

Photoluminescence spectra of polycrystalline CVD ZnSe when changing the wavelength of excitation light

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Received 30-Apr-2024; Accepted 24-May-2024

Abstract

In this work, we investigated the photoluminescence spectra of polycrystalline CVD ZnSe observed by stepwise variation of excitation energy in the region of the fundamental absorption edge, first from 420 nm to 455 nm in 5 nm steps, then 10 nm from 455 nm to 475 nm and finally 20 nm from 475 nm to 515 nm.

Keywords: polycrystalline zinc selenide, photoluminescence spectra, chemical vapour deposition-grown ZnSe

PACS: 32.50.+d; 78.55.-m; 81.15.Gh

1. Introduction

Wide-gap A2B6 semiconductors, in particular zinc selenide, are a promising material, the crystals of which are used in various fields of optoelectronics and laser technology [1, 2]. Due to the large band gap, especially pure polycrystalline ZnSe has a high resistivity, is still transparent in the visible region of the spectrum and transmits infrared radiation well.

The homogeneity region of CVD-zinc selenide has a two-sided character and, unlike other zinc chalcogenides, it is characterized by a wide range of compositions

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with an excess of oxygen and selenium - ZnSe(O)Se. In this work, the photoluminescence spectra of polycrystalline CVD (chemical vapor deposition) ZnSe were studied with a step change of 30 meV in the excitation energy in the region edges of fundamental absorption.

2. Methods and experiments

Samples of polycrystalline ZnSe 3 mm thick were obtained by chemical vapor deposition (CVD) at the Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences (Nizhny Novgorod) [3]. Growth samples specially not doped. The concentration of background impurities for the studied sample of polycrystalline CVD ZnSe was determined by two methods: atomic emission spectroscopy and laser mass spectrometry. Total impurity content $<10^{16}-10^{17} \text{ cm}^{-3}$ ($\text{Cu} \sim 10^{16} \text{ cm}^{-3}$). The oxygen concentration is controlled by chemical gas chromatographic analysis: $\text{O} \sim 10^{18}-10^{20} \text{ cm}^{-3}$ [3,4].

Photoluminescence spectra (Fig.1-3) were obtained using a universal fluorescence spectrometer – Fluo Time 300 Easy Tau. A xenon lamp with a power of 300 W was used as an excitation source in the spectrometer. All measurements were carried out at $T = 300 \text{ K}$.

