



Beynəlxalq Konfrans "Fizika-2005" International Conference "Fizika-2005" Международная Конференция "Fizika-2005"

7 - 9
İyun
June 2005
Июнь

№191
səhifə
page 722-724
стр.

Bakı, Azərbaycan

Baku, Azerbaijan

Баку, Азербайджан

OPTICAL CHARACTERIZATION OF EXCITONS IN InSe CRYSTALS DOPED WITH RARE EARTH IONS

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Investigations of exciton luminescence and absorption spectra of InSe lamellar semiconductors doped with different kinds of compounds at $T=1.8$ K are carried out. It is found that changes in the luminescence intensity of free and bound excitons are due to screening of Coulomb interaction between electron and hole. Increase of free excitons luminescence intensity in InSe crystals activated by holmium ions is attributed to "healing" of metal and chalcogenide vacancies and also to interlaminar interaction increase due to the exchange interaction of local formations, i.e. holmium ions.

1. INTRODUCTION

In nature lamellar semiconductors are known to crystallize in defective structures (vacancies, shift of the layers relative to each other, cracks, pores, disordered regions, etc.) [1], In spite of the fact that induced luminescence has been registered in lamellar compounds about a half of century ago [2] their application as active elements in quantum electronics remained a serious problem. Investigations of the character and mechanisms of the influence of dopants and rare-earth ions (RE) on the exciton states in doped semiconductors have shown that the problem can be solved only by using improved monocrystals with rare-earth elements ions as dopants. These elements have been chosen taking into consideration the following:

1. Doping "heals" structural defects caused by metal vacancies, and doping with rare-earth compounds promotes, besides the "healing" of metal and chalcogenide vacancies, also interlaminar interaction in the crystal [3 to 5].
2. The possibility to produce the active element for laser luminescence using not only the matrix but also RE ions.
3. Production of the active elements for laser luminescence using RE ions allows to reduce the number of defects caused by the shift of layers [6], hence to eliminate polytypism.

To understand more clearly the mechanism of the doping influence on the exciton spectra of the crystals we have singled out for a separate study the specific character of dopant and RE ions on exciton states. A generalized model of local formations in lamellar compounds has

been proposed. Luminescence and absorption spectra of "pure" and doped InSe crystal were studied.

InSe crystals were chosen, as certain achievements in the technology of growing and doping allowed a precise control of composition and concentration of doping compounds with known main parameters. It should be noted that the strong anisotropy of chemical bonds significantly simplifies the technology to produce thin single-crystal films which are sufficiently large and have high-quality natural surfaces.

InSe single crystals have a hexagonal lattice of space symmetry group $D_{6h-c6/mmc}^4$ large [7]; crystals are clearly lamellar. An isolated layer of InSe is formed by four hexagonal close-packed single-atom sublayers arranged in the following sequence: -Se-In-In-Se. Every In atom is almost exactly tetrahedrally surrounded by three Se atoms and one In atom. Interatomic bonding within the layers is mainly covalent and interlayer relative bonding is of weak van-der-Waals type. A number of different positions of layers relative to one another and forming different crystal polytypes (β , γ , ϵ and δ -polytypes) are possible [8 to 10]. At present, most of InSe crystals grown by the Bridgeman method are of the ϵ -polytype. However, introduction of small quantities of doping agents leads to the formation of a mixture of γ - and ϵ -polytypes [11].

2. EXPERIMENTAL

Pure and doped InSe crystal were grown from the melt using a modified Bridgman – Stockbarger method. Compounds of the RE dopants holmium (Ho) and dysprosium (Dy) were introduced during the crystals growth; their concentration varied in the range of (10^{-5} to 0.2).

Monocrystallingly, homogeneity of composition, and distribution of introduced compounds, quality of the grown crystals and their structure were analyzed using Debye powder diagrams, Laue photographs, and diffraction patterns of the investigated compositions. The crystals were easily cleaved just before measurements from large single-crystal pieces (45 x 8 mm²) along the cleaving surface and perpendicular to the optical C-axis; as they had specular surfaces they had not been subjected to further mechanical and chemical treatment. All measurements of the absorption and luminescence spectra have been performed using an installation on the basis of the ДФС-12 spectrometer with resolution not less than 0.05 nm/mm. Transmission was measured with light propagating along the optical C-axis. Photomultipliers of ФЭУ-79 and ФЭУ-62 types were used as radiation receivers. Luminescence was registered (ЛПИ – 505, $\lambda = 33.7$ nm) using reflection geometry of the surface excited by a laser beam.

