THE INFLUENCE OF STRUCTURAL DEFECTS ON THE ELECTRONIC AND ADHESIVE PROCESSES AT THE INTERFACE OF THE $Bi_{0.85}Sb_{0.15}$ SOLID SOLUTION WITH CONTACT ALLOYS

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The dependence of the resistance of the transition contact r_k and the adhesion work of extruded samples of the $Bi_{0.85}Sb_{0.15}$ solid solution on the magnetic field strength and temperature was investigated. It was found that the resistance of the transition contacts of the $Bi_{0.85}Sb_{0.15}$ -contact alloy structures is determined mainly by the resistance of the n- $Bi_{0.85}Sb_{0.15}$ solid solution - $Bi_{0.85}Sb_{0.15}$ solid solution structure heavily doped with acceptor impurity atoms Sn and Pb diffusing from the contact alloy into the near-contact region of the crystal.

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1. INTRODUCTION

Crystals of solid solutions of Bi-Sb systems are photosensitive in the infrared region of the spectrum, and are also effective low-temperature thermo- and magnetothermoelectric materials for the creation of solid-state electronic coolers for infrared photodetectors. The efficiency of photo- and thermoelectric converters, along with the fundamental parameters of the semiconductor material, is also determined by the physical properties of the transition contacts of these converters [1-5] the efficiency of thermoelements is determined by the relationship [6]

$$Z = \alpha^2 / [\chi(\rho + r_k /2\ell)] \qquad (1)$$

Where α and χ are the thermoelectric emf and thermal conductivity coefficients, ρ is the resistivity of the semiconductor material of the thermoelement legs, r_k is the resistance of the transition contact between the semiconductor and the switching plates, ℓ- is the length of the thermoelement legs. A long service life of a thermoelement can be achieved if, under operating conditions, the thermoelectric and contact materials have mutual physical and chemical resistance, and the switching method and quality ensure this resistance.

The process of contacting a metal and a semiconductor is accompanied by mutual diffusion of materials, which leads to poisoning and oxidation of the semiconductor material. In the case of soldering, the solder can release toxic components inside the thermoelement legs, especially at high temperatures. The diffusion of the contact material in the thermal branch causes a number of harmful phenomena that reduce the efficiency of the thermoelectric material, such as the formation of a second phase of a well-conducting layer that causes a local short circuit of the thermoelement, a direct reaction of the contact material with the thermoelectric, the appearance of donor or acceptor levels that change the local concentration of carriers, the dissolution of impurities from the thermal branches by the contact material, etc.

Therefore, the switching material must have high electrical and thermal conductivity, and the transition resistance at the contact section of the semiconductor with the switching material must be minimal, provided that the linear expansion coefficients of the thermoelectric and switching materials are matched. Therefore, the study of physical properties, including elucidation of the mechanisms of electron and phonon transfer in extruded samples of $Bi_{0.85}Sb_{0.15}$ solid solutions, is an urgent task in materials science.

Taking into account the above, in this work the resistance of the transition contact and the adhesive properties the effect of heat treatment on the resistance of the transition contacts of extruded samples of $Bi_{0.85}Sb_{0.15}$ solid solutions with various contact alloys were investigated [7].

2. EXPERIMENTAL PART

Samples of $Bi_{0.85}Sb_{0.15}$ solid solutions were obtained in the following process sequence:

-the synthesis was carried out by direct alloying of the components in a quartz ampoule, pre-etched in a $K_2Cr_2O_7$ solution and evacuated to a residual pressure of ~10^{-3} Pa, constantly subjected to shaking during the synthesis to improve the homogeneity of the alloy. The ampoule with the substance was sharply cooled to room temperature. The components used were bismuth of the VI-0000 brand, antimony of the SU-0000 brand.

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- extrusion was carried out on an MS-1000 hydraulic press. Extrusion process parameters: $P_{eks.}$=4.0 t/cm^2, $T_{eks.}$=475±3K.

