FEATURES OF ELECTRICAL PROPERTIES OF A^3B^6-TYPE LAYERED CRYSTALS

A.G.Kyazym-zade *, V.M.Salmanov, A.Z.Abasova, L.G.Gasanova, V.V.Dadashova

Baku State University, 23 Z.Khalilov str., 370145 Baku, Azerbaijan
*E-Mail: bsu_aydin@yahoo.com

ABSTRACT

The temperature dependencies of conductivity, Hall and drift mobility in monocrystals of A^3B^6-type layered compounds and solid solutions on their basis in different crystallographic directions were analyzed. The conclusion that observable strong anisotropy of conductivity and Hall mobility in different crystallographic directions is connected to localization of electron states near the band edges along the c-axis is made. It is supposed that localization of electron states is connected with packing defects, which arise owing to weakness of interlayes bonding. It proves to be true also by observations of photoconductivity anisotropy at high levels of optical excitation and at various configurations of current contacts.

Keywords: layered crystals, solid solitions, conductivity anisotropy, photoconductivity anisotropy, localization

I. INTRODUCTION

Widebands monocrystals of A^3B^6-type compounds, in particular monocrystals *GaSe, InSe, GaS* and solid solutions on their basis are perspective materials for solid-state power. In the given paper features of electrical properties of these crystals in different crystallographic directions are analyzed.

Monocrystals *GaSe, InSe* and *GaS* and solid solutions on their basis crystallize in layered structure [1]. The structure of these crystals will consist of consistently packed layers, each of which contains four densely connected nuclear planes *Se (S) - Ga (In) - Ga (In) - Se (S)*. Features of such structures are strong (covalent) bonding inside layers and very weak (van der Waals-type) bonding between layers. Presence weak interlayes bonding results in formation of polytypes at *GaSe* and *InSe*. Depending on joining layers monocrystals *GaSe* crystallize in 4 (ε, β, γ and δ), and monocrystals *InSe* - in 2 (ε and γ, established till now) modifications. Crystals *GaS* form only β modification. In ε and β structures the elementary cell includes 8 atoms from two layers (on 2 *Ga (In)* and 2 *Se (S)* from each layer), and in γ and δ structures - 12 atoms from three layers and 16 atoms from four layers accordingly. The hexsagonal β and ε modifications differ in the way of packing of layers, and γ and δ modification - amount of layers in an elementary cell. Formation of this or that polytype or a mixture of various modifications essentially depends on a method of reception of crystals [2].

II. MAIN PART

Crystals *GaSe* and *GaS* form a continuous line of solid solutions [3,4]. The crystal structure of GaS_xSe_{1-x} solid solutions frequently is polymorphic and depends on concentration x. In them four modifications are also observed depending on packing layers. At x>0,6 crystals GaS_xSe_{1-x} form only β-structure, and at x<0,4 the mixture of various modifications takes place.

Features of structure and distinction of chemical bounding in different crystallographic directions, first of all, are shown in electrical properties of the specified crystals and solid solutions on their basis. It frequently results in observation of abnormal strong anisotropy of conductivity and Hall mobility in different crystallographic directions. Results of numerous experiments show (for example see to [5]), that Hall mobility of the majority carriers along *c*-axis, frequently strongly depends on temperature:

$$\mu_{//} = \mu_0 \exp\left(-\Delta E_0 / k_0 T\right), \qquad (1)$$

Where μ_0 is mobility at $\Delta E_0 = 0$. Therefore activation energy of conductivity $\sigma_{//}$ in this direction is more on size ΔE_0, than activation energy of conductivity $\sigma_\perp$ in a direction, perpendicular *c*-axis. As a result of this the experimental dates for the DC dark coductivity, which was measured mentioned above crystals show a strongly temperature-dependent anisotropy:

$$\chi = \sigma_\perp / \sigma_{//} = A \cdot \exp\left(\Delta E_0 / k_0 T\right) \qquad (2)$$

where A is of the order of effective-mass ratio of the

majority carriers $m_{//}/m_{\perp}$ (for example, A=0,25 for *GaSe* [6]). At rather high temperatures χ it is really determined by parameter A. At the same time, in a direction, perpendicular *c*-axis, mobility is well described by the formula, received by Fivaz [5] in view of interaction of carriers with polar optical fonons:

$$\mu_{\perp} = \frac{e}{8m\omega\pi g^2} \frac{e^{\frac{\hbar\omega}{k_0 T}} - 1}{1 + \hbar\omega/2k_0 T} \qquad (3)$$

Here $\hbar\omega$ is energy of optical fonons, $k_0 T$ is thermal energy, g is bonding parameter. The good consent of experimental results with settlement are usually observed at the following values of parameters: g^2 = 0,25; m=0,2m_0; $\hbar\omega$ =0,04 eV for *GaSe* [7] and g^2 = 0,25; m=0,12m_0; $\hbar\omega$ =0,03 eV for *InSe* [8].

