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ELECTRICAL CONDUCTIVITY OF ZnSe : In CRYSTALS, OBTAINED BY FREE GROWTH

The electrical conductivity of ZnSe:In crystals doped by indium during growth and crystals subjected to diffusion doping by indium from a melt are investigated. It is shown that electrical conductivity of ZnSe:In crystals doped by indium during growth is controlled by donors In^{+}_{Zn}, In_i^{3+} and compensating acceptors — zinc vacancies, centers ($V_{Zn}In_{Zn}$). In crystals subjected to diffusion by indium from melt, electrical conductivity is controlled by shallow donors In^{+}_{Zn}. The annealing of ZnSe:In crystal in zinc melt gives the decrease in concentration of compensating acceptors and increase of crystal conductivity.

INTRODUCTION

Zinc selenide which band gap width is equal 2.7 eV at 300 K is the perspective material to create on its base the optoelectronic devices operating in blue spectrum [1]. The process to make radiating *p—n* junctions on the base of ZnSe consists in production of low-ohmic substrates of *n*-type conductivity and in formation of *p*-ZnSe layers on these substrates. Previously, the low-ohmic ZnSe crystals have been obtained by diffusion doping from zinc melt by elements of III group (Al, In). The most low-ohmic crystals were obtained by doping with aluminium. However, the doping by aluminium providing the decrease of resistivity up to 0.02 Ohm·cm, leads to increase in red emission and to quenching in blue one. The doping of crystals by indium is usually carried out by their annealing in melt of corresponding metal.

The attempts to increase concentration of indium doping impurities during doping out of melt result in contamination of crystal owing to contact with quartz. Besides, formation of the separate phase In_2Se_3 in ZnSe:In crystals is possible in these conditions. In the light of this, the most perspective is doping by in the process of crystal growth from vapour phase. The basis for such conclusion are the number of the latest works, e.g. [2, 3], where the possibility to dope by indium in process of crystal growth, excluding its contact to growth container, is shown. The corresponding procedure obtained the name — free growth procedure. Now, ZnSe:In crystals with indium concentration up to 10^{19} cm^{-3} have been obtained [3]. However, the nature of intrinsic and impurity defects, formed in the process to grow such crystals, is not simply proved.

The aim of this study is to clear up the nature of indium donor centers, responsible for electrical conductivity of zinc selenide crystals doped by indium in growth process.

EXPERIMENTAL

The investigated single crystals of zinc selenide were grown at Physical Institute of Russian Academy of Sciences by free growth procedure in ampoule placed in furnace with vertical temperature gradient. The fitting of temperature profiles and construction of growth container excluded the possibility for crystal contact to its walls. Vapour phase doping of crystals by indium is carried out during the growth process. As the doping material In_2Se_3 is used. The detailed description of procedure to growth crystals and their properties is presented in [2, 3]. Indium concentration was determined by atomic — emission procedure and was varied from 10^{16} to 10^{19} cm^{-3}.

As the research object, ZnSe:In crystals, doped by indium during their growth from vapour phase, were used. To decrease resistivity, ZnSe:In crystals were subsequently annealed in zinc melt. The annealing of ZnSe:In crystals in zinc melt is carried out in the preliminary pumped and evacuated quartz ampoules at temperatures 1170—1220 K during 50—100 hours. To exclude indium extraction from the crystals, some amount of indium was added to zinc melt.

For comparison, ZnSe crystals, obtained by free growth process and subjected to diffusion doping with indium, were investigated. Diffusion of indium was carried out by crystal annealing in indium melt at 1100 K during 10 hours. It is founded, that indium concentration in near-surface layer of such crystals was lower than 10^{17} cm^{-3}, and the average value of resistivity was of order 10^3 Ohm·cm.

Electrical contacts of indium were formed by crystal thermal treatment in vacuum at temperature 600 ч 650 K. The contact ohmic properties were controlled by measurements of current-voltage characteristics.

