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BANDFILLING EFFECT IN GaSe AND InSe AT HIGH OPTICAL EXCHANGE LEVELS

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The absorption and luminescence spectra of thin films of gallium and indium monoselenide under the action of laser radiation are experimentally investigated. It is shown that the edge of the absorption band in the studied samples is due to direct optical transitions. The band gap, GaSe and InSe, determined from the $\alpha^2 \sim f(h\nu)$ dependence turned out to be 2.03 eV and 1.32 eV, respectively. At low excitation intensities by the 2nd harmonic of the YAG: Nd laser, luminescence is observed in the region of the edge of the absorption band. At high levels of optical excitation in the short-wave region of the spectrum, a narrow luminescence line with a half-width of ~ 10 A^0 was detected. The most possible mechanism of the observed radiation can be the effect of filling the zones with laser radiation.

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1. Introduction

It is known that, layered III-chalcogenides are van der Waals crystals having direct-band gaps in the visible (GaSe) and near infrared (InSe). Thanks to their optical properties and controllable n- or p-type doping [1], these materials possess significant promise for van der Waals heterostructures, and will enable a range of band alignments and potential profiles when combined with graphene and other 2D crystals. In contrast to transition metal dichalcogenides (TMDCs) where light emission occurs only in films with a single unit cell thickness [2 – 4], III-VI materials are bright light emitters in a range of thicknesses [5, 6] and offer useful properties for applications [2, 7, 8] in the emerging 2D materials-based technology.

In this work, we investigated the luminescence spectra of thin films of GaSe and InSe under the action in a wide range of intensity of optical excitation.

2. Samples and experimental methods

Bulk GaSe and InSe studied in this work was grown by the Bridgman-Stockbarger method. InSe and GaSe films were exfoliated from bulk using a mechanical cleavage method. The thickness of the studied samples was 30-100 microns.

Pulsed Nd: YAG lasers equipped with built-in second and third harmonic generators capable of generating 1064, 532 and 355 nm wavelengths and a dye laser with tunable wavelengths (594-643) nm were used as the light source. The laser-pulse duration was 3 ns with a maximum output power density of about 12 MW/cm^2. The absorption and photoluminescence spectra of GaSe and InSe were studied using an M833 double-dispersive automated monochromator equipped with a computer controller and photodetector capable of registering radiation in the range of wavelengths from 350 to 2000 nm.

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3. Experimental results and discussion

Fig. 1 shows the absorption spectra of GaSe crystals at low (curve 1) and high (curve 2) levels of optical excitation dye laser. As can be seen from the figure, at high levels of excitation, a decrease in the absorption near the band gap occurs and at the same time a shift of the edge of the absorption band towards high energies of ~ 40 meV.

Fig. 2 shows the luminescence spectra of thin GaSe and InSe films under the action of ordinary (non-laser) light. As can be seen from the figure, the maximum radiation of GaSe corresponds to the wavelength λ=623 nm. In contrast to GaSe, the luminescence spectrum of InSe is located in the near IR region with a maximum λ=935 nm.

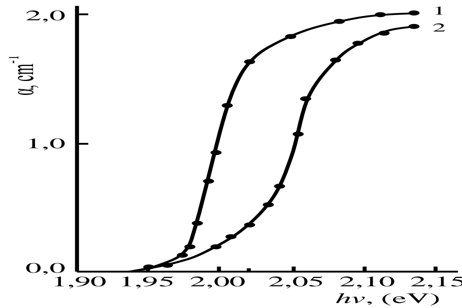

Fig. 1. The absorption spectra of GaSe crystals at low (3.5 MW/cm², curve 1) and high (12 MW/cm², curve 2) excitation intensities.

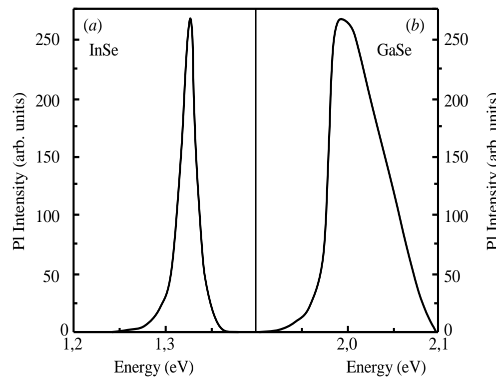

Fig. 2. The luminescence spectra of thin InSe(a) and GaSe (b) films under the action of ordinary light (non-laser).

Fig. 3 shows the luminescence spectra of thin GaSe films at various excitation levels. As can be seen from the figure, at low excitation levels (~ 0.1 MW/cm²), the emission band with a maximum of 623 nm is present in the spectrum (Fig. 3, a). As the pump power increases (~ 3.5 MW/cm²), a new emission line with a maximum of 613 nm appears in the short-wave region of the spectrum, 10 meV below the initial emission line (Fig. 3b). At very high excitation levels (~ 8.5 MW/cm²), only the short-wavelength emission band dominates the emission spectrum (Fig. 3, c). It should be noted a rather narrow band of the short-wave line (~ 15 Å) compared to the emission band with a maximum at 623 nm.

The luminescence spectra of thin InSe films are in the near infrared region. At low levels of optical absorption in the emission spectrum there is only one emission line with a maximum λ=935 nm (Fig. 4, a). At high excitation levels (~ 8 MW/cm²), a short-wavelength emission line with a maximum λ=920 nm appears in the spectrum, which dominates the spectrum with increasing pump power (Fig. 4, b).

This results in filling the states near the bottom of the conduction band by electrons and

the top of the valence band by holes. The schematics of the bandfilling process is shown in Fig. 5.

