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OPTICAL ABSORPTION AND DIFFUSION OF COBALT IN ZnS SINGLE CRYSTALS

ZnS:Co single crystals obtained by diffusion doping are investigated. The spectra of optical density in the energy range 0.3-3.8 eV are investigated. On absorption edge shift of investigated crystals the cobalt concentration is calculated. Nature of optical transitions determining optical properties of ZnS:Co single crystals in the visible and IR-region of spectrum is identified.

The diffusion profile of the Co dopant is determined via measurement of the relative optical density of the crystals in the visible spectral region. The Co diffusivities in the ZnS crystals at 1170-1270 K are calculated. The Co diffusivity at 1270 K equals 10^{-9} cm^2/s.

INTRODUCTION

Cobalt-doped ZnS single crystals have found a wide application as generating media and passive gates of lasers emitting in the IR region. In [1,2], the possibility of the use of Co^{2+}:ZnS as the efficient passive gate and active media for lasers emitting in the region of 1.5-2.1 and 0.7-0.8 μm is shown. The diffusion doping with Co has a number of advantages compared with doping during growth, among which we can distinguish the main ones, namely, the possibility of controlling the impurity concentration and doping profile.

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

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

EXPERIMENTAL

The samples under study are obtained by diffusion doping with Co of starting pure ZnS single crystals. Undoped crystals are obtained via the free growth on a single crystal ZnS (111) substrate. A detailed description of this growth method and main characteristics of the ZnS crystals are presented in [3]. 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}. The crystals were doped via diffusion of impurity from metal powderlike Co in He+Ar atmosphere. In order to avoid etching of crystals, powderlike ZnS in the ratio 1:1 was added to the Co powder. Crystals were annealed in evacuated quartz cells at temperatures from 1170 to 1270 K (see Table 1). The duration of the diffusion process was 10 h. After annealing the ZnS:Co crystals acquired a turquoise colour, in contrast to the colourless of undoped ZnS crystals.

Diffusion of Co 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

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

where C_0 is the activator concentration at the surface and the symbol "*erf*" denotes the error function (the Gaussian function).The optical density D^* spectra were measured using a MDR-6 monochromator with 1200, 600, and 325 grooves/mm diffraction grates. The first grate was used to analyze the absorption spectra in the 3.8-1.6 eV photon energy range, the second, in the 1.6-0.6 eV one, and third, in the 0.6-0.4 eV one. A 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 300 K.

When measuring the diffusion profile of the 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 the Fe-doped crystals was performed using an MF-2 microphotometer. This device allowed us to measure the 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.

ANALYSIS OF OPTICAL DENSITY SPECTRA

The spectra of optical density of undoped ZnS crystals at 77K are feature 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 of crystals with cobalt leads in the absorption edge shift towards lower energies (Fig. 1, curves 2-3). The shift value increases with annealing temperature and is due to the 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, impurity concentration in cm^{-3}, $\varepsilon_s = 8.3$ is ZnS dielectric constant, ε_0, electric constant. The cobalt concentration in the studied crystals was calculated from band gap width changing (see Table 1). The maximum Co concentration ($3\cdot 10^{19}$ cm^{-3}) for the crystals annealed at 1270 K.

Table 1.

Optical characteristics of ZnS:Cr crystals in the absorption edge region

Sample No	Type of the crystal	E_g, eV	ΔE_g, meV	N, cm^{-3}
1	ZnS starting	2.75	---	---
2	ZnS:Co, annealing 1170 K	2.74	10	$4\cdot 10^{16}$
3	ZnS:Co, annealing 1220 K	2.68	70	$8\cdot 10^{18}$
4	ZnS:Co, annealing 1270 K	2.64	110	$3\cdot 10^{19}$

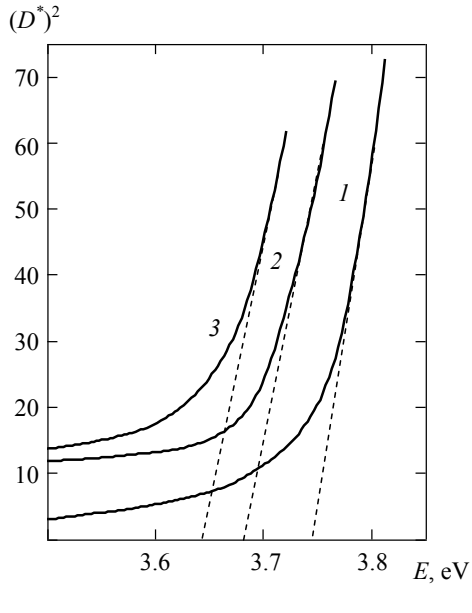

Fig. 1. Spectra of optical density of ZnS (*1*) and ZnS:Co samples 3 (*2*) and 4 (*3*).

