UDC 621.315.592

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INFLUENCE OF 3D-IMPURITIES (Cr, Fe, Co, Ni) ON THE POSITION OF ABSORPTION EDGE IN ZINC CHALKOGENIDES

The zinc chalkogenides (ZnS, ZnSe, ZnTe) single crystals doped with 3d-impurityes (Cr, Fe, Co, Ni) are investigated. The diffusion doping is carried out from metallic nickel and chromium or powderlike iron and cobalt in helium and argon atmosphere. The optical density spectra are investigated in the fundamental absorption range of ZnS, ZnSe, ZnTe crystals. The transition-metal elements doping of crystals results in the absorption edge shift toward lower energies. From the value of the absorption edge shift, the 3d-impuryty concentrations in crystals under investigation is determined.

Last years researches of zinc chalcogenides (ZnS, ZnSe, ZnTe) crystals doped with elements of transition metals (Cr, Fe, Co, Ni) are actual. It is related to that for such crystals intracenter absorption and luminescence transitions are characteristic in unfilled 3d-shells these atoms is characterized by a spectrum in an infra-red (IR) region (1—5 μm) and high quantum output. The explored crystals can used as an active environments for lasers with the reconstructed wave-length IR-emission. Such lasers are applied in medicine, biology, and different spectroscopy researches. Substantial progress in making of the IR-emission lasers is presently attained. The laser generation on the ZnSe and ZnS crystals doped with chrome is realized [1, 2]. In [3], efficient lasing in the spectral range of 3.77—5.05 μm is realized for ZnSe:Fe crystals.

In spite of certain success, there is the row of unresolved important problems, that restrains further application in practice of zinc chalcogenides crystals doped with transition-metal ions. Among them such: perfection of technology obtaining crystals doped with the set concentration of doping impurity, insufficient researches of optical properties in the visible region of spectrum.

There are two basic methods of doping zinc chalcogenides crystals elements of transition-metal is doping during the growing process from a vapour phase and diffusion doping. In [4] ZnSe:Fe and ZnSe:Ni single crystals were obtained from a vapour phase by the free growth method on a single crystal substrate with the use of chemical transport in hydrogen. The possibility of controlling the impurity concentration and doping profile is advantage of the diffusion doping. In [5] the ZnSe:Fe crystals are obtained by the doping from a solid phase metallic source (a metallic layer). The diffusion doping in the iron vapours is carried out in [6]. Duration of diffusion process and small iron impurity concentrations in the obtained crystals are the lacks of these diffusion doping methods.

In this study we describe the diffusion technique of doping which allows to obtaining ZnS, ZnSe, ZnTe single crystals with predicted transition-metals impurities concentration. The optical absorption spectra in the area of fundamental absorption edge has been studied. Basing on the optical absorption edge shift, the impurity concentration has been determined.

The goals of this study is the determination of transition-metal impurities influencing on the fundamental absorption edge position of the ZnS, ZnSe, ZnTe crystals.

1. EXPERIMENTAL

The samples for the study were prepared by the transition-metal elements diffusion doping of pure ZnS, ZnSe and ZnTe single crystals. The undoped crystals were obtained by free growth on a ZnSe single crystal substrate with the (111) growth plane. The method and the main characteristics of the ZnS, ZnSe and ZnTe crystals were described in details in [7]. Selection of temperature profiles and design of the growth chamber excluded the possibility of contact of the crystal with chamber walls. The dislocation density in obtained crystals was no higher than 10^4 cm^{-2}.

Doping of crystals by the nickel or chromium impurity was carried out by diffusion from the metallic nickel or chrome layer deposited on the crystal surface in the He + Ar atmosphere. The nickel or chromium diffusion was carried out under conditions in which the impurity concentration in the source (the metallic nickel or chromium layer) remained nearly constant. A metallic layer sneaked up such thickness, that the condition of impurity diffusion from a source was executed, in which concentration of her during all process remains practically permanent. The crystals were annealed at the temperatures $T_a = 1020$—1270 K. The diffu-

sion process time was about 5—10 hours. After annealing the crystals changed the color: crystals ZnS:Ni, ZnS:Cr got a yellow color, ZnSe:Ni was light-brown, ZnSe:Cr was red-brown and ZnTe:Ni, ZnTe:Cr was dark-brown.