RESULTS AND DISCUSSION

The investigation in electrical conductivity of ZnSe: In crystals cleared up some essential especiallities, which were not characteristic for typical donor. Dependence of resistivity, determined by Van-der-Paw at 300 K, on indium concentration in the investigated crystals, is shown in Figure 1. In case when indium diffusion leads to donor formation, resistivity of crystals must decrease with increasing of doping impurity concentration. This really takes place in ZnSe:In and ZnSe:In:Zn crystals with indium concentration $4\cdot10^{16}$—$1\cdot10^{18}$ cm^{-3}. But with increase of indium concentration from $1\cdot10^{18}$ to $3\cdot10^{19}$ cm^{-3}, the resistivity of crystals increases (Fig. 1). The increasing of resistivity can be explained by formation of compensating acceptors. Such acceptors, in accordance with [4], can be zinc vacancies and associative defects of $(V_{Zn}In_{Zn})$ type too. It is confirmed by the fact that after annealing of the investigated crystals ZnSe:In in zinc melt their resistivity decreases by some orders.

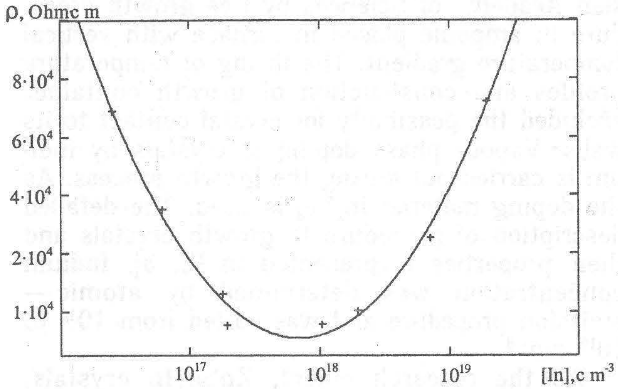


Fig. 1. Specific resistance dependence from indium concentration of ZnSe:In crystals (the points designate experimental data)

The temperature dependencies for dark current of ZnSe:In crystals with various indium concentrations are presented in Figure 2. It is stated that for all samples the electrical conductivity increased with temperature raise and characterised by two linear sections with different slopes in high-temperature and low-temperature regions. So, ZnSe:In crystals are characterised by two energies of donor activation. In crystals with indium concentration $4\cdot10^{16}$ cm^{-3} these energies are 0.03 and 0.6 eV (Fig. 2, curve *1*). The first corresponds to the previously known donor centers In^{+}_{Zn}. The donors with activation energy 0.6 eV, in accordance with [5], correspond to interstitial atoms of zinc Zn^{+}_{i} and characterise undoped crystals mainly. For the crystals with indium concentration $> 10^{17}$ cm^{-3}, the electrical conductivity is defined by activation

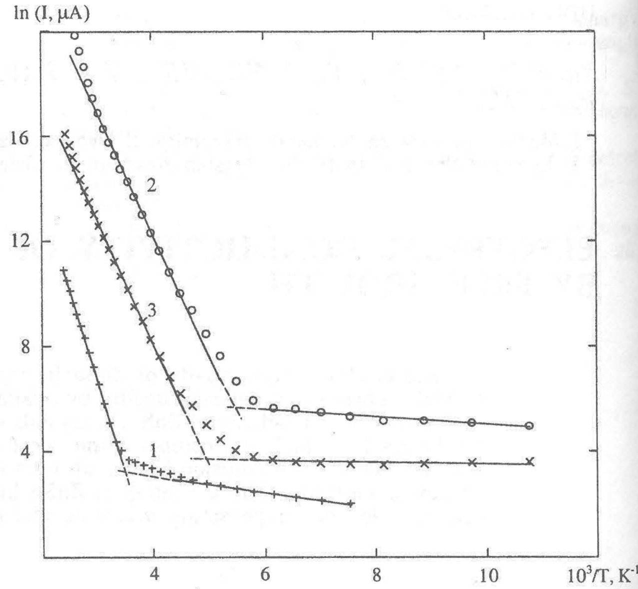


Fig. 2. Dark current temperature dependence of ZnSe:In crystals with indium concentration $4\cdot10^{16}$ (*1*), $3\cdot10^{17}$ (*2*), $3\cdot10^{18}$ cm^{-3} (*3*)

