Optical absorption and diffusion of iron in ZnS single crystals

Yu.A.Nitsuk, Yu.F.Vaksman, V.V.Yatsun, Yu.N.Purtov,

I.Mechnikov National University, 2 Dvoryanskaya str.,
65026 Odesa, Ukraine

ZnS:Fe single crystals obtained by diffusion doping were investigated. Spectra of optical density in the range of energies 0.4–3.8 eV were obtained. The concentration of iron in the studied crystals was determined using a magnitude of the shift of the absorption edge. Optical transitions determining the impurity absorption spectrum of ZnS:Fe single crystals were identified. The diffusion profile of Fe impurity was determined by measuring the relative optical density of the crystals in the visible spectral region. The diffusivities of Fe in ZnS crystals in the temperature range of 1220–1320 K were calculated for the first time. At 1270 K the diffusivity of Fe is $2 \cdot 10^{-10}$ cm^2/s.

Методом диффузионного легирования получены монокристаллы ZnS:Fe. Исследованы спектры оптической плотности в области энергий 0.4–3.8 эВ. По величине смещения края поглощения определена концентрация железа в исследуемых кристаллах. Идентифицированы оптические переходы, обуславливающие спектр примесного поглощения монокристаллов ZnS:Fe. Диффузионный профиль примеси железа определен путем измерения относительной оптической плотности кристаллов в видимой области спектра. Впервые рассчитаны коэффициенты диффузии железа в кристаллах ZnS при температурах 1220–1320 К. При 1270 К коэффициент диффузии железа составляет $2 \cdot 10^{-10}$ см^2/с.

1. Introduction

The zinc sulfide single crystals doped with transition metal ions (Cr, Fe, Co, Ni), can be used as active media and passive gates for the mid infrared (IR) spectral region lasers. The effective laser generation in the spectral region 2.35 µm has been realized in ZnS:Cr crystals [1]. Iron-doped ZnS crystals are less studied as compared to crystals doped with cobalt and chrome. In the work [2] it was reported about creation of impulsive laser based on ZnS:Fe crystal with continuous tuning of the laser wavelength within the range of 3.49–4.65 µm. Lasing in this crystal was obtained at room temperature under pumping by 40 ns pulses of Er:YAG laser at 2.94 µm wavelength. Therefore the obtaining of ZnS:Fe crystals and research of their optical properties is actual.

The goals of current study are: development of a procedure of diffusion doping of ZnS crystals with Fe, identification of the optical absorption spectra, and determination of diffusivity of Fe in ZnS crystals.

In this investigation the procedure of diffusion doping is realized, which allows one to obtain ZnS:Fe single crystals with a specified concentration of Fe impurity. The structure of optical absorption spectra in the visible and infrared wavelength regions is studied and identified. The maximum concentration of Fe impurity is determined by means of a magnitude of the absorption edge shift. Analysis of the profile of relative optical density allowed us to determine the diffusivity of Fe in ZnS crystals.

2. Experimental

The samples under study are obtained by diffusion doping with Fe of ZnS single crystals. Undoped crystals are obtained via free growth on a single crystal ZnS (111) substrate. No polytypes were discovered in the crystals structure. A detailed description of this growth method and main characteristics of ZnS crystals are described in [3]. Selection of temperature profiles and design of the growth chamber excluded any contact between the crystal and the chamber walls. The dislocation density in the crystals was no higher than 10^4 cm^{-2}.

The crystals were doped via diffusion of impurity from powdery Fe in He + Ar atmosphere. In order to avoid etching of crystals, powdery ZnS in the ratio 2:1 was added to the powder of Fe. The crystals were annealed in evacuated quartz cells at temperatures from 1170 to 1320 K (see Table 1). Duration of the diffusion process was 10 h.

