STUDY OF EDGE LUMINESCENCE UPON CHANGING THE WAVELENGTH OF THE EXCITING LIGHT WITH AN INTERVAL CLOSE TO THE LO PHONON ENERGY IN ZnSe

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The specific features of the photoluminescence (PL) spectra at T=300 K in the 451-468 nm wavelength range of a special undoped polycrystalline CVD (chemical vapor deposition) ZnSe were studied when the excitation light wavelength was changed from 400 to 435 nm with an interval 5 nm close to the LO phonon energy in ZnSe. The proposed study makes it possible in the terms of polaritons to clarify more correctly the "anomalous edge" luminescence observed in this wavelength range as localized excitons for ZnSeO (Se) samples with a small excess of selenium and at extremely saturated oxygen.

1. INTRODUCTION

Study of ZnSe luminescence provides information about the mechanisms of luminescence and the parameters of recombination centers, and also helps to identify the necessary technological conditions for growing sufficiently high-quality samples with low concentrations of uncontrolled impurities [1-4]. To obtain more complete information, it is necessary to excite the sample by different methods and different light sources. In particular, this is of interest when the wavelength of the exciting light can be changed insignificantly, since this makes it possible to excite spatially separated luminescence centers in the bulk of the sample. In the given paper, the measured PL spectra of polycrystalline CVD ZnSe in the 451-468nm wavelength range are analyzed on a Fluo Time 300 Easy setup with a change in the exciting light wavelength from 400 nm to 435 nm with an interval close to the LO phonon energy in ZnSe (31-35 meV) [1,2].

2. EXPERIMENTAL

Photoluminescence spectra (Fig. 1) were obtained using a universal fluorescence spectrometer (Fluo Time 300 Easy Tau). A 300W xenon lamp was used as the excitation source for the sample. The sample was excited at wavelengths of 400, 410, 420-435 nm, and all measurements were carried out at T=300K.

Monochromators allow achieving spectral resolution up to 0,1 nm in a wide wavelength range from 200 to 1700 nm. The spectrally filtered excitation radiation from the output slit of the monochromator is first collimated using a quartz lens. The design provides a high measurement rates of up to 10 million counts/sec and provides a high stable, crystal-calibrated time resolution of 4 ps.

3mm-thick polycrystalline ZnSe samples were obtained by chemical vapor deposition (CVD) at the Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences (Nizhny Novgorod) [5]. Crystal growth from the vapor phase occurs at a lower temperature compared to melt technology. This contributes to reduce the concentration of bulk defects, and also makes it possible to reduce the growing crystal contamination by the material of the ampoule. The concentration of background impurities for the polycrystalline CVD ZnSe sample under study was determined by two methods: atomic emission spectroscopy and laser mass spectrometry. The total impurity content is $<10^{16}$~10^{17} cm^{-3} (Cu~10^{16} cm^{-3}). Oxygen concentration is controlled by chemical gas chromatographic analysis: O ~ 10^{18}-10^{20} cm^{-3}. Quantitative X-ray microanalysis determined the composition of the ZnSe phase and distribution of chemical elements on the surface of the sample under study (Fig. 2). The analysis of the results obtained shows the homogeneity of the surface and the change in stoichiometry within the homogeneity region towards the excess of selenium.

3. RESULTS AND DISCUSSION

When the sample was excited by light with wavelengths of 400 and 410 nm, no maxima were observed in the PL spectrum, but a maximum in the spectrum at λ_{max}=453 nm (2.74 eV) was observed at λ_{ex}=420 nm (2.95 eV). There cannot be such a maximum at T=300K (since the quantum energy corresponding to the maximum is greater than E_g). If we take E_g=2.714 eV, then it appears that the energy of the quantum corresponding to the maximum is 26 meV higher than E_g. The energy 26 meV is the energy of TO phonons in ZnSe. Further excitation of the sample was carried out at wavelengths of 425, 430, 435 nm, while the quantum energy decreased by 35 meV each time, i.e. at the same energy of LO phonons in ZnSe. Upon excitation by light with λ_{ex}=425 nm (2,92 eV), the maximum is formed at λ_{max}=458 nm (2.71 eV), the second has not yet formed completely, and at λ_{ex}=430 nm (2,88 eV), a maximum is recorded at λ_{max}=463 nm (2,68 eV) and the second at λ_{max}=451 nm (2,75 eV), and if the sample is excited with light with λ_{ex}=435 nm (2,85 eV), the maxima are observed at λ_{max}=468 nm (2,65 eV) and λ_{max}=457 nm (2,71 eV).

