OPTIMIZATION OF ENERGY PARAMETERS-INDEMNIFICATION OF IMPURITY LEVELS IN CHALCOGENIDES OF LEAD AND BISMUTH

Ahmedli G.T*, Aliyeva A. P **, S.A.Seyidzadeh Sabounchi*, KuliyevA.Z****.**

** Azerbaijan Medical University, Department of physics. St. Bakikhanov 23. Baku, Azerbaican*
*** The Azerbaijan Technical University, the Republic of Azerbaijan*
**** University of Tabriz, Faculty of Physics. Tabriz, Iran*
*****SPA ˝Selenium˝ SAS AZ/R, st. F.Aqayeva 14, Baku, Azerbaican*
samir@maccenter.baku.az

ABSTRACT

Influence of indemnification on properties of chalcogenides of bismuth and lead is investigated. Crystals PbTe<$PbCl_2$, B>> and Bi_2Te_3<$CdCl_2$, B> with low concentration of the hole carriers of current. The measured and calculated parameters (electro-conductivity, thermoelectromotive, concentration of carriers of current testify the strong compensating influence of boron. Adjusting with complex impurity ($PbCl_2$-B) and ($CdCl_2$-B) it was possible to receive a set of samples with concentration of the hole carriers down to P=6,2-10^{17} cm^{-3}. The reason of strong indemnification is, on seen, linkage of vacancies of lead in complexes with ions of chlorine (in case PbS and PbTe). In Bi_2Te_3 strong p-type influence of boron results in indemnification of donor levels of chlorine.

Keywords: electro-conductivityб thermoelectromotive, impurities, indemnification, concentration, defects, self-indemnification, located, complexes.

I. INTRODUCTION

In impurity semiconductors except for the impurity giving the basic carriers of a charge, there are compensating impurities. Usually for their characteristic the measure of indemnification is entered and properties of semiconductors in a wide interval of a degree of indemnification are investigated. Influence of indemnification on properties of alloys is expressed that in the forbidden zone there are additional resolved power levels. Indemnification influences dispersion of carriers of a charge. These two factors strongly change such characteristics, as concentration and mobility of carriers of a charge (including electro-conductivity and thermoelectromotive of semiconductors).

Researches of the author [1] have shown, that crystals of indium phosphide and arsenide of gallium contain a plenty of compensating impurity; creating special technology of clearing, it is possible to receive crystals with the much greater mobility of rriers of a charge [1]. The method of indemnification of semiconductors is known depending on concentration of carriers of current and impurities in the initial material at impurity doping process by fast diffused impurity by repeated diffusion of them [1]. So copper quickly diffuse from the surface in volume of many semiconductors, creating donors and being dissolved in big quantities (for example, in Bi_2Te_3 and its firm solutions) [2]. Using temperature dependence of solubility Cu, on the same crystals at different temperatures it is possible to carry out repeated diffusion of copper. Thus crystals with a different degree of indemnification turn out. The first diffusion should be carried out at the lowest temperature, each following diffusion – at higher. After each technological process all researched phenomena [1-2] are measured. The impurity can be entered and during synthesis and cultivation of a crystal; it will be considered the best temperature during diffusion for this or that crystal. It is obvious, that it is possible to apply any quickly diffused element (for example, Li, Na, Cu, B, Ni) to change the degree of indemnification. It is possible to compensate impurity (donor and p-type) levels not only by easily diffused impurity. So self-indemnification of donor effect of chlorine by complexes of a vacancy - ion in PbTe is carried out by authors [3]. In opinion of the authors' data [3] the essence of the phenomenon of self-indemnification is in the introduction of electrically active impurity in a crystal own defects compensating alloying action of the impurity are formed. For such semiconductors as PbTe and Bi_2Te_3 there is also practically the major problem of reception of as much as possible compensated crystals with low concentration of carriers of current. The maximal degree of self-indemnification in chalcogenide of lead is received, when the sample is in thermodynamic balance with sated ferry Pb for p-type impurity [1]. In case of maximal self-indemnification of p-type effect of thallium in sulfide and selenide Pь, the good consent of the theory and experiment is received at indemnification by single twice ionized by vacancies of chalcogenide (in PbSe) [4].

With the help of measurements of Hall effect in system PbTe <Bi, $T_{sur.}$> by the authors [5] the phenomenon of self-indemnification of alloying effect of the impurity of bismuth is investigated. It is shown, that the experimental data will well be coordinated to the theory advanced in the given work if to assume, that the significant number of atoms Bi links in complexes with single vacancies Pb with energy of link of a complex ~ 0,3 eV.

The found out [4] phenomenon of self-indemnification of alloying effect of impurity Tl by vacancies of chalcogenide allows to receive simply enough samples with low concentration of carriers of a current. Owing to strong indemnification a number of interesting features in temperature dependences of factor of Hall (R_x), allowing to reveal the presence of localized impurity conditions in semiconductors with narrow forbidden zone are shown. For all investigated compensated samples the significant falling R_x with growth of temperature is typical. In not compensated samples of chalcogenide of lead with the same concentration of the holes $R_x(T)$ =const or grows with temperature. This peculiarity $R_x(T)$ in the compensated systems does not contact own conductivity [4]. All received experimental data the authors [4] explain assuming the existence in the compensated samples appreciable quantity of complexes. As the observable located conditions in the compensated samples are not connected to isolated dot defects, it is supposed, that they are connected to complexes. Elementary of which the complexes of vacancies are the complexes of impurity - impurity and complexes vacancy - impurity.

