Semiconductor Physics, Quantum Electronics & Optoelectronics, 2015. V. 18, N 4. P. 416-421.
doi: 10.15407/spqeo18.04.416

PACS 81.65.Cf

Development, optimization and improvement of ZnSe crystal surfaces mechanical and chemical treatment and washing methods

A.S. Stanetska[1], V.N. Tomashyk[1], I.B. Stratiychuk[1], Z.F. Tomashyk[1], M.Yu. Kravetskyy[2], S.N. Galkin[1]
[1]V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine
41, prospect Nauki, 03680 Kyiv, e-mail: stanetska_anna@ukr.net
[2]Institute for Scintillation Materials, National Academy of Sciences of Ukraine,
60, Lenin Ave, Kharkiv

Abstract. The process of cutting, mechanical and chemical treatment of the undoped and doped ZnSe crystal surface has been studied. The chemical interaction of zinc selenide surface with bromine emerging solutions of H_2O_2 – HBr and H_2O_2 – HBr – organic solvent has been studied. The surface states after chemical etching have been investigated using electron, metallographic and atomic force microscopy, and it was shown that the surface state is improved after chemical etching. Etchant selection to develop slow polishing compositions for chemical-mechanical polishing of investigated materials has been made. Efficient methods for washing samples solutions have been developed after different types of ZnSe surface treatment: cutting of the crystal, mechanical surface treatment, chemical removing the surface damaged layer.

Keywords: zinc selenide, etchant, crystal, semiconductor, surface treatment, chemical polishing.

Manuscript received 27.04.15; revised version received 27.08.15; accepted for publication 28.10.15; published online 03.12.15.

1. Introduction

Crystal quality is characterized by its topographical surface (roughness), the crystalline perfection of the surface layers and the degree of physical and chemical purity (absence of phase films and other contaminations). The traditional technology of modern electronics provided production of operation elements for devices based on II-VI semiconductor compounds involves using the abrasive or chemical treatment methods at all stages of their manufactoring [1]. Therefore, it is very important to develop technology for production of defect-free single crystals, which includes transaction oriented cutting plates from single-crystal ingots, the application work pieces manufacturing of given configuration and obtaining the required wafer surface geometry. In practice, chemical-mechanical (CMP) and chemical-dynamic polishing (CDP) in specially selected etching compositions are generally used for preparation of surface with required quality [2].

The main purpose of this work is to investigate the process of chemical treatment of the undoped and doped ZnSe crystal surface by bromine emerging in H_2O_2–HBr solutions, to establish the surface state after chemical etching using metallographic, electron and atomic force microscopy as well as low temperature photoluminescence, and to find the concentration regions of polishing solutions for various types of ZnSe surface treatment: to remove the damaged layer, to control the etching rate and to obtain samples of a given thickness.

Chemical modification of crystal surfaces in II-VI semiconductor compounds is often carried out using bromine containing mixtures [3-8]. To obtain a more perfect polished surface of ZnSe crystals bromine containing etching compositions such as Br_2 in methanol or ethanol with different bromine content has been used [9-15]. For chemical etching of ZnSe crystals with orientation (111), the solution of 0.4 vol.% Br_2 in CH_3OH at the boiling point can be used [10]. In [11, 12] the zinc selenide semiconductor wafers were treated with 2 vol. % solution of Br_2 in CH_3OH at 273-283 K. When treating ZnSe surfaces with 0.5 vol. % solution of Br_2 in CH_3OH, formation of etching pits on the polished plane (111) was observed [13]. In [14] after the previous mechanical treatment of ZnSe (111) crystals with diamond pastes of 0.25 μm graininess, they carried out their etching by the 0.5 vol.% solution of Br_2 in CH_3OH. The processes of doped ZnSe sample etching were carried out using solution that contains 10 vol.% Br_2 in C_2H_5OH for 2 min [15].

