CYSENI 2013, May 29–31, Kaunas, Lithuania
ISSN 1822-7554, www.cyseni.com

OBTAINING OF THE SUBSTRATES OF II-VI COMPOUNDS AND SOLID SOLUTIONS FOR NANOPOROUS STRUCTURES

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ABSTRACT

The wide band-gap II-VI semiconductors and solid solutions on their basis have large perspectives to be used in optoelectronics, solar energy and spintronics. Substrates of these materials could be widely utilized for fabrication of nanoporous matrices (templates) used for obtaining nanowires and nanotubes with various diameters and lengths. These nanostructures can be used as elements of LEDs, plate lenses, components of integrated optical circuits etc. One of the most interesting applications is solar energy converters with improved performance and cost effectiveness due to increased optical absorption in the region of nanostructured p-n junction and smaller necessary thickness of corresponding layers. The easiest and cost-effective method to obtain nanoporous structures is anodic etching. However, the technology development for II-VI compounds is still on the beginning stage.

This paper deals with the problems of growing homogeneous substrates of the widest band gap II-VI semiconductors (ZnSe, ZnS, ZnO) and solid solutions on their basis (ZnCdS, ZnSSe) with controlled electrical parameters. Prospects of these materials utilization for preparing nanoporous matrices by means of electrochemical etching are also estimated. Various methods of growth and doping of II-VI compounds are analyzed by examination of their morphology, electrical, luminescence and optical properties. The results of nanostructuring using various electrolytes are shown. The prospects of ZnSe and ZnCdS utilization for obtaining nanoporous arrays with porous diameters up to 30 nm are demonstrated. Also, the complexity of obtaining the nanoporous matrices on ZnS, ZnSSe and ZnO substrates is analyzed.

Keywords: zinc oxide (ZnO), zinc selenide (ZnSe), solid solution, anodic etching, nanoporous structure

1. INTRODUCTION

Wide band-gap II-VI semiconductors, such as ZnSe, ZnS and ZnO, have wide perspectives for application in photonics, optoelectronics and spintronics, for example, as solar energy converters, light emitting devices, substrates for nanoporous matrices. They have wide potential to produce the sets of nanowires and nanotubes of various materials with defined values of diameter and length [1–3]. These nanostructures are interesting for investigation of contact phenomena between nanotube materials grown in the nanoporous semiconductor matrix. They may be used as flat lenses, elements of complex integrated circuits, high-efficient solar energy cells etc. [4, 5].

The easiest and cost-effective method of obtaining nanoporous matrices is electrochemical etching. The important technological task is the development of fabrication technology for nanotemplates based on wide band gap II-VI semiconductors (ZnSe, ZnS, ZnO), as the properties of these nanostructures can be easily controlled by external irradiation, applied electric field etc. However, to use electrochemical etching technology, it is necessary to manipulate with electrical parameters of initial material (substrates), which allows controlling the pore diameter. For example, the first test nanoporous structures with minimal diameter of the pore of 400 nm were obtained using commercially available ZnSe substrates with electrical conductivity of 10^{-1} $(\Omega\cdot\text{cm})^{-1}$. In addition, porous layers were non-uniform because of non-homogeneous substrates.

The present paper deals with ZnSe, ZnS, ZnO compounds and solid solutions on their basis, such as ZnSSe and ZnCdS. Growth technology of uniformly doped materials with controlled electrical parameters, electrical and luminescent properties of these materials, as well as estimation of their prospects for obtaining nanoporous structures by electrochemical etching are discussed.

2. EXPERIMENTAL TECHNIQUE

The growth of the II-VI semiconductors and solid solutions on their basis was carried out in sealed evacuated quartz ampoules using physical or chemical vapor transport method (PVT or CVT respectively). The influence of the growth temperature (from 975 to 1080 °C), post-growth cooling (from 0.5 to 10 °C), design and temperature profile of the growth chamber, as well as growth rate (from 0.5 to 10 mm/day) on the structural perfection of the samples was analyzed. The ZnSe and ZnS samples were obtained by PVT method; ZnO – by CVT method using HCl, H_2 and CO as vapor transport agents, and ZnCdS, ZnSSe solid solutions using HCl vapors.

