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DIFFUSION OF TRANSITION-METAL IONS (Fe, Ni) IN ZINC CHALKOGENIDES

The ZnS, ZnSe, ZnTe single crystals doped with iron and nickel are investigated. The diffusion doping is carried out from metallic nickel and powderlike iron in helium and argon atmosphere. The optical density spectra are investigated in the wavelength range of 2–3.8 eV. From the value of the absorption edge shift, the nickel and iron concentrations in crystals under investigation is determined. It is shown that nickel and iron doping results in appearance of absorption lines in the visible spectral region.

The nickel and iron impurity diffusion profile is determined by measuring the relative optical density of crystals in the visible spectral region. The diffusivities of nickel and iron in ZnS, ZnSe, ZnTe crystals are calculated at temperatures of 1020–1320 K.

The last years wide interest was paid to zinc-chalcogenides (ZnS, ZnSe, ZnTe) due to their new application fields. The ZnS and ZnSe crystals doped with transitional metals have been used as active media and gates in lasers of medium infrared (IR) radiation range [1,2]. The ZnTe crystals doped with iron and nickel are perspective materials for a photorefraction [3]. Therefore the fabrication of zinc chalcogenides crystals doped with transition-metal ions is actual problem.

There are two basic methods of zinc-chalcogenides doping with transition-metal ions. The first one is doping during the growing process from vapor phase and the second one is diffusive doping. In [4] the ZnSe:Fe and ZnSe:Ni single crystals were obtained from a vapor phase by free growth on a single crystal substrate with the use of chemical transport in hydrogen.

The advantage of the diffusion doping is the exact adjusting of profile and level of doping. In [2] the ZnSe:Fe crystals are obtained by the doping from a solid phase metallic source (a metallic layer). The diffusion doping in the iron vapor is carried out in [5]. Duration of diffusion process and small iron impurity concentrations in the obtained crystals are the lacks of these diffusion doping methods.

In this study we describe the diffusion technique of doping which allows to obtaining zinc-chalcogenides single crystals with predicted iron and nickel-impurity concentration. The structure of optical absorption spectra has been studied and identified in the visible region. Basing on the optical absorption edge shift, the nickel and iron concentration has been determined. The analysis of the relative optical density profile in the visible region enabled us to calculate the diffusivity of nickel and iron in ZnS, ZnSe, ZnTe crystals.

The purpose of this study is the development of the diffusion technique of zinc-chalkogenides crystals doping with iron and nickel and the determination of the diffusivity.

1 EXPERIMENTAL

The samples for the study were prepared by nickel and iron diffusion doping of pure ZnS, ZnSe and ZnTe single crystals. The undoped crystals were obtained by free growth on a ZnSe single crystal substrate with the (111) growth plane. The method and the main characteristics of the ZnS, ZnSe and ZnTe crystals were described in details in [6]. 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 ZnS:Ni, ZnSe:Ni and ZnTe:Ni crystals were doped by diffusion of impurity from the metallic nickel layer deposited on the crystal surface in the He + Ar atmosphere. The crystals were annealed at the temperatures T_a = 1020–1270 K. The diffusion process time was about 5 hours. After annealing the crystals changed the color: the crystals ZnS:Ni got a yellow color, ZnSe:Ni was light-brown, and ZnTe:Ni was dark-brown.

The first experiments with Fe diffusion were carried out according to a procedure similar for Ni diffusion. The crystals were doped via impurity diffusion from a metal Ni layer deposited on the crystal surface in an evacuated quartz cell. It was found that at 1220 K, the metal Ni layer ~10 mkm dissolved completely in the crystals in the span of no longer than 30 min. The optical absorption spectra showed that the obtained crystals were lightly doped. However, these crystals were found to be convenient objects for studying the optical absorption spectra.

To obtain heavily doped crystals the diffusion by impurity from metal powderlike Fe in He + Ar atmosphere was carried out. In order to avoid etching of crystals, powderlike ZnSe in the ratio 1:2 was added to the Fe powder. Crystals were annealed in evacuated quartz cells at temperatures from 1120 to 1320 K. The duration of the diffusion process was 10–30 hours. After annealing the ZnS:Fe crystals acquired a yellow-brown color, ZnSe:Fe was red-brown, and the ZnTe:Fe crystals were dark-brown.

