LUMINESCENCE OF POROUS ZNSE LAYERS

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ZnSe based II-VI compounds have been extensively investigated for their potential application in the blue-near ultraviolet light emitters [1] and spintronic devices [2,3]. The nanostructuring of these materials is expected to expand the field of application to photonic devices including random lasers and photonic crystals. Photon-assisted electrochemical etching of semiconductor materials provides a cheap nonlithographic method for preparation of random media with controlled morphology starting from discrete scatterers with strong short-range disorder, up to smooth long-range inhomogeneity in weakly disordered media. These media can be used as resonators in random lasers. Gain of luminescence was recently observed in specific porous CdSe nanostructures and attributed to the formation of ring microcavities for light in the porous network [4].

In this paper we compare the luminescence properties of bulk ZnSe crystals and porous layers prepared by photon-assisted electrochemical etching.

ZnSe single crystals were grown by chemical transport techniques using iodine as transport agent. The technological conditions of electrochemical etching were described elsewhere [5]. The morphology of etched samples was studied using a TESCAN Scanning Electron Microscope (SEM) equipped with an Oxford Instruments INCA Energy EDX system operated at 20 kV. Photoluminescence (PL) was excited by the 351 nm line of an Ar^+ SpectraPhysics laser and analyzed through a double spectrometer. The resolution was better than 0.5 meV. The samples were mounted on the cold station of a LTS-22-C-330 cryogenic system.

Fig. 1 presents the top view SEM image taken from a porous ZnSe layer. One can estimate from Fig. 1 that the respective etching conditions result in an average pore density of 1×10^{10} cm^{-2} with a random distribution of pores with average dimensions of 50 nm. EDX microanalysis proved the stoichiometric composition of the skeleton in porous ZnSe. Fig. 2 compares the PL spectra of as-grown and porous ZnSe samples. The inset shows the excitonic luminescence in more details.
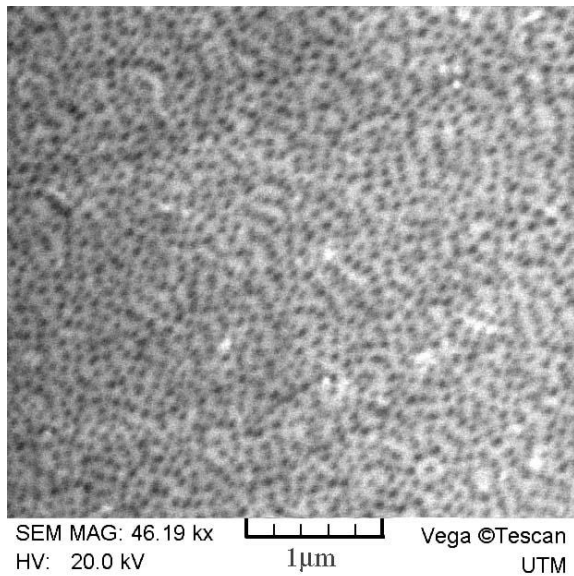
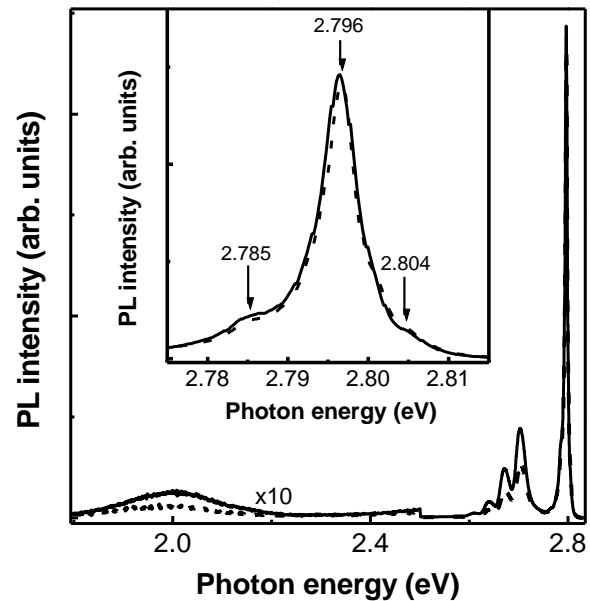Fig. 1. SEM image taken from a porous ZnSe layer.

