INTENSE LUMINESCENCE FROM POROUS ZnSe LAYERS

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Abstract

We report on the possibility to prepare ZnSe porous layers with different degrees of porosity by means of electrochemical methods. The prepared porous structures were characterized using scanning electron microscopy (SEM), photoluminescence (PL) and cathodoluminescence (CL) techniques. The PL of the as-grown material and porous layers measured at low temperatures (10 K) was found to be dominated by an emission band at 2.796 eV as well as a band at 2.700 eV with several phonon replicas. The analysis of the dependence of these bands upon the excitation power density and temperature suggests that free-to-bound and respectively donor-acceptor electron transitions are responsible for the emission bands involved. The comparison of SEM and CL images taken from the same porous regions demonstrated that cathodoluminescence intensity from layers with small characteristic sizes of the porous entities (around 50 nm) is weaker than that inherent in bulk material, while porous layers with the pore diameter of around 500 nm exhibit much stronger luminescence.

Introduction

The porous form of III-V semiconductors was extensively studied during the last decade. Porosity enhanced phenomena such as optical second harmonic generation and Terahertz emission have been reported [1-4]. Porosity induced increase of cathodoluminescence (CL) intensity was observed in GaP [5]. In spite of the huge surface inherent in porous matrix, gallium phosphide in the porous form shows CL intensity one order of magnitude higher than that of bulk crystals under the same excitation conditions. On the other hand, relatively little attention has been previously paid to the study of porosity-induced changes in the properties of II-VI compounds. The effect of photoetching on photoluminescence (PL) of n-CdSe was studied many years ago [6], but the authors claimed the formation of etch pits rather than pores. Formation of porous network which extends more than 100 μm below the initial surface was recently reported in p-$Cd_{1-x}Zn_xTe$ by Erné *et al.* [7, 8]. Besides, Zenia *et al.* subjected p-ZnTe crystals to electrochemical etching and observed the formation of needlelike structures exhibiting a blueshift of the excitonic transition energies [9]. Porous CdSe layers have been recently produced by anodic etching of crystalline substrates in a HCl solution. It was found that anodization under in-situ UV illumination results in the formation of uniformly distributed parallel pores with the diameter of 30 nm, stretching perpendicularly to the

initial surface. At the same time pronounced non-uniformities in the spatial distribution of pores were evidenced in samples subjected to anodic etching in dark [10]. Gain of luminescence was observed in some porous regions and attributed to the formation of ring microcavities for light in the porous network [11].

ZnSe is one of the most important wide-band-gap semiconductors suitable for nanostructuring by means of electrochemical methods. This material is especially interesting in connection with the development of random lasers. Nanocomposite materials prepared on the basis of porous semiconductor templates are most suitable for this purpose, due to the possibility of integration with other optical or electronic functions. Strong light scattering in the porous ZnSe network can ensure the necessary conditions for a resonant feedback. On the other hand, since ZnSe is a direct wide-band-gap semiconductor, it can play the role of a dense exciton system, and assures lasing effects due to exciton-exciton scattering and stimulated emission of electron-hole plasma. The band gap of ZnSe allows emission in the blue spectral region.

In this paper we report on the possibility to prepare ZnSe porous layers with different degrees of porosity including the one ensuring strong light scattering by means of electrochemical methods.

1. Experimental details

Zincblende-phase n-ZnSe single crystals were grown by chemical transport techniques using iodine as transport agent. Electrochemical etching was carried out at room temperature under potentiostatic conditions as described elsewhere [12]. The morphology and chemical composition microanalysis of etched samples were studied using a TESCAN Scanning Electron Microscope (SEM) equipped with an Oxford Instruments INCA Energy EDX system. 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. Cross-sectional CL images of the anodized samples were recorded in a Hitachi S2500 SEM at 90 K with an accelerating voltage of 20 kV, by using a Hamamatsu R928 photomultiplier.