The diffusion of nickel and iron was carried out under conditions, where the impurity concentration in the source (the metallic nickel layer) remained almost constant. In this case, the solution of the Fick diffusion equation for the one dimensional diffusion has the form

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

where C_0 is the activator concentration near the surface, the symbol "erf" designates the error function (the Gauss function), D is the diffusivity, x is the coordinate, and t is the time.

The optical density spectra in the visible region were measured by means of an MDR-6 monochromator with diffraction gratings 1200 lines/mm. A FEU-100 photomultiplier was used as a light flow receiver. The optical density spectra were measured at 77 and 300 K.

To measure the diffusion profile of the impurities, a thin (0.2–0.4 mm) plate of the crystal was cleaved in the plane parallel to the direction of the diffusion flow. The measurements of the optical density profile of the Ni and Fe-doped crystals were carried out using an MF-2 microphotometer. This device provides the optical density measurement with the step 10 mkm in the direction of the diffusion flow. In this case, the integrated optical density in the spectral range 2.0–2.8 eV was measured.

2. OPTICAL DENSITY SPECTRA IN THE VISIBLE REGION

The optical density spectra (D* — optical density) of the ZnS:(Fe,Ni), ZnSe:(Fe,Ni), ZnTe:(Fe,Ni) crystals have been measured. The iron and nickel doping of crystals results in the absorption edge shift toward lower energies. The shift value increases with annealing temperature. The band gap varies due to the Coulomb interaction between impurity states. Thus correlation between ΔEg (in meV) and impurity concentration N (in sm^{-3}) is determined by the relation:

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

Table 1

Results of calculation of doping impurities concentrations in crystals under investigation.

Annealing temperature, T_a, K	Impurity concentration, cm^{-3}					
	Ni-doped crystals			Fe-doped crystals		
	ZnS:Ni	ZnSe:Ni	ZnTe:Ni	ZnS:Fe	ZnSe:Fe	ZnTe:Fe
1020	---	---	$3\cdot10^{17}$	---	---	---
1070	---	$2\cdot10^{17}$	$4\cdot10^{18}$	---	---	$2\cdot10^{17}$
1120	$4\cdot10^{17}$	$2\cdot10^{18}$	$6\cdot10^{19}$	---	---	$3\cdot10^{18}$
1170	$2\cdot10^{19}$	$4\cdot10^{19}$	---	$2\cdot10^{16}$	$3\cdot10^{16}$	$4\cdot10^{19}$
1220	$5\cdot10^{19}$	$8\cdot10^{19}$	---	$2\cdot10^{17}$	$2\cdot10^{17}$	$8\cdot10^{19}$
1270	$2\cdot10^{20}$	10^{20}	---	$7\cdot10^{17}$	$8\cdot10^{17}$	---
1320	---	---	---	$9\cdot10^{18}$	$2\cdot10^{18}$	---

where e, electron charge, ε_s is the static permittivity of ZnS, ZnSe or ZnTe. Using the shift of the band gap, we calculated the nickel and iron concentration in the studied crystals (see Table 1).

In the visible spectral region the crystals doped with nickel feature had series of absorption lines, caused by the intrastate transitions from the lower $^3T_1$(F)-state to the excited G-states in the limit of the Ni^{2+} ion.

The crystals doped with iron in the visible region are characterized by the series of absorption lines, which are due to intrastate transitions from the basic state ^5E(F) on the high-power excited states of Fe^{2+} ion. The absorption spectra of undoped ZnSe crystals and ZnSe:Fe and ZnSe:Ni crystals, doped at temperature 1170 K presented in Fig. 1 as an example. The investigation of optical properties of zinc chalkogenides doped with Fe and Ni were described in details in [7,8].

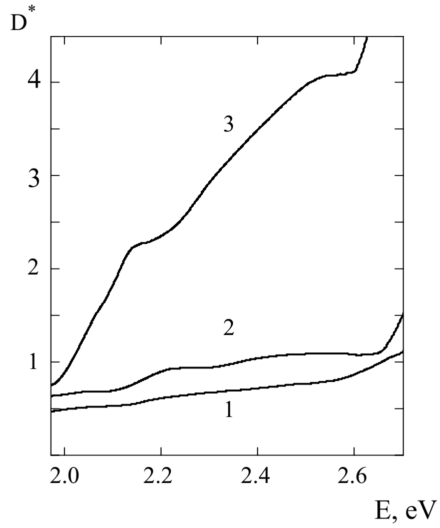

Fig. 1. Spectra of the optical-density D* in the visible region of (1) ZnSe, (2) ZnSe:Fe and (3) ZnSe:Ni crystals.

