Semiconductor physics

Some optoelectronic properties of $FeGaInSe_4$ crystals under laser excitation

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Abstract. Photoconductivity and photoluminescence of layered $FeGaInSe_4$ crystals at high levels of optical excitation have been studied. It has been found out that decrease in the lifetime at high excitation intensities is due to the high concentration of non-equilibrium charge carriers generated by high-power laser radiation. The linear nature of the lux-ampere characteristic of photoconductivity is due to the transition of carriers from the valence band to the conduction band when $FeGaInSe_4$ crystals are excited by the second harmonic of a neodymium laser. The photoluminescence band may be associated with a transition from the conduction band to the valence band or with a radiative transition from the trap levels below the bottom of the conduction band to the valence band.

Keywords: $FeGaInSe_4$ crystals, laser excitation, photoconductivity, photocurrent relaxation, lux-ampere characteristic, photoluminescence.

https://doi.org/10.15407/spqeo28.01.033
PACS 42.55.-f, 42.60.Jf, 73.50.Pz, 78.55

Manuscript received 29.07.24; revised version received 06.12.24; accepted for publication 12.03.25; published online 26.03.25.

1. Introduction

Intensive development of semiconductor electronics stimulates a detailed study of new properties of already known substances as well as a search and study of new semiconductor materials that meet modern requirements. In this regard, new ternary compounds of the type $A^{II}B_2^{III}X_4^{VI}$ (where A is Mn, Fe, Co, or Ni, B is Ga or In, and X is S, Se, or Te) containing elements with unfilled *d*-shells are of great scientific and practical interest [1–14]. These compounds have unique physical properties, which suggests their perspective for manufacturing a number of new-class optoelectronic devices controlled by magnetic field. Based on these compounds, Schottky diodes have been created [6]. Moreover, nanostructures from $FeIn_2S_4$ and $MnIn_2S_4$ compounds have been synthesized [7, 8].

Recent theoretical and experimental investigations have shown that the mentioned compounds and heterojunctions based on them are promising for photovoltaic, thermoelectric and photocatalysis applications [9–11]. At the same time, it has been shown in [12] that these compounds with a spinel structure of the MIn_2S_4 type (where M is Mn, Fe, or Co) have practical significance as a new type of anode materials for stable storages of sodium and lithium ions.

The properties of the above-mentioned compounds can be improved by changing their chemical composition with cation and anion substitutions. As a result, new materials with multifunctional electric, optical, and magnetic properties can be obtained [13, 14]. This evidences the relevance of the research aimed at obtaining more complex phases and solid solutions based on AB_2X_4-type compounds and studying their physical properties.

In this work, photoconductivity and photoluminescence of $FeGaInSe_4$ crystals under laser excitation are investigated for the first time.

2. Experimental

The starting compounds $FeGa_2Se_4$ and $FeIn_2Se_4$ were synthesized by fusing stoichiometric amounts of high-purity elemental components purchased from a German company Alfa Aesar. Syntheses were carried out in quartz ampoules sealed and evacuated to a residual pressure of 10^{-2} Pa at temperatures 20 K above the melting point for 8 hours. Then the furnace was turned off.

The single-phase nature of the synthesized compounds was confirmed by X-ray diffraction technique. Based on the X-ray diffraction data, $FeGa_2Se_4$ was determined to have cubic crystallographic structure of the space group $F\bar{4}3m$ with a = 5.5006 Å. $FeIn_2Se_4$ had trigonal crystallographic structure of the space group *R*3*m* with the lattice parameters $a = 4.0219$ Å and $c = 39.161$ Å. The obtained characteristics were in good agreement with the literature data [15].

$FeGaInSe_4$ was synthesized by fusing a 1:1 mixture of the compounds mentioned above in evacuated quartz ampoules, followed by long-term (500 hours) thermal annealing at 800 K. The crystallographic parameters of the $FeGaInSe_4$ lattice were determined from the analysis of the diffraction patterns. It was found that this compound crystallizes in a trigonal structure (space group *R*3*m*, $a = 3.9290$ Å, and $c = 38.542$ Å), which is consistent with the literature data [15].

X-ray phase analysis was carried out by recording powder patterns on a "D2 Phaser" diffractometer. Crystal lattice parameters were calculated and refined using the EVA and TOPAS 4.2 programs (Bruker, Germany. CuKα was a radiation source, the angle range was $5° \leq 2\theta \leq 80°$, and the shooting speed was 0.03°×0.2 min). To measure the photocurrent, plates of the thickness ~0.1 mm were cut from the obtained crystals. Contacts to the samples were created by melting indium into the opposite surfaces of this plate.