2. Results and discussion

Multilayer porous ZnSe structures were prepared by changing the parameters of electrochemical etching. Different samples as well as different layers on the same sample are characterized by different degrees of porosity, different pore diameters and different thicknesses of the porous skeleton walls. Fig. 1 compares the CL spectra of three samples measured at 85 K. Samples 1 and 2 represent multilayer porous structures with the sizes of the porous entities varying from 50 to 500 nm in different layers, while sample 3 is a uniform porous structure with the diameter of pores around 500 nm. As one can see from Fig. 1 the CL spectra recorded in all the samples are practically identical, except a high energy wing in sample 3. The samples show a broad band centered at 2.0 eV related to the recombination involving deep centers. There is no near bandgap emission, neither in porous layers, nor in the bulk substrate. In spite of the identical spectral distribution, the samples exhibit different CL intensities. The integral CL intensity in samples 1 and 2 is lower than the intensity in the bulk substrate (see Figs 2 and 3). The CL intensity in sample 3, on the contrary, is higher than that of the bulk substrate (see Fig. 4). The differences in the CL intensities are attributed to differences in the sizes of the porous entities of samples. Sample 3 with the bigger diameter of pores exhibits

the highest CL intensity. In order to analyze this issue we have compared the SEM and CL images in samples 1 and 2, which represent multilayer porous structures.
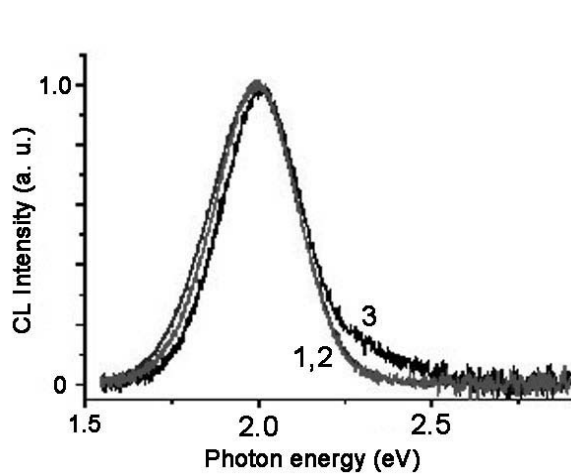

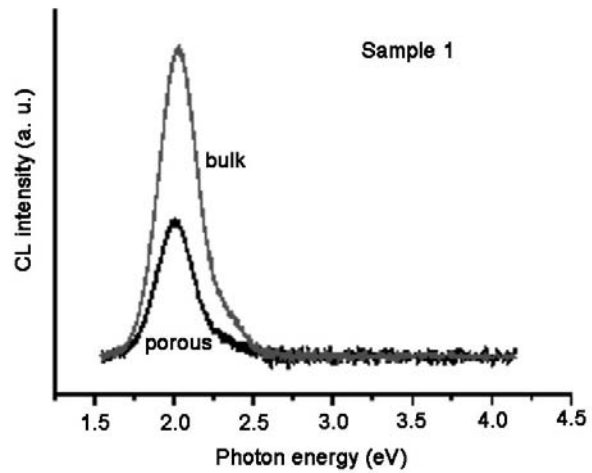Fig. 1. CL spectra of three porous ZnSe samples.

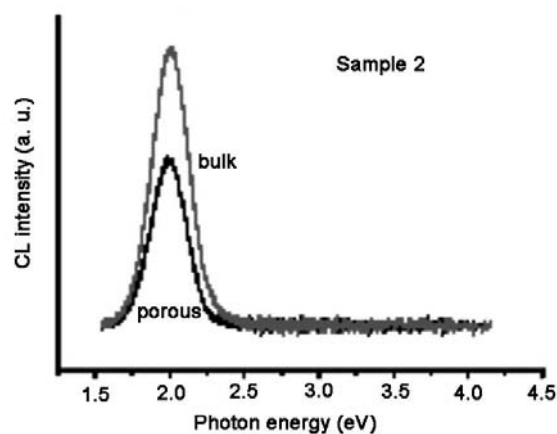Fig. 2. The comparison of the integral CL intensity in sample 1 and the bulk.