The first experiments with iron and cobalt diffusion were carried out according to a procedure similar for nickel and chromium diffusion. The crystals were doped via impurity diffusion from a metallic layer deposited on the crystal surface. At the same time, this method was uneffective for the receipt of high-doped crystals. It is explained it by the technological problems related to impossibility deposite the thick cobalt or iron layer, from what in the process of annealing all layer dissolved completely in the crystals in the span no longer than 30 minutes. The optical absorption spectra showed that the obtained crystals were lightly doped.

To obtain heavily doped crystals the diffusion by impurity from metal powderlike iron or cobalt in He + Ar atmosphere was carried out. In order to avoid etching of crystals, powderlike ZnS, ZnSe or ZnTe depending on the crystals type in the ratio 1:2 was added to the metallic powder. Crystals were annealed at temperatures from 1070 to 1320 K. The duration of the diffusion process was 10—30 hours. After annealing the ZnS:Fe crystals acquired a yellow-brown colour, ZnS:Co was turquoise, ZnSe:Fe was red-brown, ZnSe:Co was brown and the ZnTe:Fe ZnTe:Co crystals were dark-brown.

The optical density spectra in the visible region were measured by means of an MDR-6 monochromator with diffraction gratings 1200 lines/mm. A FEU-100 hotomultiplier was used as a light flow receiver.

2. INVESTIGATIONS IN THE ABSORPTION EDGE REGION

The absorption spectra (the optical density D^*) of undoped ZnS crystals at 300 K are characterized by an absorption edge with the energy $E_g = 3.75$ eV, ZnSe crystals are characterized by an absorption edge with the energy $E_g = 2.68$ eV and ZnTe are characterized by the energy $E_g = 2.24$ eV.

The transition-metal elements doping of crystals results in the absorption edge shift toward lower energies. Figure 1 shows the absorption spectra of the ZnSe and ZnSe:Co crystals. The absorption edge shift value increased with annealing temperature and conditioned by the Coulomb interaction between impurity states. The absorption edge shift values in the ZnS, ZnSe and ZnTe crystals doped with transition-metal elements are presented in the Tables 1—4. At the change of temperature from 300 to 77 K shift values are saved.

The band gap varies ΔE_g depending on the introduced impurity concentration is determined in [8] by the relation

$$\Delta E_g = -2 \cdot 10^5 \left(\frac{3}{\pi}\right)^{1/3} \frac{eN^{1/3}}{4\pi\varepsilon_0\varepsilon_s}, \qquad (1)$$

where e — electron charge, N — impurity concentration in cm^{-3}, ε_s is the static permittivity of ZnS, ZnSe or ZnTe, ε_0 — permittivity constant. Using the band gap shift, we calculated the doping impurity concentration in the studied crystals (see Tables 1—4).

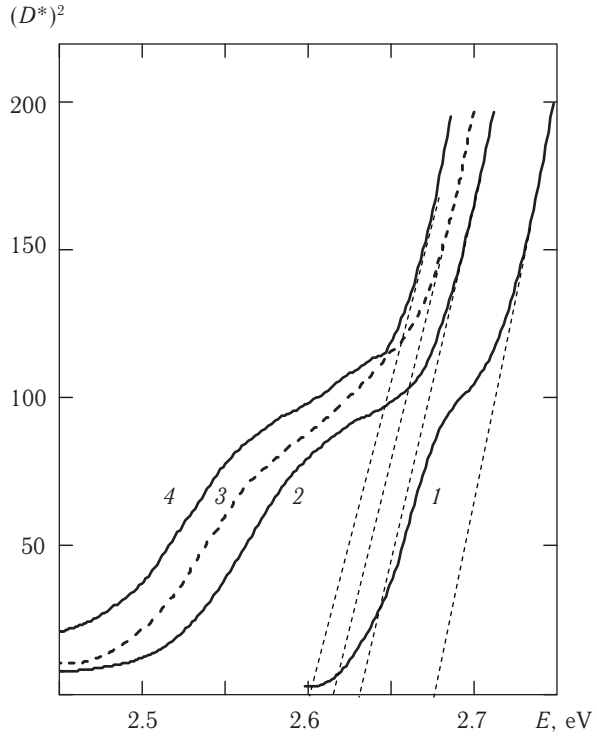

Fig. 1. Spectra of the optical-density D^* of (*1*) ZnSe, and (*2—4*) ZnSe:Co crystals obtained at annealing temperature T_a = (*2*) 1070, (*3*) 1120, and (*4*) 1170 K