The samples of II-VI compounds and solid solutions were cut on plain substrates with ~1 mm thickness for thermal treatment. Finally, the samples were exposed to mechanical and chemical polishing using $Br\text{-}CH_3$ solution and boiling water solution of NaOH.

Photoluminescence (PL) was excited by a nitrogen laser ($E_{exc} \approx 3.68$ eV, $I_{exc} \sim 10$ mW/mm^2) and registered in the 350 to 800 nm range using a monochromator with reciprocal dispersion of 1.4 nm/mm. Electrical parameters were calculated from the Hall effect measurements using a six-probe method.

Electrochemical etching was carried out in various electrolytes in the dark at room temperature. Anodization was performed in potentiostatic regime [6]. Applied voltage to Pt electrodes was varied from +5 to +30 V depending on the substrate conductivity. The light-induced etching treatment of ZnO crystals was carried out using ultraviolet (UV) mercury lamp with 350 W power. A TESCAN Scanning Electron Microscope (SEM) was used to study morphology of the samples.

3. RESULTS AND DISCUSSION

3.1. ZnSe single crystals

The best results were achieved for the ZnSe crystals grown by the PVT method with the subsequent thermal annealing in Zn+Al melt. Doping conditions (900 °C, 100 hours, 1 at.% Al) allowed obtaining of homogeneous ZnSe substrates with large area and conductivity of 20 $(\Omega\cdot cm)^{-1}$ (Fig. 1(a)) [7]. Homogeneous nanoporous structures were fabricated on their basis with the diameters up to 40 nm using $K_2Cr_2O_7:H_2SO_4:H_2O$ electrolyte (Fig. 1(b)) [8]. However, technology for other II-VI semiconductors and solid solutions on their basis, which have wider band gap, as well as their prospects as nanoporous matrices, are of great interest.

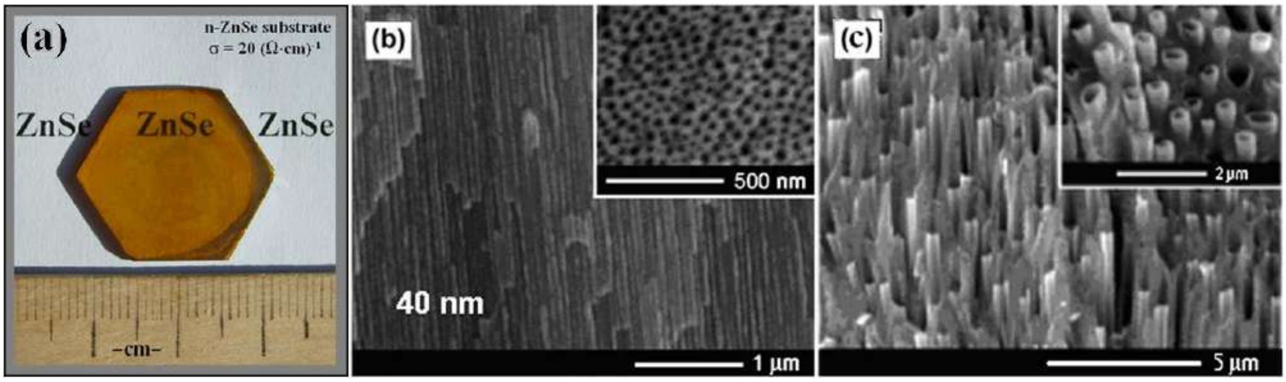

Fig. 1. Exterior view of the high-conductive ZnSe substrate (a), SEM images of nanopores fabricated on the ZnSe substrates with electron concentration of $2 \cdot 10^{18}$ cm^{-3} (b), and Pt nanotubes grown in these pores (c). The insets illustrate a top view

3.2. ZnS single crystals

The ZnS samples grown by PVT method with growth temperature and rate of 1050 °C and 1–1.5 mm/day respectively, have a high density of subgrain boundaries. This is attributed to lower pressure of the ZnS vapours (approximately 0.3 mmHg at 1050 °C) and liability to polytypism [9]. The most optimal parameter of the growth rate is 0.5 mm/day at 1050 °C providing lower density of structural defects.