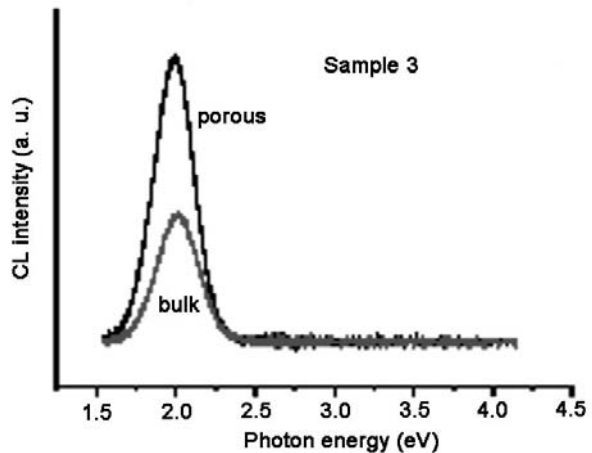Fig. 3. The comparison of the integral CL intensity in sample 2 and the bulk.

Fig. 4. The comparison of the integral CL intensity in sample 3 and the bulk.

Three regions with different degrees of porosity are well identified in the SEM image (Fig. 5). The sizes of the porous entities in the first layer are about 50 nm. The diameter of pores is 100 – 200 nm in the second layer, and about 500 nm in the third layer. One can see from Fig. 6 that the CL intensity increases with increasing sizes of the porous entity. Very bright spots are observed in some regions of the third layer indicating the gain of luminescence. This gain is attributed to the formation of ring microcavities for light in the porous network like that recently observed in CdSe porous layers [11].

Sample 2 also consists of layers with different porosity (Fig. 7). However, the distribution of porous entity sizes is more uniform in these layers, in contrast to the third layer of sample 1. The CL image is also more uniform inside each layer, no bright spots being formed. The layer with very small pore diameters (region 6) practically exhibits no CL, while the intensity of luminescence is highest in the region with bigger pore diameter.
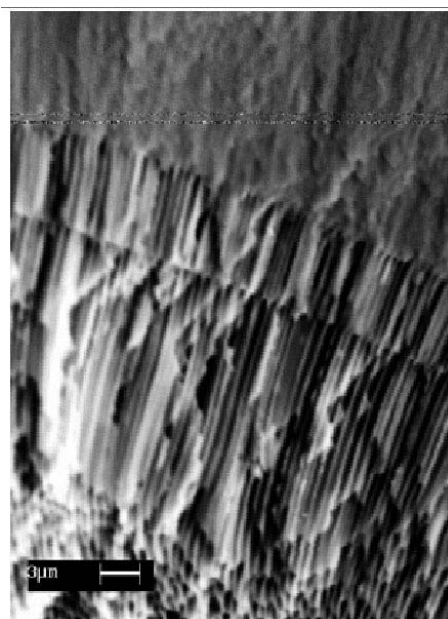
Fig. 5. SEM image taken in cross section from sample 1.
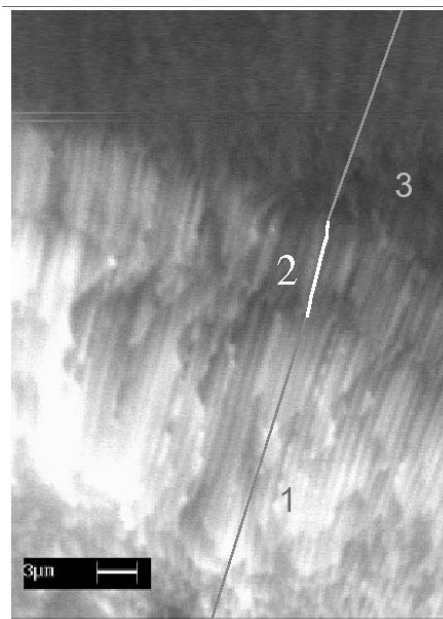