A pulsed YAG:Nd laser (L5Q29B) with built-in 2nd and 3rd harmonic generators, designed to generate radiation with wavelengths of 1064 and 532 nm, was used as a radiation source. The laser pulse duration was 12 ns and the maximum power in a pulse was 12 MW/cm^2. The duration of photocurrent and laser radiation pulses were recorded using a technique that allowed single nanosecond pulses to be recorded on the screen of a storage oscilloscope (Tektronix TDS-1002B).

3. Results and discussion

Fig. 1 shows photocurrent relaxation curves of the $FeGaInSe_4$ samples measured under excitation by laser radiation with $\hbar\omega = 2.33$ eV ($\lambda = 532$ nm) at 300 K. The photocurrent relaxation obeys the following exponential law:

$$J_f = J_f^{max} e^{-\frac{t}{\tau}},$$

where J_f^{max} is the maximum value of the photocurrent, J_f is the value of the photocurrent at time *t*, and τ is the lifetime of nonequilibrium current carriers, respectively.

At low excitation intensities ($I \approx 10^{22}$ quanta/cm^2 s), the photocurrent relaxation curve reveals fast recombination processes (Fig. 1, curve *1*). Using the data of this curve, the lifetime of non-equilibrium current carriers, is estimated to be $\tau_1 = 258$ µs. With an increase in the intensity of the excitation radiation ($I \approx 10^{24}$ quanta/cm^2 s), the lifetime of non-equilibrium carriers significantly decreases, $\tau_2 = 135$ µs (Fig. 1, curve *2*). This decrease is apparently due to the substantial increase in the concentration of generated non-equilibrium charge carriers ($\tau \sim 1/\Delta n$, where Δn is the concentration of non-equilibrium charge carriers).

The lux-ampere characteristic (LAC) of photoconductivity of the $FeGaInSe_4$ crystals is shown in Fig. 2. As can be seen from this figure, the LAC of photoconductivity is linear. It should be noted that the band gap of the $FeGaInSe_4$ crystal is not determined. But since $E_g = 1.55$ eV for $FeIn_2Se_4$ at room temperature [4], E_g of the $FeGaInSe_4$ crystal should be close to this value. Excitation of the $FeGaInSe_4$ crystals by the second harmonic of a neodymium laser ($\hbar\omega = 2.33$ eV and $\hbar\omega > E_g$) induces transition of carriers from the valence band to the conduction band and, hence, the LAC of photoconductivity becomes linear.

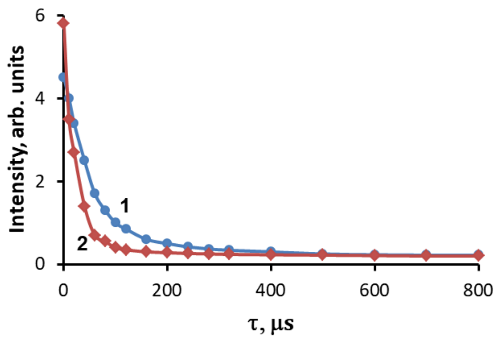

Fig. 1. Photocurrent relaxation curve measured at excitation of the $FeGaInSe_4$ samples by laser radiation with $\hbar\omega = 2.33$ eV at 300 K. *I*, quanta/cm^{2}s: *1* – 10^{22}, *2* – 10^{24}.

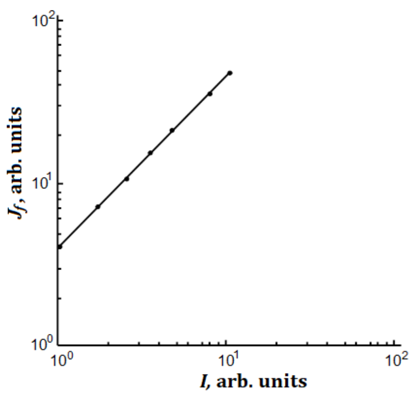

Fig. 2. Lux-ampere characteristic of photocurrent of the $FeGaInSe_4$ crystal at 300 K.