Diffusion of Fe was performed under conditions in which the impurity concentration in the source remained virtually constant. In this case the solution of Fick's diffusion equation for the one dimensional diffusion has the form

$$C(x,t) = C_0 \left(1 - \text{erf}\frac{X}{\sqrt{4Dt}}\right), \qquad (1)$$

where C_0 is the activator concentration at the surface, D is the impurity diffusivity and the symbol "erf" denotes the error function (the Gaussian function).

After annealing ZnS:Fe crystals were characterized by the presence of diffusion profile with a thickness increasing with the annealing temperature elevation. The profile color varied from yellow-green to yellow-brown with the temperature increasing.

Optical density D^* spectra were measured using MDR-6 monochromator with 1200, 600, and 325 grooves/mm diffraction grates. The first grate was used to analyze
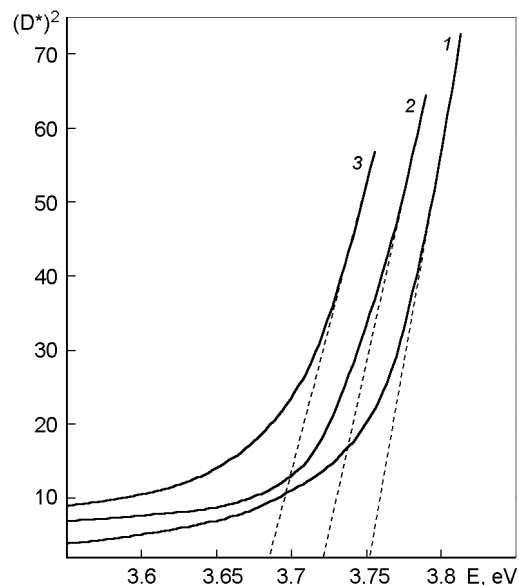

Fig. 1. Spectra of optical density of ZnS (*1*) and ZnS:Fe samples 4 (*2*) and 5 (*3*).

the absorption spectra in the 3.8–1.2 eV photon energy range, the second, in the 1.2–0.6 eV one, and third, in the 0.6–0.4 eV one. FEU-100 photomultiplier was used as a light flow receiver in the visible spectral region, while FR-1P photoresistor working in the alternating current mode in the IR region. The optical density spectra were measured at 77 and 293 K. The optical windows of cryostat chamber used to study the optical density were of 3 mm diameter.

For measuring the diffusion profile of Fe impurity a thin plate of the crystal (0.2–0.4 mm) was cleaved in the plane parallel to the direction of the diffusion flux. The measurement of the profile of optical density of Fe-doped crystals was performed using MF-2 microphotometer. This device allowed us to measure a magnitude of optical density with a step of 10 μm in the direction of the diffusion flux. In this case the integrated optical density was measured in the spectral range of 2.8–2.4 eV.

Table 1. Optical characteristics of ZnS crystals in the absorption edge region

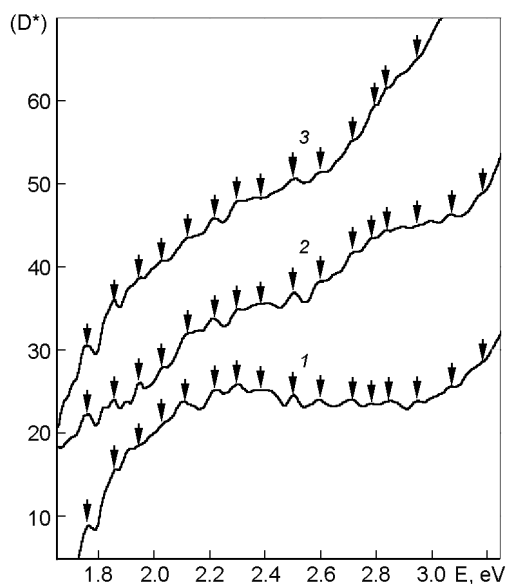| Sample No.	Type of the crystal	E_g, eV	ΔE_g, meV	N, cm^{-3}
1	ZnS starting	3.75	–	–
2	ZnS:Fe, annealing 1170 K	3.74	10	$2 \cdot 10^{16}$
3	ZnS:Fe, annealing 1220 K	3.73	20	$2 \cdot 10^{17}$
4	ZnS:Fe, annealing 1270 K	3.72	30	$7 \cdot 10^{17}$
5	ZnS:Fe, annealing 1320 K	3.68	70	$9 \cdot 10^{18}$