The process of radiative recombination that occurs upon excitation of a sample with λ_{ex}=420-435nm is would be better to be considered in the language of polaritons [6] and on the basis of the band model, which is proposed in [3,7,8]. Interpretation of the spectra (Fig. 1) in the language of polaritons consists in the transformation of external photons inside crystals into polaritons. For absorption to occur, polaritons must undergo inelastic-weak scattering by phonons, i.e., relax with the help of phonons: high-energy polaritons belonging to branch I [6] have strong photonic components in their wave functions (and are therefore referred to as photon-like). They interact weakly with phonons (it can be assumed that they interact with TO phonons) and have a high probability of leaving the medium. It is with this that we associate the observation of the maximum at λ=453 nm with the excitation of the sample at λ_{ex}=420 nm. Furthermore, it can be expected that polaritons as a result of elastic scattering by defects, i.e. effectively losing their energy pass to branch II [6], where the wave functions have a large exciton component (exciton-like) and thus dissipation of the energy of polaritons inside the medium occurs, which leads to optical absorption. In this case, it can be assumed that polaritons are more strongly scattered by phonons, which leads to the interaction of polaritons not only with TO phonons, but

also with LO phonons, and therefore, the observation of exciton maxima upon excitation of a sample with λ_{ex}=425-435 nm can be asserted. We have all these maxima observed at T=300K, while in [3, 6-8] they are considered only at low temperatures. The authors of [3,7,8], using the theory of anti-intersecting bands, which takes into consideration the effect of an isoelectronic oxygen impurity on the band structure that is invariably present in the ZnSe lattice, showed that, depending on the oxygen content, the change in the band structure is different and this determines the formation of a complex multizone structure in ZnSe·Se (O).

In ZnSe·Se(O) samples with an excess of selenium and oxygen close to p-type conductivity, segregation of oxygen-containing complexes at stacking faults (SF) [3,8] is observed, where the oxygen concentration $[O_{Se}]$ ~10^{20} cm^{-3}, however, in "pure" layers, it can be ~10^{19}cm^{-3}.