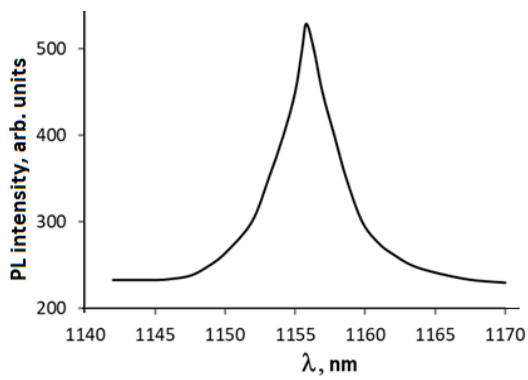

Fig. 3. $FeGaInSe_4$ emission spectrum under excitation by the second harmonic of a Nd:YAG laser ($\lambda = 1064$ nm).

Fig. 3 shows the emission spectrum of the $FeGaInSe_4$ crystals under excitation by the second harmonic of a $YAG:Nd^{3+}$ laser (λ = 1064 nm). The spectrum reveals one narrow band with a maximum at 1156 nm (1.07 eV), covering the wavelength region of 1145…1170 nm. The photoluminescence band may be associated with transitions from the conduction band to the valence band or with radiative transitions from the trap levels below the bottom of the conduction band to the valence band [16, 17]. We note that a narrow band with a maximum at 1259 nm was also observed in the 1255 to 1265 nm wavelength range of the emission spectrum of a $FeGaInS_4$ single crystal [16].

4. Conclusions

In this work, photocurrent relaxation, lux-ampere characteristic of photoconductivity and photoluminescence of layered $FeGaInSe_4$ crystals excited by the second harmonic of a pulsed $YAG:Nd^{3+}$ laser were experimentally investigated for the first time. The lifetime of non-equilibrium current carriers was determined. It was shown that the decrease in the lifetime at high excitation intensities is due to the high concentration of non-equilibrium charge carriers generated by powerful laser radiation. The observed linear region in the lux-ampere characteristic of photoconductivity is due to transitions of carriers from the valence band to the conduction band when the $FeGaInSe_4$ crystal was excited by laser radiation with $\hbar\omega$ = 2.33 eV. The photoluminescence band may be associated with transitions from the conduction band to the valence band or with radiative transitions from the trap levels below the bottom of the conduction band to the valence band.

Conflict of interest

The authors declare that they have no conflict of interest.

