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Optimization of conditions for treatment of ZnSe crystal surfaces by chemical etching

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Abstract. The process of chemical polishing the undoped and doped ZnSe crystals surface with H₂O₂ – HBr etchants has been studied. The dependence of the samples polishing rate on the concentration of H₂O₂ in HBr solution has been investigated. Surface states after chemical etching have been established using electron and atomic force microscopies, and it was shown that the surface state is improved after chemical etching. Etchant selection to develop slow polishing compositions for chemical-mechanical polishing the investigated materials has been made. Concentration regions of polishing solutions have been found for various types of ZnSe surface treatment: to remove the damaged layer, to control the etching rate, to obtain samples of a given thickness.

Keywords: semiconductor, zinc selenide, etchant, crystal, chemical-mechanical polishing, chemical-dynamic polishing.

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1. Introduction

The traditional technology of modern electronics for manufacturing elements of devices with semiconductor II-VI compounds involves the use of abrasive or chemical treatment methods at all stages of their production [1]. In this regard, great importance is the development of defect-free single crystals manufactured technology, which includes transaction oriented cutting plates from monocrystalline ingots, the application workpieces manufacturing of given configuration and obtaining the required wafer surface geometry using chemical mechanical (CMP) and chemical dynamic polishing (CDP) technologies that prevent formation and transformation of defects [2].

Chemical modification of the II-VI semiconductor compounds surfaces is often carried out using bromine containing mixtures [3-8]. To obtain more perfect

polished surface of ZnSe crystals, bromine containing etching compositions such as Br₂ in methanol or ethanol with different bromine content has been used [9-15] (Table 1). For chemical etching the ZnSe crystals with orientation (111) a solution of 0.4 vol.% Br₂/CH₃OH at the boiling point can be used [10]. In [11, 12], zinc selenide semiconductor wafers were treated with 2 vol.% solution of Br₂ in CH₃OH at $T = 273-283$ K. At the treating of ZnSe surfaces with 0.5 vol.% solution of Br₂ in CH₃OH, formation of etching pits on the polished plane (111) were observed [13]. In [14], after the previous mechanical treatment of ZnSe (111) crystals with the diamond paste of 0.25- μm graininess, carried out was etching them with the 0.5 vol.% solution of Br₂ in CH₃OH. The processes of etching the doped ZnSe samples were carried out in the solution that contains 10 vol.% Br₂ in C₂H₅OH for 2 min [15].

Table 1. The etchant compositions for chemical treatment of ZnSe crystals.

1.	0.4% Br ₂ in CH ₃ OH	Using the hot solution at its boiling point, the orientation of crystals (111)	[10]
2.	0.5% Br ₂ in CH ₃ OH	The etching pits are located on a (111) plane	[13]
3.	0.5% Br ₂ in CH ₃ OH	The pretreatment was performed by diamond paste (0.25 μm), orientation of crystals (111)	[14]
4.	2% Br ₂ : 98% CH ₃ OH	$T = 273-283$ K	[9, 11,12]
5.	10% Br ₂ in C ₂ H ₅ OH	The process of etching was carried out for 2 min	[15]

The high toxicity and difficulty of process conditions, when using the bromine containing etchants, require searching for a new, less toxic and more technological etching compositions with low dissolution rates of semiconductor surfaces. An alternative to bromine containing etchants is bromine emerging compositions, including solutions based on H₂O₂ – HBr, which can be used even at 291-298 K. In these mixtures, free bromine is produced in the process of interaction between components disappears. It means that all bromine takes part in the chemical etching.

In this paper, we report peculiarities of the chemical-mechanical etching of undoped and aluminum or tellurium doped ZnSe crystals in H₂O₂ – HBr – ethylene glycol (EG) etching compositions and surface morphology after chemical etching, optimization of etchant compositions for semiconductors chemical polishing and technological conditions of CMP to use them in producing materials for making operation elements for optical and electronic devices, and selection of slow zinc selenide polishing compositions for CMP.

2. Experimental

The research was carried out using crystal wafers of undoped ZnSe(I) (without thermal annealing), ZnSe(II) (after thermal annealing) and doped ZnSe(Al) and ZnSe(Te) crystals grown by the Bridgman method.

The surface pretreatment of undoped and doped ZnSe before chemical polishing process included the following operations:

- cutting the relevant crystal ingots to wafers;
- mechanical treatment of surface (polishing with abrasives, mechanical polishing);
- removing the surface damaged layer by CMP;
- surface inter-cleaning after each stage of treatment.

For each of these steps we have developed the technological modes and recommendations to these operations.