Unfortunately, bromine containing etchants are very toxic and have difficulties with its using under laboratory conditions; therefore, there is a necessity to search less toxic and more technological etching compositions with low dissolution rates of semiconductor surfaces. The bromine emerging compositions (bromine produced in the process of components interaction, it means that all the bromine takes part in the chemical etching) are an alternative to bromine containing etchants.

In this work, we optimize and improve the developed by us methods for cutting, mechanical, CMP, CDP of undoped and aluminum or tellurium doped ZnSe crystals using the etching compositions based on H_2O_2 – HBr solution. We analyze surface morphology after each stage of semiconductor treatment by using various microscopy methods. We have optimized etchants composition and technological conditions for chemical polishing semiconductors to use them in producing materials for making operation elements of optical and electronic devices. We investigate ZnSe crystal surface before and after chemical treatment by using the X-ray fluorescent analysis to confirm efficiency of the developed washing method.

2. Experimental

All the researched processes were carried out with crystal wafers of undoped ZnSe (I) (without thermal annealing), ZnSe (II) (after thermal annealing) and doped ZnSe(Al) and ZnSe(Te) crystals that were grown using the Bridgman method.

Before the chemical polishing process, undoped and doped ZnSe crystals should be cut for a more convenient research. Our method is as follows: semiconductor samples are cut from grown monocrystalline ingots by using wire cutting unit with a diamond coating. The process is performed using installation under the following technological conditions (the string was moisten with distilled water in the cutting process): the diameter of the string is 300 μm, speed of its movement – 0.5 m/s, the pressure on a crystal – 15 g, the duration process – 10–20 min, the cutting width – 350 mm, while the rate of crystal cutting is 200 mm/min.

The samples for investigations were cut with 1.2 mm thickness; the area of substrate was not less than 25 mm^2. Cutting semiconductors is usually accompanied by intensive mechanical effect on the crystal, and, as a result, the obtained surface contains irregularities and damaged layer of different thickness that depends on the material nature. Such irregularities and damaged layer can be partially removed by mechanical polishing. According to preliminary assessments, the thickness of the damaged layer on the ZnSe surface is 50…60 μm as a result of cutting by using the developed method, while after cutting ZnSe with a diamond wheel it is much thicker and equal to 100…150 μm [1, 2].

That is why, after cutting process we perform mechanical treatment process of semiconductor surface with polishing abrasives. Polishing the ZnSe (I), ZnSe (II), ZnSe(Al), ZnSe(Te) plates after cutting by the developed method should be performed using abrasive powder with grain sizes M 10, M 5 and M 1, or diamond powders ASM 28/20, ASM 10/7, ASM 5/3, ASM 3/2, ASM 2/1 and ASM 1/0. The polishing mixture is prepared in the form of abrasive powders aqueous suspensions with distilled water. The process should be carried out on a glass grinder, alternately treating the plate with both sides within 1 to 5 min by each abrasive (in order to decrease abrasive grit) depending on the thickness of the damaged layer that must be removed. After these treatments, the samples should be thoroughly washed with warm distilled water using addition of a small amount of detergent, then several times with distilled water and dried in air. The elimination rate of the surface layer is different depending on the nature of these materials and abrasive grit (Table 1). The ZnSe(Al) material elimination rate is 6 μm/min, when we polish by abrasive diamond powders ASM 28/20, and by powder ASM 5/3 amounts to 4 μm/min. For ZnSe(Te) crystals the surface layer elimination rate with abrasives ASM 28/20 is equal to 18 μm/min and 2 μm/min with diamond powder ASM 5/3. Such small surface layer elimination rate of the ZnSe(Al) samples may be related to the fact that these crystals were thermally annealed in an atmosphere of zinc, while ZnSe(Te) crystals were prepared without thermal annealing.

Table 1. The elimination rates of ZnSe crystals surface layer during mechanical polishing by free abrasives.

