EXCITON-EXCITON INTERACTION IN GaSe CRYSTAL ELECTROLUMINESCENCE SPECTRUM

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Stimulated emission from the quasi-two-dimensional lamellar semiconductor GaSe was investigated under high electric fields and at the temperature 77 K. Increase of the polarized optical spectrum and quantum yield have been determined. Versus defects concentration and direction of the electric field applied to the specimens relative to optical *C* axis. The presence of three processes of intensification at the boundary of the fundamental absorption region, connected with mutual interaction of defects, free direct and non-direct excitons, has been confirmed.

INTRODUCTION

GaSe is a quasi-two-dimensional semiconductor with the indirect transition (space group $D^{1}_{3h}-\bar{p}\bar{6}\,m2$) with the peak of the valence band in the *G*-point of the Brillouin zone and the bottom of the conduction band in *M*-point, i.e. two equivalent minima are situated on second order axes [1-5]. Moreover, an additional subband with the upward energy shift of 40 meV exists in the *G*-point. Fundamental direct and indirect transitions at 77 K are E_g^{dir}=2.177eV and E_g^{ind}=2.065eV, respectively. Binding energies of corresponding excitons are E^{dir}=20 meV and E^{ind}=43 meV [6-8]. Due to crystal structure, this free exciton becomes the resonance state (Philips, [9]) with the continuum of free electron states of indirect conduction band botton. Meanwhile impurities and phonon scattering might provide strong binding of these two types of state.

Large oscillator strength of the direct free exciton transition can provide free excitons recombination at energy substantially higher than E^{ind}. These processes become more probable at sufficiently high temperatures for electronic jumps to free exciton levels and will be maintained by high excitation density.

Results of investigations of stimulated emission in GaSe [10] with various intensities of the electric field applied along and normally to layers at *T*=77 K are given in the present paper. Three different lines of the stimulated emission in the region of direct and indirect excitons were observed.

In accordance with works [11-13] process of exciton-exciton interaction causes presence of the emission line shifted from the free exciton line to the region close to the bound exciton energy. Thus, mechanisms of optical spectrum intensification, which are responsible for observed lines, could be associated with joint exciton processes.

EXPERIMENTAL

Crystals were grown by Bridgman-Stockbarge method.

Experiments were carried out on monocrystalline plates of p-GaSe with mobility of holes and electrons 30÷40 and 150÷180 cm^2/V·s respectively at the room temperature. Specimens with dimensions 3x5x0.1 mm^3, specific resistance $10^5 \div 10^6$-Ω·cm at 300 K, obtained by simple cleaving along the cleavage plane, were used. Contacts were placed on the fresh-cleaved surface. In-Ga eutectic mixture was used as the electrode. Intercontact distance was 0.1-0.2 mm. The electrod-crystal contact processes have been excluded by measurement of all investigated volt-ampere characteristics at two opposite voltage directions. Crystals were cooled by direct immersion into the liquid nitrogen. Excitation was accomplished by the alternating voltage with the frequency 50 Hz. Electroluminescence was registered in two directions: from the surface normal to $\vec{C}$ axis and from the layer plane, containing $\vec{C}$ axis. Obtained spectra were analyzed by the DFC-24 spectrometer.

RESULTS

Electroluminescence spectra of available GaSe crystals in the region of the fundamental absorption edge can be combined into 4 groups. In accordance with *X*-ray analysis data, the ε-polytype is prevalent in specimens of No.1 type in comparison with other modifications; respectively crystals of this group are more perfect [14]. It could be seen from fig.1 that different distribution of lines intensities is observed for different groups of specimens: *A*–595 nm, *B*–615 nm, *C*–667 nm, *D*–688 nm. Short-wavelength line *A* having the same energy as line observed in the transmission spectrum and induced by free electron – hole pairs formation, can be ascribed to recombination of a direct free exciton. Strong resonance line of *A* exciton in specimens of No.1 type confirms that they are more perfect in comparison with specimens of other groups. Thus, for complex investigations of electroluminescence spectra, crystals of No.1 type with clearly defined exciton luminescence, have been chosen.