Cutting the crystal ingots to wafers. According to our methods, the samples of undoped and doped ZnSe crystals were cut from grown single crystal ingots in a special unit by cutting wire with a diamond coating. The process was performed on stall at the following technological conditions (the string was moisten with distilled water in the cutting process): the diameter of the wire string 300 μm; speed of its motion 0.5 m/s; load on a crystal 15 g; process duration 10 to 20 min; cutting width 350 mm, while the rate of crystal cutting was 200 mm/min.

The investigated samples were cut with a 1.2 mm thickness; the area of the substrate was not less than 25 mm². The semiconductor cutting was followed by an intensive mechanical effect on the crystal, and, as the result, the obtained surface contained irregularities and damaged layer of different thickness that depends on the material nature. These irregularities and damaged layer can be partially removed by mechanical polishing. According to preliminary assessments, the damaged layer of ZnSe surface was 50-60 μm as a result of cutting by the developed method, while after cutting ZnSe with a diamond wheel, it is much larger and reaches 100...150 μm [1, 2].

Mechanical polishing the samples. Polishing ZnSe(I), ZnSe(II), ZnSe(Al), ZnSe(Te) plates after cutting by our 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 1-5 min by each abrasive (in order to decrease abrasive grit) depending on the thickness of the damaged layer that must be removed. After this, the samples should be thoroughly washed with warm distilled water using the addition of a small amount of detergent, then several times with distilled water and dried in air. The elimination rate of the surface layer was different depending on the nature of these materials and abrasive grit (Table 2). The ZnSe(Al) material elimination rate was 6 μm/min when we made polishing 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.

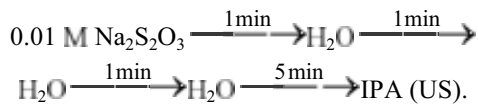
This small surface layer elimination rate of ZnSe(Al) samples may be related to the fact that these crystals were thermally annealed in atmosphere of zinc, and ZnSe (Te) crystals were prepared without thermal annealing. After mechanical polishing of undoped and doped ZnSe, the damaged layer thickness was about 10 to 30 μm [1], and the layer can be removed using CMP.

Table 2. The elimination rates of ZnSe crystals surface layer during mechanical polishing by free abrasives.

Semiconductor	The elimination rate of the surface layer, $\mu\text{m}/\text{min}$	
	M10	M5
ZnSe (I)	154.5	47
ZnSe (II)	145.5	30
ZnSe(Al)	109	67
ZnSe(Te)	89.5	71

Chemical-mechanical polishing. Elimination of the surface damaged layer should be carried out using the CMP method. To make the CMP process for ZnSe(I), ZnSe(II), ZnSe(Al), ZnSe(Te) samples, we developed polishing solution at a volume ratio of components: 10 H₂O₂:10 HBr:80 EG characterized by small etching and high polishing ability. We recommend holding the etching mixture for 2 hours in order to achieve the maximum concentration of free bromine, which is formed during interaction of etching components. The CMP process of wafers that are prepared in etching solution with the rate 2 ml/min was carried out for 5 min at $T = 298 \text{ K}$ using a cambric tissue covered glass polisher, and CMP rate do not exceed 20 $\mu\text{m}/\text{min}$ (Table 3).

After CMP process, the samples were immediately washed in 0.01 M aqueous solution of Na₂S₂O₃, distilled water and isopropyl alcohol (IPA) using ultrasound (US) at $T = 308 \text{ K}$ as follows:



Then the samples were dried in air flow. As a result of our treatment techniques, the shiny polished surface of ZnSe(I), ZnSe(II), ZnSe(Al) and ZnSe(Te) crystals was obtained, which was not oxidized against time and not covered by cloudy films. It was found that the storage of ZnSe samples after CMP is better in solution (isopropanol or dimethylformamide) than in air, as the polished surfaces did not lose their properties for several months.

Table 3. The CMP rates of undoped and doped ZnSe crystal surfaces.

Semiconductor	The CMP rates, $\mu\text{m}/\text{min}$
ZnSe (I)	17.1
ZnSe (II)	14.5
ZnSe(Al)	13.8
ZnSe(Te)	18.2

Inter-cleaning the ZnSe surface after each stage of treatment.

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

The crystal dissolution rates were registered by reducing its thickness before and after etching with an electronic indicator TESA DIGICO 400 with an accuracy $\pm 0.2 \mu\text{m}$.

The investigation of ZnSe surface state after different stages of mechanical and chemical treatments were carried out using the universal stage microscope ZEISS JENATECH INSPECTION with a digital camcorder with magnification from 25 \times to 1600 \times .