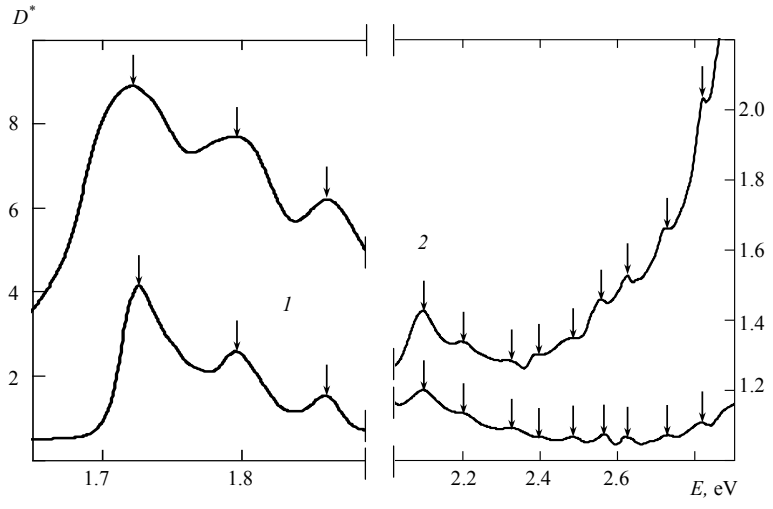

Fig. 2. Spectra of optical density of ZnS:Cr crystals in the visible region. Samples (*1*) 3 and (*2*) 4

In the visible spectral region, the spectra of the optical density of the ZnS:Co crystals involve a series of poorly resolved lines (Fig. 2). The absorption of the light in this region increases as the cobalt concentration. In the absorption spectrum of the lightly-doped ZnS:Co crystals obtained at 1170 K, twelve absorption lines can be distinguished, namely, at 2.82, 2.73, 2,61, 2.55, 2.48, 2.39, 2.32, 2.19, 2.09, 1.86, 1.8, 1.73 eV (Fig. 2, curve 1). As the doping level increased, 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 conduct 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 in the limits of the Co^{2+} ion and their identification are given. This table is constructed based on our experimental results and our calculations of the Co^{2+} ion energy states in ZnS lattice performed on the Tanabe-Sugano diagrams [6]. It is achieved the best accordance of experiment and theory at the parameters of the crystalline field of Δ=4000 cm^{-1} and B=750 cm^{-1}. Values of Δ and B parameters correspond with the results of the calculations performed in [7]. Lines of absorption at 2.73, 2.61, 2.55 eV was observed before in [8,9]. The energy of $^4A_2(F)\rightarrow{}^4T_1(P)$ transition corresponds with energy position of $^4T_1(P)$ level, calculated in [10].

Table 2.

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

Line no.	E_{exp}, eV	E_{calc}, eV	Transition
1.	2.82	2.85	$^4A_2(F)\rightarrow{}^2E(D)$
2.	2.73	2.82	$^4A_2(F)\rightarrow{}^2T_2(D)$
3.	2.61	2.81	$^4A_2(F)\rightarrow{}^2T_1(P)$
4.	2.55	2.58	$^4A_2(F)\rightarrow{}^2E(H)$
5.	2.48	2.42	$^4A_2(F)\rightarrow{}^2T_1(H)$
6.	2.39	2.40	$^4A_2(F)\rightarrow{}^2T_2(H)$
7.	2.32	---	---
8.	2.19	2.21	$^4A_2(F)\rightarrow{}^2T_1(H)$
9.	2.09	2.06	$^4A_2(F)\rightarrow{}^2A_1(G)$
10.	1.86	1.81	$^4A_2(F)\rightarrow{}^2T_2(G)$
11.	1.8	1.78	$^4A_2(F)\rightarrow{}^2T_1(G)$
12.	1.73	1.72	$^4A_2(F)\rightarrow{}^4T_1(P)$
13.	1.48	1.48	$^4A_2(F)\rightarrow{}^2E(G)$
14.	0.89	---	---
15.	0.84	0.85	$^4A_2(F)\rightarrow{}^4T_1(F)$
16.	0.77	---	---
17.	0.43	0.4	$^4A_2(F)\rightarrow{}^4T_2(F)$

In the near IR-region the spectra of optical density of ZnS:Co crystals are characterized by the broad absorption band at 1.48 eV. The optical density of the crystals increased with cobalt concentration growth. The location of this band was unchanged under the temperature varying from 77 to 300 K and cobalt temperature varying. According to our calculations (see Table 2), the absorption band at 1.48 eV can be explained by $^4A_2(F) \rightarrow {}^2E(G)$ transitions occurring in the limits of Co^{2+} ion.