To increase the electrical conductivity of the ZnS samples, the doping from Zn+Al melt was carried out at various temperatures (from 900 to 1040 °C) and Al concentrations (0–2 at.%). From the dependence of the resistivity on Al concentration and doping temperature (Fig. 2(a)), the optimal conditions of annealing are determined to be 900 °C during 100 hours and 0.5 at.% Al. In this case, the charge carrier concentration is ~ $2 \cdot 10^{16}$ cm^{-3} and resistivity is 0.3 Ω·cm. However, the investigated material has extreme surface resistance (~ $M\Omega/mm^2$) due to the surface levels which influence the electrical properties of the material because of the raised conduction band bottom (Fig. 2(b)).

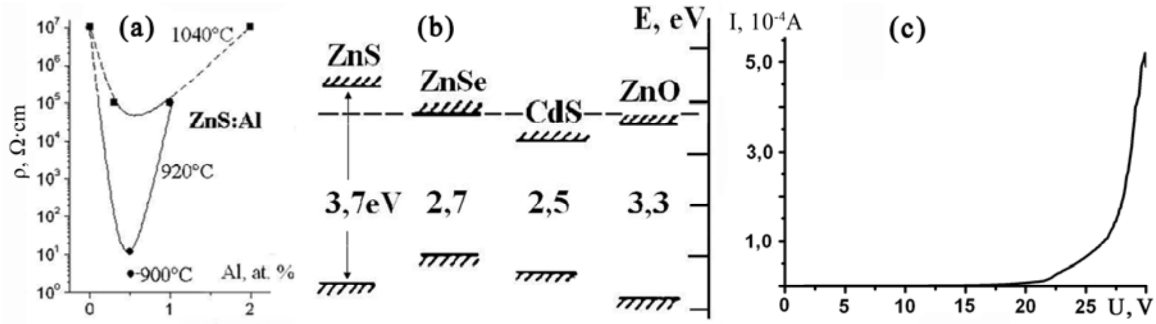

Fig. 2. (a) Resistivity of the crystals (T = 300 K) after annealing during 100 hours at various temperatures and Al concentrations in Zn+Al melt. (b) Energy diagram of II-VI compounds. (c) Volt-ampere characteristic of the ZnS single crystal during electrochemical etching

The attempts to realize electrochemical etching using various electrolytes (HCl, $HCl:H_2SO_4$, $HCl:H_3PO_4$) were unsuccessful. The sample surface has been intact after 20 minutes etching at the voltages up to 30 V, as a result of extremely low values of current due to high surface resistance (Fig. 2(c)).

In this regard, we propose to use the solid solutions on the ZnS and ZnSe basis, which have lower surface resistance and wider band gap comparing to ZnS and ZnSe respectively.

3.3. ZnSSe single crystals

It is advisable that the final material corresponds to the composition of the initial material of growth for solid solution. This is very difficult to achieve using PVT method, because of the different pressures of the saturated vapours (for ZnS and ZnSe, these values differ for 3 times [9]). Thus, it is better to use CVT method and HCl vapors as transport agent due to effective interaction with both sulphides and selenides. The results of the thermodynamic calculation for chemical vapour transfer for ZnS, ZnSe and CdS compounds are presented in Fig. 3(a).

