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Photostimulated Ga diffusion in zinc sulfide

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Effect of coherent illumination (using LGI-23 and LGN-222 lasers) of ZnS powders during thermal annealing on zinc sulfide structure properties and on Ga diffusion in ZnS has been studied using photoluminescence method. The photostimulated Ga diffusion in ZnS is shown to be more efficient when the material is illuminated at $\lambda = 632.8$ nm as compared to the UV illumination. Illumination by He–Ne laser during the annealing results in appearance of a band at $\lambda_{max} = 470$ nm in the photoluminescence spectrum as well as in an afterglow (10 s).

Проведены фотолюминесцентные исследования влияния когерентного светового облучения (использовалось излучение лазеров ЛГИ-23, ЛГН-222) порошков ZnS в процессе их термического отжига на структурные свойства сульфида цинка и диффузию Ga в ZnS. Показано, что стимулированная диффузия Ga в ZnS более успешно реализуется при облучении материала излучением с $\lambda = 632.8$ нм по сравнению с УФ излучением. Облучение He–Ne лазером в процессе отжига приводит к появлению в спектре ФЛ полосы $\lambda_{max} = 470$ нм, а также послесвечения (10 сек).

Today, a big attention is given to study of ionizing and micro-wave irradiation influence on degradation processes in solids (metals, alloys, and semiconductors). The studies of light illumination influence on semiconductor properties are still actual. There are few works aimed at photostimulated diffusion and the data presented are often contradictory [1–4]. However, studies of photostimulated diffusion and its features has a considerable scientific and practical interest. The purpose of this work is studying of the effect of coherent light illumination of ZnS powder during thermal annealing on its luminescence and structure properties as well as on Ga diffusion in ZnS.

Investigated ZnS powders (ETO.035.295 TU) were annealed at 800°C under limited access of environmental atmosphere in the presence of Ga metal at simultaneous illumination either by $\lambda = 337.1$ nm (LGI-23 laser) or $\lambda = 632.8$ nm (LGN-222 laser). Powders were investigated for structural changes of the lattice as well as for the possibility of Ga diffusion under light illumination. The LGN-222 power was about 50 mW/cm^2, the LGI-23 pulse had about 1.5 kW/cm^2. The laser and the furnace were switched on and off simultaneously. The sample heating due to light irradiation was neglected since it was within the accuracy limits of the annealing temperature control. The annealing was carried out within time intervals of 30 to 60 min in a tubular quartz furnace with temperature control accuracy of at least ±10°C. The furnace heating time up to the annealing temperature was 10 to 15 min, the cooling time about 2 h. The reference samples were annealed in the same temperature and time conditions but without external irradiation. To restrict the environmental atmosphere access, a gas seal made from activated carbon was used. The photoluminescence (PL) spectra were recorded using a KSVU-23 with nitrogen laser ($\lambda = 337.1$ nm) as the exciting source. Investigations were made at room temperature. PL spectra were measured immediately after samples annealing and cooling to the room temperature.

It is seen from Fig. 1 that the PL spectrum of initial (unannealed) ZnS powder is a rather broad complex band peaked about λ_{max} 500 nm and with half-width of about

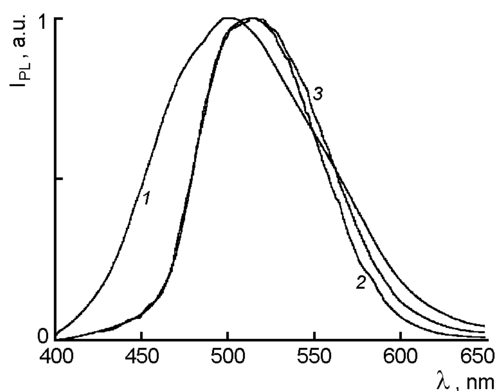

Fig. 1. PL spectra of ZnS powders: initial (*1*), annealed at 800°C (*2*), annealed at 800°C under UV irradiation (*3*).

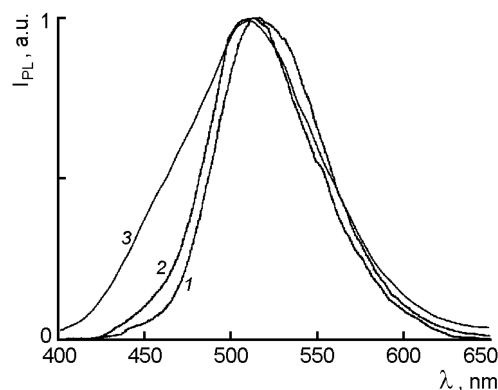

Fig. 2. PL spectra of ZnS:Ga powders: annealed at 800°C (*1*); annealed at 800°C under UV irradiation (*2*); annealed at 800°C under illumination at λ = 632.8 nm (*3*).

