

Optical anisotropy in GaSe

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Optical anisotropy of the layer semiconductor GaSe has been studied by photoluminescence (PL) and Fourier Transform Infrared Spectroscopy (FTIR). The PL spectra are dominated by two closely positioned emission bands resulting from the free exciton and the bound exciton connected direct band edge of GaSe. Photoluminescence and transmission spectra of GaSe crystals have been measured for two cases in which the propagation vector k is perpendicular ($k \perp c$) and parallel to the c -axis ($k // c$). Peak position of the PL emission band and the onset of the transmission have been found to be significantly different for these two cases. This observed anisotropy is related to anisotropic band structure and the selection rules for the optical absorption in layered GaSe. FTIR transmission spectrum is in good agreement with PL results.

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1 Introduction

Being a member of the group III-VI, GaSe is a layer semiconductor whose c -axis is perpendicular to the layer planes. The sandwich layer consists of four covalently bound sheets of hexagonal close-packed atoms, arranged in the sequence Se-Ga-Ga-Se. In literature, four different periodic stacking sequences of the layers have been reported as β , γ , ϵ , and δ [1]. The ϵ and β - phases are 2H Hexagonal polytypes, and the modification γ and δ have a 3R trigonal structure. The layers are bound by weak Van der Waals forces while intralayer – bonding forces are primarily ionic-covalent in nature [2].

GaSe is a highly anisotropic material due to its layer structure. The structural anisotropy results in anisotropy in the electrical and optical properties of GaSe. Optical anisotropy of GaSe have been investigated by transmission, absorption or reflectivity measurements, where it was found that optical constants (e.g. absorption coefficient or refractive index) are different for $E // c$ and $E \perp c$ [3-8]. This difference was attributed to the selection rules related to the anisotropic band structure of GaSe.

In this work, we present the results of PL and transmission spectroscopy for GaSe samples that we have grown by the Bridgman method with emphasis to the optical anisotropy in GaSe. This paper is a complementary work to our previous publications [9, 10] where we reported electrical transport properties of the same structure. The optical anisotropy in the PL emission is clearly demonstrated with the dependence of the PL emission on the k vector of the exciting photons.

2 Experimental procedure

The GaSe single crystals were grown by the Bridgman technique and they were found to have hexagonal structure having lattice parameters in accordance with the literature. Preparation of the ampoules and growth processes were explained in our previous works [9, 10]. The samples used in this study were prepared by cleaving an ingot parallel to the layers. Typical sample dimensions were about of 1cm^2 and 0.5 to 2.0 mm of thickness. For PL measurements, each sample was mounted to a cold finger and placed into a closed cycle helium cryostat which provides a temperature variation from 10 K to 300 K. Sample was exposed to a laser with a wavelength of 337.1 nm and an average power of 7 mW. The luminescence emitted was focused by two convex lenses onto the entrance slit of Oriel model 77700a monochromator which is equipped with four

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gratings. The Hamamatsu C7041 (S7031-1008 series with number of pixel) multi-channel detector was used to detect the PL signals. The transmission measurements were carried out by using Bruker Equinox 55 FTIR spectroscopy.

3 Results and discussion

Fig. 1 shows the PL spectrum of GaSe that was obtained with an incidence angle of about 10° with respect to the *c*-axis, at 20 K. By using a commercially available computer program, we identified 2 peaks with energies 2.086 eV, 2.067 eV, respectively. The peak with the higher energy is obviously corresponding to the free exciton (FE) of the direct band edge. From the activation energy analysis of the temperature dependent PL spectra we found the binding energy to be 26.4 meV [11]. The bandgap of the crystal is then found to be 2.112eV which is quite consistent with the commonly accepted value for GaSe [12-18].

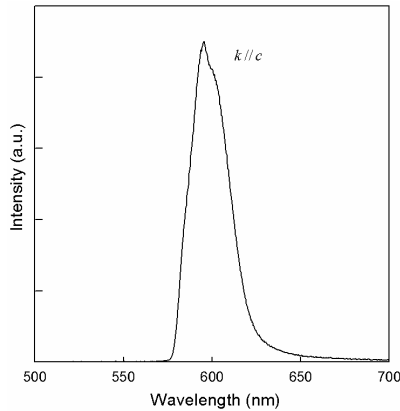


Fig. 1 Photoluminescence spectra of as-grown GaSe single crystal at 20 K. ($k//c$).

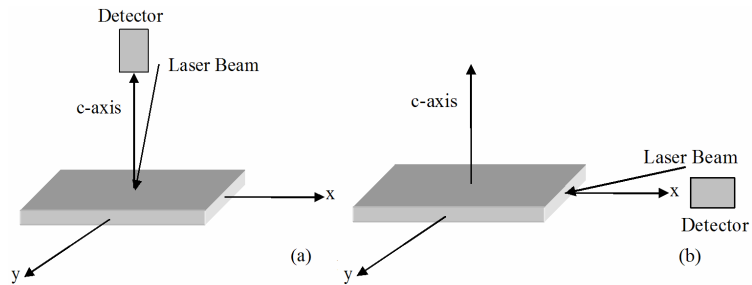


Fig. 2 (a) Experimental conditions for the measurement of PL emission. Laser beam is directed to the sample surface with an angle of $\sim 10^\circ$ with respect to *c*-axis. The detector is positioned along the *c*-axis ($k//c$). (b) Laser beam is directed on the side of the sample. The detector's position is along the direction perpendicular to the *c*-axis ($k \perp c$).