Crystal surface morphology was studied at room temperature by atomic force microscope (AFM) Nano Scope IIIa Digital Instrument company using the periodic contact mode. The silicon probes NCH-50 with a nominal tip radius of curvature $\approx 10 \text{ nm}$, with the resonance frequency of 320 kHz, and console stiffness 42 N/m were used for measurements.

3. Results and discussion

When we were studying chemical polishing peculiarities of undoped and doped ZnSe crystals in H₂O₂ – HBr solutions, it was found that the most perspective for the creation of polishing etchants with average speeds of material removal (12-22 $\mu\text{m}/\text{min}$) are solutions containing 10-16 vol.% H₂O₂ in HBr. An introduction of the solvent in such etchant reduces the concentration of an active component in the solution. As a result, we 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 H₂O₂:10 HBr:80 EG at $v \approx 13 \mu\text{m}/\text{min}$. This etchant is characterized by high polishing ability and small etching rates (Table 3).

The results of electron microscopy for ZnSe surface after treatment by CMP methods in solution H₂O₂ – HBr – EG suggest high quality of treated surface (Fig. 1).

The atomic force microscopy was used to evaluate the effectiveness of our developed etching compositions. The results of electron and atomic force microscopy (Fig. 2) of ZnSe surface after treatment by CMP and CDP in 10 H₂O₂:10 HBr:80 EG solution (in vol.%)

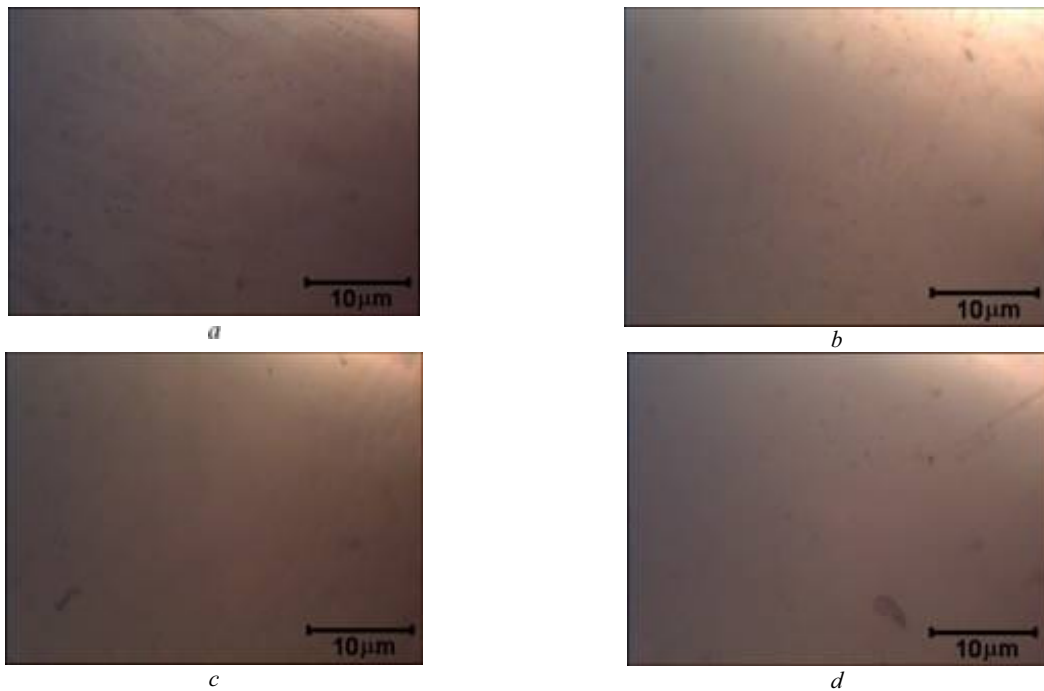


Fig. 1. Surface morphology of crystals: (a) – ZnSe(I), (b) – ZnSe(II), (c) – ZnSe(Al), (d) – ZnSe(Te) after CMP by the solution (in vol.%) 10 H₂O₂:10 HBr:80 EG.