Semiconductor	The elimination rate of the surface layer, μm/min	
	M 10	M 5
ZnSe (I)	154,5	47
ZnSe (II)	145,5	30
ZnSe(Al)	109	67
ZnSe(Te)	89,5	71

After mechanical polishing process, the samples were washed by distilled water with adding surfactants, then repeatedly in pure distilled water, using ultrasonic washing (USW) at 308 K as follows:

$$H_2O_{dist} + \text{surfactants} \xrightarrow{1\,\text{min}} H_2O_{dist} \xrightarrow{1\,\text{min}} H_2O_{dist} \xrightarrow{1\,\text{min}} H_2O_{dist} \xrightarrow{5\,\text{min}} H_2O_{dist}\ (\text{USW}).$$

The thickness of ZnSe crystal surface damaged layer after mechanical polishing was about 10…30 µm [1], and elimination of this layer should be carried out using the method of CMP. To realize CMP processing the ZnSe (I), ZnSe (II), ZnSe(Al), ZnSe(Te) samples, we developed polishing solution with the following volume ratio of components: 10 H2O2:10 HBr:80 EG, which provides small etching and high polishing ability. We recommend holding the etching mixture for 2 h in order to achieve the maximum concentration of free bromine, which is formed by the interaction of etching components. CMP processing the wafers prepared by etching solution with the rate 2 ml per minute was carried out for 5 min at 298 K using a cambric tissue covered glass polisher, and CMP rate does not exceed 20 µm/min (Table 2).

After the CMP process, the samples should be immediately washed by 0.01 M aqueous solution of Na2S2O3, distilled water and isopropyl alcohol (IPA) using USW at 308 K in accord with the scheme:

$$0.01\ \text{M Na2S2O3} \xrightarrow{1\,\text{min}} \text{H2Odist} \xrightarrow{1\,\text{min}} \text{H2Odist} \xrightarrow{1\,\text{min}} \text{H2Odist} \xrightarrow{5\,\text{min}} \text{IPA (USW)}.$$

Then the samples were dried in air flow. As a result of our treatment, the shiny polished surface of ZnSe (I), ZnSe (II), ZnSe(Al) and ZnSe(Te) crystals was obtained, which was not oxidized with time and not covered by cloudy films. It was found that even storage of ZnSe samples in air after CMP doesn’t worsen quality of the polished surface for several months.

The crystal dissolution rates were determined by measuring changes in its thickness (before and after etching) by using the electronic indicator TESA DIGICO 400 with an accuracy of ±0.2 µm.

The investigation of ZnSe surface state after different stages of mechanical and chemical treatments was carried out using the desktop electron microscope JEOL JCM-5000 NeoScope with magnification ×10,000. Low vacuum mode allows investigating all the samples without coating. Investigated plates were placed onto a camera sliding table, then it automatically created low vacuum 10–3 Pa for 3 min (accelerating voltage –15 kV).

Table 2. The CMP rates of undoped and doped ZnSe crystal surfaces.

Semiconductor	The CMP rates, µm/min
ZnSe (I)	17,1
ZnSe (II)	14,5
ZnSe(Al)	13,8
ZnSe(Te)	18,2

Crystal surface morphology was studied at room temperature using metallographic microscope MIM-7 with 8 Mpix digital video camcorder eTREK DCM 800 that displays the image on a monitor by using the ScopePhoto program.

The elemental composition analysis of ZnSe crystal surface before and after chemical treatment was performed using the X-ray fluorescent analysis based on precise express analyzer of the crystal structure EXPERT 3L Enterprise “Institute of analytical control methods” with measurement range of the elements mass fraction 0.01–99.9%.

3. Results and discussion

It was found that the most perspective solution composition for creation of polishing etchants with average removal rates of material (12…22 µm/min) is solution containing 10 to 16 vol.% H_2O_2 in HBr. The compositions of etchants for zinc selenide chemical polishing were optimized. A controlled polishing rate of these materials allows to develop polishing etchants for thinning wafers to the specified sizes. The processes of CMP and CDP enable to improve the surface quality of undoped and doped ZnSe crystals [16]. Introduction of the solvent into this etchant reduces the concentration of an active component in the solution. As a result, one can obtain lower polishing rates and significantly better polishing properties.