The formula (3) is generally replaced with the approached expression $\mu \sim T^{-\gamma}$ where γ depends on fonon energy. Experimental value γ for monocrystals InSe and GaSe usually makes 1,9 ÷2,1. Dispersion of carriers on polar optical fonons proves to be true also by absorption of light with free carriers, induced by laser radiation. In particular, it is established by us, that intensity of the probing light past through crystals InSe, it is strongly modulated by radiation of a pulse of the ruby laser that is connected by absorption of probing light by the nonequilibrium carriers created by laser radiation. Dependence of a signal of modulation *dI* on length of a wave of probing light looks like $dI \sim \lambda^n$, where *n*=2,2÷2,4, that testifies to dispersion of carriers on optical fonons. At the same time measurement of drift mobility in monocrystals p-*GaSe* has shown [8], that irrespective of crystallografic directions dependence as $\mu \sim T^{-\gamma}$ (where γ=1,9±0,1) is observed, that is predicted by Fivaz theory and can be explained by band conductivity of holes in view of dispersion on polar optical fonons. Observable anisotropy of conductivity thus is determined by the effective-mass ratio of carriers $m_{//}/m_{\perp}$. According to [9,10], such distinction between Hall and drift mobility can take place in the disorder structures, in which take place a non-uniform relief of potential (i.e. casual modulation of band edges) or the localized states. In this case conductivity of a sample is defined by concentration of carriers at a perculation level of course which strongly depends on temperature ($n_c \sim \exp(-\Delta E/k_o T)$) even at constant concentration in a zone, and the Hall constant *R* is define by average on a sample concentration $\overline{n}$. Due to this the magnitude of $\mu = cR\sigma$ does not reflect behaviour of true (drift) mobility, and differs from it on

a multiplier $n_c/\overline{n}$, which it is less than unit and sharply falling with downturn of temperature. Numerous experimental results show also, that the parameter ΔE_0 strongly varies at transition from one series of monocrystals in another and receives values in a range ΔE_0 =15÷120 meV in various series the specified layered crystals. Except for it there are informations on reduction of parameter ΔE_0 in solid solutions [11], with growth of enclosed electric field [12] and concentration of the majority carriers [13], in the crystals doped by non-isoelectronic impurity atoms [14], and also about increase ΔE_0 in intercalated InSe monocrystals [15].

Experimentally observable dependence of a kind (1) or (2) in the specified crystals frequently spoke a basis of hopping conductivity. However the nature of hopping conductivity thus remains non-found out. In particular, it was supposed, that electron wave functions of separate layers are not blocked, owing to what carriers jump from one layer to another, overcoming interlayered barriers with height of ΔE_0. However the similar explanation of observable anisotropy of conductivity causes doubts. As the distance between layers has a few A^0, it is clear, that carriers can easily pass from one layer in another in the way by tunneling. Nevertheless, many electron properties of the perfect monocrystals of the specified compounds are well described by the three-dimensional band structure calculated by a method of pseudo-potential, that, first of all, is shown at research of optical properties [1]. Here we shall note, that hopping character of conductivity has been found out only in [16], in specially alloyed crystals *n-GaSe* and *n-GaS* in area of impurity conductivity. The received results thus will well be coordinated to the theoretical formulation suggested by Shklovsky for poorly alloyed semiconductors, and conductivity on a variable field close and below room temperature submits to the theoretical formulation of the Pollak and Geballe [17] down to frequencies of 10^5 Hz. The specified conductivity does not depend on a direction of movement of carriers and is connected with anion vacancies which, probably, are responsible for conductivity of n-type.