1. Experimental Results

Spectra of pure and Dy-doped InSe

The luminescence and absorption spectra of InSe single crystals, pure and doped with Dy ions at T=1.8 K are shown in Fig.1. The spectrum obtained for pure InSe contains the same components as that described in [12]; several components observed in the energy region 1.310 to 1.302 eV are more pronounced. Comparing the luminescence spectra one can see that the luminescence in the long-wavelength region of the InSe (Dy) spectrum is more intensive than the luminescence A-line which coincides with the line near the fundamental absorption edge at E= 1.332 eV (T=1.8 K). At low doping levels of InSe with Dy ions a broader luminescence band appears instead of the group of narrow maxima (B to F) at E = 1.300 eV and the intensity of the A-line as well as the absorption coefficient decrease. With increasing concentration further broadening of the A-line and the luminescence band in the long-wavelength region is observed. It should be noted that with increase of the doping level at E = 1.332 eV the absorption coefficient decreases, while the energy position coinciding with that of the luminescence A-line does not change.

Spectra of pure and Ho-doped InSe

The luminescence and absorption spectra of InSe single crystals, pure and doped with Ho ions at T=1.8 K, are shown in Fig.2. Doping with low concentrations of Ho (up to 10⁻⁵ at%) leads to an intensity decrease in the wide band region, redistribution and extinction of E and F lines. With n increasing up to 10⁻² at % (Fig.2, curve 2) the E and F luminescence lines disappear completely, and bright narrow lines are well observed in the energy region of 1.310 to 1.318 eV. From Fig. 2 one can see that on doping with 0.2 at % in the long –wavelength region of the spectrum a slight smeared luminescence maximum formed by the forbidden phonon satellite A and B lines is observed [12]. The nature of the structure observed below 1.302 eV (Fig.2, curve 2) has not yet been investigated.

3. DISCUSSION OF RESULTS

The coincidence of the energy positions of the luminescence line (1.332 eV) and the maximum near the

fundamental absorption edge caused by the free exciton formation at 1.8 K indicates that the luminescence line in the short- wavelength region of the spectrum is due to resonance annihilation of free excitons.

A comparison of the luminescence spectra observed for pure and doped InSe single crystals shows that introduction of the dopant changes considerably the luminescence intensity (1.332 eV for InSe). As can be seen doping seriously affects the luminescence spectrum, i.e. the formation of structural defects in the crystal undoubtedly depends on the doping level.

It is known [13] that lamellar InSe crystals usually have multiple structural defects caused by Se, In vacancies (up to 10¹⁸ cm⁻³).

When RE chalcogenide compounds are used as dopants, simultaneous «healing» of structural defects caused by Se and In vacancies takes place. Thus, in InSe crystals activated by Dy ions with increasing doping level nearly complete quenching of free exciton luminescence line and of the line in the long-wavelength region is observed. The observed dependence of free and bound exciton luminescence intensity on the doping level of the samples can be explained as follows.

Excitons, being electron – hole pairs bound by Coulomb attraction, interact within the crystals with charged doping ions. In the region of low doping concentrations, when the average distance between the dopants significantly exceeds the exciton radius, this interaction is not strong and does not provoke a considerable disturbance of free exciton states. It is revealed mainly in exciton scattering on the doping ions and can also lead to a localization of exciton near dopants, i.e. to «bound» exciton formation [14 to16].

