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OBTAINING AND OPTICAL PROPERTIES OF ZnS:Ti CRYSTALS

ZnS:Ti 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 titan concentration is calculated. Nature of optical transitions determining optical properties of ZnS:Ti single crystals in the visible and IR-region of spectrum is identified.

The diffusion profile of the Ti dopant is determined via measurement of the relative optical density of the crystals in the visible spectral region. The Ti diffusivities in the ZnS crystals at 1270-1370 K are calculated. The Ti diffusivity at 1270 K equals 10-10 cm^2/s.

INTRODUCTION

The zinc sulphide single crystals, doped with transitional metals ions can be used as active media for the lasers of mid-infrared (IR) spectral region. In particular, the effective laser generation in the spectral region of 2.35 mkm were fabricated based on the ZnS:Cr crystals [1]. 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 mkm. At the same time, essentially nothing is known about possibility of infrared laser radiation realization using ZnS:Ti crystals.

The ZnS crystal doping during the growing process is difficult because the transitional metal evaporation temperatures exceed considerably than of zinc sulphide sublimation. In [3], we have described the procedure of ZnS crystals doping with nickel. A method for diffusion doping of ZnS single crystals with titanium is offered in this work that provides crystals with known titanium impurity concentration. The structure of the optical absorption spectra for the ZnS:Ti crystals has been studied and identified in the visible and infrared regions. The analysis of the profile of the relative optical density allowed us to determine the diffusivity of Ti in the ZnS crystals.

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

EXPERIMENTAL

The samples under study are obtained by diffusion doping with Ti of starting pure ZnS single crystals in P.N. Lebedev physical institute of Russian Academy of Sciences. A detailed description of this growth method and main characteristics of the ZnS crystals are presented in [4].

The crystals doping was carried out by impurity diffusion from a metal Ti layer deposited on the crystal surface. A titanium is deposited on one of the large surfaces of the crystalline plate (10×5×1mm) cut out parallel to the plane (111). The nickel layer thickness made the order 10μm. Crystals were annealed in He+Ar atmosphere at the temperatures of 1270-1370 K. The diffusion process was 5h long. After annealing, the ZnS:Ti crystals were characterized by the presence of diffusion profile with a thickness increasing with the annealing temperature elevation. The profile color varied from light yellow to dark yellow as the temperature increases, in contrast with colourless undoped crystals.

Diffusion of Ti 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

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

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 Ti 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 Ti-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 titanium 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 [5] by the

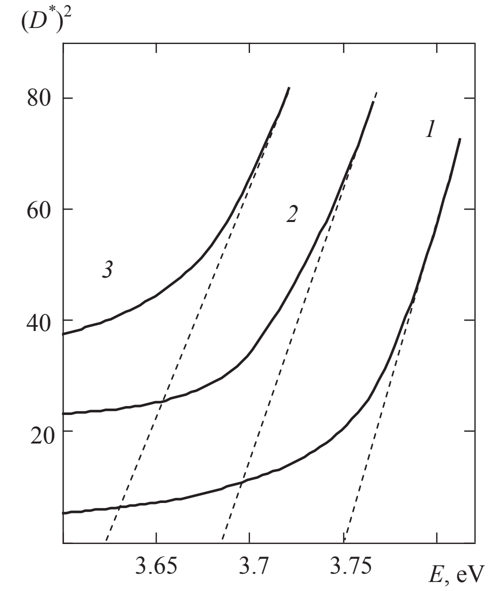

Fig. 1. **Spectra of optical density of ZnS (1) and ZnS:Ti samples 3 (2) and 4 (3)**

Table 1.

Optical characteristics of ZnS:Ti 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:Ti, annealing 1270 K	3.69	60	$5\cdot10^{18}$
3	ZnS:Ti, annealing 1320 K	3.65	100	$2\cdot10^{19}$
4	ZnS:Ti, annealing 1370 K	3.62	130	$5\cdot10^{19}$

relation:

$$\Delta E_g = 2\cdot10^5\left(\frac{3}{\pi}\right)^{1/3}\frac{eN^{1/3}}{4\pi\varepsilon_0\varepsilon_s}, \qquad (2)$$

where e is electron charge, N, impurity concentration in cm^{-3}, e_s = 8.3 is ZnS dielectric constant, e_0, electric constant. The titanium concentration in the studied crystals was calculated from band gap width changing (see Table 1). The maximum Ti concentration ($5\cdot10^{19}$ cm^{-3}) for the crystals annealed at 1370 K.