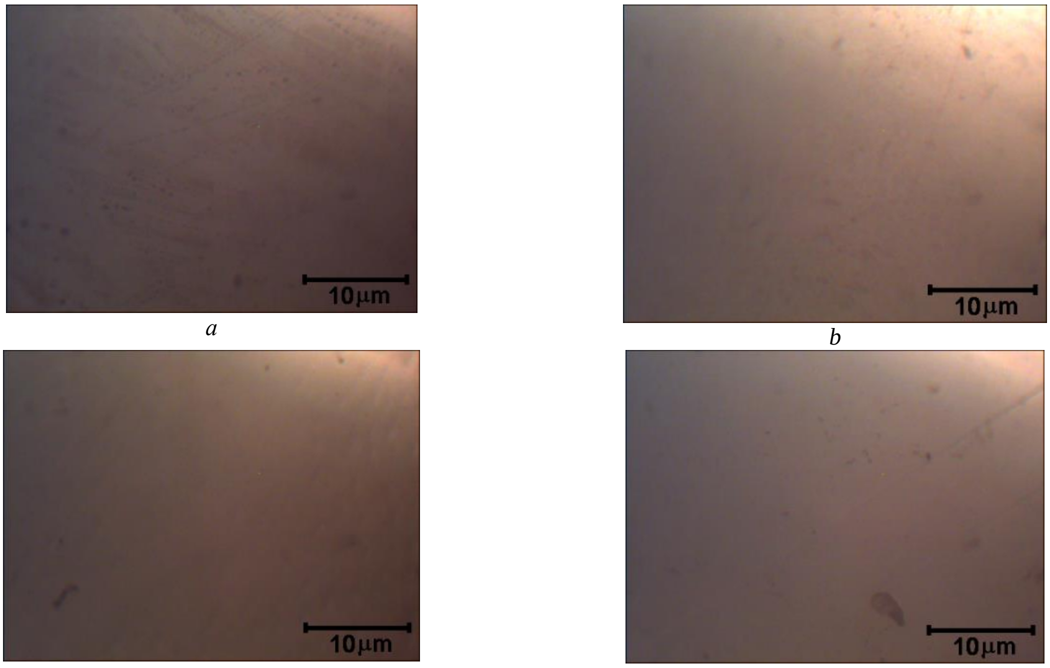
For CMP of undoped and aluminum or tellurium doped zinc selenide samples, we have developed the polishing solution (in vol. %):10 H_2O_2:10 HBr: 80 EG at $v \approx 13$ µm/min. This etchant is characterized by high polishing ability and low etching rates (Table 2).

The results of electron microscopy applied to ZnSe surface after treatment with CMP methods in solution H_2O_2 – HBr – EG show high quality of the treated surface (Fig. 1).

The atomic force microscopy was carried out to evaluate the effectiveness of our developed etching compositions. The results of electron microscopy (Fig. 2) of ZnSe surface after cutting, mechanical polishing and treatment by CMP and CDP in (vol. %) 10 H_2O_2:10 HBr:80 EG solution confirms high quality of treated surface, because its roughness parameters corresponding to polished surface semiconductor materials reach 2…14 nm (Table 3).

Table 3. Surface roughness of undoped and doped ZnSe after chemical treatment in the new bromine emerging etchants.

Semiconductor	rms value, nm	
	CMP	CDP
ZnSe	6,0	13,5
ZnSe (Al)	2,0	11,1
ZnSe (Te)	2,1	9,6



a *b*

c *d*

Fig. 1. The surface morphology of crystals: (a) – ZnSe (I), (b) – ZnSe (II), (c) – ZnSe(Al), (d) – ZnSe(Te) after CMP by the solution (in vol. %) 10 H_2O_2:10 HBr:80 EG.