Post-extrusion annealing was carried out in ampoules evacuated to ~10^{-3} Pa at ~503 K for 5 hours. The experiments were carried out in the temperature range from ~77 to ~300 K and magnetic field strength up to 74x10^4 A/m. Electrical measurements were carried out along the extrusion axis. Samples that had not undergone heat treatment after extrusion and the same samples that had undergone heat treatment.

3. RESULTS AND ITS DISCUSSION

Fig. 1 shows the dependences of $(r_k-r_{k0})/r_{k0}$ and $(\rho-\rho_0)/\rho_0$ at ~77 K on the magnetic field strength in the case of the contact material made of alloy 1. Here r_{k0}, ρ_0 are the transition contact resistance and the specific resistance in the absence of a magnetic field, and r_k and ρ are in a magnetic field. It is evident that the nature of the change in the transition contact resistance r_k of the $Bi_{0.85}Sb_{0.15}$ solid solution with alloy 1 and the specific resistance ρ of the solid solution itself of the extruded $Bi_{0.85}Sb_{0.15}$ sample on the magnetic field strength are the same. However, the change in $(r_k-r_{k0})/r_{k0}$ with an increase in the magnetic field strength is greater in all cases than the change in $(\rho-\rho_0)/\rho_0$. For example, at ~77 K with a magnetic field strength greater than ~23x10^4 A/m, the ratio $[(r_k-r_{k0})/r_{k0}]/[(\rho-\rho_0)/\rho_0]$ for samples based on annealed solid solution reaches 1.5. With increasing temperature to 300 K, the dependence of r_k and ρ on the magnetic field strength weakens, however, the patterns observed at ~77 K on the effect of the magnetic field on r_k and ρ are preserved at high temperatures.

Similar results at ~77 and 300 K were obtained in the case of contact alloy 2.

The magnetoresistance results obtained in extruded $Bi_{0.85}Sb_{0.15}$ samples are well described by the results of theory and experimental data available in the literature [8].

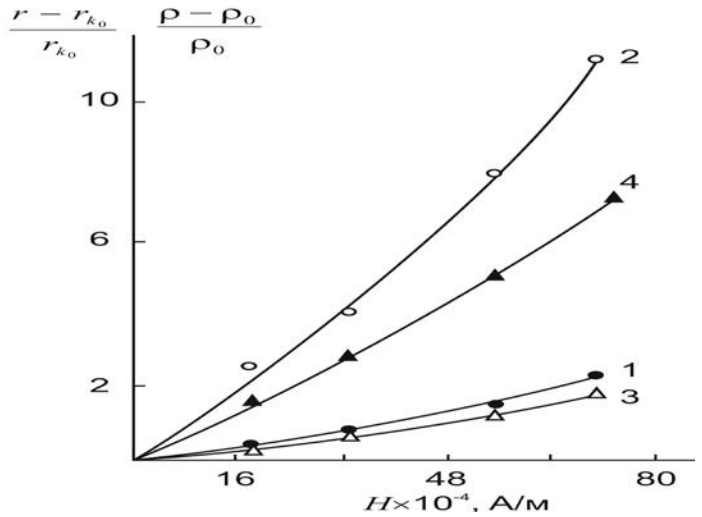

Fig. 1. Dependences of the transient contact (1, 2) and specific magnetoresistance (3, 4) at ~77K on the magnetic field strength. Curves 1, 3 relate to $Bi_{0.85}Sb_{0.15}$ samples that have not undergone heat treatment, and 2 and 4 to samples that have undergone heat treatment after extrusion.

The following considerations can explain the rather strong dependences r_k of the transition contact of $Bi_{0.85}Sb_{0.15}$ with contact alloys on the magnetic field strength, compared to the specific resistance ρ. When applying the contact to the ends of extruded $Bi_{0.85}Sb_{0.15}$ samples, mutual diffusion of the components of the solid solution and the contact alloy in each other occurs.