3. DETERMINATION OF NICKEL AND IRON DIFFUSIVITY IN THE ZNS, ZNSE, ZNTE CRYSTALS

The presence of the absorption bands in the visible range (Fig. 1) indicates the possibility of determining the diffusion profile of the impurity by measuring the relative optical density (Δ). This magnitude is the function of the coordinate x in the 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 the crystal as a function of the coordinate x, $D^*(0)$ is the optical density of the crystal in the near surface layer with the coordinate $x = 0$, and $D^*(\infty)$ is the optical density of the crystal in the region where the impurity concentration is negligibly low (crystal is undoped). The selected definition of the relative optical density allows us to compare the dependence $\Delta(x)$ with the concentration profile of the impurity $C(x)/C_0$ calculated by formula (1).

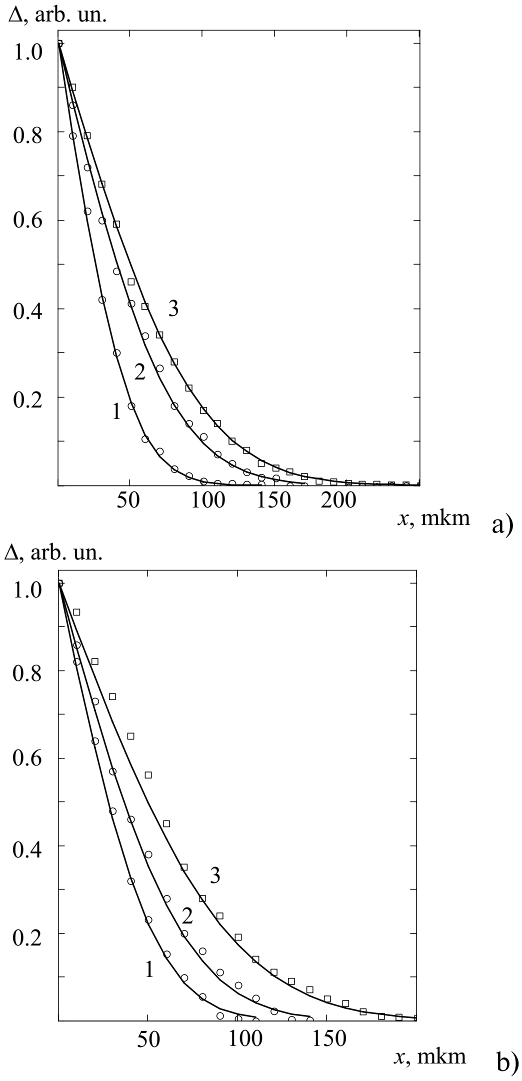

Fig. 2. Profiles of relative optical density (points in the curves) and diffusion profiles (solid lines) of Ni impurity in the ZnTe:Ni crystals (a) and Fe impurity in the ZnTe:Fe crystals. The diffusion temperature is 1070 (1), 1120 (2), 1170 K(3).

In Fig. 2. we show relative optical density profiles (points on curves) and diffusive profiles (solid lines) of nickel impurities in the ZnTe:Ni crystals and iron in the ZnTe:Fe crystals. By means of selection of diffusivity in (1), we obtained good agreement between profiles of the relative optical density and impurities concentration in investigated crystals. The diffusivities of Ni and Fe in the ZnS, ZnSe, ZnTe crystals at temperatures T_a=1020–1320 K were calculated similarly. In the Table 2 presented the nickel and iron diffusivities in the investigated crystals at the temperature T_a=1220 K. It is established that nickel diffusivities are two orders of magnitude higher than iron diffusivities in all types of the investigated crystals.

The temperature dependence of the difusivities (fig. 3) is described by the Arrhenius equation

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

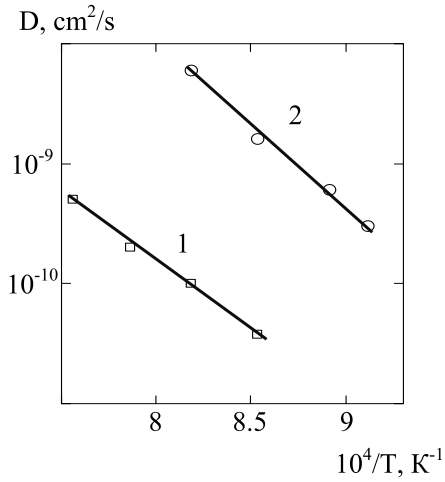

Fig. 3. The temperature dependences of iron diffusivities in ZnS:Fe crystals (1) and nickel diffusivities in ZnS:Ni (2) crystals.