energy of 0.03 and 0.39 eV (Fig. 2, curves *2*, *3*). The value of the first activation energy is characteristic for all ZnSe:In crystals. The slope of low-temperature linear section in the curves for dependence $\ln I$ on $1/T$ decreases with raise of indium concentration. Donors with activation energy 0.39 eV were not observed in undoped crystals. We suppose that these donors are stipulated by interstitial indium atoms In^{3+}_{i}. Centers In^{3+}_{i} in ZnSe crystals doped with indium were found first. It is obvious, that their generation becomes possible owing to crystal doping in growing process. Indeed, the investigation of electrical conductivity, carried out in ZnSe:In crystals being subjected to indium diffusion from Zn-In melt, does not point to generation of donors with $E_d = 0.39$ eV. For such crystals, the activation energy of donors about 20—30 meV is characteristic one. This indicates that in diffusion doped crystals the donor centers In^{+}_{Zn} form.

The view for temperature dependence of dark conductivity for ZnSe:In:Zn crystals differs essentially from temperature dependence of dark conductivity for ZnSe:In crystals. Figure 3 presents temperature dependencies of dark resistance for ZnSe:In:Zn crystals. In low-temperature region the conductivity insignificantly raises as temperature increases. Activation energy of donors to be equal to 30 meV and to correspond to centers In^{+}_{Zn} was determined by the slope of linear section in this area, obtained in $\ln R$ on $1/T$ coordinates. Donor level with activation energy 0.39 eV were not found.

It was founded that ZnSe:In crystals after annealing in zinc melt became grey in colour. Optical density of such crystals strongly depends on indium concentration in crystals. Investigations, carried out by optical microscope, revealed the creation of extended indium macrodefects with length of some tens μm and with

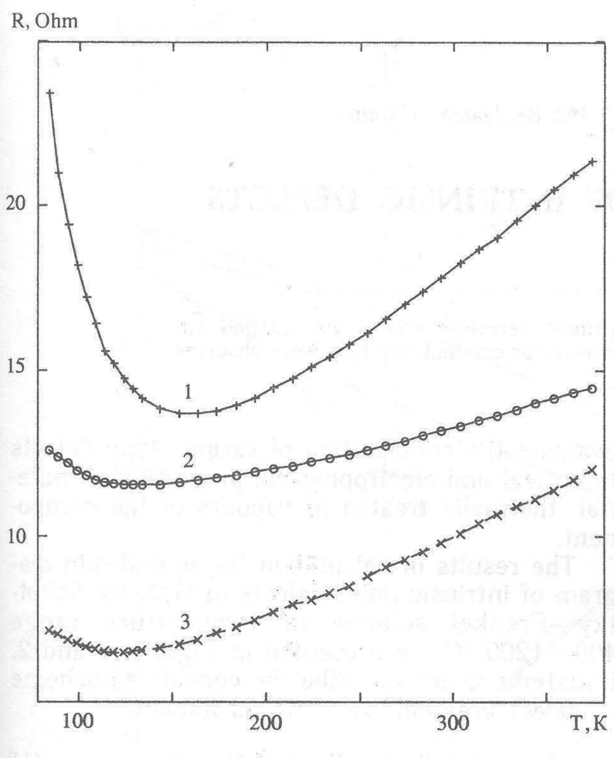
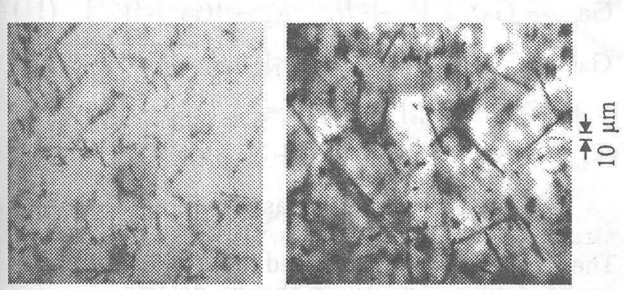