Therefore, as a result of the diffusion of Pb and Sn atoms from the contact alloy into the $Bi_{0.85}Sb_{0.15}$ solid solution, a near-contact layer of this solid solution is formed near the contact, doped with lead and tin atoms (or only tin in the case of a contact alloy wt %: 57 Bi + 43 Sn). As a result, the following structure is formed: $Bi_{0.85}Sb_{0.15}$ solid solution - intermediate layer of $Bi_{0.85}Sb_{0.15}$ solid solution, heavily doped with acceptor lead and tin atoms - contact alloy. The specific resistance of the intermediate layer at ~77 K (solid solution $Bi_{0.85}Sb_{0.15}$ doped with Pb and Sn) is several times higher than the specific resistance of pure $Bi_{0.85}Sb_{0.15}$ In addition, $Bi_{0.85}Sb_{0.15}$ samples doped with Pb or Sn atoms with a concentration of more than 0.01 at.% have p-type conductivity at ~77 K. Therefore, the transient contact resistance of the structure will be mainly determined by the transient resistance of the transition $Bi_{0.85}Sb_{0.15}$ solid solution - intermediate layer. In a magnetic field, with an increase in the magnetic field strength to 74x10^4 A/m, the specific resistance of $Bi_{0.85}Sb_{0.15}$ increases strongly (by ~7.3 times). At the same time, the specific resistance of the intermediate layer also increases (for example, experiments have shown that extruded samples with 0.1 at.% Pb have ~77 K $\rho \approx 5{\cdot}10^{-4}$ (Ohm·cm) at ~77 K and with an increase in the voltage to 74x10^4 A/m, ρ increases almost linearly and reaches a value of $6{\cdot}10^{-4}$ (Ohm·cm). Because of this, the growth of r_k of the $Bi_{0.85}Sb_{0.15}$ - intermediate phase structure under the action of a magnetic field is stronger than the growth of the specific resistance of pure $Bi_{0.85}Sb_{0.15}$.

At temperatures above ~120 K, the conductivity type of the $Bi_{0.85}Sb_{0.15}$ solid solution doped with Pb or Sn becomes electronic [9]. In addition, at high temperatures, the effect of Pb and Sn impurities on the ρ of the $Bi_{0.85}Sb_{0.15}$ solid solution, including the ρ of the intermediate layer, is weakened. Therefore, at ~300 K, despite the fact that the value of the specific resistance of both the $Bi_{0.85}Sb_{0.15}$ solid solution and the intermediate layer (the $Bi_{0.85}Sb_{0.15}$ layer doped with Pb or Sn atoms) differs insignificantly from the values of ρ at ~77 K, the contact resistance r_k at ~300 K is ~2 times lower than at ~77 K. The change in r_k of the structure under the action of a magnetic field at ~300 K also correlates well with the change in ρ of pure $Bi_{0.85}Sb_{0.15}$ and the intermediate layer. In extruded samples of $Bi_{0.85}Sb_{0.15}$, there are stressed regions that create scattering centers for charge carriers [2]. Annealing of the rods after extrusion leads to the disappearance of these regions, which ends with an increase in the mobility of charge carriers. As a result, the magnetoresistive effect and the change in r_k under the influence of a magnetic field in annealed samples are stronger than in non-annealed ones.

In addition to electrical parameters, contacts are also characterized by mechanical properties. The bond and adhesion between the extruded $Bi_{0.85}Sb_{0.15}$ solid solution and the contact alloy is determined by the process of wetting the crystal surface with this contact alloy.

It is known that the wetting of a solid by a liquid and the bond of a liquid with a solid can be determined by two types of forces acting between the phases:

- physical interaction combining dipole, induction and dispersion forces. By analogy with adsorption, this type of contact can be called physical, reversible wetting, i.e. such a contact when the contacting surfaces after contact can be separated, while remaining unchanged;

- chemical forces - ionic and homopolar. This type of contact and wetting can be called chemical, irreversible wetting.