Thus, from temperature dependences of nickel and iron diffusivities the diffusion process activation energies E_a and the preexponential factor D_0 in the Arrhenius equation were calculated for the proper crystals (see Table 2). Comparing obtained the diffusion process activation energies, it was established that in the ZnSe crystals both for nickel impurity and for the iron impurity the diffusion process activation energy has maximal value.

Table 2

The results of diffusion process investigations

Type of the crystal	Ni-doping			Fe-doping		
	D, cm^2/s at 1220 K	D_0, cm^2/s	E_a, eV	D, cm^2/s at 1220 K	D_0, cm^2/s	E_a, eV
ZnS	$4\cdot10^{-7}$	10^3	2.6	$8\cdot10^{-11}$	0.16	2.2
ZnSe	$7\cdot10^{-7}$	$8.8\cdot10^6$	3.5	$1\cdot10^{-10}$	$3.3\cdot10^3$	2.9
ZnTe	$8\cdot10^{-7}$	0.03	1.5	$4\cdot10^{-9}$	$5.6\cdot10^{-3}$	1.6

It evidences that in crystals ZnSe diffusion of transitional metal ions is due to dissociative mechanism. High activation energies of 4.45 eV and 3.8 eV were obtained for a diffusive process in the ZnSe:Cr and ZnSe:Co crystals [9,10].

4. CONCLUSION

The investigations enable us to draw the following conclusions.

The diffusion nickel and iron doping technique is developed for ZnS, ZnSe, ZnTe single crystals. Concentrations of doping impurities in the investigated crystals are determined.

It is shown that the diffusion profile of a nickel and iron impurities can be determined by measuring the relative optical density of crystals in the visible region.

The nickel and iron diffusivities in ZnS, ZnSe, ZnTe crystals are calculated in the temperature range of 1020–1320 K. The analysis of the temperature dependences $D(T_a)$ enables us to determine the activation energies E_a of diffusion processes in the proper crystals and the factors D_0 from the Arrhenius equation.

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Abstract

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Key words: zink chalkogenides, diffusion doping, optical-density, diffusivity.

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ДИФФУЗИЯ ИОНОВ ПЕРЕХОДНЫХ МЕТАЛЛОВ (FE, NI) В ХАЛЬКОГЕНИДАХ ЦИНКА

Резюме

Исследованы монокристаллы ZnS, ZnSe, ZnTe, легированные железом и никелем. Диффузионное легирование осуществлялась из металлического никеля и порошкообразного железа в атмосфере гелия и аргона. Исследованы спектры оптической плотности в области энергий 2–3.8 эВ. По величине смещения края поглощения определены концентрации никеля и железа в исследуемых кристаллах. Показано, что легирование никелем и железом приводит к появлению полос поглощения в видимой области спектра.

Диффузионный профиль примеси никеля и железа определен путем измерения относительной оптической плотности кристаллов в видимой области спектра. Рассчитаны коэффициенты диффузии никеля и железа в кристаллах ZnS, ZnSe, ZnTe при температурах 1020–1320К.

Ключевые слова: халькогениды цинка, диффузионное легирование, оптическая плотность, коэффициенты диффузии.

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ДИФУЗІЯ ІОНІВ ПЕРЕХІДНИХ МЕТАЛІВ (FE, NI) В ХАЛЬКОГЕНІДАХ ЦИНКУ

Резюме

Досліджено монокристали ZnS, ZnSe, ZnTe, леговані залізом та нікелем. Дифузійне легування виконувалось з металевого нікелю та порошкоподібного заліза в атмосфері гелію та аргону. Досліджено спектри оптичної густини в області енергій 2–3.8 еВ. За величиною зсуву краю поглинання визначені концентрації нікелю і заліза в досліджуваних кристалах. Показано, що легування нікелем і залізом призводить до виникнення смуг поглинання в видимій області спектру.

Дифузійний профіль домішок нікелю і заліза визначено шляхом вимірювання відносної оптичної густини кристалів в видимій області спектру. Розраховані коефіцієнти дифузії нікелю і заліза в кристалах ZnS, ZnSe, ZnTe при температурах 1020–1320К.

Ключові слова: халькогеніди цинку, дифузійне легування, оптична густина, коефіцієнти дифузії.