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OPTICAL PROPERTIES OF ZnSe:Mn CRYSTALS

ZnSe single crystals with diffusion doping of Mn have been investigated. Absorption, luminescence and photoconductivity of ZnSe:Mn crystals have been studied and analyzed in the visible region of the spectrum. Concentration of Mn impurity was estimated from absorption edge. The electron transition scheme in ZnSe:Mn was proposed.

1. INTRODUCTION

Semiconductor compounds A_2B_6 with dopants of transition metals are described by internal transitions in 3d states — absorption and luminescence. Investigation of internal transitions luminescence on these states and luminescent centers formed by Mn is interesting because ZnS:Mn and ZnSe:Mn crystals are rather good phosphors [1]. In this work, diffusion doping of ZnSe single crystals with Mn is described. The optical absorption, luminescence and photoconductivity of ZnSe:Mn crystals have been investigated and analyzed in the visible range of the spectrum. Concentration of Mn impurity was estimated from absorption edge shift.

The purpose of this study is to develop the procedure of diffusion Mn doping of the ZnSe crystals, to identify the optical absorption, luminescence and photoconductivity spectra of obtained samples.

2. EXPERIMENTAL

The samples for study were prepared via diffusion Mn doping of pure ZnSe single crystals. Undoped crystals were obtained by the method of free growth on a single-crystal ZnSe substrate with the growth plane (111) or (100). This method was described in detail, and the main characteristics of the ZnSe crystals were obtained in [2, 3]. The selection of temperature profiles and design of the growth chamber excluded the possibility of a contact between the crystal and chamber walls. The dislocation density in the crystals obtained was no higher than $10^4 cm^{-2}$.

Initially, the crystal doping was provided by impurity diffusion towards crystal bulk from evaporated surface layer of metallic Mn in He+Ar atmosphere. Then, the crystals have been annealed at 1173-1223K. Diffusion process time was 5 hours. However, this method didn't form crystals with high concentration of Mn, thus Mn atoms diffused into the crystal bulk resulted from high diffusion coefficient of Mn. As result, ZnSe:Mn crystals with low Mn concentration (10^{16} cm^{-3}) were obtained.

The method described in [4,5] was used for highly doped ZnSe:Mn crystals obtaining. Metal powder-like Mn was used as the source of impurity. To prevent crystal etching, Mn powder was mixed with ZnSe powder in 1:1 ratio. Diffusion process was performed in He+Ar atmosphere in the temperature range from 1173 to 1223 K. The diffusion process was 5h long.

The spectra of optical density were measured using an MDR-6 monochromator with diffraction grating 1200 grooves/mm in the visible region. The light intensity was registered by photomultiplier FEU-100. The optical density spectra were measured at 77 and 293 K.

Photoluminescence spectra were measured by ISP-51 quartz prism spectrograph. Photoluminescence excitation was provided by super luminescent diode EDEV-3LA1 Edison Opto Corporation with λ_{max}=400 nm.

Indium contacts were deposited on the surface of crystals for photoconductivity measurements. The contacts were formed by firing in vacuum at 600 K. Monochromator MUM-2 was used for photoconductivity spectra measurements. Halogen lamp was used for excitation of the spectra.

3. OPTICAL ABSORPTION OF ZnSe:Mn IN THE VISIBLE REGION SPECTRUM

The optical density (D^*) spectra of ZnSe:Mn crystals, obtained at different annealing temperatures, are presented in fig.1. The spectra of undoped ZnSe crystals characterized by absorption edge at 2.82 eV (fig 1, curve 1) at T =77K. The second linear area was located at 2.76 eV, associated with an unresilient exciton-exciton interaction [3]. No features was observed at the energies lower than 2.6 eV.