100 nm. Thermal annealing of that powder at T = 800°C results in the half- width reduction down to about 80 nm and in a shift of the main PL maximum (λ_{max} = 515 nm). These changes in the PL band character are due mainly to the extinguish of lines forming its short-wavelength edge, what results eventually in the maximum position shift of the band as a whole. In non-activated ZnS, the λ_{max} = 515 nm band is ascribed to the emission of self-activated ZnS [5] as well as to changes in sulfur sublattice [6, 7]. The spectral redistribution of PL intensity resulting from anneal is caused by several factors. Sulfur is well-known to be the volatile component of zinc sulfide [8]. Therefore, heat influence on ZnS results in sulfur desorption and increased concentration of sulfur vacancies (V_S). The powder annealing causes also removal of radicals from the material surface [9].

UV illumination of ZnS powder during annealing results only in an insignificant increase of the PL spectrum half-width up to about 88 nm. This increase is due (as is seen in Fig. 1) to the shift of long-wavelength spectrum edge towards longer wavelengths by about 8 nm, the short-wavelength edge position remaining unchanged. The PL maxima are coincident in both above cases.

The Ga metal presence at the ZnS powder annealing results in the PL band half-width reduction down to 70 nm due to decreasing of its short-wavelength edge. This, in turn, results in that the PL maximum is shifted by 5 nm (λ_{max} = 520 nm). The comparative analysis of PL spectra for ZnS powders (Fig. 2) annealed in the presence of Ga metal under simultaneous coherent illumination has shown that the PL band maxima (λ_{max} = 510 nm) are the same as well as their long-wavelength edges. Moreover, the coherent irradiation during the annealing results in that the whole spectrum shifts by 10 nm towards shorter wavelengths, while the UV illumination without Ga metal causes only the long-wavelength edge shift without PL maximum shift. In literature [7], the bands peaked at 505 to 510 nm are ascribed to formation of a $ZnO(ZnS)_x$ solid solution but only at x < 0.3.

While the PL maxima (λ_{max} = 510 nm) are the same and long-wavelength edges, the PL spectrum half-width increases up to 100 nm in the case of He–Ne laser action (Fig. 2, curve 3). This is due to increased intensity of bands forming the short-wavelength PL edge. Moreover, the PL edge shape points to the presence of at least one line in the region of 470 nm. In [10, 11], this line is ascribed to Ga presence in ZnS. It has been supposed [10, 11] that the CA center model in non-activated ZnS may be similar to that of blue emission centers in ZnS activated with 3B subgroup elements. Emission of those centers is due to recombination of electrons trapped at shallow Ga^*_{Zn} donors with holes at A centers of $\{V''_{Zn}Ga^*_{Zn}\}'$ type. In non-activated ZnS, the CA center may include interstitial Ga as the Zn_i donor and A center $\{V''_{Zn}Zn^*_i\}'$ as acceptor.

Afterglow (up to 10 s) is one more feature of ZnS powders annealed in the presence of Ga under He–Ne laser irradiation. This allows to conclude that such a treatment of ZnS powders results in formation of deep traps (or activation those present in

the material) capable of capture a fraction of excited carriers. According to calculations presented in [12], the trap level depth E_τ at room temperature can be estimated to be about 0.5 eV in this case. Thus, the UV illumination of ZnS powder during its annealing can be concluded to result neither in any essential changes in the PL properties of ZnS nor in Ga diffusion activation into ZnS lattice. The possible reason is that the UV energy is absorbed essentially completely within a very thin surface ZnS layer and so does not penetrate into the material volume. The LGI-23 emission is higher than the fundamental absorption edge even at room temperature, as at 800°C it exceeds the absorption edge by about 0.5 eV.

At the temperature increase during the annealing, the band gap of the material varies as

$$E_g = E_{g0} - k\Delta T; \qquad (1)$$

where k is the bias factor, $k = 6.0\times10^{-4}$ eV·K^{-1} [5].

Knowing the band gap width at 300 K, $E_{g0} = 3.709$ eV [5], and using (1), the E_g for 1073 K can be estimated as 3.245 eV. There is another situation as ZnS powder is illuminetad by a He–Ne laser during the annealing. The PL studies show an increased Ga diffusion rate in ZnS. This effect can be elucidated by the model where electrons (or holes) localized at both surface and volume structure defects act as Ga trapping centers. The illumination causes changes in the value of the ionization of the structure defects, in other words, the electron and hole occupancy of corresponding local levels. Thus, the trapping center concentration becomes changed and, as a consequence, the material surface absorbability.

To conclude, the photostimulated Ga absorption in ZnS is more efficient under illumination by $\lambda = 632.8$ nm light as compared to that at UV illumination.

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Фотостимульована дифузія Ga у сульфіді цинку

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Проведено фотолюмінесцентні дослідження впливу когерентного світлового опромінення (використовувалось випромінювання лазерів ЛГИ-23, ЛГН-222) порошків ZnS у процесі їх термічного відпалу на структурні властивості сульфіду цинку і дифузію Ga у ZnS. Показано, що стимульована дифузія Ga у ZnS більш успішно реалізується при опроміненні матеріалу випромінюванням з $\lambda = 632.8$ nm у порівнянні з УФ випромінюванням. Опромінення He–Ne лазером у процесі відпалу приводить до проявлення в спектрі ФЛ смуги $\lambda_{max} = 470$ нм, а також післясвітіння (10 сек).