According to profilographic determination of ZnSe crystals surface roughness after chemical treatment with H_2O_2 – HBr – EG solutions by different methods corresponds: after CMP rms = 1.95…6.03 nm, and after CDP rms = 9.6…13.5 nm.

The results of ZnSe samples morphology after CDP by solution composition (vol.%) 16 H_2O_2:84 HBr (Fig. 2d) suggest that there is a surface deterioration in contrast to results obtained after the CMP process (Fig. 2c). It may be caused by the presence of various dopants in the studied crystals (Al or Te) and their influence on the process of material dissolution.

Appearance of “terraces” can be traced, which may result from the transition between the blocks or from wurtzite to sphalerite modification during crystal growth. The presence of shallow grooves (Fig. 2d) may indicate etching of tellurium inclusions. The surface roughness value of crystals after the CDP process is slightly higher in comparison with its value after CMP (Table 3), which may be due to insignificant deterioration of the surface, and to formation of oxide film (ZnO), and this oxide film is removed by CMP, probably because of the mechanical component of the process. All the etching compositions that we use in CMP have good polishing properties for both undoped and doped ZnSe crystals, while the etching rate is decreased from 22.5 to 0.5 µm/min.

After each stage of mechanical treatment, surface intercleaning the undoped and doped ZnSe single crystals should be carried out for removing dirt from the surface of plates produced during cutting, grinding and mechanical polishing. First, to remove the physical or mechanical contaminations (dust, abrasive particles, metallic materials and semiconductor crumbs that are formed during grinding) by rinsing in distilled water with addition of surface-active substances. Removal of organic contaminants (grease, glue, residues, suspension, and fingerprint) was performed by degreasing in organic solvents (ethanol, acetone), after which the crystals should be thoroughly dried in flow of purified air before the next technological operations.

The study of ZnSe crystal surface composition before and after chemical treatment by X-ray fluorescent analysis confirms efficiency of the developed and optimized methods for chemical polishing and washing methods of both undoped and doped ZnSe crystal wafers after chemical treatment, thus cleaning surface from the etching mixture residual components and other related impurities. For CMP processing the ZnSe, ZnSe(Al), ZnSe(Te) crystal surfaces, we used a polishing solution with the volume ratio of components: 10 H_2O_2:10 HBr:80 EG. When we analyzed data of measuring the mass fraction (in %) for surface elements: Zn 43.45±0.07 and Se 56.07±0.07, these fully correspond to crystal stoichiometric composition before and after chemical treatment, and content of other elements was considerably lower or completely absent. For example, the silicon content found on the surface before the chemical etching and washing was 0.37±0.04, after – was not revealed, sulphur – before 0.05±0.01, after CDP – 0.04±0.01, after CMP was 0.05±0.01, and iron – before 0.07±0.01, while after CDP and after CMP was 0.05±0.01 (Table 4).

