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Optical properties of ZnS:Ni crystals obtained by diffusion doping

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ZnS:Ni single crystals obtained by nickel diffusion doping have been investigated. The diffusion was performed from nickel metallic layer in helium and argon atmosphere. The optical density spectra in the 3.8–0.4 eV region have been measured. Basing on the absorption edge shift, the nickel concentration in the studied crystals is calculated. The optical absorption and luminescence spectra of ZnS:Ni crystals are identified.

Исследованы монокристаллы ZnS:Ni, полученные методом диффузионного легирования никелем. Диффузия осуществлялась из металлического слоя никеля в атмосфере гелия и аргона. Исследованы спектры оптической плотности в области 3.8–0.3 эВ. По величине смещения края поглощения определена концентрация никеля в исследуемых кристаллах. Идентифицированы спектры оптического поглощения и люминесценции кристаллов ZnS:Ni.

1. Introduction

The zinc sulfide single crystals doped with transition metal ions are used as active media for the mid-infrared (IR) spectral region lasers. In particular, the effective laser generation in the spectral region of 2.35 μm has been realized in the ZnS:Cr crystals [1]. At the same time, essentially nothing is known about possibility of infrared laser radiation realization using ZnS:Ni crystals.

The ZnS crystal doping during the growing process is difficult because the transitional metal evaporation temperatures exceed considerably that of zinc sulfide sublimation. In [2], we have described the procedure of pure ZnS crystals with cobalt. A method for diffusion doping of ZnS single crystals with nickel is offered in this work that provides crystals with known nickel impurity concentration. The structure of the optical absorption and luminescence spectra for the ZnS:Ni crystals has been studied and identified in the visible and infrared regions. Basing on the optical absorption edge shift, the nickel concentration has been determined.

The purpose of this study is to develop a procedure for diffusion Ni doping of ZnS crystals and to identify the optical absorption and luminescence spectra.

2. Experimental

The samples for the study were prepared by Ni diffusion doping of pure ZnS single crystals. The undoped crystals were obtained by free growth on a ZnS single crystal substrate with the (111) growth plane. No polytypes were discovered in the crystals structure. The method and the main characteristics of the ZnS crystals were described in detail in [3]. The selection of temperature profiles and design of the growth chamber excluded any contact between the crystal and chamber walls. The dislocation

density in the crystals obtained did not exceed 10^4 cm^{-2}.

The crystals were doped by impurity diffusion from a metal Ni layer deposited on the crystal surface. Nickel was deposited on one of the large surfaces of a crystal plate ($10\times5\times1$ mm^3) cut out parallel to the (111) plane. The nickel layer thickness was about 10 μm. The crystals were annealed in He + Ar atmosphere at 1100–1270 K. The diffusion process was 5 h long. After annealing, the ZnS:Ni 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 increased, in contrast with colourless undoped crystals.

The nickel layer remaining on the crystal surface was etched out using hydrochloric acid. Then the large surfaces of the crystal plate were polished. To study photoluminescence, the samples were etched in boiling hydrochloric acid to obtain a mat surface, because the luminescence was examined in the reflected light to eliminate the reabsorbtion influence.

The optical density spectra were measured using a MDR-6 monochromator with 1200, 600, and 325 grooves/mm diffraction gratings. The first grating was used to analyze 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 0.6–0.3 eV one. A FEU-100 photomultiplier was used as a light flow receiver in the visible spectral region, while a FTG-5 phototransistor and a PbS photoresistor working in alternating current mode in middle IR region. The optical density spectra were measured at 77 and 293 K. The optical windows of cryostat chamber used to study the optical absorption were of 3 mm in diameter.

The photoluminescence spectra were measured using an ISP-51 prism spectrograph. The luminescence was excited (at an angle of ~45°) using an EDEV-3LA1 light-emitting diode having the emission spectrum in the visible region of ZnS:Ni crystal impurity absorption. When analyzing the luminescence spectra, the emitted light reabsorbtion was not taken into account.

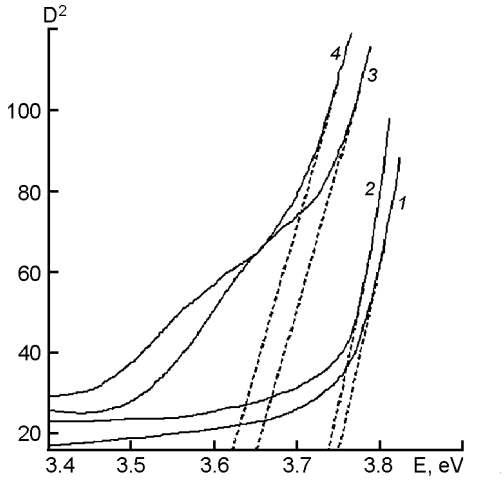

Fig. 1. Optical density spectra of ZnS (*1*) and ZnS:Ni ZnSe (*2–4*) crystals obtained at annealing temperatures (K): 1100 (*2*), 1170 (*3*) and 1220 (*4*).