References

1. Gainza J., Guinazu O.N., Cespedes E. *et al.* Tunable inversion degree of $MnIn_2S_4$ thiospinels prepared by high-pressure synthesis, and its implication in the optical and magnetic properties. *J. Alloys Compd.* 2023. **969**. Art. ID 172413. https://doi.org/10.1016/j.jallcom.2023.172413.
2. Niftiyev N.N., Dashdemirov A.O., Mammadov F.M., Muradov M.B. Frequency dispersion of dielectric coefficients of $MnGaInTe_4$ crystals. *SPQEO.* 2024. **27**. P. 189–193. https://doi.org/10.15407/spqeo27.02.189.
3. Niftiev N.N., Dashdemirov A.O., Mamedov F.M., Muradov M.B. Dielectric properties of layered $MnGaInSe_4$ single crystals in an alternating electric field. *Surf. Eng. Appl. Electrochem.* 2023. **59**. P. 644–648. https://doi.org/10.3103/S1068375523050137.
4. Hwang Y., Choi J., Ha Y. *et al.* Electronic and optical properties of layered chalcogenide $FeIn_2Se_4$. *Curr. Appl. Phys*. 2020. **20**. P. 212–218. https://doi.org/10.1016/j.cap.2019.11.005.
5. Boledzyuk V.B., Kovalyuk Z.D., Kudrynskyi Z.R. *et al*. Physical properties of layered $FeIn_2Se_4$ single crystals. *Funct. Mater*. 2016. **23**. P. 557–560. https://doi.org/10.15407/fm23.04.382.
6. Bodnar I.V., Osipova M.A., Rud V.Yu. *et al.* MSP 1P Shottky barriers on the base of $MnIn_2S_4$ single crystals. *Conf. "Materials Science and Condensed Matter Physics"*, Chișinău, Moldova, 13-17 sept. 2010. P. 71.
7. Kim H., Tiwari A., Hwang E. *et al*. $FeIn_2S_4$ nanocrystals: A ternary metal chalcogenide material for ambipolar field-effect transistors. *Adv. Sci.* 2018. **51**. P. 800068. https://doi.org/10.1002/advs.201800068.
8. Lei S., Tang K., Fang Z. *et al.* Preparation of manganese indium sulfide urchins in aqueous solution-immiscible organic solvent. *Mater. Res. Bull.* 2006. **41**. P. 2325–2333. https://doi.org/10.1016/j.materresbull.2006.04.015.
9. Song Y., Guoa Y., Qia Sh. *et al.* $Cu_7S_4/MnIn_2S_4$ heterojunction for efficient photocatalytic hydrogen generation. *J. Alloys Compd*. 2021. **884**. P. 161035. https://doi.org/10.1016/j.jallcom.2021.161035.
10. Kushnir B.V., Kovalyuk Z.D., Katerynchuk V.M. *et al.* Layered crystals $FeIn_2Se_4$, In_4Se_3 and heterojunctions on their basis. *Funct. Mater.* 2017. **24**. P. 372–375. http://doi.org/10.15407/fm24.03.372.
11. Sharan A., Sajjad M., Singh D.J. *et al*. Two-dimensional ternary chalcogenides FeX_2Y_4 (X = Ga, In; Y = S, Se, Te): Promising materials for sustainable energy. *Phys. Rev. Mater*. 2022. **6**. P. 094005. https://doi.org/10.1103/PhysRevMaterials.6.094005.
12. Yan D., Li K., Yan Y. *et al.* Cubic spinel XIn_2S_4 (X = Fe, Co, Mn): A new type of anode material for superfast and ultrastable Na-ion storage. *Adv. Energy Mater.* 2021. **11**. P. 2102137. https://doi.org/10.1002/aenm.202102137.
13. Sardarli R., Salmanov F., Alieva N., Abbasli R.M. Impedance spectroscopy of $(TlGaSe_2)_{1-x}(TlInSe_2)_x$ solid solutions in radio frequency range. *Mod. Phys. Lett. B*. 2020. **34**. P. 2050113. https://doi.org/10.1142/S0217984920501134.
14. Moroz N.A., Lopez J.S., Djieutedjeu H. Indium preferential distribution enables electronic engineering of magnetism in $FeSb_{2-x}In_xSe_4$ *p*-type high-tc ferromagnetic semiconductors. *Chem. Mater.* 2016. **28**. P. 8570. https://doi.org/10.1021/acs.chemmater.6b03293.
15. Mammadov F.M., Amiraslanov I.R., Imamaliyeva S.Z., Babanly M.B. Phase relations in the FeSe–$FeGa_2Se_4$–$FeIn_2Se_4$ system. Refinement of the crystal structures of the $FeIn_2Se_4$ and $FeGaInSe_4$. *J. Phase Equilib. Diffus*. 2019. **40**. P. 787–796. https://doi.org/10.1007/s11669-019-00768-2.
16. Niftiyev N.N., Dashdemirov A.O., Mammadov F.M., Mamedov R.M. Optical properties of $FeGaInS_4$ single crystals under laser excitation. *J. Appl. Spectrosc.* 2023. **89**. P. 1147–1149. https://doi.org/10.1007/s10812-023-01480-3.
17. Guk M., Merschjann C., Tyborski T., Dermenji L. Photoluminescence $MnIn_2S_4$ single crystals. *Mold. J. Phys. Sci.* 2011. **10**. P. 137–142.

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Mammadov F.M.: research concept, investigation, writing – review and editing, discussion of the results.

Mamedov R.M.: investigation, software, writing – original project, visualization.

Babanly M.B.: scientific supervision, research concept, final conclusions.

Деякі оптоелектронні властивості кристалів $FeGaInSe_4$ при лазерному збудженні

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Анотація. Досліджено фотопровідність і фотолюмінесценцію в шаруватих кристалах $FeGaInSe_4$ при високих рівнях оптичного збудження. Встановлено, що зменшення часу життя при високих інтенсивностях збудження зумовлене високою концентрацією нерівноважних носіїв заряду, генерованих потужним лазерним випромінюванням. Лінійний характер люкс-амперної характеристики фотопровідності викликано переходами носіїв з валентної зони в зону провідності при збудженні кристалів $FeGaInSe_4$ другою гармонікою неодимового лазера. Смуга фотолюмінесценції може бути пов'язана з переходами з зони провідності у валентну зону або з випромінювальними переходами з рівнів пасток, що лежать нижче дна зони провідності, у валентну зону.

Ключові слова: кристали $FeGaInSe_4$, лазерне збудження, фотопровідність, релаксація фотоструму, люкс-амперна характеристика, фотолюмінесценція.