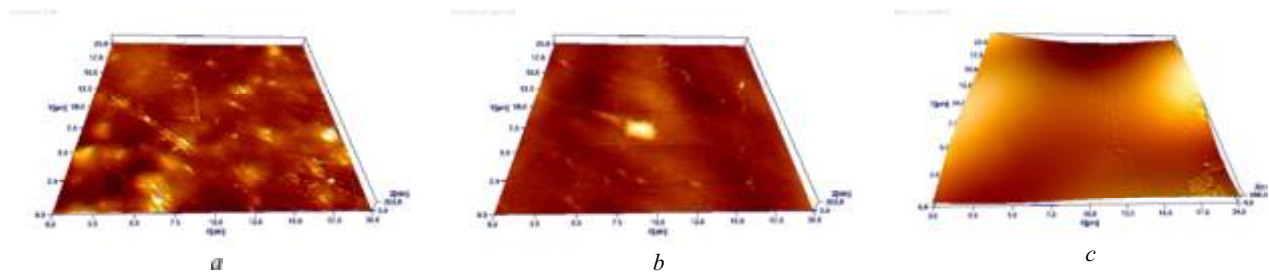


Fig. 2. Atomic force microscopy of the surface after the CMP process in the solution (in vol.%) 10 H₂O₂:10 HBr: 80 EG to (a) ZnSe, (b) – ZnSe(Al), (c) – ZnSe(Te).

confirms the high quality of treated surface, because its roughness parameters corresponding to polished surface semiconductor materials 2-14 nm (Table 4).

According to profilographic researches of ZnSe crystals, the surface roughness after chemical treatment with H₂O₂ – HBr – EG solutions from data of 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 AFM after CDP by solution composition (in vol.%) 16 H₂O₂: 84 HBr (Fig. 3) suggest that there is a surface deterioration in contrast to results obtained after the CMP process. This may be due to the presence of different dopants in researched crystals (Al or Te) and their influence on the process of dissolution of the material.

The 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. 3c) may

indicate the etching of tellurium inclusions. The surface roughness value for crystals after the CDP process is slightly higher in comparison with its value after CMP (Table 4), 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.

Table 4. 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

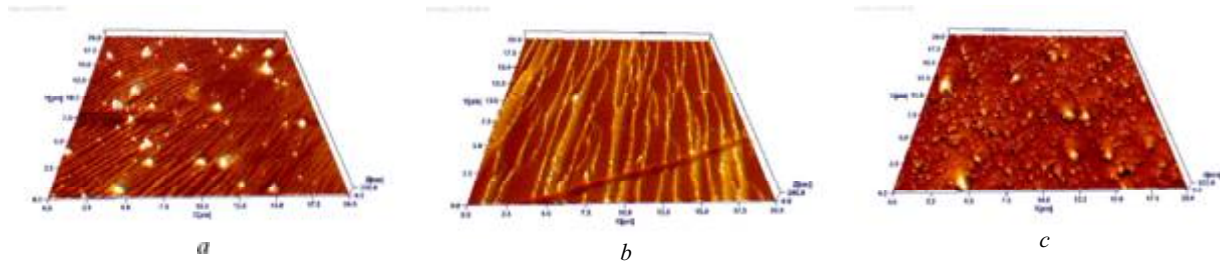


Fig. 3. Atomic force microscopy of the surface after the CDP process in the solution (in vol.%) 16 H₂O₂:84 HBr to (a) – ZnSe, (b) – ZnSe(Al), (c) – ZnSe(Te).