The simultaneous availability of an electron and a hole state with momentum k is determined by the so-called bandfilling factor,

$$A(\varepsilon)= 1 - f_e(\varepsilon) - f_h(\varepsilon) \quad (1)$$

where f_e and f_h are the Fermi functions for the electrons and holes, respectively. The bandfilling factor arises from the consideration that for a valence-to-conduction-band (v→c) transition to occur, the valence–band state has to be filled by an electron (~f_v) and the conduction-band state has to be empty (~$1-f_c$), so the transition rate is proportional to the product,

$$A_{v\to c} = f_v\,(1- f_c\,) \quad (2)$$

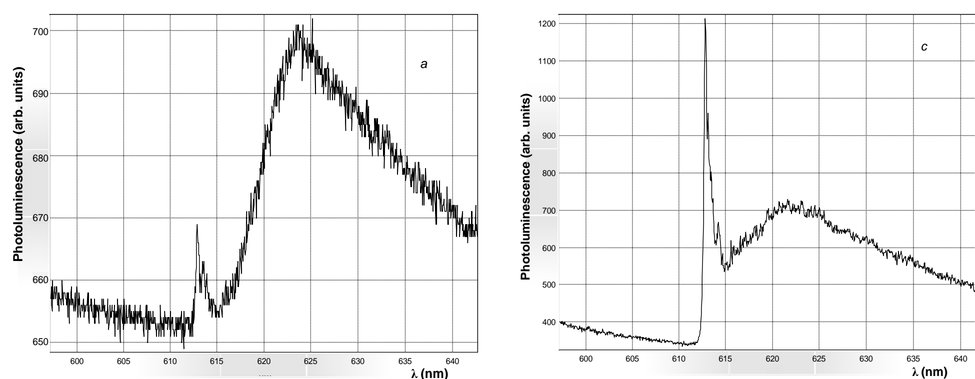

Fig. 3. Luminescence spectra of thin GaSe films by the 2-nd harmonic of a YAG: Nd laser at different levels of optical excitation I (MW/cm^2): a-1.2; b -9.4.

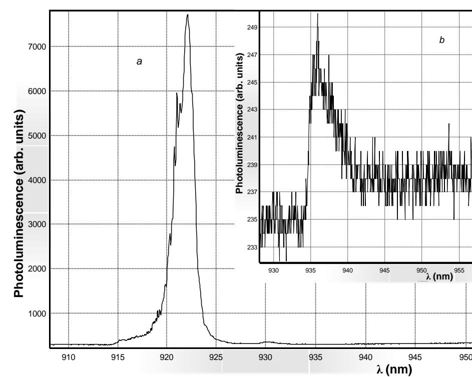

Fig. 4. The luminescence spectra of thin InSe films by the 2nd harmonic of a YAG: Nd laser at different levels of optical excitation I (MW/cm^2): a - 1,2; b - 10.0.

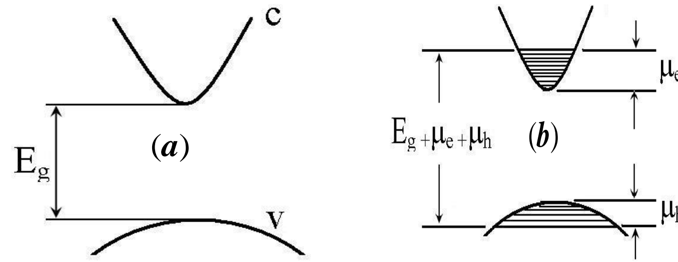

Fig. 5. Schematic representation of optical absorption due to the bandfilling effect in semiconductor crystals. (a) The semiconductor band structure in the absence of electron-hole pairs. (b) The bands when a large electron-hole density is generated, causing filling of the bands near their extrema.

Furthermore, to obtain the net transition rate, one has to subtract the inverse process (i.e., the conduction-to-valence-band-transition rate (c→ v) that describes carrier recombination)

$$A_{c\to v} = f_c\,(1- f_v\,) \tag{3}$$

since it leads to a reduction of the bandfilling. Subtracting Eq. (3) from (2) and using f_v=1- f_h yields Eq. (1). . Knowing the concentration of nonequilibrium carriers generated by laser light, it is possible to determine the height of the filling zones ΔE:

$$\Delta n = \frac{8\pi}{3h^3}(2m_e\Delta E)^{3/2} \tag{4}$$

Using the values of the effective mass for GaSe ($m_h = 0{,}5m_0$)] and knowing the concentration of nonequilibrium carriers ($\Delta n = 4{,}5\times 10^{19}$ cm^{-3}), using equation (1) can be determined ΔE. The values obtained are in good agreement with the observed magnitude of the shift (~ 40 meV) of the GaSe emission line (see Fig. 3).

In InSe, the shift of the emission line in InSe (ΔE=20 meV) is two times smaller compared to GaSe (see Fig. 4). Estimates according to formula (4), taking into account the value of the effective mass for InSe ($m_h = 0{,}15m_0$), shows that a non-equilibrium carrier concentration of $\Delta n \approx 7.5\times10^{17}$ cm^{-3} is required for an offset of ~ 20 meV. This suggests that the curvature of the bottom of the conduction band of InSe is significantly greater than in GaSe.

4. Conclusions

GaSe and InSe thin films are obtained by mechanical detachment of a crystal grown by the Bridgman-Stockbarger method. At high levels of optical excitation in the luminescence spectra of the samples studied, luminescence exceeding the band gap by an amount of 20–40 meV was detected. The concentration of non-equilibrium carriers created by laser radiation is determined $\Delta n=4.5\times10^{19}$ cm^{-3}. Estimates show that filling the InSe conduction band by 20 meV requires concentration of nonequilibrium carriers ~ 7.5×10^{17} cm^{-3}, and in the case of GaSe filling the band by 40 meV requires ~ 1.2×10^{19} cm^{-3} concentrations.

Acknowledgements

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