OBTAINING OF II-VI COMPOUND SUBSTRATES WITH CONTROLLED ELECTRICAL PARAMETERS AND PROSPECTS OF THEIR APPLICATION FOR NANOPOROUS STRUCTURES

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Investigation objectives and experiment

- Substrates of wide band-gap II-VI semiconductor compounds could be widely used in fabrication of nanoporous matrices (nanotemplates), which give the possibility to obtain nanowires and nanotubes of various materials with good application prospects in various fields. The easiest and cost-effective method to obtain nanotemplates is electro-chemical etching (ECE), which, however, depends on conductive properties of the substrates.
- The growth of the single crystals was carried out in sealed evacuated quartz ampoules using physical and chemical vapor transport methods (PVT and CVT respectively) at 950-1050°C.
- Electrical parameters were calculated from the Hall effect measurements using a six-probe method. Photoluminescence (PL) was excited by a pulsed nitrogen laser ($E_{exc} \approx 3.68$ eV, $I_{exc} \sim 10$ mW/mm^2).
- Electrochemical etching was carried out in the dark at room temperature in various electrolytes. Anodization was performed in a potentiostatic regime [1]. Applied voltage to Pt electrodes was varied from +5 to +30 V, depending on the substrate conductivity.

Experimental results

ZnSe

- The best results of the nanostructuring were achieved using ZnSe single crystals grown by means of seeded PVT method in vacuum at 1050°C. A special furnace temperature profile was used to eliminate the attachment to the growth chamber walls that allowed to obtain the crystals free of twins and subgrain boundaries, with dislocation density ≤ 10^4 cm^{-2} [2].
- The subsequent thermal annealing in Zn+Al melt (900°C, 100 h) allows to obtain homogeneously doped substrates with controlled concentration of the charge carriers (n) and conductivity (σ) varied in the ranges of $2\cdot10^{15}$-$2\cdot10^{18}$ cm^{-3} and $1\cdot10^{-2}$-20 (Ω·cm)$^{-1}$ respectively.

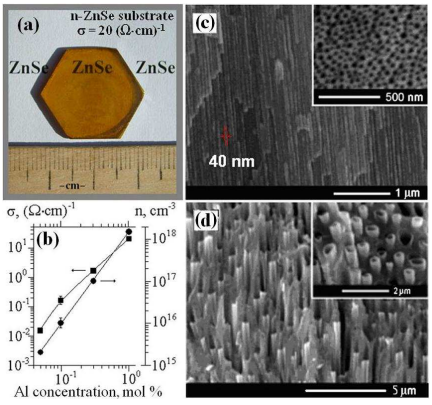

Fig.1. *View of the ZnSe substrates (a), electrical properties of the ZnSe:Al versus impurity concentration in the annealing medium (b), nanopores obtained by ECE (c), and an example of the Pt nanotubes grown by electrochemical depositing (d) (top view in the insets).*

- Depending on the charge carrier concentration in the ZnSe substrates, the use of $K_2Cr_2O_7$:H_2SO_4:H_2O electrolyte allows to obtain nanopores with medium diameter from 400 down to 40 nm (for the most conductive material). The width of the nanopore walls correlates with the pore diameter, as a result, the pore diameter is about the same in all the samples [3].

ZnS and ZnSSe

- Conductivity up to 0.3 (Ω·cm)$^{-1}$ could be achieved in the ZnS single crystals grown by PVT method and doped with Al impurity [4], as well as in the ZnSSe:Cl grown by CVT method using HCl as a transport agent. However, these materials are characterized by the enormous surface resistance (~MΩ·mm^2 for ZnS) due to the surface levels, which influence the electrical properties because of the raised conduction band edge.
- Nanostructuring of these materials in various electrolytes (HCl, HCl:H_2SO_4, HCl:H_3PO_4) was unsuccessful because of extremely low values of current due to high surface resistance.

ZnO

- The ZnO single crystals free from subgrain boundaries and voids were grown by CVT method using H_2+HCl gas mixture as a transport agent at 950°C. Varying of the loaded HCl concentration give possibility to vary n and σ values in the respective intervals of (2-6)·10^{17} cm^{-3} and 0.5-9 (Ω·cm)$^{-1}$.

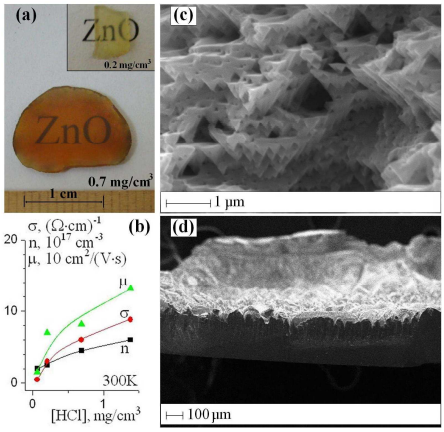

Fig.2. *View of the ZnO substrates (a), electrical properties of the ZnO versus HCl concentration in the growth medium (b), nanopores obtained by ECE (c), and an example of the substrate dissolution by a long-term ECE (d).*

- Porous layers obtained in aqueous HCl solution are characterized by specific morphology and absence of order. This is considered to be due to low chemical stability of the ZnO to acid solutions that causes the gradual dissolution of the pore walls during ECE.

ZnCdS

- The ZnCdS:Cl single crystals were grown by CVT method using HCl (1.3 mg/cm^3) as a transport agent at 1000°C. Band-gap energy (E_g) was estimated from the shift of the edge PL band and fundamental optical absorption (OA) edge. Composition of the crystals is closed to that of the growth source. The most conductive $Zn_{0.4}Cd_{0.6}S$ materials have the following values: n – $2\cdot10^{18}$ cm^{-3}, σ – 20 (Ω·cm)$^{-1}$ and mobility (μ) – 70 cm^2/(V·s). Only investigated $Zn_{0.67}Cd_{0.33}S$ compound is characterized by the substantial surface resistance of about 10 kΩ·mm^2.
- ECE in aqueous HCl solution gives possibility to obtain nanotemplates with hexagonal pore diameter down to 30 nm and pore wall width down to 20 nm.

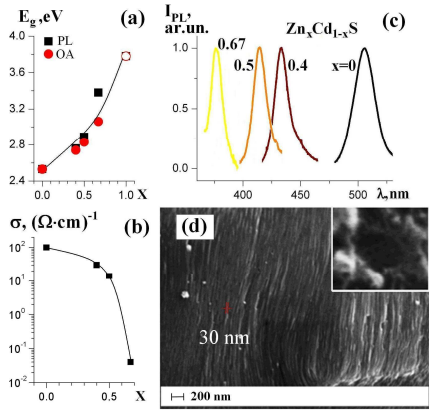

Fig.3. *The value of E_g, calculated from the shift of the edge PL band and fundamental absorption edge (OA) (a), and conductivity (b) versus the composition of the growth source for $Zn_xCd_{1-x}S$ crystals; normalized spectra of the edge PL (c), and nanopores obtained by ECE (d).*

Conclusions

- Porous layers with pore diameters from 400 down to 40 nm may be obtained on the homogeneous substrates of the ZnSe:Al grown by PVT.
- Use of the ZnS and ZnSSe is restricted by high surface resistance. The ZnO nanostructuring is limited by chemical instability.
- The ZnCdS single crystals grown by CVT, with band-gap energy larger than that of ZnSe, is a promising material for obtaining nanotemplates with the pore diameter down to 30 nm.

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