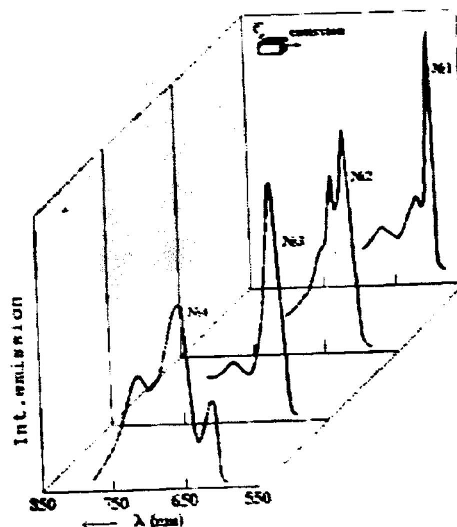

Fig.1. Electroluminescence spectra for various specimens of GaSe at 77 K

Figures 2, 3 demonstrate series of electroluminescence spectra obtained for GaSe at 77 K in emission directions $\vec{q} \perp \vec{C}$ and $\vec{q} \| \vec{C}$ respectively, with increase of the electric field intensity. Enlarged exciton electroluminescence spectrum at various intensities of the applied electric field ($\vec{q} \| \vec{C}$) is given in fig.4. Dependence of the energy position and relative intensity (E) are given in inset to fig.4. This dependence is represented by intersection of two curves in the region close to E=450 V/cm; they reflect two mutually incompatible phenomena: at E<450 V/cm lines are continuously shifting towards the low energy region, and beginning from E>450 V/cm, steep rise in intensity is observed which excludes longwavelength shifts.

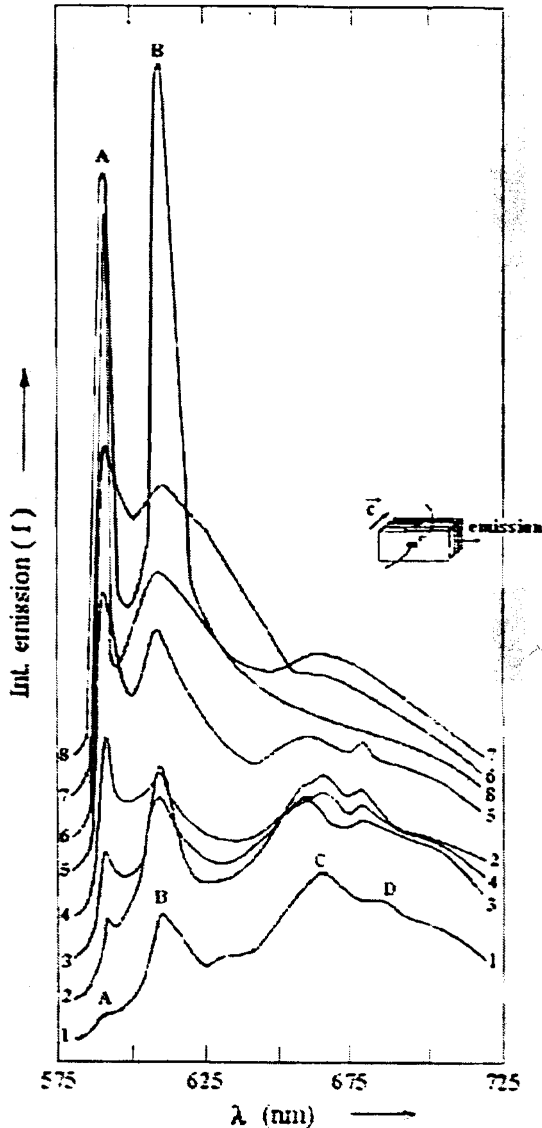

Fig. 2. Electroluminescence spectra for various specimens of GaSe (type No.1) in different fields, geometry q⊥C at 77 K 1-450; 2-530; 3-550; 4-660; 5-720; 6-760; 7-820; 8-840V/cm

With increase of E at $\vec{q} \| \vec{C}$ both A and B lines of a free exciton move to longwavelength region and have asymmetrical form with the low-energy tail. Meanwhile, C and D-lines demonstrate shortwavelength shifts. In case of $\vec{q} \perp \vec{C}$ geometry there is no energetic shift of lines.