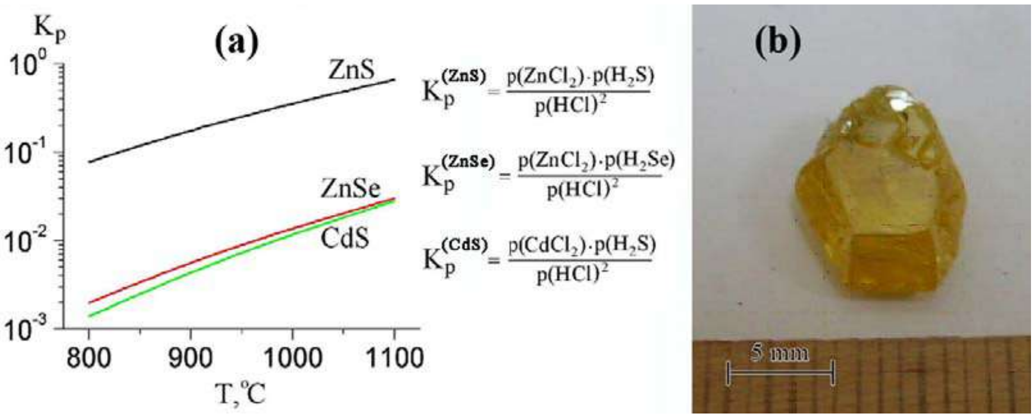

Fig. 3. (a) Temperature dependence of reaction constants corresponding to the CVT process, (b) view of obtained $ZnS_{0.5}Se_{0.5}$ single crystal

Another difficulty in obtaining of ZnSSe solid solutions is the absence of commercially available substrates of these compounds with various compositions and controlled parameters. Thus, it was necessary to synthesize the seed which was extended to the size of 1 cm^3. Homogeneous crystals with ZnSe:ZnS proportion of 2:1, as well as 1:1 (Fig. 3(b)), were grown using HCl as a transport agent.

The values of the band gap of ZnSSe solid solution were estimated from investigations of exciton PL band. PL spectra are presented in figure 4 for $ZnS_{0.5}Se_{0.5}$ and $ZnS_{0.33}Se_{0.67}$ solid solutions, as well as ZnSe sample doped with Cl impurity for comparative analysis. The value of band gap energy increases depending on the ZnS concentration in the solid solution (Fig. 4, inset). The presence of Cl impurity in the samples is indicated by self-activated long-wave PL band.

Similar to ZnS, the resistivity of grown ZnSSe samples is high (10^8 Ω·cm). The decrease of the resistivity can be achieved by thermal annealing in Zn vapours at the following conditions: temperature – 900 °C, duration – 30 hours, Zn vapour pressure – 1 atm. However, even in this case, the surface resistance of the sample cannot be dropped to the level of 1 $K\Omega/mm^2$, and it increases with increasing Zn concentration in the samples. At the same time, electrical conductivity of the crystals is approximately equal to 0.3 $(\Omega\cdot cm)^{-1}$.

As in the case of ZnS samples, current intensity at electrochemical etching is very low for obtaining some results with the use of HCl, $HCl:H_2SO_4$, $HCl:H_3PO_4$ electrolytes. Voltage of 30 V and duration of 20 minutes were useless for obtaining of ZnSSe-based nanotemplates.

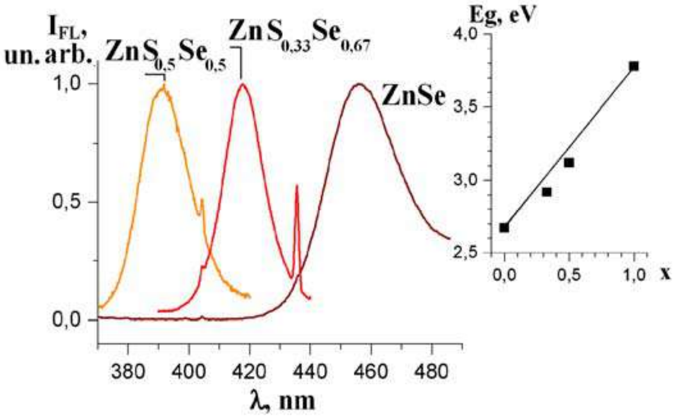

Fig. 4. Edge PL spectra for $ZnS_{0.5}Se_{0.5}$, $ZnS_{0.33}Se_{0.67}$ and ZnSe samples. Inset: the band gap energy calculated from the edge PL band shift