Fig. 2. PL spectra of a bulk ZnSe single crystal (solid line) and a porous ZnSe layer (dash line) measured at T = 10 K.

The excitonic PL is dominated by overwhelming D^0X exciton recombination emission with the maximum at 2.796 eV and FWHM of 4 meV. The right and left side shoulders at 2.785 eV, and 2.804 eV are related to acceptor bound (AX) and free excitons (FX), respectively. One can see, that the excitonic luminescence is identical for as-grown and porous material, while the donor-acceptor pair (DAP) related emission at 2.702 eV with 1LO and 2LO phonon replicas at 2.670 and 2.638 eV, respectively, is by a factor of two lower in the porous material. Apart from this near band gap emission, a week red PL band with the maximum at 2.0 eV, related to deep impurity levels is observed in both as-grown and porous ZnSe. However, the intensity of this PL band in porous material is by a factor of three lower in comparison with the as-grown material. The deep level related luminescence is commonly believed to come from structural defects [6,7], and the relative PL intensity ratio of the near-band edge emission to the deep level related emission is used as a parameter for estimation the quality of the material. One can conclude that the quality of the porous skeleton is higher.

Fig. 3 shows the evolution of PL spectra of ZnSe with the temperature increase. The PL intensity is redistributed in the favor of free exciton emission with increasing temperature, especially for temperatures higher than 200 K as evident from the inset. This redistribution is

explained by the more effective quenching of the luminescence related to bound excitons, since the binding energy of bound excitons is lower than the binding energy of free excitons.
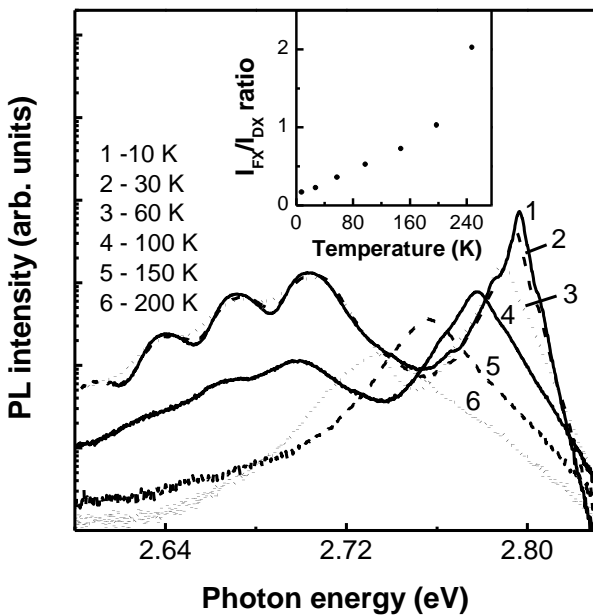

Fig. 3. PL spectra of ZnSe measured at different temperatures with the excitation power density of 50 W/cm².
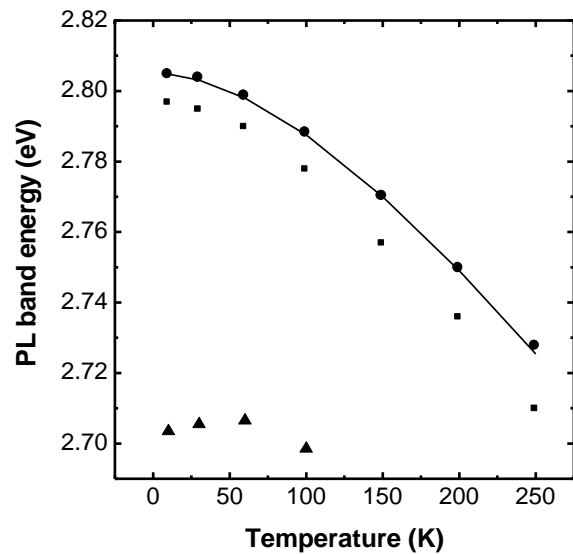

Fig. 4. Temperature dependence of PL bands position in ZnSe: circles are for FX band, squares are for D^0X band, and triangles are for DA band.

The intensity of the DA luminescence is stable up to 60 K, and sharply decreases at higher temperatures. The temperature dependence of the PL bands position is illustrated in Fig. 4. The position of the DA PL band is shifted to higher photon energies with the temperature increase up to 60 K. This behavior is attributed to the ionization of the impurity with smaller binding energy involved in DAP transitions. Therefore, the free-to-bound transitions dominate at temperatures higher than 60 K, and the position of this PL band is red-shifted with the temperature increase above 60 K.