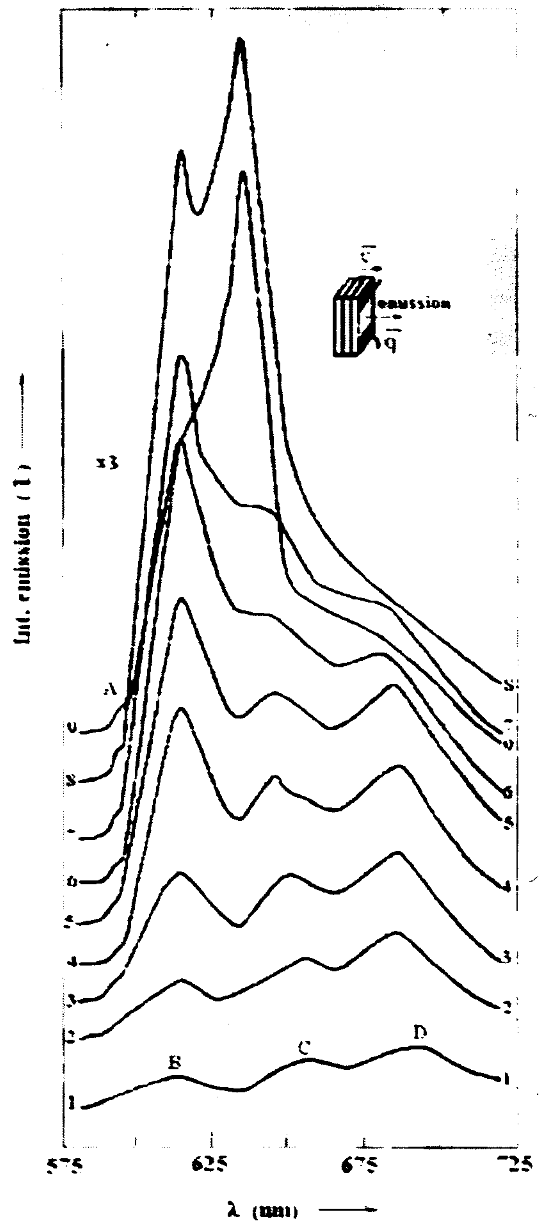

Fig. 3. Electroluminescence spectra for various specimens of GaSe (type No.1) in different fields, geometry q‖C at 77 K 1-230; 2-280; 3-340; 4-390; 5-450; 6-500; 7-560; 8-670; 9-780 V/cm

Alongside with increase of E up to the certain critical value E^{cri} in both observation directions, absolute value of the emission intensity rises. It is always higher in $\vec{q} \perp \vec{C}$ direction than in case of $\vec{q} \| \vec{C}$. Rise of the value E leads also to decrease of A and B lines half-widths in geometry $\vec{q} \perp \vec{C}$ (B and C in case of $\vec{q} \| \vec{C}$). Line A (B) is narrower in comparison with B (C). This shows that emission mechanism connected with A (B) is more favourable at higher intensities of electric fields. It is confirmed by the spectrum at E=760V/cm (580V/cm) for geometry $q \perp C$ ($q \| C$) where A (B) line dominates.

DISCUSSION

For the A-line the observed superlinear dependence on E excludes an impurity emission radiative recombination of the

bound exciton and phonon replica of the free exciton. Superlinearity, narrowing at E=720 V/cm $\vec{q}\perp\vec{C}$ with geometry (at E=450V/cm $-\vec{q}\|\vec{C}$), polarization and direction for the A-line emission allows to reveal stimulated emission in the course of annihilation of free direct excitons due to exciton-exciton interaction. Moreover the A-peak is badly observed in case of $\vec{q}\|\vec{C}$ geometry because reabsorption effect is strong when the light passes through the specimen and the low-energy tail of B-line is observed as the wide band with the peak of 2.015eV. It has been suggested [15] that B-line is a result of impurity-impurity emitting transition; authors [16] consider this line as phonon replica of the indirect bound exciton. However, further investigation [17] did not confirm these suggestions.

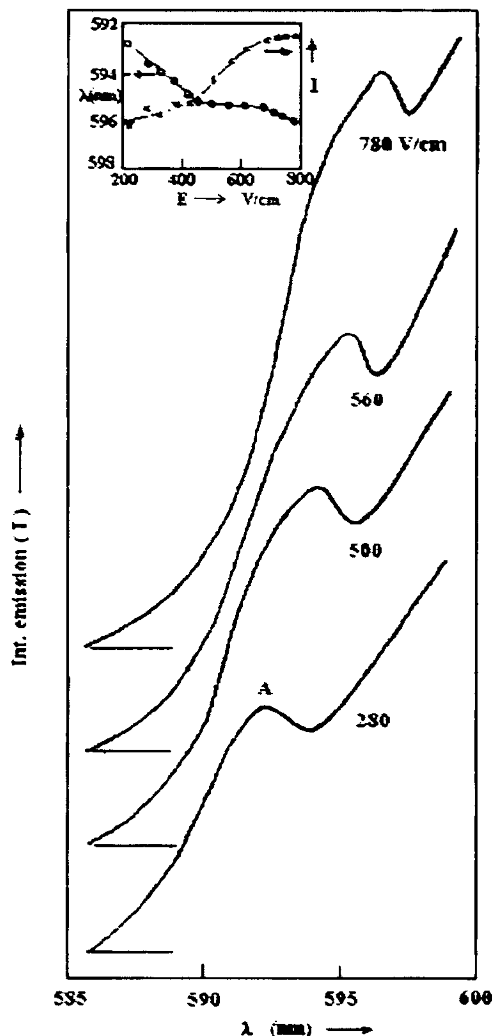

Fig.4. Exciton electroluminescence spectrum of GaSe specimen (type No.1) in different fields, geometry q‖C Inset to Fig.4 is the dependence of energy position and relative intensity of A-line on E.