3.4. ZnO single crystals

The growth of ZnO single crystals by PVT method needs considerable values of saturated vapours pressure of initial material, which, unfortunately, could not be reached even at the temperature of quartz softening. Therefore, the CVT method was used with H_2, HCl and CO transport agents [10]. Thermodynamical calculation of corresponding reactions is shown in Fig. 5.

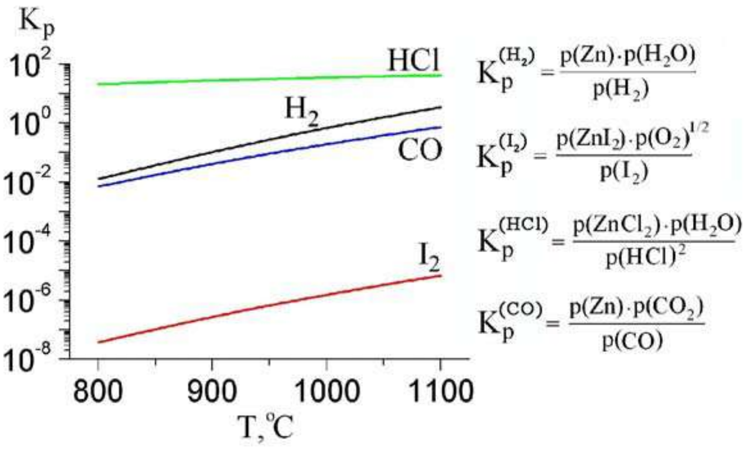

Fig. 5. Temperature dependence of reaction constants corresponding to the CVT method for ZnO

The use of H_2 as a transport agent provides high growth rate of the crystals, however, the strong mechanical contact between the sample and the quartz walls of growth chamber leads to the destruction of both growth chamber and grown crystals during a post-growth cooling (Fig. 6(a)). HCl transport agent is more favourable for the growth of ZnO single crystals due to insignificant mechanical contacts between the crystal and the walls of growth chamber that reduces structural defects generated during a post-growth cooling. At the same time, ZnO:HCl single crystals have a large ratio between the crystal length and diameter that is a disadvantage, in our view (Fig. 6(b)). Thus, in order to combine the advantages of the both growth technologies, a mixed H_2+HCl transport agent was proposed. The high growth rate of the single crystals (1 mm/day) and moderate mechanical contact between the crystals and ampoules were obtained experimentally. Thus, the crystals with controlled values of the electric conductivity of 0.5–9 $(\Omega\cdot cm)^{-1}$ and charge carrier concentration of $(2–6)\cdot 10^{17}$ cm^{-3} were obtained [7, 10].