The solid curve in Fig. 4 represents the fit of the FX band position to the experimental data by the phenomenological Varshni formula [8]:

$E(T) = E_0 - \alpha T^2/(T+\beta)$, with $E_0 = 2.805$ eV, $\alpha = 7 \times 10^{-4}$ eV K^{-1}, and $\beta = 300$ K parameters.

Note that these data corroborate the previously reported α and β parameters of ZnSe [9].

The analysis of the dependence of PL intensity in porous ZnSe layer on excitation power density (Fig. 5) shows a sublenear dependence for the DA band with a slope of 0.63 and a nearly linear dependence for the excitonic bands. The position of the excitonic PL bands is independent on the excitation power density, while the DA band shifts to higher energies when increasing

excitation power (Fig. 6), which is consistent with the saturation of distant pairs under increasing excitation, as expected for DAP recombination.
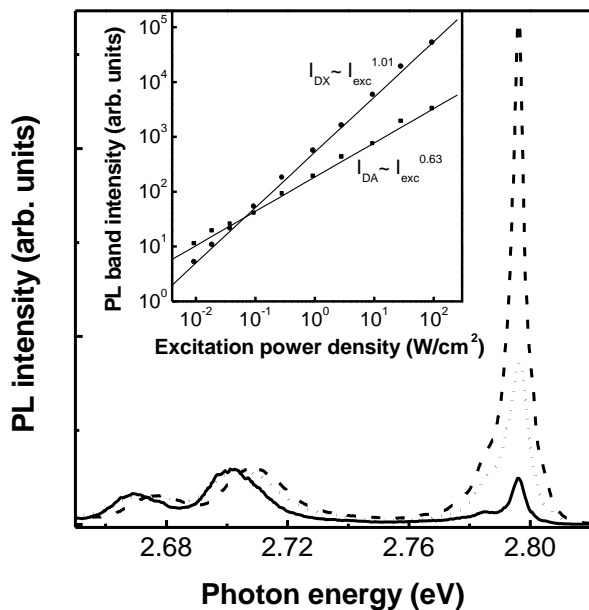

Fig. 5. Excitation power density dependence of PL in porous ZnSe. Excitation power density is 0.04 W/cm^2 (solid curve), 1 W/cm^2 (shot dash curve), and 30 W/cm^2 (dash curve). In the inset circles are for the D^0X band, and squares are for the DA band.
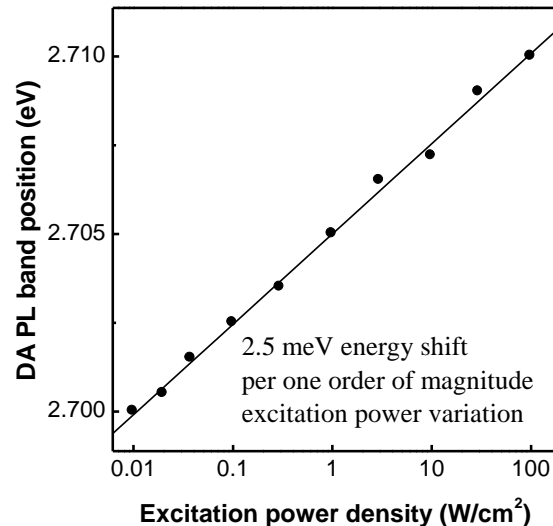
Fig. 6. The spectral peak position of the DAP emission in porous ZnSe layer as a function of the excitation power density. The solid line represents the linear least square fit of experimental data.

Note that no energy shift of excitonic PL bands and no deviation from linearity of the DAP emission peak position as a function of the excitation power density was observed up to 300 W/cm^2. This is in contrast with the behavior of a porous InP layer with average pore dimensions of 200 nm in which the excitonic PL bands shift to lower energies and the saturation of the DAP emission intensity with the increase of excitation power density was attributed to the trapping of the laser light inside the porous network. One can conclude that ZnSe layers with the average pore dimensions of 50 nm are optically homogeneous and no light trapping occurs. Moreover, the porous layers are of an optical quality better that the bulk material.

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