In the middle IR-region, the spectra of optical density of the crystals involve the absorption bands at 0.89, 0.84, 0.76 and 0.43 eV (Fig. 3). The optical density of the crystals increased as the cobalt concentration increased. The location of this band was unchanged as the temperature and the cobalt concentration varied. According to our calculations (see Table 2), the absorption band at 0.84 eV are related to the $^4A_2(F) \rightarrow {}^4T_1(F)$ transitions. Two other bands can be conditioned by the presence of the spin-orbit splitting of $^4T_1(F)$ state of Co^{2+} ion.

The absorption band at 0.43 eV was observed by us before in ZnS:Co, ZnSe:Co and ZnTe:Co crystals [11-13]. According to our calculations and calculations [10] this absorption band is conditioned by $^4A_2(F) \rightarrow {}^4T_2(F)$ transitions between $^4A_2(F)$ ground state and $^4T_2(F)$ first excited state of Co^{2+} ion.

It should be noted that, as the doping level of the crystals increased, the absorption bands broadened. 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 the Co^{2+} ions.

DETERMINATION OF THE COBALT DIFFUSIVITY IN THE ZnS CRYSTALS

The presence of characteristic cobalt-absorption lines in the visible region of the spectrum indicates that it is possible to determine the impurity-diffusion profile by measuring the relative optical density (Δ^*). This quantity is a function of the coordinate x in the direction of the diffusion flux and is defined by the expression

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

where $D^*(x)$ is the crystal's optical density as a function of the coordinate x, $D^*(0)$ is the optical density of the crystal in the surface layer with the coordinate $x = 0$, and $D^*(\infty)$ is the optical density of the crystal in the region, where the cobalt concentration is negligible (the crystal is not doped). The chosen definition of relative optical density makes it possible to compare the dependence $\Delta^*(x)$ with the impurity concentration profile $C(x)/C_0$ calculated by formula (1). By choosing the value of the diffusivity in Eq. (1), we managed to obtain good agreement between the relative optical density and cobalt concentration profiles in the crystals (Fig. 4). The diffusivities of Co in ZnS crystals at temperature 1170-1270 K were calculated similarly. The temperature dependence of diffusivity $D(T)$, 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=2.39 cm^2/s, while the activation energy of diffusion E=2.34 eV. At the crystals annealing temperature of 1270 K the diffusivities of chromium is 10^{-9} cm^2/S. This value is a few orders less than cobalt diffusivity in ZnSe crystals, which we determined according to the procedure described in [12].

CONCLUSIONS

The study allows a number of conclusions. These are as follows:

1. The method of cobalt diffusion doping of ZnS single crystals was developed. The maximum concentration of cobalt impurity determined by the shift of the absorption edge in ZnS:Co crystals was $3 \cdot 10^{19}$ cm^{-3}.
2. The nature of absorption lines of ZnS:Co crystals in the visible and IR regions of the spectrum was identified.

3. The diffusivities of cobalt in ZnS crystals in the temperature range 1170-1270 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=2.39 cm^2/s and *E*=2.34 eV. At 1270 K the diffusivity of Co is 10^{-9} cm^2/s.

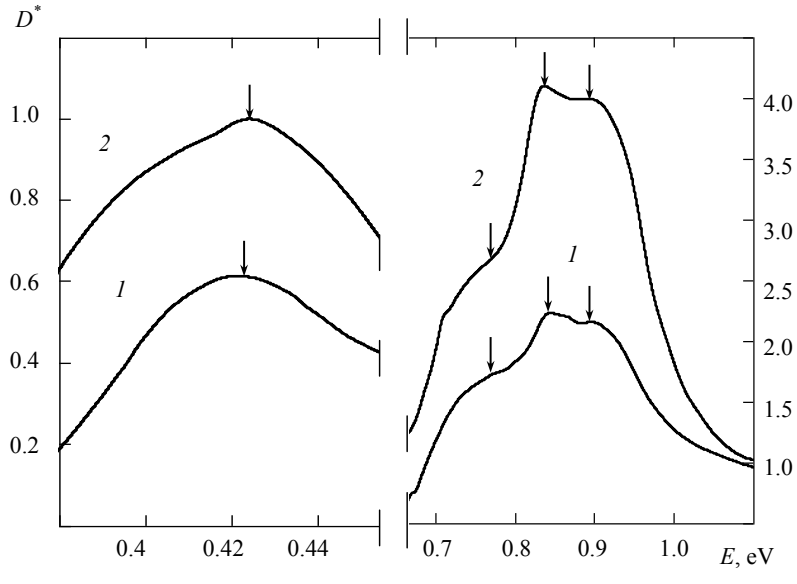

Fig. 3. Spectra of optical density of ZnS:Co crystals in the IR-region. Samples (*1*) 3 and (*2*) 4.