Tables 1—4 show that the maximal band gap shift value and doping impurity concentration is observed in the crystals doped with cobalt and nickel. In the researches of the ZnSe:Co crystals absorption edge [9] there was band gap shift to 400 meV, that evidenced at formation of the $Zn_{1-x}Co_xSe$ alloy.

Table 1

Results of calculation of the chromium concentration in the ZnS:Cr, ZnSe:Cr, ZnTe:Cr crystals

Annealing temperature, K	Crystal type					
	ZnS:Cr		ZnSe:Cr		ZnTe:Cr	
	ΔE_g, meV	N, cm^{-3}	ΔE_g, meV	N, cm^{-3}	ΔE_g, meV	N, cm^{-3}
1070	—	—	20	$2 \cdot 10^{17}$	30	10^{18}
1120	—	—	30	10^{18}	60	$8 \cdot 10^{18}$
1170	20	$2 \cdot 10^{17}$	70	10^{19}	100	$4 \cdot 10^{19}$
1220	50	$3 \cdot 10^{18}$	90	$2 \cdot 10^{19}$	—	—
1270			120	$5 \cdot 10^{19}$	—	—

Table 2

Results of calculation of the iron concentration in the ZnS:Fe, ZnSe:Fe, ZnTe:Fe crystals

Annealing temperature, K	Crystal type					
	ZnS:Fe		ZnSe:Fe		ZnTe:Fe	
	ΔE_g, meV	N, cm^{-3}	ΔE_g, meV	N, cm^{-3}	ΔE_g, meV	N, cm^{-3}
1070	—	—	—	—	20	$2 \cdot 10^{17}$
1120	—	—	—	—	40	$3 \cdot 10^{18}$
1170	10	$2 \cdot 10^{16}$	10	$3 \cdot 10^{16}$	100	$4 \cdot 10^{19}$
1220	20	$2 \cdot 10^{17}$	20	$2 \cdot 10^{17}$	130	$8 \cdot 10^{19}$
1270	30	$7 \cdot 10^{17}$	30	$8 \cdot 10^{17}$	—	—
1320	70	$9 \cdot 10^{18}$	40	$2 \cdot 10^{18}$	—	—

Table 3

Results of calculation of the cobalt concentration in the ZnS:Co, ZnSe:Co, ZnTe:Co crystals

Annealing temperature, K	Crystal type					
	ZnS:Co		ZnSe:Co		ZnTe:Co	
	ΔE_g, meV	N, cm^{-3}	ΔE_g, meV	N, cm^{-3}	ΔE_g, meV	N, cm^{-3}
1020	—	—	—	—	90	$3 \cdot 10^{19}$
1070	—	—	40	$2 \cdot 10^{18}$	110	$5 \cdot 10^{19}$
1120	—	—	50	$3 \cdot 10^{18}$	120	$7 \cdot 10^{19}$
1170	—	—	80	10^{19}	—	—
1220	130	$5 \cdot 10^{19}$	120	$5 \cdot 10^{19}$	—	—

Table 4

Results of calculation of the nickel concentration in the ZnS:Ni, ZnSe:Ni, ZnTe:Ni crystals

Annealing temperature, K	Crystal type					
	ZnS:Ni		ZnSe:Ni		ZnTe:Ni	
	ΔE_g, meV	N, cm^{-3}	ΔE_g, meV	N, cm^{-3}	ΔE_g, meV	N, cm^{-3}
1020	—	—	—	—	20	$3 \cdot 10^{17}$
1070	---	—	20	$2 \cdot 10^{17}$	50	$4 \cdot 10^{18}$
1120	10	$4 \cdot 10^{17}$	40	$2 \cdot 10^{18}$	110	$6 \cdot 10^{19}$
1170	100	$2 \cdot 10^{19}$	110	$4 \cdot 10^{19}$	—	—
1220	130	$5 \cdot 10^{19}$	140	$8 \cdot 10^{19}$	—	—
1270	200	$2 \cdot 10^{20}$	160	$1 \cdot 10^{20}$	—	—