Mn doping led to absorption edge shift (fig.1, curves 2-4). The shift value increased with annealing temperature raise. The change of the band gap (meV) as the function of impurity concentration was discussed in [3]:

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

where *e*-electron charge, *N*-impurity concentration (cm^{-3}), ε_s=8.66 — ZnSe dielectric constant. As result, Mn-dopant concentrations have been calculated. The obtained values are presented in Table. Maximum of Mn concentration was observed ($6 \cdot 10^{19}$ cm^{-3}) for the samples annealed at 1223K.

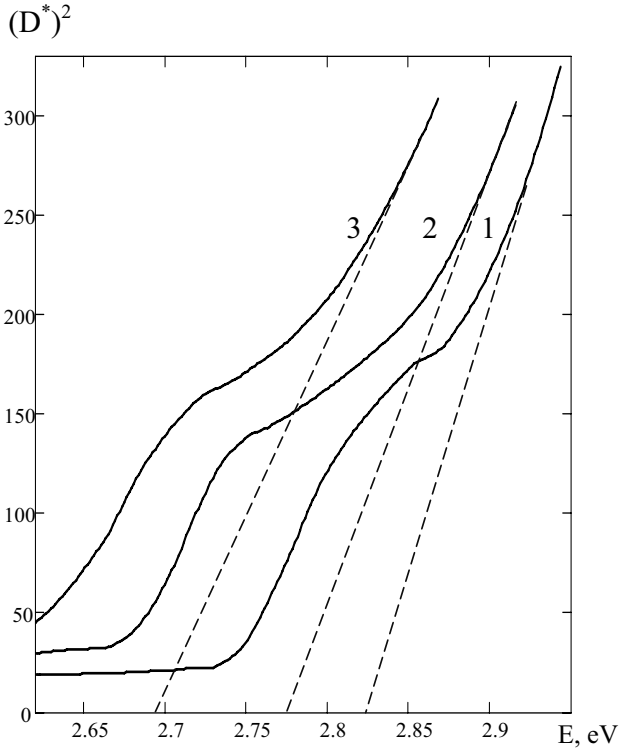

Fig. 1. The optical-density spectra of ZnSe (1) and ZnSe:Mn (2,3) crystals doped with Mn at temperatures of (2) 1173 and (3) 1223K. T_m=77 K.

In the visible region ZnSe:Mn optical-density spectra have several absorption lines, which intensity increases with Mn concentration enhance (fig.2). Three absorption lines at 2.31, 2.47 and 2.67 eV can be separated

Table

The change of the band gap (meV) in the ZnSe:Mn crystals

Crystal type	77 K	300 K	ΔE_g, meV	N, cm^{-3}
ZnSe, undoped	2.82	2.68	---	---
ZnSe:Mn, doped at 1173K	2.78	2.64	40	$2 \cdot 10^{18}$
ZnSe:Mn, doped at 1223K	2.69	2.55	130	$6 \cdot 10^{19}$

Absorption measurements at 77-300K showed that lines at 2.31, and 2.47 eV didn't change their positions with temperature raise. Line at 2.67 eV at 300 K is located at the conductivity band because the band gap of ZnSe:Mn is 2.55-2.64 eV at this temperature. The one can suppose that intracenter transitions are the origins of those lines. According to [6], absorption line at 2.31 eV is due to transition from the ground state $^6A_1(G)$ to excited state $^4T_1(G)$ of Mn^{2+} ion. The line at 2.47 eV is due to $^6A_1(G) \rightarrow {}^4T_2(G)$ transitions and the line at 2.67 eV is due to $^6A_1(G) \rightarrow {}^4E_1(G)$ intracenter transitions.

3. ZnSe:Mn PHOTOLUMINESCENCE SPECTRA

Photoluminescence measurements have been performed at 77-600 K. At 77K ZnSe:Mn crystals spectra had two narrow lines at 2.12 and 2.31 eV. The intensity of the lines increased with Mn concentration increase (fig.3, curves 1,2). Lines positions didn't change with the temperature increase that evidences about intracenter nature of this lines.