Chalcogenide of bismuth. Concentration of carriers of a charge in Bi_2Te_3 strongly depends on presence of extraneous impurity and defects at crystal. At telluride of bismuth there are such dot defects as: vacancies Te and Bi, their atoms in internode, anti-structural defects (atoms Bi on places of tellurium and on the contrary), impurity atoms on places Bi, Those and in internodes; complexes such as " vacancy - impurity atom " and more complex formations. In all chalcogenide of bismuth quasi- stoichiometric samples have surplus of more electronegative element. It results in formation donor and p-type the centers. For samples the anti-structural model of defects is a lot of bismuth which are investigated more often is inherent; it is equal-0,4 eV, that is approximately three times less than energy of formation of vacancy of tellurium; occurrence of anti-structural defect energetically more profitable. Beside that electro-physical properties Bi_2Te_3 are determined not only by impurity atoms, but also by electrically active own defects. On the whole heterogeneity and deficiency of structure of chalcogenide of bismuth alongside with impurity influence reception of optimal concentration of carriers of a charge [6]. All stated factors should influence essentially on self-indemnification and reception of a set of samples with various concentration of carriers of current. In this connection the purpose of work was selection of the effective impurity, playing role of the compensating additive of donors in PbTe and Bi_2Te_3.

II. MAIN TEXT

Samples PbTe <Te, B> were prepared by a method of synthesis with the subsequent slow cooling in ampoules in diameter 9mm (samples were burned during 4 day at 900°K in vacuumed quartz ampoules. Samples Bi_2Te_3 <$CdCl_2$, B>, (Bi_2Te_3- Bi_2Se3)<Cu, B> received by a method of the directed crystallization in diameter (8-9) mm. Factor Thermo-Electromotive (a), electroconductivity and Hall factor $_{(Kx)}$ were measured. Preliminary researches of $R_x(T)$ crystals Bi_2Te_3 <B> have shown, that in all samples it is possible to receive by method of indemnification a set of various concentration of carriers of current. In samples Bi_2Te_3<Cu, B> extremum R_x are observed at temperatures below 300°K. In the table electric properties of not alloyed and alloyed samples PbTe, PЬS, Bi_2Te_3 and a firm solution on its basis are given.

Table

Thermo-electromotive, electrocunductivity and concentration of current carriers of lead and bismuth chalcogenides at temperature 300ºK

	Plain and alloyed compounds and alloys	$\alpha \cdot 10^{-6}$ V/K	$\delta \cdot 10^{-6}$ Cm/m	n_x, p_x R_x cm^{-3}
1	PbTe	-260	300	$5{,}8 \cdot 10^{18}$
2	PbTe<$PbCl_2$>	-80	2200	$3{,}5 \cdot 10^{19}$
3	PbTe<$PbCl_2$,B>	-20	280	$8{,}1 \cdot 10^{17}$
4	PbS	-275	260	$2 \cdot 10^{18}$
5	PbS<$PbCl_2$>	-60	3000	$5{,}9 \cdot 10^{19}$
6	PbS<$PbCl_2$,B>	-280	250	$7{,}3 \cdot 10^{17}$
7	Bi_2Te_3	-200	1000	$5{,}6 \cdot 10^{19}$
8	Bi_2Te_3<$CdCl_2$>	-120	3000	$8{,}1 \cdot 10^{19}$
9	Bi_2Te_3<B>	+260	500	$6{,}2 \cdot 10^{17}$
10	Bi_2Te_3<$CdCl_2$,B >	-230	800	$9{,}8 \cdot 10^{18}$
11	Bi_2Te_3<$CdCl_2$,B >	+240	700	$8{,}1 \cdot 10^{18}$
12	(Bi_2Te_3- Bi_2Se_3) <$CdCl_2$,B>	-210	1000	$9{,}2 \cdot 10^{19}$

Apparently from the table, the measured parameters evidently testify the strong influence of a boron and its complex impurity ($PbCl_2$-B) and ($CdCl_2$-B) on thermoelectric properties PbTe, PbS and telluride of bismuth, including on its firm solution with selenium. The boron in telluride of bismuth is not only the strongest acceptor, but also plays a role of compensating influence on chalcogenide of lead and bismuth. It is possible to say, that complex impurity ($PbCl_2$-B) and ($CdCl_2$-B) almost on the order reduce concentration of carriers of a charge (see in the table a sample №3, 6 and 11). In a firm solution (Bi_2Te_3-Bi_2Se_3) adjusting quantity $CdCl_2$ and B it is possible to receive a set of samples with concentration of carriers of a current from $n=2 \cdot 10^{19}$

cm^{-3} up to $n=9{,}8\cdot10^{18}cm^{-3}$ Samples of telluride of bismuth alloyed only boron have hole conductivity with α=+260V/K and $P_x=6{,}2\cdot10^{17}$ cm^{-3} (at quantity of boron of equal 0,01 % weight.). Such combination of impurity ($CdCl_2$-B) has the important applied value.