Fig. 2. Spectra of optical density of ZnS:Fe crystals in the visible region. Samples (*1*) 2, (*2*) 3 and (*3*) 4.

3. Analysis of the optical density spectra

The spectra of optical density of undoped ZnS crystals at 77 К are characterized by an absorption edge with energy of 3.75 eV (Fig. 1, curve *1*). In the range 0.40–3.6 eV, no features of the absorption spectra of undoped crystals are found.

Doping crystals with iron results in the absorption edge shift towards lower energies (Fig. 1, curves *2–3*). The shift value increases with annealing temperature and it is conditioned by interimpurity Coulomb interaction. The band gap width variation ΔE_g (in meV) as a function of impurity concentration depending on concentration of introduced impurities is determined in [4] by the relation:

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

where e is electron charge, N is impurity concentration in cm^{-3}, $\varepsilon_s = 8.3$ is ZnS dielectric constant, ε_0 — electric constant. The concentration of iron in the studied crystals was calculated from band gap width changing (see Table 1). The maximum concentration of Fe was $9{\cdot}10^{18}$ cm^{-3} for the crystals annealed at 1320 K.

In the visible spectral region the spectra of optical density of ZnS:Fe crystals contain a series of poorly resolved lines (Fig. 2).

Table 2. Optical transitions in the limits of Fe^{2+} ion

Line No.	E_{exp}, eV	E_{theor}, eV	Transition
1	3.18	3.15 [4]	$^5E(D) \to {}^1E(G)$
2	3.06	3.05 [4]	$^5E(D) \to {}^1A_1(G)$
3	2.94	2.95 [4]	$^5E(D) \to {}^3T_2(F)$
4	2.84	2.85 [4]	$^5E(D) \to {}^1T_2(I)$
5	2.78	2.80 [4]	$^5E(D) \to {}^3E(G)$
6	2.72	2.72 [4]	$^5E(D) \to {}^1T_1(I)$
7	2.60	2.60 [4]	$^5E(D) \to {}^1A_2(I)$
8	2.50	2.50 [4]	$^5E(D) \to {}^1A_1(I)$
9	2.39	2.40 [4, 5]	$^5E(D) \to {}^3T_2(P)$
10	2.30	2.32 [4, 5]	$^5E(D) \to {}^3T_1(F)$
11	2.22	2.25 [4, 5]	$^5E(D) \to {}^3T_2(F)$
12	2.11	2.14 [4, 5]	$^5E(D) \to {}^3A_1(F)$
13	2.03	2.07 [4, 5]	$^5E(D) \to {}^3A_2(P)$
14	1.94	1.92 [4, 5]	$^5E(D) \to {}^3T_2(H)$
15	1.85	1.81 [4, 5]	$^5E(D) \to {}^3T_1(H)$
16	1.75	1.68 [4, 5]	$^5E(D) \to {}^3E(H)$
17	1.35	1.28 [6]	$^5E(D) \to {}^3T_1(H)$
18	0.44	0.44 [4]	$^5E(D) \to {}^5T_2(D)$

