsilon_1^\rho(x = 0.005) = 0$ meV. By analyzing the dependences of the occupation degrees of the atomic Co and (Ti,V) positions on the composition of $Ti_{1-x}V_xCoSb$ [1] and the corresponding variation of the activation energy ε_1^ρ, we can assert that the growth of $\varepsilon_1^\rho(x)$-values occurs in the section, where the occupation degrees of the Co and (Ti,V) atomic positions are minimal.

In its turn, the increase of the activation energy ε_1^ρ evidences an increase of the energy barrier between the Fermi level and the percolation level in the conduction band, which means that the Fermi level drifts towards the valence band. Such a behavior of the Fermi level is possible only if the compensation degree in the semiconductor changes; the rate of acceptor impurity generation must exceed the introduced concentration of the donor impurity at that. This conclusion is confirmed by the variation character of the dependence of the atomic position occupation degree on the donor impurity concentration [1].

An almost linear reduction of the activation energy ε_1^ρ starts, when the generation rates of acceptor and donor impurities become equal to each other, which testifies to the reverse of the drift of the Fermi level which moves now towards the conduction band. This becomes possible, provided that the rate of donor impurity introduction exceeds the rate of acceptor impurity generation.

In the specimens, for which no low-temperature activation sections were observed in the $\ln\rho(1/T)$-dependences, i.e. the hopping conductivity ε_3^ρ was absent ($0 \leq x \leq 0.02$), the depth of small-scale fluctuations was insignificant ($\varepsilon_3^\alpha \approx 0.3$ meV), because the majority charge carriers “fill in” the small-scale relief [5].

If the compensation degree of the semiconductor increases (the acceptor impurity concentration in a semiconductor of the *n*-type grows), the fluctuation amplitude and the depth of the potential well of small-scale fluctuations also increase (see the Table). It gives rise to the initiation of the hopping mechanism of charge transfer. The dependence of the compensation degree in specimens on the donor impurity concentration is complicated; nevertheless, it allows the relationship between the impurity concentration, on the one hand, and the large-scale fluctuation amplitude and the averaged depth of the potential well of small-scale fluctuations (a fine structure), on the other hand, to be traced, as it was done, in particular, in works [3, 4, 7].

3. Conclusions

Thus, a conclusion drawn on the basis of the results of calculations concerning the electron density distribution finds its confirmation; namely, the doping of the intermetallic *p*-TiCoSb semiconductor with the donor V impurity is accompanied by a simultaneous occupation of crystallographic positions of Ti and Co atoms by dopant atoms. This means a simultaneous introduction of both donor and acceptor defects into the semiconductor and gives rise to a change of the compensation degree in the semiconductor and to a modification of the Fermi level position.

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МЕХАНІЗМ ГЕНЕРАЦІЇ АКЦЕПТОРНОЇ ДОМІШКИ В ІНТЕРМЕТАЛІЧНОМУ НАПІВПРОВІДНИКУ p-TiCoSb ПРИ СИЛЬНОМУ ЛЕГУВАННІ ДОНОРНОЮ ДОМІШКОЮ V. 2. ЕЛЕКТРОКІНЕТИЧНІ ДОСЛІДЖЕННЯ

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Р е з ю м е

Досліджено температурні та концентраційні залежності питомого електроопору та коефіцієнта термо-ерс інтерметалічного напівпровідника p-TiCoSb, сильнолегованого донорною домішкою V ($N_D^{\mathrm{V}} \approx 9,5 \cdot 10^{19} \div 1,9 \cdot 10^{21}$ см$^{-3}$, $T = 80 \div 380$ K). Виявлено перехід провідності діелектрик–метал–діелектрик, зумовлений зміною взаємного розташування рівнів Фермі та протікання зони провідності внаслідок зміни ступеня компенсації напівпровідника за механізмом, встановленим у нашій попередній роботі.