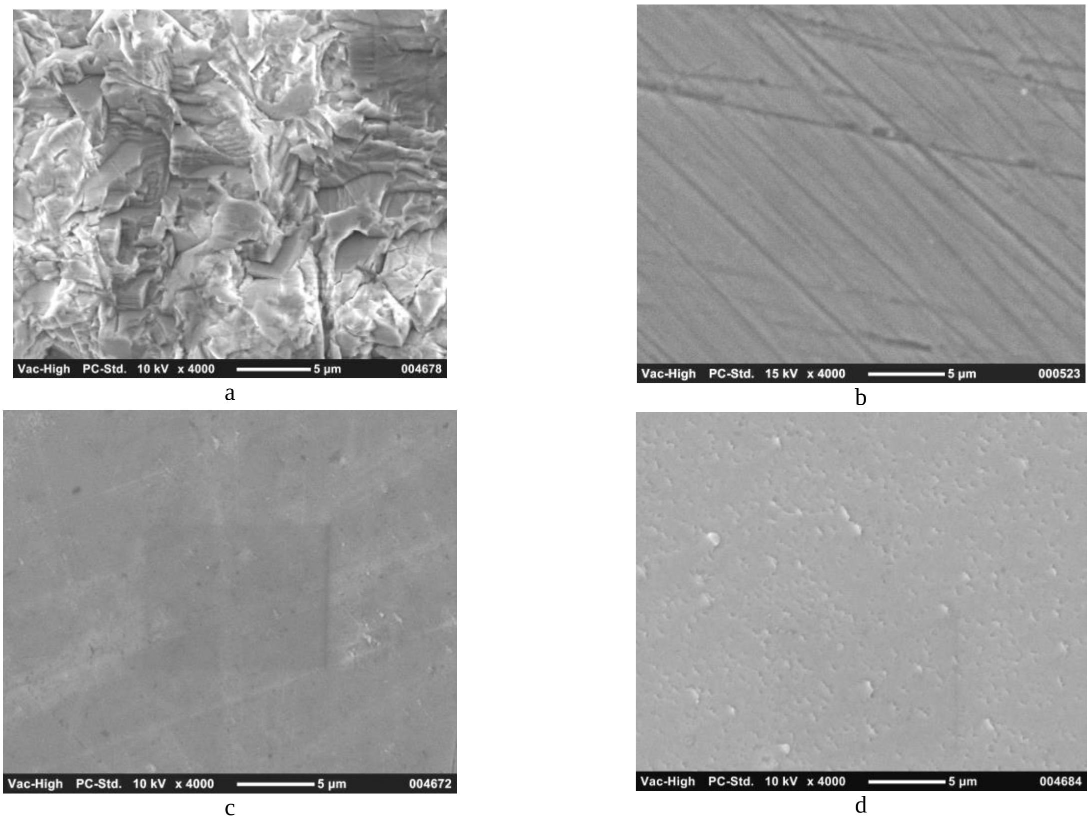


Fig. 2. The surface morphology of ZnSe crystals after different types of treatment: (a) – cutting, (b) – mechanical polishing, (c) – CMP, (d) – CDP.

Table 4. The results of ZnSe crystal structure surface analysis before and after chemical treatment by X-ray fluorescence method.

Semiconductor	Type of treatment	Mass fraction of element, %				
		Zn	Se	Si	S	Fe
ZnSe	mechanical polishing	43.45±0.07	56.07±0.07	0.37±0.04	0.04±0.01	0.07±0.01
ZnSe	CDP	43.68±0.07	56.23±0.07	—	0.05±0.01	0.05±0.01
ZnSe	CMP	43.56±0.07	56.29±0.07	0.05±0.02	0.05±0.01	0.05±0.01
ZnSe(Al)		43.57±0.07	56.35±0.07	—	0.020±0.004	0.05±0.01
ZnSe(Te)		43.75±0.07	56.19±0.07	—	0.016±0.005	0.05±0.01

4. Conclusions

We have developed, optimized and improved mechanical and chemical treatment, and also the washing method for ZnSe crystal surfaces after cutting, mechanical treatment and chemical etching (CDP, CMP).

We have found that H_2O_2 – HBr – EG etchants are stable in time and keep their polishing properties for 24 h after preparing. The controlled polishing rate for these materials lies within 12…22 μm/min, which allows development of polishing etchants for thinning wafers to the specified sizes. The methods of electron and metallographic microscopy confirmed the high quality of the semiconductor surface after the chemical polishing process. The X-ray fluorescent analysis confirmed the efficiency of developed and optimized methods for chemical polishing and also of washing methods for ZnSe crystals surface after cutting, mechanical and chemical treatment.

The absence of dirt, dust, etchant molecules suggests that our method of crystals washing after cutting, mechanical and chemical treatment is the most effective in this case of treatment and can be used for washing similar semiconductor crystals.

The developed etching compositions can be used for controlled thinning the plates to the specified size and finish polishing of single crystals and thin films. The developed etchant is characterized by a high polishing ability and small etching rates.