In the visible spectral region, the spectra of the optical density of the ZnS:Ti crystals involve a series of poorly resolved lines (Fig. 2). The absorption of the light in this region increases as the titanium concentration. In the absorption spectrum of the lightly-doped ZnS:Ti crystals obtained at 1270 K, nine absorption lines can be distinguished, namely, at 1.58, 1.72, 2.0, 2.13, 2.37, 2.52, 2.75, 2.85 and 3.26 eV(Fig. 2, curve 1).

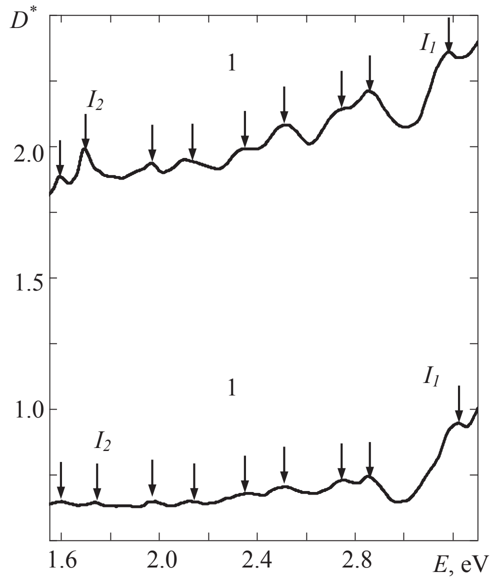

Fig. 2. **Spectra of optical density of ZnS:Ti crystals in the visible region. Samples (1) 2 and (2) 3**

As the doping level increased, the location of the lines at 1.58, 2.0, 2.13, 2.37, 2.52, 2.75, 2.85 eV 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 [6]. In the Table 2, the energies of optical transitions in the limits of the Ti^{2+} ion and their identification are given. This table is constructed based on our experimental results and our calculations of the Ti^{2+} ion energy states in ZnS lattice performed on the Tanabe-Sugano diagrams [7]. It is achieved the best accordance of experiment and theory at the parameters of the crystalline field of Δ=3800 cm^{-1} and B=770 cm^{-1}. Values of Δ and B parameters correspond with the results of the calculations performed in [8].

Table 2.

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

Line no.	E_{exp}, eV	E_{calc}, eV	Transition
1.	3.26	---	$^3A_2(F)+h\nu\rightarrow {}^2E(D)+e_{-c.b}$.
2.	2.85	2.87	$^3A_2(F)$®$^1T_2(G)$
3.	2.75	2.76	$^3A_2(F)$®$^1E(G)$
4.	2.52	2.55	$^3A_2(F)$®$^1T_2(G)$
5.	2.37	2.39	$^3A_2(F)\rightarrow {}^1A_1(G)$
6.	2.13	2.10	$^3A_2(F)\rightarrow {}^3T_1(P)$
7.	2.0	1.98	$^3A_2(F)$®$^1T_2(D)$
8.	1.72	1.72[8]	$^2E(D)+h\nu\rightarrow {}^3A_2(F)+e^+_{v.b}$
9.	1.58	1.55	$^3A_2(F)$®$^1E(D)$
10.	0.78	0.77	$^3A_2(F)\rightarrow {}^3T_1(F)$
11.	0.48	0.47	$^3A_2(F)\rightarrow {}^3T_2(F)$

It is established that the 3.26 eV line (I_1-line) change their position under variations in the Ti concentration. I_1-line shift towards lower energies at 40 meV with the increase of titan concentration from $5\cdot10^{18}$ cm^{-3} to $2\cdot10^{19}$ cm^{-3} (Fig 2, curve 2). Such shift corresponds to the concentration change of zinc sulfide band gap width by titan doping (see Table 1). At the increase of crystals temperature from 77 to 300 K I_1-line shift towards lower energies at 110 meV. Such shift corresponds to the temperature change of zinc sulfide band gap. Thus, the I_1-line absorption can be conditioned by Ti^{2+} ion photoionization

$$Ti^{2+}+h\nu\rightarrow Ti^{3+}+e^-_{c.b.} \qquad (3)$$

This is also confirmed by a photoconductivity presence in this region.

The behavior of the absorption line at 1.72 eV (I_2-line) is identical to the behavior of the I_1-line. I_2-line also shift towards lower energies at 40 meV with the increase of titan concentration from $5\cdot10^{18}$ cm^{-3} to $2\cdot10^{19}$ cm^{-3} (Fig. 2, curve 2). At the increase of crystals temperature from 77 to 300 K I_2-line shift towards lower energies at 110 meV. The corresponding absorption process can be represented as

$$Ti^{+}+h\nu \rightarrow Ti^{2+}+e^{+}_{v.b.} \quad (4)$$

In the IR-region the spectra of optical density of ZnS:Ti crystals are characterized by the broad absorption bands at 0.48 and 0.78 eV. The optical density of the crystals increased with titanium concentration growth. The location of this band was unchanged under the temperature varying from 77 to 300 K and titanium concentration varying. These absorption lines were observed before in [8]. According to our calculations (see Table 2), the absorption band at 0.48 eV can be explained by $^3A_2(F)$®$^3T_1(F)$ transitions occurring in the limits of Ti^{2+} ion. The absorption band at 0.78 eV is due to the $^3A_2(F)$®$^3T_2(F)$ intracenter transitions. At excitation by light corresponding to the high-energy intrinsic absorption region of Ti^{2+} ions intracenter emission $^3T_1(F)\rightarrow{}^3A_2(F)$ transitions were observed.