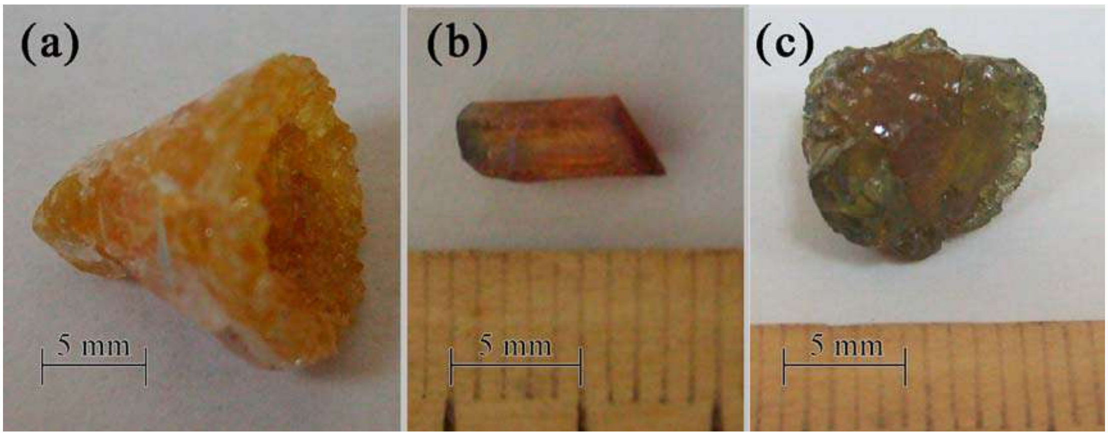

Fig. 6. View of the ZnO single crystal obtained by CVT method using transport agent: (a) H_2, (b) HCl, (c) H_2+HCl

The CO transport agent allows growing the most qualitative ZnO single crystals (Fig. 7(a)). The crystals have no volume structural defects, are optically transparent in the visible spectral range after annealing in vacuum (in comparison with ZnO:H and ZnO:HCl) and are characterized by intense edge luminescence (Fig. 7). Deviation from the ZnO:CO crystal stoichiometry allows both varying the electrical parameters for one order of magnitude (Fig. 7(b)) and essential modification of PL and optical properties of the crystals (Fig. 7(c, d)) [10].

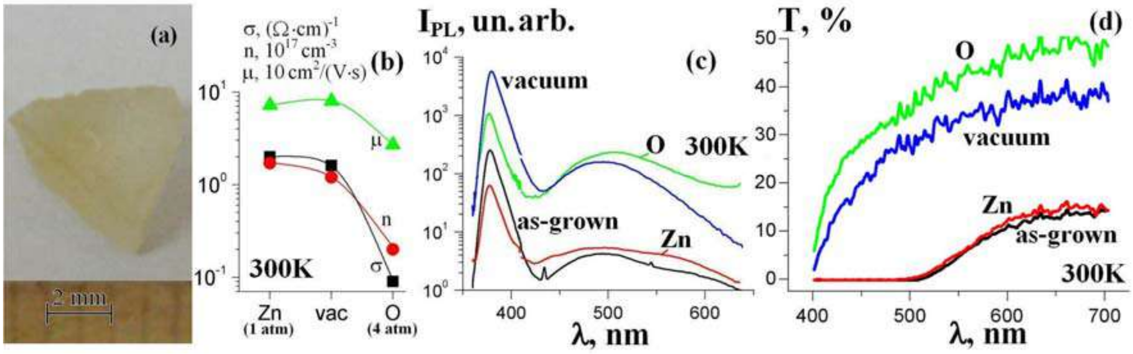

Fig. 7. (a) ZnO single crystal grown with the use of CO transport agent, (b) electrical, (c) PL and (d) transmission properties of ZnO:CO before and after annealing in various media

The NaCl (0.1 M) and KOH (0.1 M) electrolytes have no substantial influence on the surface states of the ZnO samples (Fig. 8(a)) after light-induced electrochemical etching during 15 minutes. Light-induced etching treatment with oxalic acid (0.3 M) allows realization of nanostructuring on the zinc oxide surface. However, the obtained nanostructures do not represent arranged pores as in the case of ZnSe samples (Fig. 1, 8(b)).

The results of nanostructuring performed during 10 minutes in the dark, at 20 V, in 3% water solution of HCl at room temperature are shown in Fig. 8(c). It is clearly seen that the obtained pores have specific geometry that is caused by gradual dissolution of the pore walls during electrochemical etching due to instability of zinc oxide relative to acid solution.