Polarization of B-line ($\vec{E}\|\vec{C}$) corresponds to indirect transition $M_3^+ - \Gamma_4^-$ allowed in GaSe that takes place with participation of the symmetry phonon M_1^+ [18]. Magnitude of such phonon with dispersion contribution $\hbar\omega$=13meV [19]. Energy position $h\upsilon_e$=2.015eV of line satisfies to equation $h\upsilon_B = E^{ind}_{g.exc.} - \hbar\omega$, where $E^{ind}_{g.exc.}$=2.028eV is the value of indirect exciton zone in GaSe which is in good agreement with works [6-8], with the accuracy within several meV.

In our opinion the B-line is a result of stimulated emitting annihilation of free indirect excitons occurring at low temperatures with phonon emission. Important factor in favour of its exciton nature is coincidence of this line position in the luminescence spectrum with the energy position in the line caused by emitting decay of free indirect excitons.

It is difficult to understand the nature of the process responsible for the C-line. Indeed reliable data for a binding energy of indirect free exciton and for effective masses bound with M minimum of the conduction band are not given in literature. Nevertheless, we can observe that the functional dependence I_c on E is similar to the dependence of I_e vs E but it has different threshold voltage value. Larger halfwidth of C-line (52meV) can be ascribed to band-impurity emitting transitions in the energy region E>1.86eV. However, short-wavelength shift with E rising up to E_{thr} for indirect free exciton, superlinear dependence and narrowing beginning from E>E_{thr} allow to assume that C-line is linked respectively by recombination through donor-acceptor pairs [20] and by exciton-exciton interaction (indirect excitons).

On the contrary, there might be no D-line due to joint exciton processes remoteness from exciton transition region and absence of stimulation even at high E values. Short wavelength shift with rise of E and long-wavelength shift with increase of time delay of registration relative to initiating pulse show that most probable mechanism stipulating this band must be recombination through donor-acceptor pairs.

Thus, in the region of the fundamental absorption edge of GaSe at 77 K we discovered three stimulated emission channels with $\vec{q}\perp\vec{C}$ ($\vec{q}\|\vec{C}$) geometry respectively working at various intensities of the applied electric field. In other words there are three mechanisms of inverse population with different threshold voltage in GaSe.

It should be noted that intensification of the optical spectrum and strong quantum yield of various optical intensification processes were registered which confirm the importance of GaSe material as the coherent light source. These results allow to suggest various methods of laser application in lamellar compounds.

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GaSe-NİN ELEKTROLÜMİNESSENSİYA SPEKTRİNDƏ EKSİTON-EKSİTON QARŞILIQLI TƏSİRİ

77K temperaturunda və elektrik sahəsinin yüksək qiymətlərində kvaziikiölçülü laylı yarımkeçiricinin stimullaşmış şüalanması öyrənilmişdir.

Defektlərin konsentrasiyası və nümunəyə tətbiq olunan elektrik sahəsinin optik ox $\bar{C}$ ilə təşkil etdiyi istiqamətdən asılı olaraq polyarizə olunmuş optik spektrin və kvant çıxımının güclənməsi ilə əlaqədar ölçmələr aparılmışdır.

Sübut olunmuşdur ki, fundamental udulma sərhədinin formalaşmasında iki proses-qarşılıqlı təsirdə olan defektlər və sərbəst düz və çəp eksitonlar iştirak edir.

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ЭКСИТОН-ЭКСИТОННОЕ ВЗАИМОДЕЙСТВИЕ В СПЕКТРЕ ЭЛЕКТРОЛЮМИНЕСЦЕНЦИИ КРИСТАЛЛА GaSe

Стимулированное излучение от квазидвумерного слоистого полупроводника при высоких значениях электрического поля изучено при температуре 77 К. В зависимости от концентрации дефектов и направления прикладываемого к образцам электрического поля относительно оптической оси С, осуществлены измерения по усилению поляризованного оптического спектра и квантового выхода. Доказано наличие трех процессов усиления в области края фундаментального поглощения, связанного с совместными взаимодействиями дефектов, свободных прямых и непрямых экситонов.

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