Light absorption in this region increases as the iron concentration growth. In the absorption spectrum of the lightly-doped ZnS:Fe crystals obtained at 1170 K, sixteen absorption lines can be distinguished, namely, at 1.75, 1.85, 1.94, 2.03, 2.11, 2.22, 2.30, 2.39, 2.50, 2.60, 2.72, 2.78, 2.84, 2.94, 3.06, 3.18 eV (Fig. 2, curve *1*). With increase of the doping level the location of these lines remained unchanged (Fig. 2, curve *2*). Studies of optical density in the temperature range 77–300 K showed that the location of these lines remained unchanged. Such behaviour is characteristic for the absorption lines conditioned by the optical transitions of electrons within the impurity ion limits [5]. In the Table 2 the energies of optical transitions and their identification in the limits of Fe^{2+} ion are given. This table is created on the basis of our experimental results and calculations of Fe^{2+} ion energy states in ZnS lattice performed in [6–8]. The lines of ZnS:Fe intracenter absorption at the range of 1.7–2.3 eV was observed before in [7].

In the near IR-region the spectra of optical density of ZnS:Fe crystals contain the
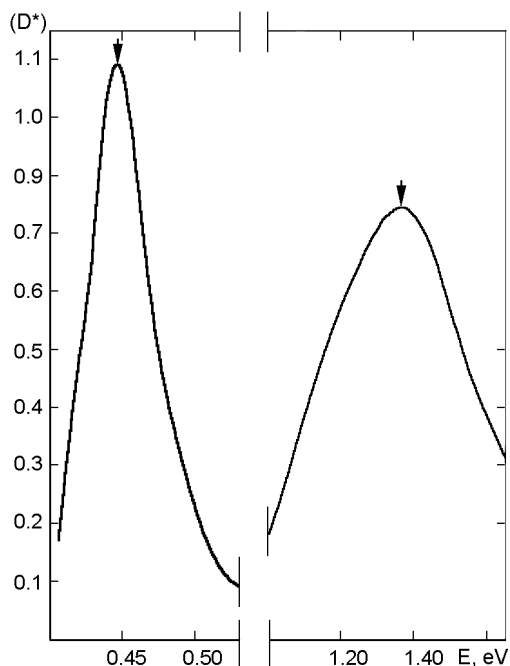
Fig. 3. Spectra of optical density of ZnS:Fe crystals in the IR region. Sample 4.

Fig. 4. Profiles of relative optical density (points in the curve) and diffusion profiles of Fe (solid lines) of ZnS:Fe crystals, samples (*1*) 3, (*2*) 4 and (*3*) 5. The temperature dependence of the diffusivity of Fe in ZnS crystals is in the inset.

absorption band at 1.35 eV (Fig. 3). The optical density of the crystals increased with iron concentration growth, while a location of the spectral lines was unchanged as the temperature varied from 77 to 300 K. The absorption line at 1.35 eV was observed before in [8, 9]. According to calculations (see Table 2), this absorption line can be explained by $^5E(D) \rightarrow {}^3T_1(H)$ transitions occurring in the limits of Fe^{2+} ion.

In the middle IR-region the optical density spectra of the crystals are characterized by the absorption band at 0.44 eV (Fig. 3). The optical density of the crystals increased with iron concentration growth. The location of this band was unchanged under the temperature and iron concentration varying. The absorption band at the range 0.3–0.6 eV was observed before in [10]. The absorption band at 0.44 eV is related to $^5E(D) \rightarrow {}^5T_2(D)$ transitions occurring in the limits of Fe^{2+} ion (see Table 2).

It should be noted that the absorption bands broadened with an increase of the crystals doping level. A similar broadening of the structure of the lines takes place in the absorption spectra in the visible spectral region. This is apparently associated with manifestation of the impurity-impurity interaction of Fe^{2+} ions.
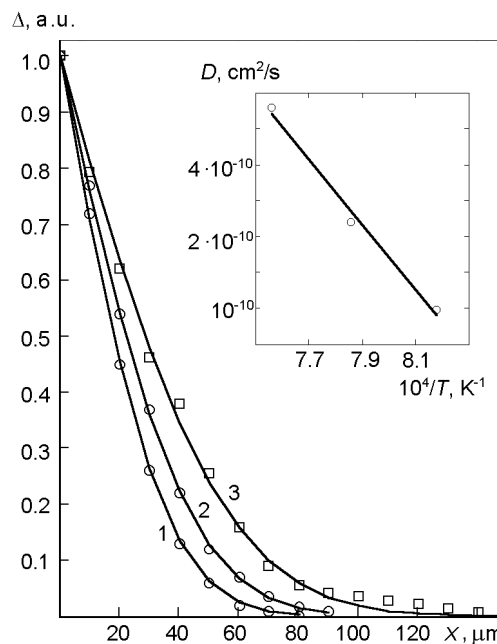
4. Determination of iron diffusivity in ZnS crystals

