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INTERFERENCE OF ADDITIONAL WAVES OF EXCITONIC POLARITONS IN SnSe SINGLE CRYSTALS

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Absorption, reflection, photoluminescence, wavelength modulation reflection and transmission spectra at temperatures 300–10 K in energy rage 1.1–1.5 eV were investigated. Contours of excitonic reflection spectra were calculated and the binding energy (Rydberg constant), translation (M) and reduced (μ^*) effective masses of excitons were determined. Effective masses of electrons and holes were estimated. In the region of A and B excitonic series sparse and thick interference fringes were observed in measured spectra. The sparse fringes are due to Fabry-Perot interference of excitonic polaritons of lower polaritonic branch (ω_T). The thick interference is caused by the mutual interference of excitonic polaritons of lower (ω_T) and upper (ω_L) polaritonic branches.

Key words: tinmonoselenide; optical spectroscopy; excitonic polaritons; electron transitions; direct transitions.

INTRODUCTION

Tin selenides (SnSe) attract an attention because of possible application. SnSe crystals are used in holographic record systems, optical and optoelectronic devices, infrared electronic and switching memory devices and photoelectrical structures [1]. The SnSe compound, with orthorhombic lattice structure, are of interest due to their low thermal conductivity and high power factor, which have potential advantages in increasing the thermoelectric conversion efficiency [2]. The crystal lattice structure of SnSe prevents the phonons

propagation and temperature vibrations along axis *b*, therefore high thermoelectric efficiency is observed in these crystals. A significant Seebeck coefficient was found in tin selenide, which provides a high power factor and low thermal conductivity.

High-performance devices development and advantages and properties of the material using, a necessary condition (prerequisite) is a thorough study of the optical, optoelectronic properties and band structure of SnSe crystals and nanostructures. A number of works are devoted to the investigation of material properties, Raman and infrared reflection and absorption spectra [3], edge absorption spectra [4], electroreflectance [5] and temperature dependences of optical properties of thin films of SnS [6] were investigates. The band gaps associated with indirect transitions vary from 0.58 eV [7] to 1.076 eV [8]. A scatter of direct band gap is larger 1.02 eV [9], 1.24–1.74 eV [10], 1.60 eV [11], and 1.9–2.3 eV [12]. The theoretical calculations of SnSe band structure effectuated by different authors give contrasictory results [11].

EXPERIMENTAL METHODS

SnSe single crystals were grown by the zone melting method in sealed ampoules. The received ingots had sized around 1×1×1.5 cm and cleaved easy. This fact allows to receive the mirror surfaces of samples with different thicknesses (100 μm–3 mm). The thinner samples (7–10 μm) were exfoliated by an adhesive scotch type. The crystals quality and their space groups were controlled by x-ray methods. The presence of structural phases, for example, $SnSe_2$ in the SnSe crystalline ingot was monitored under a microscope and by Raman spectra measured in various regions of ingot.

Optical transmission and reflection spectra were measured on the double grating high-aperture spectrometer SDL-1 with aperture 1:2 and linear dispersion 7 Å/mm. The low temperature spectra were recorded from samples deposed in closed helium optical cryogenic system LTS-22 C 330. Al optical measurements were performed when entrance and exit spectrometer slits not exceeding 70 μm, i.e. with a resolution of ~ 0.5 meV. Surfaces of investigated samples were perpendicular to *b* axis and had a high reflectivity. Some room temperature reflection and transmission spectra measurements were carried out at spectrophotometers Specord-M40 and Jasco V-670. Wavelength modulation spectra of reflection and transmission were measured by help of spectrometer MDR-2 (aperture 1:2 and linear dispersion Å/mm).

EXPERIMENTAL RESULTS AND DISCUSSION

SnSe crystals attracted much attention of researchers due to the ultra-low lattice thermal conductivity and pronounced thermoelectric effect [1]. Recently it was established that thin films of metastable SnSe with cubic structure of NaCl type grown by epitaxy have the properties of crystalline topological insulator [13]. Under conditions of quasi-hydrostatic compression higher than 27 GPa the superconductivity was observed in SnSe [4]. At this pressure, SnSe undergoes a structural transition to a phase of CsCl type (space group *Pm3m*). Tin monoselenide crystalized in layered structure of orthorhombic syngony with space group *Pnma* (lattice parameters $a = 0.447$ nm, $b = 0.419$ nm, $c = 1.148$ nm and $Z = 4$). Thus this orthorhombic crystal structure can be considered as a deformed structure of rock salt NaCl. In the wavelength modulation reflection ($\Delta R/\Delta\lambda$) spectrum shown in Fig. 1 the both $n^A = 1$ and $n^A = 2$ maximums are more clear. The maximum $n^A = 2$ is situated at the same energies (1.195 eV) like in the case of reflection spectrum. Taking into

account the positions of ground and excited states the binding energy of excitonic state A is equal to 94 meV.