Formation of the $Zn_{1-x}Fe_xSe$ alloy was observed in [10]. Careful analysis of optical absorption in the fundamental absorption region of the ZnSe:Fe, ZnSe:Ni crystals, executed by us in [8,11], showed that crystals with doping impurity concentration higher than 10^{18} sm^{-3} showed strong impurity absorption in this region, that difficult determination of fundamental absorption edge. The impurity absorption bands in the fundamental absorption region were observed in the ZnSe:Cr, ZnSe:Co, ZnS:Co and ZnS:Ni crystals [9, 11—13].

The author is grateful to Drs. *Yu. Vaksman* and *Yu. Purtov* for their suggestions, and is also thankful to his aspirant *V. Yatsun* for technical assistance.

4. CONCLUSIONS

The investigations enable us to draw the following conclusions.

1. The diffusion 3d-impuryties doping technique is developed for the ZnS, ZnSe, ZnTe single crystals. The method allows to obtaining zinc-chalcogenides single crystals with predicted 3d-impuryty concentration.

2. It is shown that doping by transition-metal elements results in diminishment of band gap in the explored crystals.

3. Concentrations of doping impurities in the investigated crystals are determined on values band gap shift. The maximal value of doping impurity concentration ($\sim 10^{20}$ cm^{-3}) is observed in the crystals doped with cobalt and nickel.

REFERENCES

1. *Воронов А. А., Козловский В. И., Коростелин Ю. В., Ландман А. И., Подмарьков Ю. П., Фролов М. П.*, Лазерные характеристики кристалла Fe: ZnSe в диапазоне температур 85—255 K // Квант. Электроника. — 2005. — В. 35, № 9. — С. 809—812.

2. *I. T. Sorokina, E. Sorokin, S. B. Mirov, V. V. Fedorov.* Broadly tunable compact continuous-wave Cr^{2+}:ZnS laser // Optics Letters— 2002. — Vol. 27, No. — P. 1040—1042.

3. *Fedorov V. V., Mirov S. B.* et. al. 3.77—5.05-μm tunable solid-state lasers based on Fe^{2+}-doped ZnSe crystals operating at low and room temperatures // Journal of quantum electronics — 2006. — V. 42, № 9. — P. 907—917.

4. *J. Kreissl, H.-J. Schulz.* Transition-metal impurities in II—VI semiconductors: characterization and switching of charge states // J. Cryst. Growth. — 1999. — V. 161. — P. 239—249.

5. *Кулешов Н. В., Щербицкий В. Г., Кисель В. Э., Левченко В. И., Постнова Л. И.* Fe^{2+}:ZnSe — новый материал для пассивных затворов лазеров с длиной волны излучения 3 мкм // Сборник докладов Международной научной конференции «Актуальные проблемы физики твердого тела», http://ifttp.bas-net.by.

6. *Demirbas U., Sennaroglu A.*, Somer M. Synthesis and characterization of diffusion-doped Cr^{2+}:ZnSe and F^{e2+}:ZnSe // Optical Materials — 2006. — V. 28 P. 231—240.

7. *Korostelin Yu. V., Kozlovsky V. I., Nasibov A. S., Shapkin P. V.* Vapour growth of II—VI solid solution single crystals // J. Cryst. Growth. — 1999. — V. 159. — P. 181—185.

8. *Ваксман Ю. Ф., Ницук Ю. А., Яцун В. В., Насибов А. С., Шапкин П. В.* Получение и оптические свойства кристаллов ZnSe:Ni // ФТП. — 2010. — Т. 44, В. 2. — С. 149—153.

9. *Ваксман Ю. Ф., Павлов В. В., Ницук Ю. А., Пуртов Ю. Н., Насибов А. С., Шапкин П. В.* Получение и оптические свойства монокристаллов ZnSe, легированных кобальтом // ФТП. — 2006. — Т. 40, №. 7. — С. 815—818.