The above-stated reasonings allow to draw a conclusion that observable anisotropy of conductivity and Hall mobility in the specified layered crystals is connected to presence in them of packing defects. The similar explanation for the first time was offered in [18] for crystals *GaSe*. We assume, that owing to weakness of interlayered bounding at grown and machining of monocrystals of the specified crystals there is a displacement of group of layers from each other in a direction parallel to layers. Thus there is a casual infringement of symmetry of potential along an *c*-axis owing to what in this direction on a crystal

operates additional one-dimensional fluctuating potential. According to model of Anderson [10] it to result in localization of electron states near to band edges just as it takes place in the disorder structures. The structure disordering it is facilitated also by that in real crystals of the specified compounds the mixture of the various modifications distinguished by position of band edges frequently takes place. For example, in ε and β modifications *GaSe* the width of the forbidden gap and bonding energy of exitons differs on size ~50 meV [3]. Therefore it is possible to accept, that in real crystals practically always alternation of separate modifications occurs in the casual image and the one-dimensional disorder along c-axis. Parametr's ΔE_0 shows width of the localized states and only those carriers which are activated on nob-localized states participate in conductivity.

Concentration of packing defects can be characterized by introduction of parameter $\alpha = N_h / N$ which corresponds to a relative share of the displaced layers in relation to the general number of layers. The one-dimensional potential created at it changes positions of band edges. At small fluctuations of concentration of packing defects change of position of band edge can be spread out in a line on deviations of concentration of the displaced layers $\Delta\alpha$ from average:

$$E_{c,v} = E_{c,v}(\alpha) + U_{c,v}\Delta\alpha, \qquad (4)$$

$$U_{c,v} = \left(\frac{\partial E_{c,v}}{\partial \alpha}\right)\bigg|_{\Delta\alpha=0}, \qquad (5)$$

where the first composed corresponds to approximation of a virtual crystal, and the second composed describes fluctuating potential changing along an *c*-axis. This casual potential is one-dimensional and consequently in its field movement of carriers along an *c*-axis should be localized. Unfortunately, by present time there is no more strict theoretical proof about an opportunity of one-dimensional localization of electron states in three-dimensional crystals and calculation of energy of localization in a field of such one-dimensional disorder. It complicates comparison of experimental values ΔE_0 with settlement. Here only we shall note, that in works [19] influences of the one-dimensional disorder on exiton states in semiconductors are considered. It is shown, that the one-dimensional disorder results localization and non-uniform broadening of exsiton lines. In particular, localization of exitons in *GaSe* was observed in [20], that in turn testifies to presence of packing defects in these crystals.

Character of low-temperature hopping conductivity on the localized states was analyzed by us in [21]. It is established, that low-temperature hopping conductivity on the localized states in *InSe* single crystals corresponds to Mott law [10]. It allowed to estimate radius of localization. It is established, that wave functions of electrons are localized in limits of twenty layers.

It is necessary to note, that in [18] the structure of *GaSe* is considered as the one-dimensional disorder chain. Be agrees modern representation about localization of Anderson [10] conductivity in an one-dimensional case should equal zero at low temperatures. Therefore, movement of carriers in layered crystals should be considered in three-dimensional space. Really, as states along layers are not localized, it is possible to count, that carriers always possess making speed and in a direction, perpendicular *c*-axes.

As the parameter ΔE_0 thus is defined by a degree of infringement of ideal packing of layers on the basis of the specified model the observable disorder of parameter ΔE_0 in various samples well speaks, increase in factor of conductivity anisotropy in deformed and intercalated crystals and its reduction in alloyed nonisoelectronic admixture atoms crystals and at rather high electric fields. In particular, in the latter case transition of carriers of a current from the located conditions in delocalized is facilitated by an electric field as it takes place at thermo-field devastation fine admixture levels in semiconductors.

Reduction of parameter ΔE_0 and factor of anisotropy of conductivity in crystals doped by non-isoelectronic impurity atoms is not trivial and the separate explanation demands. Apparently, at replacement of a part of the basic atoms of a lattice by non-isoelectronic impurity atoms appear valent electrons which do not participate in bounding inside a layer. At rather big concentration of impurity atoms, such empty valencies the next layers close disordered areas where impurity usually accumulate, incorporate among themselves covalent bridges. It is to result in strengthening interlayered bonding and to ordering structure. The estimation of concentration by Mott criterion [22] at which formation of the bonding one-dimensional chains from impurity atoms is possible, gives value ~10^{18} cm^{-3} in *GaSe* crystals. However thus it is possible to neglect conductivity on these chains as it is usual impurity atoms are distributed casually and, therefore impurity states are strongly located [10, 22].