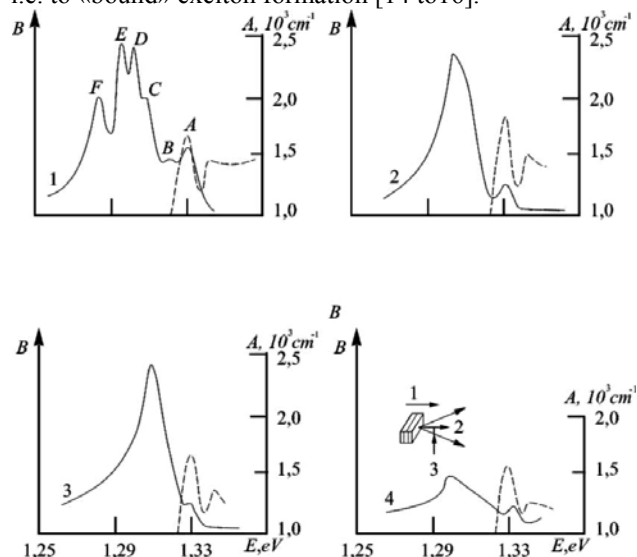


Fig.1. Luminescence (solid lines) and absorption (dashed lines) spectra of InSe single crystals, pure and doped with Dy ions at T=1.8 K. (1) Pure InSe, (2) to (4) n=10⁻⁴, 10⁻⁵, and 0.005 at.% Dy, respectively.

In the region of higher doping levels the Coulomb interaction is weaker due to the screening effect that naturally affects the internal state of an exciton. This phenomenon is probably caused by the deformation occurring in the course of crystal doping. It is known [17] that when the crystal is placed in a disturbing field the

crystal symmetry is lowered and the relative motion of electron and hole is changed. Further increase of the doping level raises the effect of the potential of randomly distributed doping centers on electron-hole interaction.

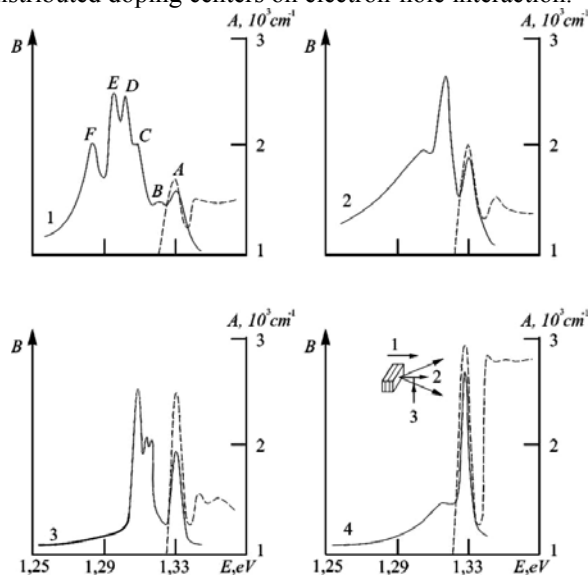


Fig.2. Luminescence (solid lines) and absorption (dashed lines) spectra of InSe single crystals, pure and doped with Ho ions at $T=1.8$ K. (1) Pure InSe, (2) to (4) $n=10^{-2}$, 10^{-5} , and 0.02 at.% Ho, respectively.

This effect is revealed in the Coulomb potential screening as follows:

$$V(r) = (-e^2/\epsilon r) \exp(-r/r_0),$$

Where r_0 is the screening radius.

As the average distance between the charge carriers or charged dopants approaches the exciton radius, i.e. $a_{exc} \approx r_0$, the disturbance caused by the dopants becomes comparable with the energy of Coulomb interaction of electron and hole in the exciton. Decay of the exciton into its components takes place, i.e. the exciton no longer exists. The breaking of the exciton state on screening was

found experimentally by Rogachev and Asnin [18,19] for excitons at the direct transition in germanium.

Unlike Dy, the activation by Ho ions favours the appearance of rather intensive luminescence line of free excitons with maximum value at 0.2 at%. The rather substantial increase of the free exciton luminescence line intensity (seven times larger than with pure InSe) and the considerable decrease of the line intensity in the long-wavelength region allow to assert that activation of InSe by Ho ions «heals» the structural defects caused by Se and In vacancies. At the same time, as a result of exchange interaction between Ho ions located in the nearest-packed sublayers of neighbouring layers [20], the interlayer interaction rises (this is confirmed by the increase of the mechanical strength of the crystal) as the number of packing defects caused by the shift of layers relative to each other decreases, which in turn leads to the elimination of polytypism. The interpretation of the obtained results is in good agreement with the model of local doping in lamellar crystals. The investigations have shown that among the numerous RE compounds Ho compounds are of utmost interest: using optimal concentrations of these compounds one could achieve maximum attainable perfection of lamellar semiconductors.

2. CONCLUSIONS

The following has been found:

1. Doping with Dy ions results in quenching of the luminescence lines of free and bound excitons is due to the effect of the potential of randomly distributed doping centres on electron-hole interaction.
2. Doping with Ho ions allows to control the degree of single crystal perfection.

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