We studied the optical anisotropy in GaSe by measuring the PL emission and transmission spectra in two different experimental configurations. In Case 1, the laser light is sent to the sample parallel to the *c* axis ($k//c$) as shown in Fig. 2(a). In case 2, the exciting laser light was directed to the side of the crystal layers ($k \perp c$) as shown in Fig. 2(b).

Fig. 3 shows the corresponding PL spectra of two experimental configurations. The most striking feature of this graph is the difference on the peak position of the PL spectra for $k//c$ and $k \perp c$ cases. The peak energy of the PL spectrum for the $k//c$ case is about 50 meV greater than that of $k \perp c$ case at 50K. This result clearly demonstrates the strong anisotropy in the PL emission of the GaSe crystal. It is in agreement with the reflectance measurement reported previously [3].

In order to verify that the anisotropy observed in the PL spectrum is related to the absorption by the GaSe rather than emission-related process, we carried out FTIR measurements with the same experimental condition. Transmission spectra measured by FTIR spectroscopy in the wavelength range of 500 to 1000 nm is shown in Fig. 4. The onset of the transmission is seen to be at 630 nm (1.97 eV) for the $k//c$ orientation, whereas in the case $k \perp c$ it is about to be at 645 nm with energy 1.92 eV. The transmission edge depends on whether or not the *k*-vector of light is perpendicular or parallel to the *c*-axis of the GaSe crystal. The difference between two configurations is about 44 meV which is in agreement with the PL results, indicating that the optical anisotropy commonly observed in layer semiconductors is an absorption related phenomenon.

Optical anisotropy in GaSe was discussed by considering its electronic band structure [3, 4]. According to the band structure calculation, energy position of p_x , p_y , and p_z states are not the same. p_z valence band states are situated slightly higher energy than p_{xy} states. It was suggested that the transition with $E//c$ is derived from the bonding-antibonding bands of the p_z orbitals, while the transitions with $E \perp c$ is derived from the p_{xy} antibonding (valence) band and the p_z antibonding (conduction) band. Selection rules require that transitions for $E \perp c$ are allowed only between bands having the same parity and the transitions for $E//c$ are allowed only

between bands having the opposite parity. One can then understand that the high energy peak observed in the $k//c$ ($E \perp c$) case (Fig. (3)), is due to the allowed transitions between antibonding states of the p_{xy} and p_z bands. In the second measurement condition, $k \perp c$, the perpendicular component of electric field is weak. The transitions with low energy emission dominate the PL spectra in this case due to smaller energy difference between p_z states. An interesting feature of the second case is that the PL band consists of a single peak which does not appear to be a combination of several other peaks. Although the asymmetry in the PL band indicates the existence of different peaks within the main PL band, these peaks are not resolvable. It is likely that one of the transitions dominates the whole PL emission and gives the observed spectra.

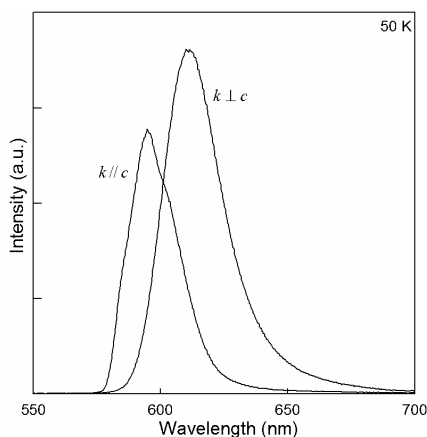


Fig. 3 Photoluminescence spectra of GaSe with respect to $k//c$ and $k \perp c$ axis.

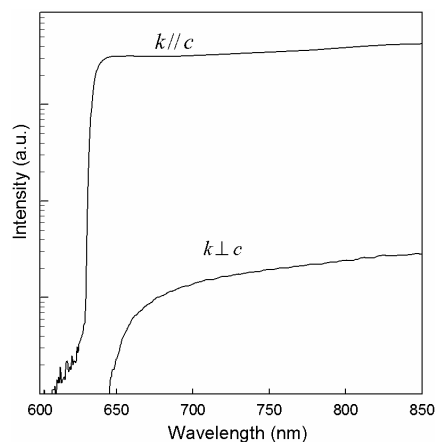


Fig. 4 Transmission spectra of GaSe at room temperature.

4 Conclusion

Optical anisotropy in the photoluminescence and transmission spectra of GaSe were studied by considering two cases which are classified according to the direction of k vector of the exciting photons with respect to the c -axis of the layers. Energy positions of the PL emission band and FTIR transmission edge were found to be different for $k//c$ and $k \perp c$ cases. The difference observed in the measured spectra is connected with the anisotropic band structures and selection rules for the light absorption in GaSe. The agreement between FTIR and PL measurements has shown that the anisotropy is an absorption related phenomenon.

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