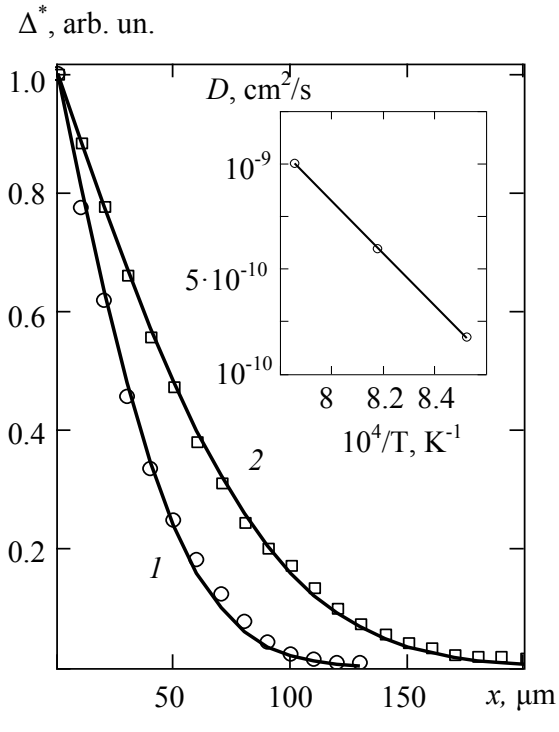

Fig. 4. Profiles of relative optical density (points in the curve) and diffusion profiles of Co (solid lines) of ZnS:Co crystals, samples (*1*) 3 and (*2*) 4. The temperature dependence of the Co diffusivity in ZnS crystals is in the inset.

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Abstract

ZnS:Co single crystals obtained by diffusion doping are investigated. The spectra of optical density in the energy range 0.4-3.8 eV are investigated. On absorption edge shift of investigated crystals the cobalt concentration is calculated. Nature of optical transitions determining optical properties of ZnS:Co single crystals in the visible and IR-region of spectrum is identified.

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Key words: zinc sulfide, diffusion doping, cobalt impurity, optical density, diffusivity.

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ОПТИЧЕСКОЕ ПОГЛОЩЕНИЕ И ДИФФУЗИЯ КОБАЛЬТА В МОНОКРИСТАЛЛАХ ZnS

Резюме

Исследованы монокристаллы ZnS:Co, полученные методом диффузионного легирования. Исследованы спектры оптической плотности в области энергий 0.4-3.8 эВ. По величине смещения края поглощения определена концентрация кобальта в исследуемых кристаллах. Идентифицирована природа оптических переходов, определяющих оптические свойства монокристаллов ZnS:Co в видимой и ИК-области спектра.

Диффузионный профиль примеси кобальта определен путем измерения относительной оптической плотности кристаллов в видимой области спектра. Рассчитаны коэффициенты диффузии кобальта в кристаллах ZnS при температурах 1170-1270 К. При 1270 К коэффициент диффузии кобальта составляет 10^{-9}см^2/с.

Ключевые слова: сульфид цинка, диффузионное легирование, примесь кобальта, оптическая плотность, коэффициент диффузии.

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ОПТИЧНЕ ПОГЛИНАННЯ І ДИФУЗІЯ КОБАЛЬТУ В МОНОКРИСТАЛАХ ZnS

Резюме

Методом дифузійного легування отримані монокристали ZnS:Co. Досліджено спектри оптичної густини в області енергій 0.4-3.8 еВ. За величиною зсуву краю поглинання визначена концентрація хрому в досліджуваних кристалах. Ідентифіковані оптичні переходи, що визначають спектр поглинання монокристалів ZnS:Co в видимій та ІЧ області спектру.

Дифузійний профіль домішки Co визначався за вимірюваннями відносної оптичної густини кристалів у видимій області спектру. Вперше розраховано коефіцієнти дифузії кобальту в кристалах ZnS при температурах 1170-1270 К. При 1270 К коефіцієнт дифузії кобальту становить 10^{-9} см^2/с.

Ключові слова: сульфід цинку, дифузійне легування, домішка кобальту, оптична густина, коефіцієнт дифузії.