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 Ti^{2+} ions.

DETERMINATION OF THE TITANIUM DIFFUSIVITY IN THE ZnS CRYSTALS

The presence of characteristic titanium-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

$$\Delta^* = \frac{D^*(x) - D^*(\infty)}{D^*(0) - D^*(\infty)}, \quad (5)$$

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^*(¥) is the optical density of the crystal in the region, where the titanium 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 titanium concentration profiles in the crystals (Fig. 3).

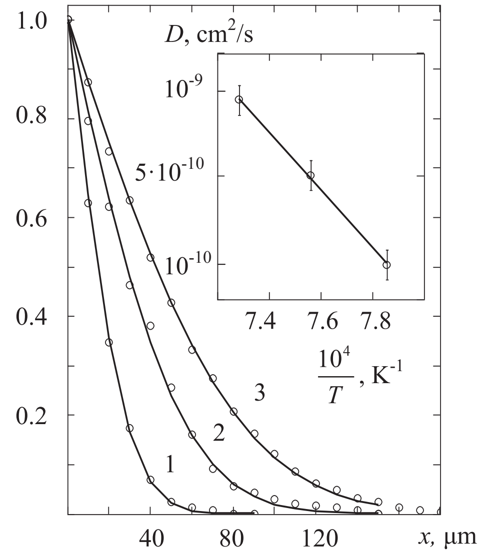

Fig. 3. **Profiles of relative optical density (points in the curve) and diffusion profiles of Ti (solid lines) of ZnS:Ti crystals, samples (1) 3 and (2) 4. The temperature dependence of the Ti diffusivity in ZnS crystals is in the inset.**

The diffusivities of Ti in ZnS crystals at temperature 1270-1370 K were calculated similarly. The temperature dependence of diffusivity $D(T)$, presented in inset to Fig. 3, is described by Arrhenius equation

$$D(T) = D_0 \exp\left(-\frac{E}{kT}\right), \quad (6)$$

where the factor D_0=2.2·10^3 cm^2/s, while the activation energy of diffusion E=2.33 eV. At the crystals annealing temperature of 1270 K the diffusivities of titanium is 10^{-10} cm^2/c. This value is the same order that iron diffusivity in ZnS crystals, which we determined according to the procedure described in [9].

CONCLUSIONS

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

1. The method of titanium diffusion doping of ZnS single crystals was developed. The maximum concentration of titanium impurity determined by the shift of the absorption edge in ZnS:Ti crystals was $5 \cdot 10^{19}$ cm^{-3}.
2. The nature of absorption lines of ZnS:Ti crystals in the visible and IR regions of the spectrum was identified.
3. The diffusivities of titanium in ZnS crystals in the temperature range 1270-1370 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=$2.2 \cdot 10^3$ cm^2/s and *E*=2.33 eV. At 1270 K the diffusivity of Ti is 10^{-10} cm^2/s.

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Abstract

ZnS:Ti 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 titanium concentration is calculated. Nature of optical transitions determining optical properties of ZnS:Ti single crystals in the visible and IR-region of spectrum is identified.

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

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ПОЛУЧЕНИЕ И ОПТИЧЕСКИЕ СВОЙСТВА КРИСТАЛЛОВ ZnS:Ti

Резюме

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

Диффузионный профиль примеси титана определен путем измерения относительной оптической плотности кристаллов в видимой области спектра. Рассчитаны коэффициенты диффузии титана в кристаллах ZnS при температурах 1270-1370 К. При 1270 К коэффициент диффузии титана составляет 10^{-10} см^2/с.

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

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ОТРИМАННЯ І ОПТИЧНІ ВЛАСТИВОСТІ КРИСТАЛІВ ZnS:Ti

Резюме

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

Дифузійний профіль домішки Ti визначався за вимірюваннями відносної оптичної густини кристалів у видимій області спектру. Вперше розраховано коефіцієнти дифузії титану в кристалах ZnS при температурах 1270-1370 К. При 1270 К коефіцієнт дифузії титану становить 10^{-10} см^2/с.

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