Fig. 3. Dark resistance temperature dependence of ZnSe:In:Zn crystals with indium concentration $4 \cdot 10^{16}$ (*1*), $3 \cdot 10^{17}$ (*2*), $3 \cdot 10^{18}$ cm^{-3} (*3*)

cross-section diameter of 1 μm order in the volume of ZnSe:In:Zn crystals (Figure 4). It was established that with increase of indium concentration in crystals from 10^{17} cm^{-3}, the dimensions and the concentration of macrodefects essentially decreased. These macrodefects distributed uniformly in crystal volume and stipulated the decrease of sample optical transparency. Taking into account the fact that indium concentration after annealing in zinc remains unvariable, it can be supposed that the source to create macrodefects are interstitial indium atoms. This explains the absence of deep donor levels in ZnSe:In:Zn crystals.



a *б*

Fig. 4. Allocation of indium macrodefects in volume of ZnSe:In:Zn single crystals. Concentration of indium $3 \cdot 10^{17}$ (*a*) и $3 \cdot 10^{18}$ cm^{-3} (*b*)

In high-temperature region, the resistivity of ZnSe:In:Zn crystals increases monotonously with temperature raise. In this temperature range, shallow donors are emptied. So, the increase in crystal resistivity as temperature raises is explained by the decrease in electron mobility.

CONCLUSION

The given results for investigations in electrical conductivity of ZnSe:In and ZnSe:In:Zn crystals, doped with indium in growing process, and ZnSe:In crystals allow to formulate the following conclusions:

1. Increase in indium concentration from 10^{18} cm^{-3} leads to decrease in electrical conductivity. It was stipulated by the compensating process of conductivity with intrinsic defects of acceptor type — zinc vacancies and associative defects of $(V_{Zn}In_{Zn})$ type.

2. Annealing of ZnSe:In crystals in zinc melt leads to decrease in concentration of cationic vacancies, that stipulates the decompensation of conductance in ZnSe:In:Zn crystals and the increase of their electrical conductivity.

3. In ZnSe:In crystals with indium concentration lower than 10^{17} cm^{-3} the electrical conductivity is controlled by donors with energies 0.03 and 0.6 eV, to which the centers In^{+}_{Zn} and Zn^{+}_{i} correspond. In ZnSe:In crystals with indium concentration more than 10^{17} cm^{-3}, the electrical conductivity is controlled by donor levels with activation energies 0.03 and 0.39 eV, corresponded to point defects In^{+}_{Zn} and In^{3+}_{i}. The interstitial indium atoms did not observed in diffusion doped crystals and were characteristic only for ZnSe crystals doped during growth.

4. The electrical conductivity of ZnSe:In:Zn crystals is controlled by point defects In^{+}_{Zn}. The interstitial indium atoms, presented in ZnSe:In crystals, form the extended macrodefects.

References

1. *Georgobiani A. N., Aminov U. A., Dravin V. A., Ilyuhina Z. P.* Luminescence of ZnSe with *p—n* junction // Neorganicheskie materiali. — 2000. — T. 36, № 2. — P. 169—172.

2. *Korostelin Yu. V., Kozlovsky V. I., Nasibov A. S., Shapkin P. V.* Vapour growth and characterization of bulk ZnSe single crystals // J. Cryst. Growth. — 1996. — V. 161. — P. 51—59.

3. *Korostelin Yu. V., Kozlovsky V. I., Nasibov A. S., Shapkin P. V.* Vapour growth and doping of ZnSe single crystals // J. Cryst. Growth. — 1999. — V. 197. — P. 449—454.

4. *Vaksman Yu. F., Nitsuk Yu. A., Purtov Yu. N., Shapkin P. V.* Intrinsic and impurity defects in ZnSe:In single crystals obtained by free growth procedure // Fisika i tehnika poluprovodnikov. — 2001. — T. 35, № 8. — P. 920—926.

5. *Nitsuk Yu. A.* Influence of intrinsic and impurity defects on electrophysical and optical properties of ZnSe:In single crystals obtained by free growth procedure: Thesis ... Candidate in Physical and Mathematical Sciences. — Odessa, 2003. — 131 p.