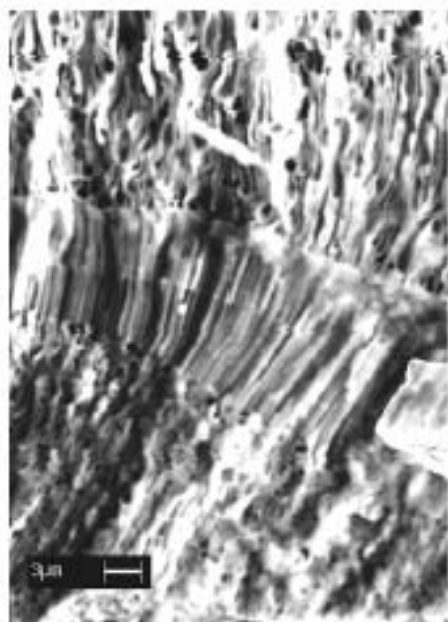Fig. 6. CL image taken from the same sample.

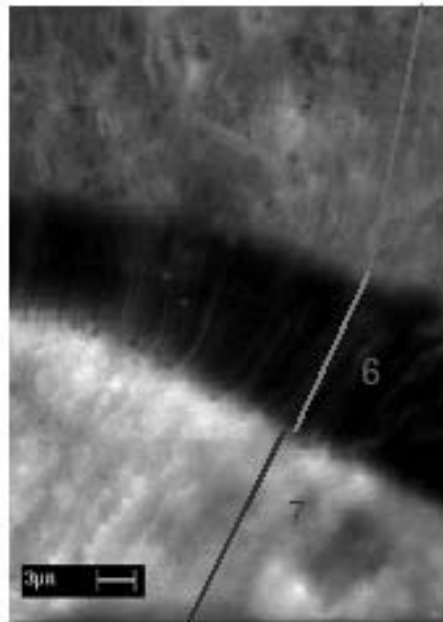Fig. 7. SEM image taken in cross section from sample 2.

Fig. 8. CL image taken from the same sample.