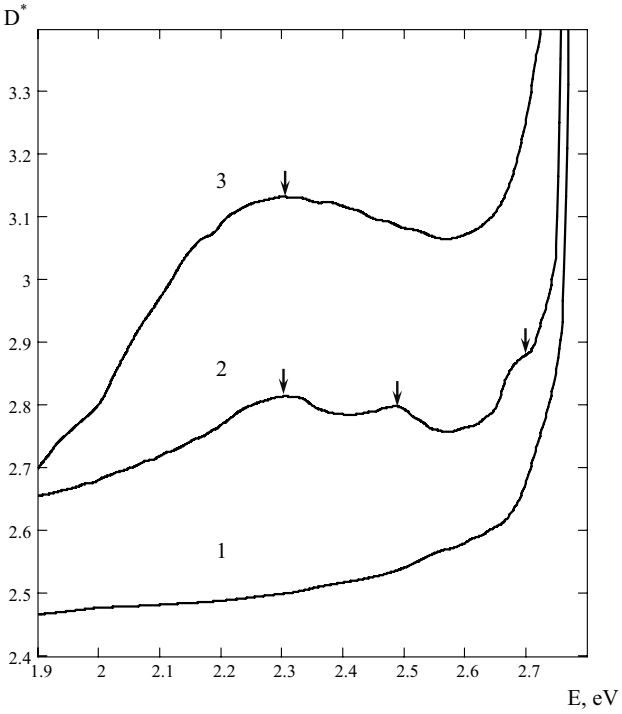

Fig. 2. The optical-density spectra of ZnSe (1) and ZnSe:Mn (2,3) crystals in the visible region of the spectrum at 77 K. Curve 2 corresponds to the sample annealed at 1173 K and curve 3 corresponds to annealing at 1223 K.

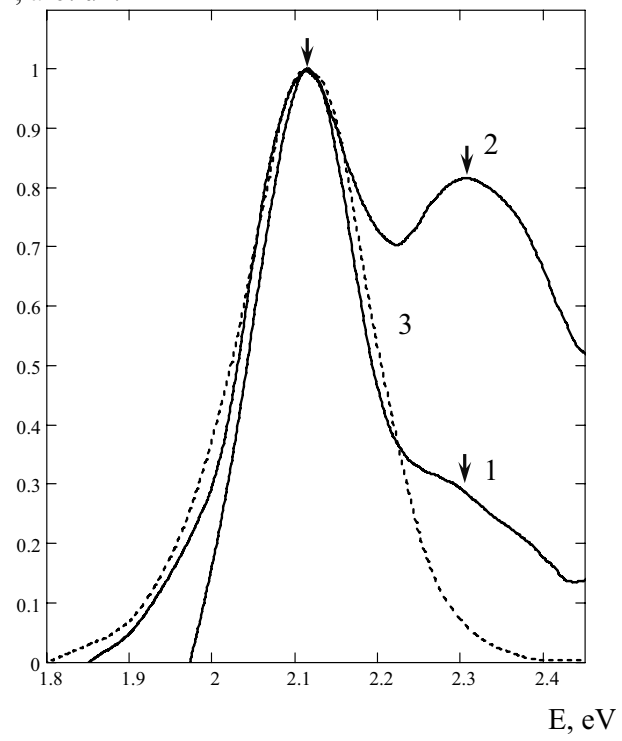

Fig. 3. The photoluminescence spectra of ZnSe:Mn crystals at 77(1,2) and 400 K (3). Curve 1 corresponds to the sample annealed at 1173 K and curves 2,3 correspond to annealing at 1223 K.

The temperature dependence of the luminescence at 300-600 K showed that line at 2.31 eV disappeared

at 400 K (fig.3, curve 3) and line at 2.12 eV disappeared at 600 K. Luminescence lines half-width increases with the temperature increase:

$$E_{1/2} = E_0 \left(\frac{2kT}{h\Omega} \right)^{1/2}, \qquad (2)$$

The equation (2) is obtained from the model of configuration coordinates, where E_0 is the lines half-width at 0 K.