3. Optical density spectra of the ZnS:Ni crystals in the fundamental absorption edge region

The optical density spectra of the undoped ZnS crystals at 77 K are characterized by absorption edge at 3.75 eV (Fig. 1, curve *1*). No peculiarities were found in the optical density spectra of undoped crystals in 0.30–3.5 eV energy region.

The nickel doping of crystals results in the absorption edge shift towards lower energies (Fig. 1, curves *2–4*). The shift value increases with annealing temperature and is due to by the interimpurity Coulomb interaction. The band gap width variation as a function of impurity concentration was determined in [4] as

Table 1. Calculation results of Ni concentration from ZnS:Ni optical absorption edge shift

Type of crystal	$Bh44\{BE_g$, eV	ΔE_g, meV	N, cm^{-3}
ZnS, initial	3.75	–	–
ZnS:Ni annealed at 1100 K	3.74	10	$2\cdot10^{16}$
ZnS:Ni annealed at 1170 K	3.65	100	$2\cdot10^{19}$
ZnS:Ni annealed at 1220 K	3.62	130	$5\cdot10^{19}$
ZnS:Ni annealed at 1270 K	3.55	200	$2\cdot10^{20}$

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

where ΔE_g is measured in meV; e, electron charge; N, impurity concentration in cm^{-3}; $\varepsilon_s = 8.3$ is ZnS dielectric constant; ε_0, electric constant. The nickel concentration in the studied crystals was calculated from the band gap width changing (see Table 1). The maximum Ni concentration (10^{20} cm^{-3}) was observed for the samples annealed at 1270 K.

4. Absorption and luminescence of ZnS:Ni crystals in the visible spectral region

The ZnS:Ni crystals show a series of absorption lines in the visible region (Fig. 2, curve *1*). In this region, the light absorption increases with Ni concentration. Seven absorption lines at 1.91, 2.01, 2.14, 2.21, 2.38, 2.68, and 2.80 eV are observed in low-doped crystals obtained at 1100 K (Fig. 2, curve *1*). The optical absorption studies in the 77–300 K temperature range has shown that the first seven line positions do not change at temperature increasing. Thus, the indicated absorption lines are caused by intracenter transitions. The high-energy absorption line at 2.80 eV changes its position as the temperature and Ni impurity concentration vary. This line was found in [5] and identified as the charge transfer band. This is also confirmed by a photoconductivity presence in this region.

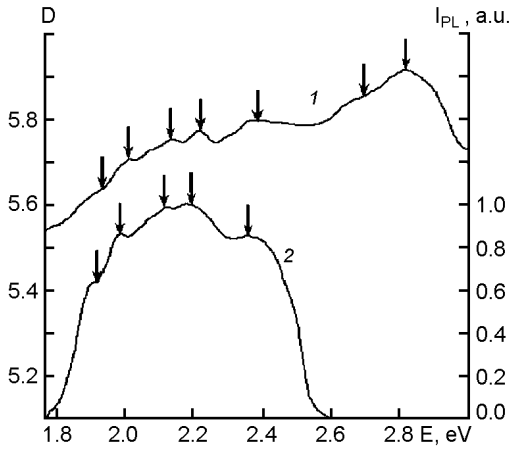

Fig. 2. Optical density (*1*) and photoluminescence (*2*) spectra of ZnS:Ni crystals in the visible region.

Optical transitions in the $ZnS:Ni^{2+}$ crystals are presented in Table 2 that is built basing on our experimental results and calculations of the Ni^{2+} ion energy states for the zinc sulfide cubic lattice. In [6–8], the Ni^{2+} ion energy states are calculated responsible for the visible spectral region absorption. The absorption line at 1.90 eV was observed before in [7].