A presence of the absorption bands in the visible range (Fig. 2) testifies to the possibility of determining the diffusion profile of the impurity by measuring the relative optical density (Δ). This magnitude is the function of x coordinate in a direction of the diffusion flux; it is determined by the relation

$$\Delta = \frac{D^*(x) - D^*(\infty)}{D^*(0) - D^*(\infty)}, \qquad (3)$$

where $D^*(x)$ is the optical density of crystal as function of x coordinate, $D^*(0)$ is the optical density of crystal in the near surface layer with coordinate $x = 0$, and $D^*(\infty)$ is the optical density of crystal in the region where Fe concentration is negligibly low (crystal is undoped). The chosen definition of the relative optical density allows us to compare the dependence $\Delta(x)$ with the concentration profile of impurity $C(x)/C_0$ calculated by formula (1). By means of diffusivity fitting in (1), we obtained good agreement between profiles of the relative optical density and Fe concentration in the

crystals (Fig. 4). The diffusivities of Fe in ZnS crystals at 1220–1320 K were calculated similarly. The temperature dependence of diffusivity presented in inset to Fig. 4 is described by Arrhenius equation

$$D(T) = D_0 \exp\left(-\frac{E}{kT}\right), \qquad (4)$$

where the factor $D_0 = 0.16$ cm^2/s, while the activation energy of diffusion $E = 2.2$ eV. At the crystals annealing temperature of 1270 K, the diffusivity of Fe is $2 \cdot 10^{-10}$ cm^2/s. This value is several times less than Fe diffusivity in ZnSe crystals, which we determined according to the procedure described in [11].

5. Conclusions

The performed studies allow us to conclude the following. The procedure of iron diffusion doping of ZnS single crystals was developed. The maximum concentration of Fe impurity determined by the shift of the absorption edge in ZnS:Fe crystals was $9 \cdot 10^{18}$ cm^{-3}. The nature of absorption lines of ZnS:Fe crystals in the visible and IR regions of the spectrum was identified.

The diffusivities of Fe in ZnS crystals in the temperature range of 1220–1320 K were calculated for the first time. Analysis of the temperature dependence $D(T)$ allowed us to determine the coefficients in Arrhenius equation: $D_0 = 0.16$ cm^2/s and $E = 2.2$ eV. At 1270 K, the diffusivity of Fe is $2 \cdot 10^{-10}$ cm^2/s.

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Оптичне поглинання і дифузія заліза в кристалах ZnS

Ю.А.Ніцук, Ю.Ф.Ваксман, В.В.Яцун, Ю.М.Пуртов

Методом дифузійного легування отримано монокристали ZnS:Fe. Досліджено спектри оптичної густини в області енергій 0.4–3.8 еВ. За величиною зсуву краю поглинання визначено концентрацію заліза в досліджуваних кристалах. Ідентифіковано оптичні переходи, що визначають спектр домішкового поглинання монокристалів ZnS:Fe. Дифузійний профіль домішки заліза визначався за вимірюваннями відносної оптичної густини кристалів у видимій області спектра. Вперше розраховано коефіцієнти дифузії заліза в кристалах ZnS при температурах 1220–1320 К. При 1270 К коефіцієнт дифузії заліза становить $2 \cdot 10^{-10}$ см^2/с.