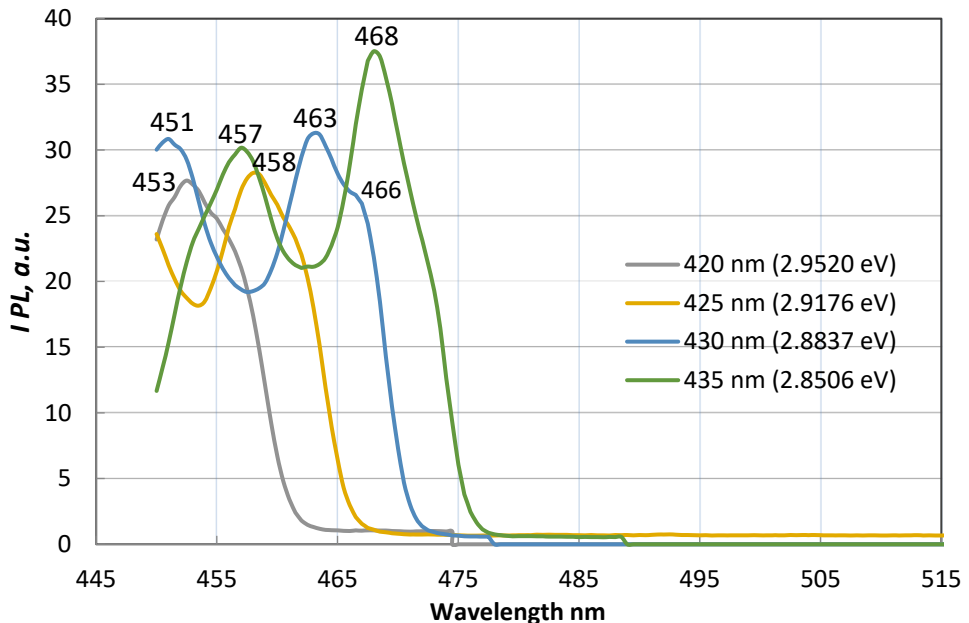


Fig. 1. PL spectra of CVD ZnSe upon excitation with lengths waves: 420–435 nm

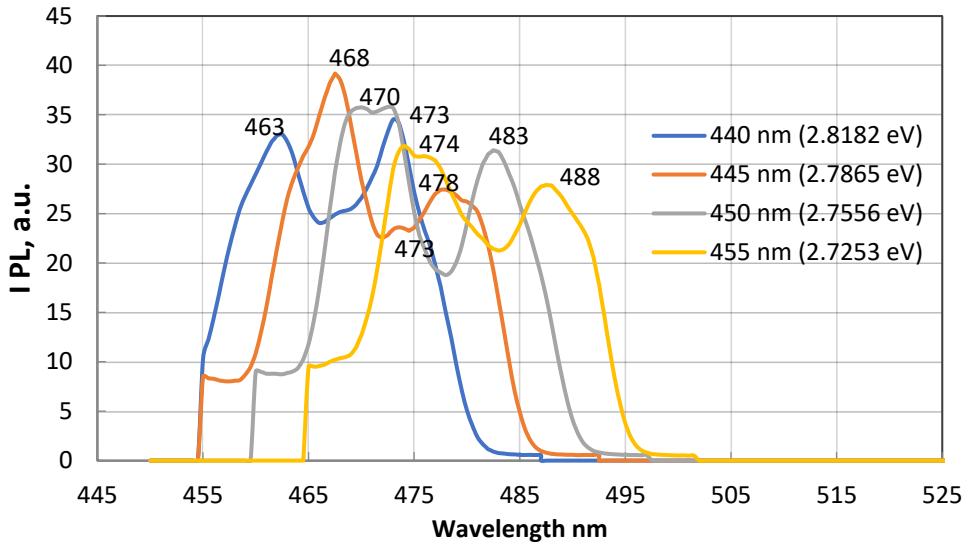


Fig. 2. PL spectra of CVD ZnSe upon excitation with lengths waves: 440–455 nm

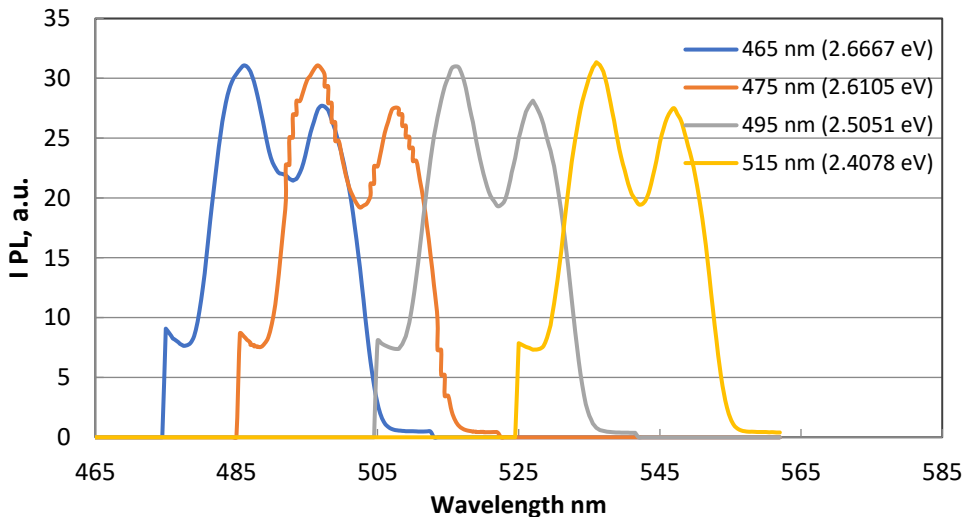


Fig. 3. PL spectra of CVD ZnSe upon excitation with lengths waves: 465–515 nm

When the excitation energy was changed stepwise with an interval of 5 nm close to the LO-phonon energy (~ 37 – 31 meV) in ZnSe, the PL spectra were observed in wavelength range 451–497 nm (Fig.1), i.e. multi-band exciton spectra were observed, and when excitation was from 455 nm to 515 nm with an interval of 10 nm and 20 nm (Fig. 2), mainly green and yellow-green spectra were observed in the

wavelength range 507-547 nm (Fig. 3). At different excitation wavelengths, different PL photoluminescence bands appear. With decreasing excitation energy, the exciton band is joined by its LO or 2LO. phonon repetitions. The low-energy shift of the photoluminescence spectra upon the excitation energy corresponds to a shift along the energy scale of the band model with a corresponding change in the type of radiative transitions.

In contrast to the cathodoluminescence spectra, when these bands are recorded only at 80 K, in the PL spectra multiphonon excitonic bands in the region of 477-490 nm are observed at 300 K.

3. Discussion of results

Wavelength range 451–497 nm, i.e. multiband exciton spectra were considered and analyzed in [5]. Green and yellow-green spectra in the wavelength range 507-547 nm can be attributed to impurity-defect luminescence of polycrystalline CVD ZnSe, which is due to oxygen centers on structural defects of the lattice, including background copper impurities [6, 7]. It can be argued that in crystals with a low copper content (as a background impurity), the green band in the luminescence spectrum is observed due to excitation by light from the intrinsic absorption region of CVD ZnSe. The authors of [8-12] have shown that the intensity of the green band depends on the oxygen content and, based on the band anticrossing model, assumed that in crystals with sp^3 , under the influence of an isoelectronic impurity (including in ZnSe under the action of oxygen), a band gap bowing has been observed. The authors [13, 14] showed that depending on the oxygen content, the change in the band structure is different and this determines the formation of a complex multiband structure. The shift of the subbands corresponds to ~ 0.1 eV per 1 mol % of dissolved oxygen in ZnSe. Copper ions $Cu^+(3d10)$, $Cu^{++}(3d9)$ form a stable complex with oxygen, the so-called associative acceptor center, where the level of $Cu^+(3d10)$ is 0.72 eV above the valence band, and $Cu^{++}(3d9)$ is 0.4 eV [15,16].

We believe that the green luminescence with maxima in the wavelength range 507-547 nm is due to electron transfer from a small donor ($E_D \sim 10-20$ meV) to an associative acceptor center including oxygen and copper- $\{Cu_i Ose\}$.

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