Table 2. Optical transitions in $ZnS:Ni^{2+}$ crystals

Line No.	Absorption			Luminescence		
	E_{expB}					
1	2.80	2.8–3.1 [5]	$d^8 \rightarrow d^7 + e$	–	–	–
2	2.68	2.70 [6–8]	$^3T_1(F) \rightarrow {}^1A_1(S)$	–	–	–
3	2.38	2.36 [6–8]	$^3T_1(F) \rightarrow {}^1A(G)$	2.36	2.38 [9]	$^1A(G) \rightarrow {}^3T_1(F)$
4	2.21	2.24 [6–8]	$^3T_1(F) \rightarrow {}^1T_1(G)$	2.19	–	$^1T_1(G) \rightarrow {}^3T_1(F)$
5	2.14	2.12 [6–8]	$^3T_1(F) \rightarrow {}^1E(G)$	2.12	–	$^1E(G) \rightarrow {}^3T_1(F)$
6	2.01	–	–	1.99	–	–
7	1.91	1.90 [6–8]	$^3T_1(F) \rightarrow {}^1T_2(G)$	1.89	–	$^1T_2(G) \rightarrow {}^3T_1(F)$
8	1.65	–	–	–	–	–
9	1.60	–	–	–	–	–
10	1.54	1.52 [10, 11]	$^3T_1(F) \rightarrow {}^3T_1(P)$	1.52	1.52 [10]	$^3T_1(P) \rightarrow {}^3T_1(F)$
11	–	1.22 [11, 12]	$^3T_1(F) \rightarrow {}^1E(D)$	–	–	–
12	–	1.18 [11, 12]	$^3T_1(F) \rightarrow {}^1T_2(D)$	–	–	–
13	1.12	1.13 [11, 12]	$^3T_1(F) \rightarrow {}^3A_2(F)$	–	–	–
14	0.56	0.54 [11, 12]	$^3T_1(F) \rightarrow {}^3T_2(F)$	–	–	–

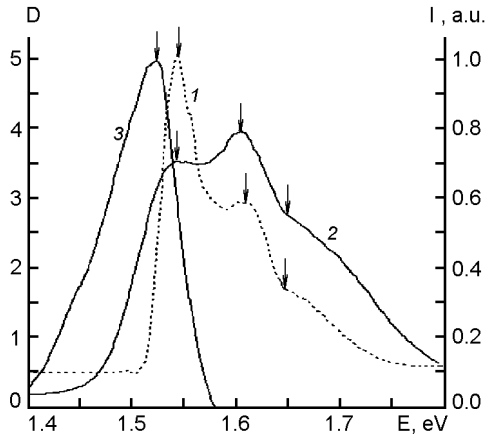

Fig. 3. Optical density (*1*) and photoluminescence (*1*, *2*) spectra of ZnS:Ni crystals in the near IR region measured at 77 (*1*, *3*) and 300 K (*2*).

The luminescence studies of high-doped crystals in the visible spectral region obtained at 1220–1270 K have revealed also a broad nonelementary emission band involving five lines at 1.89, 1.99, 2.12, 2.19, and 2.36 eV at T = 77 K (Fig. 2, curve *2*). The line positions remain unchanged as the temperature increases from 77 to 300 K. Thus, the observed emission lines are related to transitions between the high-energy excited states and the ground state $^3T_1(F)$ of Ni^{2+} ion (Table 2). As is seen in Table 2, the Stokes shift value of luminescence lines in relation to corresponding absorption lines 1.91, 2.01, 2.14, 2.21 2.38 eV is 20 meV. The line of the ZnS:Ni visible emission at 2.38 eV was observed before in [9].

5. Absorption and luminescence of ZnS:Ni crystals in IR spectral region

The nickel doping of crystals has been found result in a series of absorption line in the near IR-region. In all investigated crystals, there are three absorption lines at 1.54, 1.60, 1.65 eV. Fig. 3 (curves *1*, *2*) shows the optical density and photoluminescence spectra of the ZnS:Ni crystals obtained at 1170 K. It is established that the nickel concentration increase results in increased absorption in the observed spectral region. It has been shown that the temperature change from 77 to 300 K does not cause any noticeable shifting of these lines. This testifies to the intracenter character of optical transitions. The absorption line at 1.54 eV was observed before in [10] and, according to calculations of Ni^{2+} ion energy states in the zinc

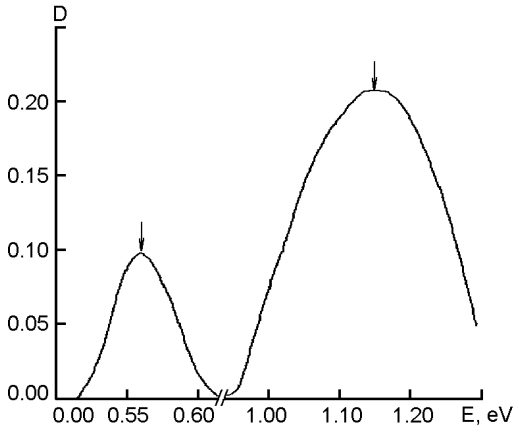

Fig. 4. Optical density spectra of ZnS:Ni crystals in the mid-IR region.

sulfide cubic lattice [11], it is due to the $^3T_1(F) \rightarrow {}^3T_1(P)$ transitions (Table 2). Two other lines are observed for the first time. Those are obviously caused by the transitions to the $^3T_1(P)$ states of the Ni^{2+} ion which are split due to the spin-orbit interaction.