References

1. B.D. Luft, V.A. Perevoshchikov, L.N. Vozmilova, I.A. Sverdlin, K.G. Marin, *Physical-Chemical Methods of Semiconductors Surface Treatment*. *Radio i sviaz', Moscow,* p. 136, 1982 (in Russian).
2. V.A. Perevoshchikov, Chemical and dynamical processes of semiconductor surface polishing // *Vysocochistye veshiestva*, **2**, p. 5-29 (1995), in Russian.
3. V.N. Tomashyk, Z.F. Tomashyk, Chemical etching of II-VI semiconductor compounds // *Neorgan. materialy*, **29**(5), p. 717-718 (1993), in Russian.
4. V.N. Tomashyk, Z.F. Tomashyk, Mechanical and chemical-mechanical treatment of II-VI semiconductor compounds // *Neorgan. materialy*, **30**(12), p. 1498-1503 (1994) (in Russian).
5. V.N. Tomashyk, Z.F. Tomashyk, A.V. Lyubchenko, A.V. Fomin, Liquid phase etching of II-VI semiconductor compounds and physical-chemical processes at the interface (review) // *Optoelektronika i poluprovodnikovaya tekhnika*, **28**, p. 3-15 (1994), in Russian.
6. V.N. Tomashyk, The selective etching of zinc, cadmium and mercury chalcogenides // *Neorgan. materialy*, **31**(3), p. 313-317 (1995), in Russian.
7. V.N. Tomashyk, Z.F. Tomashyk, Polishing etching of II-VI semiconductor compounds // *Neorgan. materialy*, **33**(12), p. 1451-1455 (1997), in Russian.
8. Z.F. Tomashyk, V.N. Tomashyk, Physical-chemical interaction of II-VI and III-V semiconductors with etching liquid compositions // *Condensirovannye sredy i mezhfaznye granitsy*, **4**(4), p. 336-341 (2002), in Russian.
9. R. Tenne, H. Flaisher, R. Triboulet, Photoelectrochemical etching of zince selenide and non-uniform charge flow in Schottky barriers // *Phys. Rev. B.: Condens. Matter*. **10**, p. 5799-5804 (1984).
10. W.C. Hughes, C. Boney, M.A.L. Johnson et al., Surface preparation of ZnSe substrates for MBE growth of V-VI light emitters // *J. Cryst. Growth*, **175/176**, p. 546-551 (1997).
11. R. Tenne, R. Haak, R. Triboulet, Electrochemical photocapacitance of zince selenide: effect of photoelectrochemical etching // *Ber. Bunsen-Ges. Phys. Chem.* **91**(6), p. 597-599 (1987).
12. R. Tenne, Y. Mirovsky, Y. Greenstein, D. Cahen D, Ternary chalcogenide-based photo-electrochemical cells II. The n-$CdZn_2Se_4$/aqueous polysulfide system // *J. Electrochem.Soc.* **129** (7), p. 1506-1512 (1982).
13. A. Sagar, W. Lehmann, I.W. Faust, Etchants for ZnSe // J. *Appl. Phys*. **11**, p. 5336-5338 (1968).
14. J. Gautron, C. Raisin, P. Lemagson, Optical and electro-optical behaviour of polished and atched zinc selenide single crystals // *J. Phys. D. Appl. Phys*. **15**, p. 153-161 (1982).
15. N. Sankar, K. Ramachandrana, C. Sanjeeviraja, Growth and characterization of ZnSe and phosphorus-doped ZnSe single crystals // *J. Cryst. Growth,* **235**, p. 195-200 (2002).
16. V.N. Tomashik, A.S. Kravtsova, Z.F. Tomashik, I.B. Stratiichuk S.N. Galkin, Dynamic chemical polishing of undoped and doped ZnSe crystals with H_2O_2–HBr–H_2O solutions // *Inorganic Materials*, **49**(10), p. 971-974 (2013).