Let's consider possible mechanisms of indemnification of complex impurity in chalcogenides Pb and Bi.

As it was already described [3,4], low concentration of carriers of a current in PbSe and PbTe, alloyed by impurity of the third group of a periodic table, can be caused at least by two reasons. The first - stabilization of a level of chemical potential in the forbidden zone due to presence in it deep impurity levels of elements of the third group. This case can be realized in firm solutions of chalcogenides of bismuth and lead. The second mechanism connected to indemnification, quite is realized in investigated by us PbS, PbTe and in firm a solution on the basis of telluride of the bismuth, alloyed also by an element of the third group - boron. Here we deal with the phenomenon of self-indemnification of donor effects of chlorine by boron. Most likely the significant number of atoms of chlorine links in complexes with single vacancies of lead (for PbS and PbTe) and bismuth (in case of telluride of bismuth). It has been confirmed, that the received good consent of the theory and experiment for a case of indemnification single twice ionized vacancies of chalcogenide in selenium[4].

As a whole experimental data are explained by the linkage of compensating vacancies in complexes with ions of chlorine.

The peculiarity of changes in properties Bi_2Te_3 <$CdCl_2$,B> and firm solutions, most likely, can be explained by dependence of such defects formed in a lattice of telluride of bismuth, from quantity of the introduced atoms of boron (including indium) and selenium. The formula of compound of telluride of bismuth can be written down as $(BiTe)_2^{+}Te^{2-}$, that reflects the character of links in this compound. It is possible to write it down as follows: $Te^{(II)}$ of extreme layers five layered packages of the elementary cell of this compound, forming by means of p-electrons δ-link with atoms of bismuth give the link Te^{I}-Bi one p-electron, that causes double ionization of atoms $Te^{(I)}$ ($Te^{(I)}$ it is internal layers of five layered package) [6]. As a result of it the link of atoms $Te^{(I)}$ with atoms of the next layers of bismuth has ionic character and isovalent replacement of chalcogenide without change of structure occurs on layers $Te^{(I)}$. Besides that p-type effect of defects Bi is the consequence of that atoms of bismuth have on one p-electron Te less than atoms Te and for realization in Bi_2Te_3 of the described above link one s-electron of atom Bi should pass to a p-level, that is accompanied by formation of vacancies in valence zone.

Atoms of boron having small nuclear radius fill not only inter-layer space $Te^{(I)}$-$Te^{(I)}$, but also vacancies in a valency zone and by that become not only acceptors, but the centers of linkage of vacancies in complexes with ions of impurity.

III. CONCLUSION

At impurity doping process $A^{IV}B^{VI}$ (Pbs and PbTe) and $A_2^{V}B_3^{VI}$ easily diffused impurity of boron appeared possible to receive samples with extremely low (for the given materials) Hall concentration of carriers of a charge. The reason of strong indemnification at the big concentration of chlorine is, most likely, linkage of vacancies Pb in complexes with ions Cl which energy of formation of which is less than of single vacancies.

REFERENCES

1. *E.E.Klotinish*, Indemnification in semiconductors, " Semiconductors and their application in electronics " IV. Riga, 1970, with. 19-38.
2. *T.G.Kerimova, S.Sh.Kahramanov, E.M.Maharramov,* "Bi_2Te_3 Doped and intercalated <Cu>: Materials for thermoelectric generators", 2nd International conference on technical and Physical Problems in Power Engineering, 6-8 September 2004, p.349-351.
3. *L.I.Bitenskiy, V.I.Kaydanov, R.F.Kuteynikov, R.B.Melnik, S.A.Nemov, Y.I.Ravich,* " Self-indemnification donor actions of chlorine by complexes a vacancy - ion of an impurity in telluride of lead ", M. Physics and techniques of semiconductors, volume 15, publication 5, 1981, p. 981-984(inRussian)
4. *L.I.Bitenskiy, V.I.Kaydanov, R.B.Melnik, S.A.Nemov, Y.I.Ravich,* " Self-indemnification of acceptors vacancies in sulfide and selenide the lead, alloyed by thallium ", M. Physics and techniques of semiconductors, volume 14, publication 1, 1980, p. 74-79(inRussian)
5. *L.I.Bitenskiy, V.I.Kaydanov, V.I.Makeenko, R.B.Melnik, S.A.Nemov,* " Self-indemnification donor actions of bismuth in telluride of lead ", M. Physics and techniques of semiconductors, volume 18, publication 3, 1984, p. 489-492. (inRussian)
6. *I.V.Gasenkova, T.E.Svechnikova,* " Structure and physical properties of monocrystals of the firm solutions $Bi_2Te_{3-x}Se_x$, alloyed by tin ", M. Non-organic materials, 2004, volume 40, № 6, p. 663-668. (inRussian)