The luminescence investigations in the near IR region exposed also an emission line at 1.52 eV at T = 77 K (Fig. 3, curve *3*). This emission line was observed before in [10] and corresponds to the $^3T_1(P) \rightarrow {}^3T_1(F)$ transitions in Ni^{2+} ion (Table 2). The Stokes shift value of luminescence line at 1.52 eV in relation to the absorption line at 1.54 eV is 20 meV.

The absorption spectra of the ZnS:Ni crystals obtained at 1220 K in the middle-IR region are presented in Fig. 4. The nickel doping results in appearance of absorption bands at 0.56 and 1.12 eV. The crystal optical density increases with nickel concentration and spectral band positions did not shift as the temperature varies from 77 to 300 K. According to the calculations (see Table 2), the absorption line at 0.56 eV is due to the $^3T_1(F) \rightarrow {}^3A_2(F)$ transitions while that at 1.12 eV, to the $^3T_1(F) \rightarrow {}^3T_2(F)$ transitions. The absorption line at 1.13 eV was observed in the ZnS:Ni crystals and the spectral evolution of this line in the ZnSSe solid solution with Se concentration increase was investigated in [12].

It should be noted that as the degree of doping of the crystal increases, the absorption bands are broadened. A similar smoothing of the line structure is observed for the absorption spectra in the near IR region and the visible region. Perhaps this phenomenon is associated with the manifestation of the interimpurity interaction of the Ni^{2+} ions.

6. Conclusions

A procedure of diffusion Ni doping of ZnS crystals has been developed allowing to obtain crystals with a different concentration of nickel impurity. The concentration of nickel impurity in the studied crystals is determined basing on the absorption edge shifting. The highest Ni impurity concentration in the ZnS:Ni crystals obtained at 1270 K is estimated to be 10^{20} cm^{-3}. The nature of absorption and emission lines of the ZnS:Ni crystals in the visible and IR spectral regions has been identified.

References

1. I.T.Sorokina, E.Sorokin, S.Mirov et al., *Opt. Lett.*, **27**, 1040 (2002).
2. Yu.F.Vaksman, Yu.A.Nitsuk, V.V.Pavlov et al., *Photoelectronics*, **16**, 33 (2006).
3. Yu.V.Korostelin, V.I.Kozlovsky, A.S.Nasibov, P.V.Shapkin, *J. Cryst. Growth*, **197**, 449 (1999).
4. Yu.I.Ukhanov, Optical Properties of Semiconductors, Nauka, Moscow (1977) [in Russian].
5. V.I.Sokolov, *Fiz. Tekhn. Polupr.*, **28**, 545 (1994).
6. S.A.Kazansky, A.I.Ryskin, G.I.Hilko, *Fiz. Tverd. Tela*, **10**, 2417 (1968).
7. H.A.Weakliem, *J. Chem. Phys.*, **36**, 2117 (1962).
8. O.Madelung, Festkorpertheorie III. Lokalizierte Zustande, Springer-Verlag, New York (1972).
9. P.Yang, M.Lu, D.Xu et al., *Opt. Mater.*, **24**, 497 (2003).
10. G.Roussos, H.-J.Schulz., *J. Luminescence*, **31–32**, 427 (1984).
11. A.Zunger, *Solid State Phys.*, **39**, 276 (1986).
12. T.P.Surkova, M.Godlewski, K.Swiatek et al., *Physica B*, **273–274**, 848 (1999).

Оптичні властивості кристалів ZnS:Ni, отриманих дифузійним легуванням

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Досліджено монокристали ZnS:Ni, отримані методом дифузійного легування нікелем. Дифузія здійснювалася з металічного слою нікелю в атмосфері гелію та аргону. Досліджено спектри оптичної густини в області 3.8–0.3 еВ. За величиною зсуву краю поглинання визначено концентрацію нікелю в кристалах, що досліджувалися. Ідентифіковано спектри оптичного поглинання і люмінесценції кристалів ZnS:Ni.