4. ZnSe:Mn PHOTOCONDUCTIVITY SPECTRA

It is established, that ZnSe:Mn crystals had photosensitivity. ZnSe:Mn crystals photoconductivity spectra at different temperatures are shown in fig.4. The one can see, one line is observed at 2.78 eV under 77 K (fig.4). This line present in spectra of undoped ZnSe crystals and could be associated with intraband transitions. Low-energy photoconductivity part increases with the temperature increase (fig4, curves 2-4).

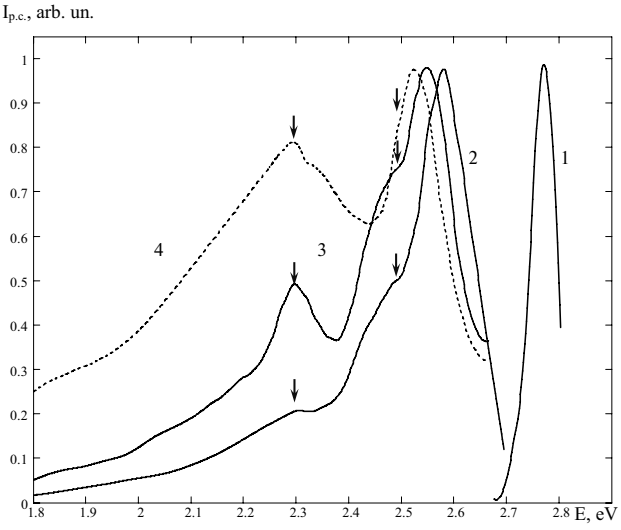

Fig. 4. The photoconductivity spectra of ZnSe:Mn crystals at 77(1), 293 (2), 323 (3) and 403K (4).

The permanent lines at 2.31 and 2.47 eV appeared in spectra at temperatures over 293 K. These lines positions are identical to absorption lines. The intensity of photoconductivity lines was changed with the temperature. At room temperatures high energy lines were dominated whereas at 403 K 2.31 eV lines intensity becomes maximal.

Electron transitions scheme of ZnSe:Mn based on optical properties investigations, is shown in fig.5.

As it is mentioned above, absorption lines at 2.31, 2.47 and 2.67 eV are the result of transitions from the ground state $^6A_1(G)$ to Mn excited states (fig.5, transitions 1-3). According to [1], the ground state of Mn ion is located 0.1 eV higher than valence band.

Photoluminescence lines at 2.12 and 2.31 eV are resulted by transitions from excited states to the ground state of Mn ion (fig.5, transitions 4,5).

Presented scheme allows to explain photoconductivity, which is due two stage process. First, optical transitions 2 and 3 take place and then thermal electron transition to conductance band starts (transitions 6 and 7). The absence of low energy photoconductivity up to 300 K, can be explained by the impossibility of thermal transitions of electrons from $^4E_1(G)$ to conductance band. It is worth to say that similar results have been obtained by us before for ZnSe:Cr [8].