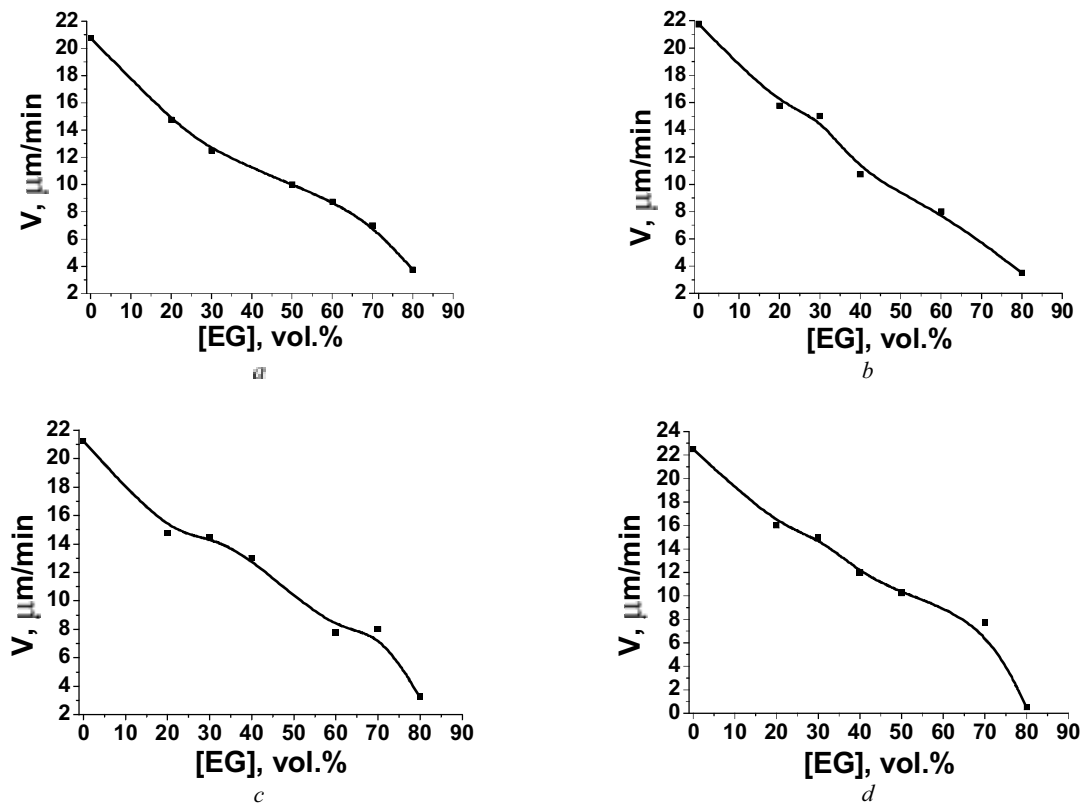


Fig. 4. Dependence of the chemical-mechanical polishing rate of ZnSe(I) (a), ZnSe(II) (b), ZnSe(Al) (c) and ZnSe(Te) (d) on the EG content in the base etchant (BS composition, in vol.% – 10H₂O₂:10 HBr:80 EG).

When we select an etchant to create on its basis the polishing compositions for CMP, we should be aware that due to mechanical component the elimination rate of semiconductor material surface by this method can be several times higher in comparison with the same etchant for CDP. According to the experiment results, the etchant composition (in vol.%) 10 H₂O₂:10 HBr:80 EG were selected as the basic solution (BS) that shows good polishing properties during CDP.

A certain amount of viscosity modifier – EG was additionally introduced to the BS in order to develop the slow polishing etchants for CMP of investigated materials, to reduce the rate of CMP (decrease in the active component content) and to improve the surface

quality directly before the CMP process. It was found (Fig. 4) that the CMP rate was gradually decreased with increasing the additionally introduced amount of EG to the basic etchant.

Thus, with increasing the EG content from 20 up to 80 vol.% in BS, the mirror shiny surface of ZnSe samples was obtained. All etching compositions of this range have the high polishing properties for both undoped and doped ZnSe crystals, while the rate of CMP was decreased from 22.5 to 0.5 μm/min.

According to the Table 5, we can evaluate expediency of using etching compositions (in vol.%) (50–80)BS : (20–50)EG for thinning the semiconductor wafers to the specified size.

Table 5. Optimized etchants compositions H₂O₂ – HBr – solvent for CMP of ZnSe crystals.

Volumetric ratio, (vol.%) [BS] : [EG]	Etching rate, $\mu\text{m}/\text{min}$			
	ZnSe (I)	ZnSe (II)	ZnSe (Al)	ZnSe (Te)
100 BS : 0 EG	20.8	21.8	21.3	22.5
80 BS : 20 EG	14.8	15.8	14.8	16
70 BS : 30 EG	12.5	15	14.5	15
60 BS : 40 EG	13	10.8	13	12
50 BS : 50 EG	10	17	15.3	10.3
40 BS : 60 EG	8.8	8	7.8	2.3
30 BS : 70 EG	7	10.8	8	7.8
20 BS : 80 EG	3.8	3.5	3.3	0.5

4. Conclusions

We have found that H₂O₂ – HBr – EG etchants are stable in time and keep their polishing properties during 24 hours after preparation. A controlled polishing rate of these materials within 12...22 $\mu\text{m}/\text{min}$ allows development of polishing etchants for thinning the wafers to the specified sizes. The methods of electron and atomic force microscopy confirmed the high quality of the semiconductors surface after the chemical polishing process. The series of slow bromine emerging etching compositions (in vol.%): (20 – 40)BS : (60 – 80)EG were developed as based on the experimental researches. They can be used for controlled thinning the plates to the specified size and finish polishing of single crystals and thin films. Thus, for CMP of undoped and aluminum or tellurium doped zinc selenide samples, we have developed polishing solution composition (in vol.%) 10 H₂O₂:10 HBr:80 EG at $v = 13.8\text{-}18.2 \mu\text{m}/\text{min}$. This etchant is characterized by a high polishing ability and small etching rates.

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