III. CONCLUSION

In summary we shall note, that presence of the localized states in the specified crystals proves to be true also by observation of photoconductivity anisotropy and Anderson transition at high levels of optical excitation when becomes possible "light doping" the semiconductor down to degeneration, and also photoconductivity anisotropies at various configurations of current contacts.

REFERENCES

1. *Belenkii G.L., Stopachinskii V.B.* Usp. Fiz. Nauk, 1983, v.140, № 2, p.233-268
2. *Balichkii A.I., Krochuk A.S., Stakhira I.M., Froniv A.V.* Fiz. Tver. Tela, 1982, v.24, № 1, p.76-80
3. *Aulich E., Bredner I.L., Mooser E.* Phys. St. Sol., 1969, v.31, № 1, p.129-131
4. *Kuhn A., Chevy A., Chevalier R.* Phys. St. Sol (a), 1976, v.36, № 1, p.181-187
5. *Fivaz R.C., Schmid P.* Transport properties of layered semiconductors. Int: Physics and Chemistry of material with layered structures. Dordrecht-Holland, 1976, № 4, p.343-384
6. *Ottaviani G., Canali C., Nava F.* And so. Sol. St. Commun., 1974, v.14, p.933-936
7. *Manfredotti C., Mancini A.M., Murri R., Rizzo A., Vasanelli L. Nuovo Cimento,* 1977, v.39, № 1, p.257-268
8. *Atakishiev S.M., Akhundov G.A.* Phys. St. Sol., 1969, v.32, K33-36
9. *Shik A.Ya.* Pisma JETF, 1974, v.20, № 1, p.14-16
10. *Shklovskii B.I., Efros A.L.* Electronic properties of doped semiconductors. Moskow, 1979, 416 p.
11. *Tagiev B.G., Mamedov G.M.* Fiz. Tekh. Poluprov., 1974, v.8, № 10, p.1873-1876
12. *Shmid P., Mooser E.* Helv. Phys. Acta., 1972, v.45, p.870-872
13. *Maschke K., Overhof H.* Phys. Rev., 1977, v.15, p.2058
14. *Kyazym-zade A.G., Mursalov E.T., Agamaliyev Z.A.* Vest. Baku Univers., 2002, №1, p.5-7
15. *Kovalyuk Z.D., Mityanskii I.V.,* Ukr. Fiz. J., 1982, v.27, № 4, p.616-618
16. *Augelli V., Manfredotti C., Murri R., Piccolo R., Vasanelli L. Nuovo Cimento,* 1977, v.38, № 2, p.327-335
17. *Pollak M., Geballe T.H.* Phys. Rev., 1961, v.122, №
18. *Maschke K., Schmid P. Phys.* Rev., 1975, v.B12, № 10, p.4312-4315
19. *Maslov A.Yu. and so.* Fiz. Tver. Tela, 1983, v.25, № 5, p.1408-1414
20. *Forney J.J., Maschke K., Mooser E. J.* Phys. C: Sol. St. Commun., 1977, v.10, p.1887-1894
21. *Kyazum-zade A.G., Abasova A.Z., Salmanov V.M., Gasanova L.G., Mamedova A.G.* Mater. Sci. Engineering, 2002, v. B88, p.282-285
22. *Mott N.F.* Metal-Insulator Transitions. Moskow, 1979, 342 p.
23. *Abdullayev G.B., Tagirov V.I., Kyazym-zade A.G., Panakhov M.M., Salmanov V.M.* Pisma JETF, 1980, v.32, № 1, p.44-46
24. *Abdullayev G.B., Tagirov V.I., Kyazym-zade A.G., Panakhov M.M., Salmanov V.M.* Fiz. Tekh. Poluprov., 1980, v.14, № 11, p.2228-2232
25. *Abdullayev G.B., Kyazym-zade A.G., Tagirov V.I., Panakhov M.M., Salmanov V.M., Asadov Kh.A.* Fiz. Tekh. Poluprov., 1982, v.16, № 4, p.612-615
26. *Kuznicki Z.T., Maschke K., Schmid P. J.* Phys. C: Sol. St.Phys., 1979, v.12, p.3749-3755
27. *Abdullayev G.B., Tagirov V.I., Kyazym-zade A.G., Panakhov M.M., Salmanov V.M.* Fiz. Tekh. Poluprov., 1980, v.14, № 9, p.1842-1845
28. Kyazym-zade A.G., Salmanov V.M., Humpanova I., Agayeva A.A. Acta Phys. Comen., 2002, v.43, №5, p.61-67
29.