In contrast to CL measured at 80 K, the PL measured at 10 K shows a series of bands in the near bandgap spectral range. The PL spectra of the bulk as-grown material and porous samples are practically identical, i. e. no changes are introduced in the PL spectrum by elect-rochemical treatment. The near bandgap PL of the as grown material and the porous layers is dominated by an emission band at 2.796 eV as well as a band at 2.702 eV with 1LO and 2LO phonon replicas at 2.670 and 2.638 eV, respectively. The analysis of the dependence of these bands upon the excitation power density and temperature suggests that free-to-bound and respectively donor-acceptor electron transitions are responsible for these emission bands.
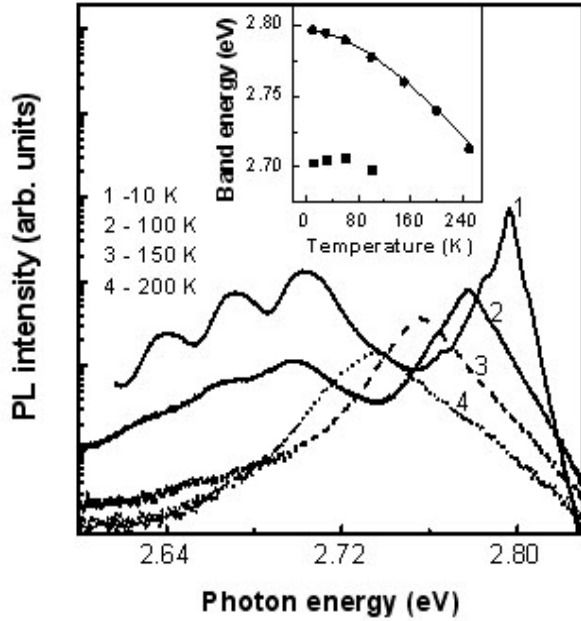
Fig. 9. PL spectra of a ZnSe sample measured at different temperatures with the excitation power density of 50 W/cm^2. Inserted is the temperature dependence of the PL band position.
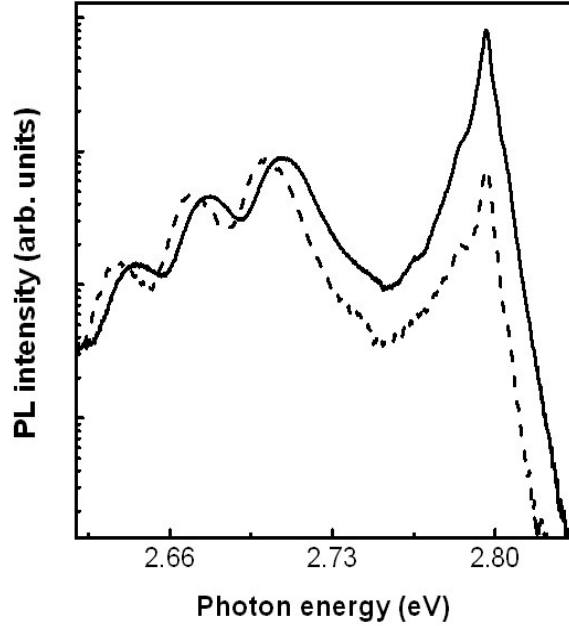
Fig. 10. Excitation power dependence of PL in a ZnSe sample. Excitation power density is 0.04 W/cm^2 (dash curve) and 30 W/cm^2 (solid curve).

Fig. 9 shows the evolution of PL spectra of ZnSe with the temperature increase. Usually, the PL bands situated at lower energies in the vicinity of free exciton bands (2.804 eV) are attributed to either bound excitons or free to bound transitions. The separation of the band at 2.796 eV from the free A-exciton band is 8 meV. If this band is associated with the recombination of bound excitons with the binding energy of 8 meV, it would result in a fast quenching at low temperatures. However, this PL band persists up to the room temperature, suggesting a free to bound origin. The solid curve in the inset of Fig. 9 represents the fit of the PL band position to the experimental data by the phenomenological Varshni formula [8]:

$E(T) = E_0 - \alpha T^2/(T+\beta)$, with $E_0 = 2.796$ 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]. One can deduce an activation energy of 23 meV of the impurity involved in this transition from the separation of the position of the PL band from the bandgap of ZnSe (2.819) eV.

The intensity of the second luminescence band at 2.702 eV is stable up to 60 K, and sharply decreases at higher temperatures. The position of this PL band is shifted to higher photon energies with the temperature increase up to 60 K. This behavior is consistent with the donor-acceptor pair (DAP) origin of the transitions responsible for this PL band. The impurity with smaller binding energy involved in DAP transitions is ionized at temperatures higher than 60 K. 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 position of the free-to-bound PL band is independent of the excitation power density, while the DA band shifts to higher energies when increasing excitation power (Fig. 10), which is consistent with the saturation of distant pairs under increasing excitation, as expected for DAP recombination.

Conclusion

The results of this work demonstrate the possibility to prepare ZnSe porous layers with different degrees of porosity by means of electrochemical methods. The comparison of SEM and CL images taken from the same porous structures demonstrates that cathodoluminescence intensity from layers with small characteristic sizes of the porous entities (around 50 nm) is weaker than in the bulk material, while porous layers with the pore diameter of around 500 nm exhibit much stronger luminescence. This gain of luminescence is attributed to the formation of ring microcavities for light in the porous network like that recently observed in CdSe porous layers.

Acknowledgements

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