Figure 2 illustrates the wavelength modulation reflection spectrum ($\Delta R/\Delta\lambda$) of thin ($d = 67$ μm) SnSe crystals in energy range 1.05–1.2 eV at temperature of 10 K. The spectrum possesses the clear interference fringes. In the long-wavelength part from the frequency of transversal exciton (ω_T) and the short-wavelength part from the longitudinal exciton (ω_L) the series of big interference bands, corresponding to Fabry-Perot case, is clearly recognized. Light waves in the through crystal passing process reflect from front and back surfaces of sample and interfere. Taking into account energy positions of maxima and minima and using relation $n = \frac{1}{2d}\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)$ (where d – thickness, λ_1 and λ_2 – positions of neighbor maxima or minima) refractive index n spectral dependence were calculated. In the interval between energies of transversal and longitudinal excitons the dense interference fringes can be recognized in the interference spectrum, Fig. 2.

In wavelength modulation transmission spectra of SnSe crystals with thicknesses of 4.5 μm recorded at temperature 10 K the dense and rare interference bands were observed (Fig. 3). The dense fringes are observed just in the region of polaritonic mods of excitons A and B. At energies $E < 1.385$ eV (energy of transversal mode ωT of exciton B) the rare fringes are more intensive and in region $E > 1.433$ eV. At energy range 1.385–1.433 eV the series of narrow interference fringes which also thicken as energies rise is observed, Fig. 3. These dense interference lines are recognized in energy range $E(\omega T) < E < E(\omega L)$. In the over energy intervals except the abovementioned the rare interference is found out.

Positions of maxima of large interference bands N corresponds to Fabry-Perot conditions

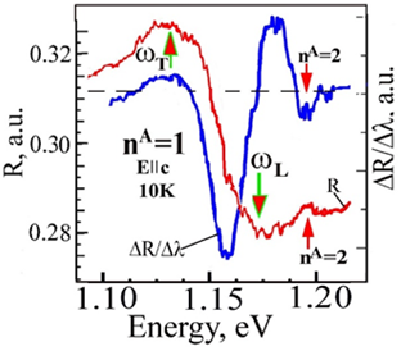

Figure 1. Reflection (R) and wavelength modulation reflection spectra ($\Delta R/\Delta\lambda$) of SnSe crystals measured at 10 K in E||c polarization

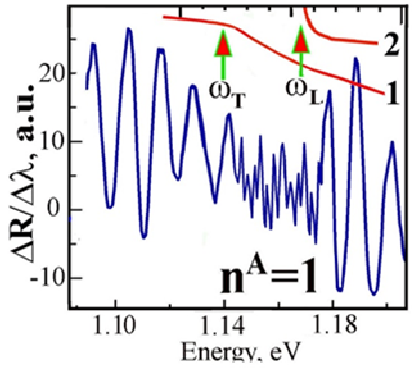

Figure 2. Wavelength modulation reflectivity ($\Delta R/\Delta\lambda$) of SnSe single crystal with thickens of 67 μm measured at temperature 10 K in polarization E||c

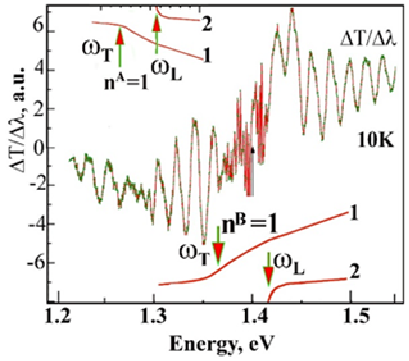

Figure 3. Wavelength modulation transmission ($\Delta T/\Delta\lambda$) spectrum of SnSe crystals with 4.5 μm thickness measured at temperature 10 K and polaritonic branches of A and B excitons

$2n_r^* d = \lambda_0 N$ where n^*_r ($r = 1.2$, $\lambda_0 = 2\pi c/\omega$ – light wavelength in vacuum). The misrepresentation of interference is due to influence of branch 2 of exciton polaritons (when $\omega < \omega_L$ decaying deep into the crystal) and exciton decay. As the crystal thickness d increases, the interference fringes become frequent, and the amplitude of additional oscillations decreases. For of these oscillations observing the condition $d \leq L_1$ ($L_1 = (n_1^* k_0)^{-1}$ – mean free path of exciton polariton branch) is necessary.

CONCLUSIONS

By investigation of different optical spectra (absorption, reflection, photoluminescence and wavelength modulation reflection and transition) measured at different temperatures in energy range 1.1–1.5 eV the main parameters of SnSe crystals were determined. In the region of A and B excitonic series two type of interference fringes (rare and dense) were found out. The dense interference fringes are due to interference of additional waves of exciton polaritons. The rare interference is caused by Fabry-Perot interference of exciton polaritons of branch ω_T. In interval ω_T–ω_L the rare oscillations superimposed on the dense fringes resulting from the mutual interference of exciton polaritons branches ω_T and ω_L.

ACKNOWLEDGMENT

The authors acknowledge financial support from the Ministry of Education, Culture and Research of Moldova under the Grants #20.80009.5007.20 and # 22.80013.5007.4BL.

ACKNOWLEDGMENT

The authors declare that they have no conflict of interest.

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