10. *Chee-Leung Mak, Sooryakumar R., Steiner M. M.* Optical transitions in $Zn_{1-x}Co_xSe$ and $Zn_{1-x}Fe_xSe$: Strong concentration-dependent effective *p-d* exchange // Phys. Rev. B. — 1999. —V. B48. — P. 11743—11747.

11. *Ваксман Ю. Ф., Павлов В. В., Ницук Ю. А., Пуртов Ю. Н., Насибов А. С., Шапкин П. В.* Оптическое поглощение и диффузия хрома в монокристаллах ZnSe // ФТП. — 2005. — Т. 39, № 4. — С. 401—404.

12. *Vaksman Yu. F., Nitsuk Yu. A., Pavlov V. V., Purtov Yu. N., Nasibov A. S., Shapkin P. V.* Optical properties of ZnS single crystals doped with cobalt // Photoelectronics. 2007. — N. 16. — P. 33—36.

13. *Vaksman Yu. F., Nitsuk Yu. A., Yatsun V. V., Purtov Yu. N., Nasibov A. S., Shapkin P. V.* Optical Properties of ZnS:Ni Crystals Obtained by Diffusion Doping // Functional Materials. — 2010. — V. 17. — N. 1. — P. 75—79.

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Abstract

The zinc chalkogenides (ZnS, ZnSe, ZnTe) single crystals doped with 3d-impurityes (Cr, Fe, Co, Ni) are investigated. The diffusion doping is carried out from metallic chromium and nickel or powderlike iron and cobalt in helium and argon atmosphere. The optical density spectra are investigated in the fundamental absorption range of ZnS, ZnSe, ZnTe crystals. The transition-metal elements doping of crystals results in the absorption edge shift toward lower energies. From the value of the absorption edge shift, the 3d-impuryty concentrations in crystals under investigation is determined.

Key words: zink chalkogenides, 3d-impuryties, optical-density, band gap shift.

УДК 621.315.592

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ВЛИЯНИЕ 3d-ПРИМЕСЕЙ (Cr, Fe, Co, Ni) НА ПОЛОЖЕНИЕ КРАЯ ПОГЛОЩЕНИЯ В ХАЛЬКОГЕНИДАХ ЦИНКА

Резюме

Исследованы монокристаллы халькогенидов цинка (ZnS, ZnSe, ZnTe), легированные 3d-примесями (Cr, Fe, Co, Ni). Диффузионное легирование осуществлялась из металлического хрома и никеля или порошкообразного железа и кобальта в атмосфере гелия и аргона. Исследованы спектры оптической плотности в области фундаментального поглощения кристаллов ZnS, ZnSe, ZnTe. Показано, что легирование элементами переходных металлов приводит к уменьшению ширины запрещенной зоны исследуемых кристаллов. По величине смещения края поглощения определены концентрации 3d-примесей в исследуемых кристаллах.

Ключевые слова: халькогениды цинка, 3d-примеси, оптическая плотность, изменение ширины запрещенной зоны.

УДК 621.315.592

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ВПЛИВ 3d-ДОМІШОК (Cr, Fe, Co, Ni) НА ПОЛОЖЕННЯ КРАЮ ПОГЛИНАННЯ В ХАЛЬКОГЕНІДАХ ЦИНКУ

Резюме

Досліджено монокристали халькогенідів цинку (ZnS, ZnSe, ZnTe), що леговані 3d-домішками (Cr, Fe, Co, Ni). Дифузійне легування виконувалось з металевого хрому та нікелю або порошкоподібного заліза та кобальту в атмосфері гелію та аргону. Досліджено спектри оптичної густини в області краю фундаментального поглинання кристалів ZnS, ZnSe, ZnTe. Показано, що легування елементами перехідних металів призводить до зменшення ширини забороненої зони в досліджуваних кристалах. За величиною зсуву краю поглинання визначені концентрації 3d-домішок в досліджуваних кристалах.

Ключові слова: халькогеніди цинку, 3d-домішки, оптична густина, зміна ширини забороненої зони.