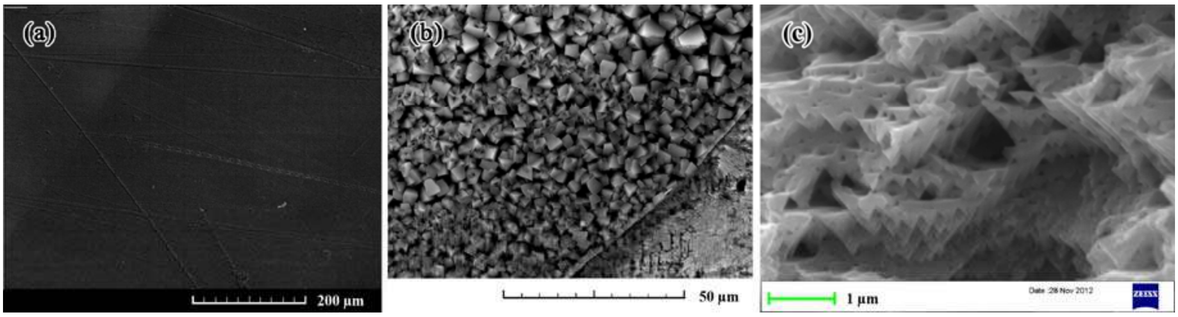

Fig. 8. Surface SEM view of the ZnO single crystals after electrochemical etching under UV irradiation using: (a) KOH electrolytes, (b) oxalic acid electrolyte (right bottom angle is the border of light-induced etching), (c) SEM view of the ZnO porous surface layer (HCl electrolyte)

3.5. ZnCdS single crystals

Taking into account big difference in saturated vapor pressures of initial components, PVT method is difficult to apply for growing ZnCdS crystals. Therefore, CVT method with HCl transport agent was used. The samples with maximum length of 1 cm and diameter of 8 mm and various ratios of the initial components (ZnS:CdS – 2:3, 1:1, 2:1) were obtained. Also, CdS and ZnS crystals doped with Cl impurity were grown for comparative analysis.

Band gap of the ZnCdS found from PL investigations at room temperature is varied from 2.5 to 3.5 eV depending on the initial material ratio (Fig. 9, inset). Thermal annealing of the ZnCdS:Cl solid solution in Zn+Cd vapors was carried out for reducing resistivity. The following results were obtained for the $Zn_{0.4}Cd_{0.6}S$:Cl sample with 2.85 eV band gap, which is larger than that of ZnSe: charge carrier concentration – $2 \cdot 10^{18}$ cm^{-3}, electrical conductivity – 20 $(\Omega \cdot cm)^{-1}$, and mobility – 70 cm^2/(V·s). These materials have no surface resistance.

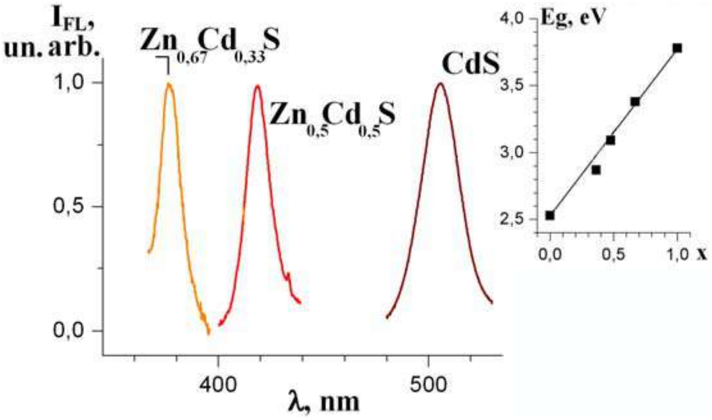

Fig. 9. Edge PL spectra of the $Zn_{0.67}Cd_{0.33}S$, $Zn_{0.5}Cd_{0.5}S$ and CdS. Inset: the band gap energy calculated from the edge PL band shift. T = 300 K

Electrochemical etching was carried out in static conditions at 18 V, in 5% HCl electrolyte, at room temperature during 20 minutes. The obtained nanoporous structure of the $Zn_{0.4}Cd_{0.6}S$:Cl solid solution (Fig. 10) is characterized by the following parameters: thickness of the pore walls – 20 nm, diameter of the pores – 30 nm, and depth – 20 μm.