The main difference between these types of contacts is the magnitude of the interphase forces. If the energy of the Van der Waals forces is a fraction or several units of kcal/mol, then for chemical interaction this energy is tens and hundreds of kcal/mol.

Thus, physical forces, although they always act, are not able to provide such energy; such energy can only be caused by chemical interaction.

A distinctive feature of chemical wetting, in addition to the large value of interfacial forces, is the relatively strong dependence of the degree of wettability on temperature; often such a dependence is characterized by a wetting threshold - the presence of a temperature, after reaching which the contact angle begins to drop sharply, and the work of adhesion to increase.

Wetting of the surface of a solid is caused, in addition to the above, by the presence of internal and surface force fields in them. The appearance of these forces causes interaction between molecules inside and on the surface of bodies.

The nature of wetting of the contact material largely depends on the value of the surface tension coefficient of their melts, the value of interfacial tension in contact with the melt of the contact material with the surface of the solid [10]. Spreading of liquids and wetting of the surface of a solid are accompanied by an increase in the surface of the liquid and are associated with overcoming the forces of surface tension.

In addition to the above, wetting of the surface of a crystal by a molten contact material largely depends on the nature of the previous treatment, the state of the crystal surface, the size and uniformity of the gap, the method of removing the oxide film, the environment, etc. Since the influence of all these factors is theoretically difficult to take into account, in practice it is determined by experiment. The process of wetting the surface of a solid with the liquid phase of the contact material and the forces that determine adhesion play a significant role in creating devices with specified properties. The characteristic of the adhesion forces of a liquid and a solid is the specific work of adhesion, equal to the work of their separation along the interphase boundary

$$A_a = \sigma_0 (1 + \cos\theta) \qquad (2)$$

where σ_0 is the coefficient of surface tension of the melt of the contact material, θ- is the contact angle, defined as the angle between the surface of the solid and the tangent to the point of contact with the liquid at the interface with the environment.

Wetting of the crystal surface with a molten contact alloy depends on the composition of the contact alloy, the state of the crystal surface, the type of medium, etc.

To determine the contact angles of wetting θ of the $Bi_{0.85}Sb_{0.15}$ surface with contact alloys, the optical method of "sessile drop" was used. The optical system of the setup provided a magnification of ~20 times, which made it possible to use drops weighing 1.5-2.0 g. The surface tension coefficient σ_0 was determined by the drop method [11].

Experiments showed that when using alloy 1 as a contact material, the contact angle is ~23-24°, and in the case of the alloy 2. ~23-24° At 410-415 K, the surface tension of alloy 1 and the alloy 2 were 424 and 410 mN/m, respectively.

The work of adhesion Aa for the specified contact alloys with the surface of the extruded sample of the $Bi_{0.85}Sb_{0.15}$ solid solution, calculated from the above expression at a temperature of 410 and 415 K, is 780 and 850 mJ/m^2, respectively.

These values of A_a indicate that good wetting of the surface of the extruded sample of the $Bi_{0.85}Sb_{0.15}$ solid solution by the above contact alloys is ensured by a sufficiently strong physicochemical interaction of the melt of the contact material with the extruded samples of the $Bi_{0.85}Sb_{0.15}$ solid solution.

4. CONCLUSION

Thus, it was found that the resistance of the transition contacts of the $Bi_{0.85}Sb_{0.15}$ -contact alloy structures is determined mainly by the resistance of the n- $Bi_{0.85}Sb_{0.15}$ solid solution - $Bi_{0.85}Sb_{0.15}$ solid solution structure heavily doped with Sn and Pb acceptor impurity atoms diffusing from the contact alloy into the near-contact region of the crystal. In the extruded samples that were not annealed after extrusion, the ratio $(r_k-r_{k0})/r_{k0}$ and $(\rho-\rho_0)/\rho_0$ at magnetic field strengths is lower than for the annealed samples. Along with this, for the samples that were not heat treated, the ratio $(r_k-r_{k0})/r_{k0}$ $(\rho-\rho_0)/\rho_0$ is lower than for the annealed samples.

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