Photoexcitation of the sample with a change in the photon energy of the exciting light in the range of 35-30 meV (and can also be changed in another way) leads to a change in the penetration of the exciting light into the bulk of the crystal, that allows to excite spatially separated luminescence centers. Hence, based on this method, we can more accurately analyze the change in the type of radiative transitions in ZnSe·Se(O).
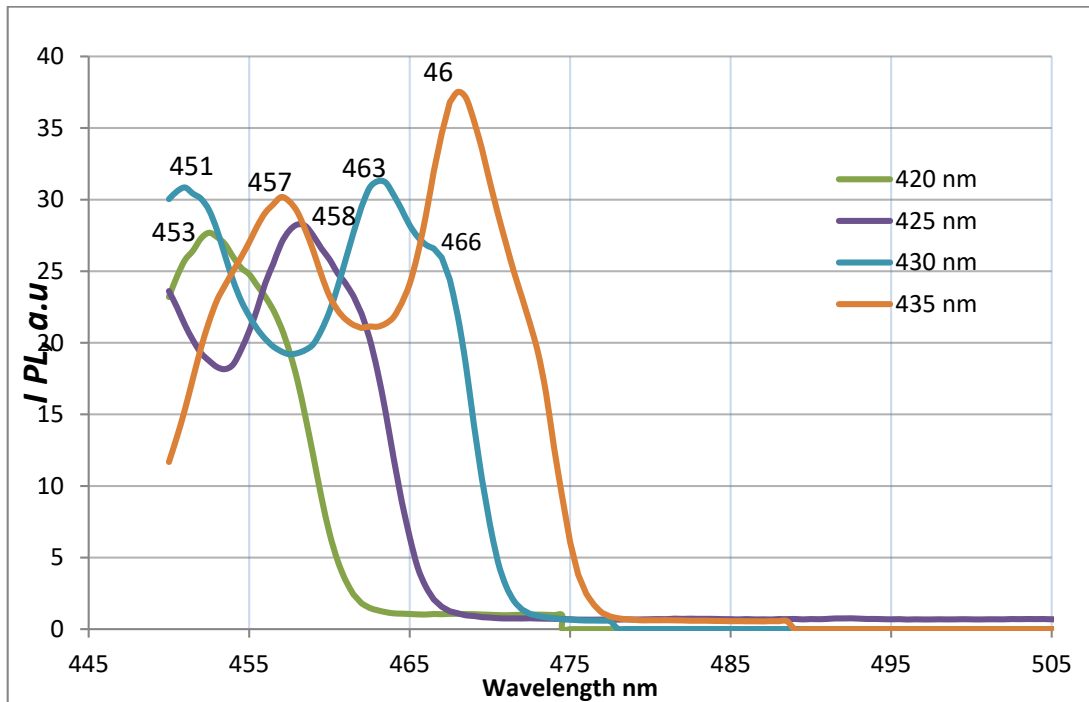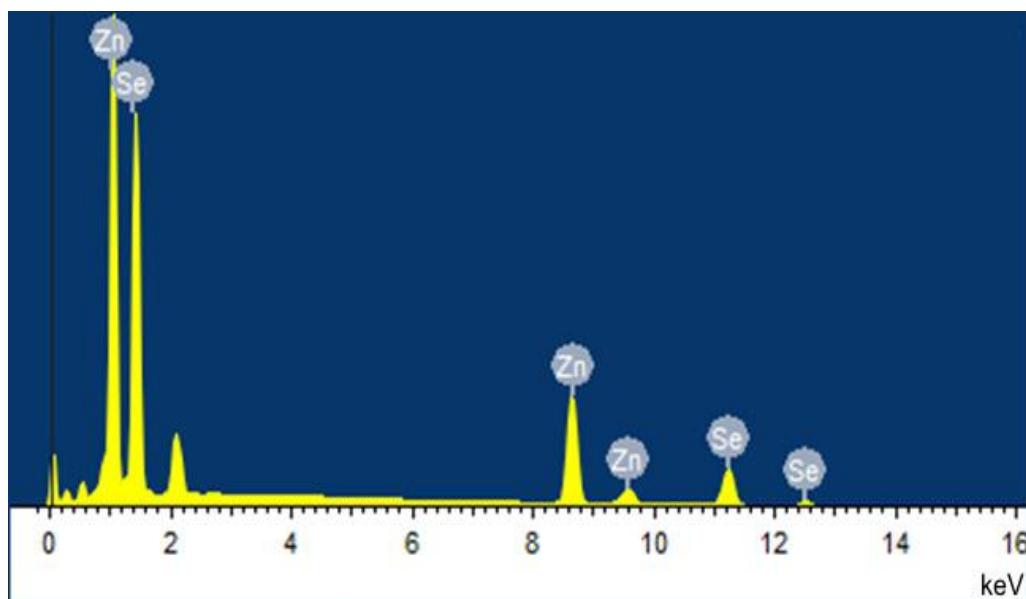

Fig. 1. PL spectra upon excitation of a CVD ZnSe sample by light with λ_{ex} (E_{ex}): 420 nm (2.95 eV), 425 nm (2.92 eV), 430 nm (2.88 eV), and 435 nm (2.85 eV).

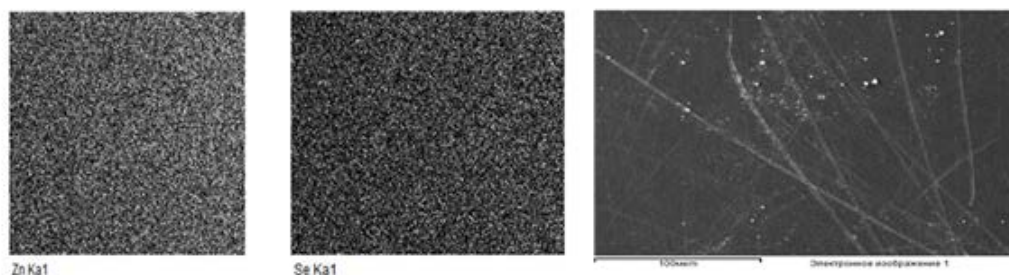| Element	Wt.%	At%
Zn K	44.08	48.78
Se L	55.92	51.22

Zn Ka1

Se Ka1

Fig. 2. X-ray microanalysis and micrographs of the CVD ZnSe crystals surface

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