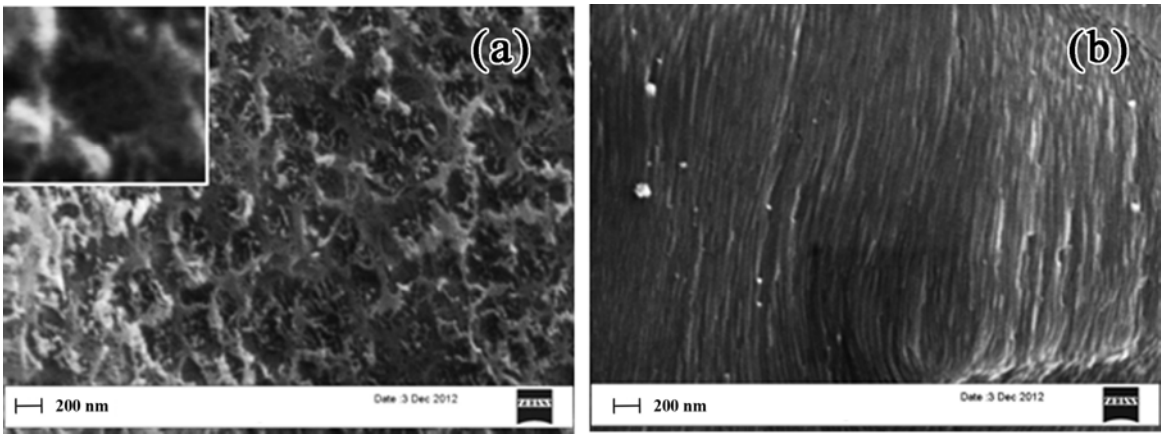

Fig. 10. Surface view of the ZnCdS after electrochemical etching: (a) top, (b) side

4. CONCLUSIONS

The obtaining of nanotemplates could not always be successfully carried out by electrochemical etching for II-VI semiconductor compounds and solid solutions on their basis. For example, despite the fact that ZnS single crystals have the maximal band gap energy among these compounds and moderate resistivity (after annealing – 0.3 Ω·cm), unfortunately, they have enormous surface resistance (> $M\Omega/mm^2$). The ZnSSe samples are also characterized by high surface resistance. We suppose this is caused by the surface levels due to the raised conduction band bottom, which influences on the electrical properties of the materials. For ZnO and $Zn_xCd_{1-x}S$ (with composition x less than 0.5), conduction band is placed lower than the conventional level corresponding to the position of the ZnSe conduction band bottom (that is not characterized by significant surface resistance). This fact is favourable for low surface resistance and opens new prospects for using these materials. Analysis of nanoporous structure obtained on the ZnSe and ZnCdS reveals vast utilizing potential for these materials due to successful obtaining of the pores with diameters down to 30 nm.

Wide band gap ZnO material is widely investigated in the nanoworld. However, this material is not so good for obtaining nanoporous structures by electrochemical etching because of its poor chemical resistance.

Summarizing, the most promising materials from the wide band gap II-VI compounds and solid solutions on their basis for nanostructuring by electrochemical etching are ZnSe and ZnCdS. If some binary II-VI compound does not suit for obtaining nanoporous structures by the discussed method, the solid solution on its basis may be used for this purpose.

ACKNOWLEDGEMENTS

We acknowledge Dr. V. Popa for help in light-induced electrochemical etching of ZnO. The research was supported by the Supreme Council for Science and Technological Development of the Academy of Sciences of Moldova under Projects 11.836.05.07A and 11.817.05.11F.

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