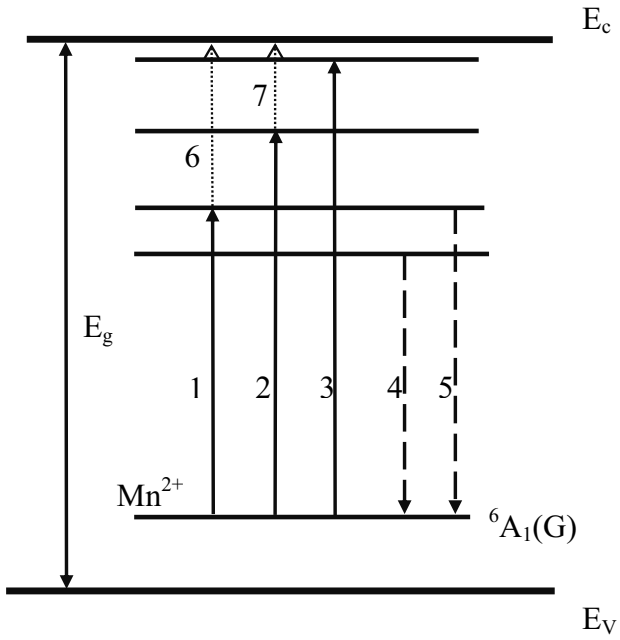

Fig. 5. The electron transition scheme in ZnSe:Mn crystals.

5. CONCLUSIONS

The studies carried out allow us to conclude the following.

1. A procedure of diffusion Mn doping of the ZnSe crystals has been developed. Maximal Mn concentration, estimated from the absorption edge, was $6 \cdot 10^{19}$ cm^{-3}.

2. The nature of ZnSe:Mn crystals absorption lines in the visible region of the spectrum have been identified.

3. The identity of absorption, photoluminescence and photoconductivity lines in ZnSe:Mn was shown.

4. The electron transition scheme in the ZnSe:Mn crystals was proposed.

References

1. Агекян В.Ф. Внутрицентровые переходы ионов группы железа в полупроводниковых матрицах типа A_2B_6 // ФТТ. — 2002. — Т. 44, №. 11. — С. 1921-1939.
2. 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.
3. Ваксман Ю.Ф., Ницук Ю.А., Пуртов Ю.Н., Шапкин П.В. Собственные и примесные дефекты в монокристаллах ZnSe:In, полученных методом свободного роста // ФТП. — 2001. — Т.35, №8. — с. 920-926.
4. 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.
5. 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.
6. Хмеленко О.В., Омельченко С.А Влияние пластической

деформации на зарядовое состояние ионов Mn^{2+} в кристаллах ZnSe // Вестник Днепропетровского университета. — 2008. — №15.
7. Буланый М.Ф., Коваленко А.В., Полежаев Б.А. Электролюминесцентные источники света на основе монокристаллов ZnSe:Mn с оптимальными яркостными характеристиками // ЖТФ. — 2003. — Т.73, №.2. — С. 133-135.
8. Ваксман Ю.Ф., Павлов В.В., Ницук Ю.А., Пуртов Ю.Н. Оптические свойства кристаллов ZnSe, легированных переходными элементами // Вісник Одеського нац. ун-ту. — 2006. — Т.11, вип. 7. — Фізика. — С. 47-53.

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Abstract
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Key words: diffusion doping, optical-density, photoluminescence, photoconductivity, intracenter transition.

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ОПТИЧЕСКИЕ СВОЙСТВА КРИСТАЛЛОВ ZnSe:Mn

Резюме
Исследованы монокристаллы ZnSe:Mn, полученные методом диффузионного легирования. Исследованы спектры оптической плотности, фотолюминесценции и фотопроводимости в видимой области. По величине смещения края поглощения определена концентрация марганца в исследуемых кристаллах. Построена схема оптических переходов в кристаллах ZnSe:Mn.
Ключевые слова: диффузионное легирование, оптическая плортность, фотолюминесценция, фотопроводимость, внутрицентровые переходы.

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ОПТИЧНІ ВЛАСТИВОСТІ КРИСТАЛІВ ZnSe:Mn

Резюме
Досліджено монокристали ZnSe:Mn, отримані методом дифузійного легування. Проведені дослідження спектрів оптичної густини, фотолюмінесценції та фотопровідності в видимій області. По зміщенню краю поглинання визначено концентрації марганцю в досліджуваних кристалах. Побудована схема оптичних переходів в кристалах ZnSe:Mn.
Ключові слова: дифузійне легування, оптична густина, фотолюмінесценція, фотопровідність, внутріцентрові переходи.