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Peculiarities of ZnSe dissolution in H_2O_2–HBr-ethylene glycol (oxalic acid) etchant compositions

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The process of chemical treatment of undoped and doped ZnSe crystals surfaces by bromine emerging solutions has been investigated. The depending of dissolution rate on the etchants composition, their mixing and temperature has been studied. Concentration bounds of polishing solutions have been determined. The surface state after chemical etching has been established using electron microscopy and low temperature photoluminescence. The etchants compositions for semiconductors chemical polishing have been optimized. The comparative characteristics of two etching compositions H_2O_2–HBr–ethylene glycol and H_2O_2–HBr–oxalic acid have been shown to obtain high-quality polished surface of zinc selenide.

Исследован процесс химической обработки поверхности нелегированных и легированных кристаллов ZnSe бромвыделяющими растворами. Изучены зависимости скорости растворения от состава травителей, их перемешивания и температуры. Определены концентрационные границы полирующих растворов. Методами электронной микроскопии и низкотемпературной фотолюминесценции установлено состояние поверхности после химического травления. Оптимизированы составы травильных растворов для химического полирования полупроводников. Показана сравнительная характеристика двух травильных композиций H_2O_2–HBr–этиленгликоль, H_2O_2–HBr–щавелевая кислота для получения высококачественной полированной поверхности селенида цинка.

Особливості розчинення ZnSe в травильних композиціях H_2O_2–HBr-етиленгліколь (оксалатна кислота). *А.С.Кравцова, В.М.Томашик, З.Ф.Томашик, І.Б.Стратійчук, А.О.Курик, С.М.Калитчук, С.М.Галкін.*

Досліджено процес хімічної обробки поверхні кристалів нелегованого та легованого алюмінієм і телуром ZnSe бромвиділяючими розчинами. Вивчено залежності швидкості розчинення від складу травників, їх перемішування і температури. Визначено концентраційні межі поліруючих розчинів. Методами електронної мікроскопії та низькотемпературної фотолюмінесценції встановлено стан поверхні після хімічного травлення. Оптимізовано склади травильних розчинів для хімічного полірування напівпровідників. Показана порівняльна характеристика двох травильних композицій H_2O_2–HBr-етиленгліколь, H_2O_2–HBr-оксалатна кислота для отримання високоякісної полірованої поверхні цинк селеніду.

1. Introduction

In recent years zinc selenide crystals are considered as the most promising materials for using in scintillation bolometers at experimental searching of double β-decay. In manufacturing of devices based on semiconductor materials the problem of getting high-quality surface on final stage of chemical treatment remains one of the topical ones in the modern semiconductor materials science [1]. In practice, to prepare surface with the needed quality, usually, it is used the chemical-mechanical (CMP) and chemical-dynamic polishing (CDP) in specially selected etching compositions [2]. Chemical etching of semiconductors is based on the processes of their dissolution. Therefore, the knowledge of kinetic peculiarities, mechanisms and character of semiconductor dissolution is an important condition of the selection of appropriate solution etchants compositions for polishing.

Chemical modification of the II–VI semiconductor compounds surfaces often carried out using bromine containing mixtures [3–8]. In particular, 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 have been used [9–15]. For chemical etching of ZnSe crystals with orientation (111) a solution of 0.4 % Br_2/CH_3OH at the boiling point can be used [10]. In [11, 12] the zinc selenide semiconductor wafers were treated with 2 % solution of Br_2 in CH_3OH at T = 273–283 K. At the treating of ZnSe surfaces with 0.5 % solution of Br_2 in CH_3OH the formation of etching pits on the polished plane (111) were observed [13]. In [14] after the previous mechanical treatment of ZnSe (111) crystals with diamond pastes of 0.25 μm graininess, they were carried out its etching by 0.5 % solution of Br_2 in CH_3OH. The processes of doped ZnSe samples etching were carried out by solution that contains 10 % Br_2 in C_2H_5OH for 2 min. [15].

However, the high toxicity and difficulty of process conditions at the using of bromine containing etchants lead to 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 H_2O_2–HBr, which can be used even at 291–298 K. In these mixtures bromine is produced in the process of components interaction that means that all bromine takes part in the chemical etching.

In this paper, we have reported the chemical dissolution peculiarities of undoped and aluminum or tellurium doped ZnSe crystals by H_2O_2–HBr–organic solvent etching compositions. We have investigated the dependence of semiconductors dissolution rate on the etchants composition, their mixing, temperature and doping of crystals, the determination of concentration regions of polishing solutions and surface morphology after chemical etching, the optimization of etchants composition for semiconductors chemical polishing and technological conditions of CDP to use them in producing materials for making working elements of optical and electronic devices.

2. Experimental

The research was carried out on crystal wafers of undoped ZnSe (I) (without thermal annealing), ZnSe (II) (after thermal annealing) and doped ZnSe(Al) and ZnSe(Te) crystals, which were grown by Bridgman method. Cylinders with 51 mm in diameter and 44–50 mm in height were cut from the crystal ingots using a diamond wheel with internal cutting edge. Then they were divided into plates 5×5 mm^2 and 1–2 mm thickness and sample area ≈25 mm^2 using diamond-wire cutting technology, when in the cutting process the string was moistened with distilled water.

The semiconductor cutting is accompanied by intensive mechanical effect on the crystal, and as a result the obtaining 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 the mechanical polishing. There it was noted [1, 2] that the damaged layer of ZnSe is 100–150 μm after cutting diamond blades, that’s why it is necessary to carry out the process of mechanical polishing.

The mechanical polishing of ZnSe (I), ZnSe (II), ZnSe(Al), and ZnSe(Te) samples was performed using the aqueous suspensions abrasive powder M 10 and M 5 graininess. After mechanical polishing undoped and doped ZnSe a thickness of the damaged layer was about 10–30 μm [1] and it can be removed using CMP.

The etching mixtures were prepared using HBr, H_2O_2 and organic solvent, and held them before etching for two hours to complete the interaction of components:

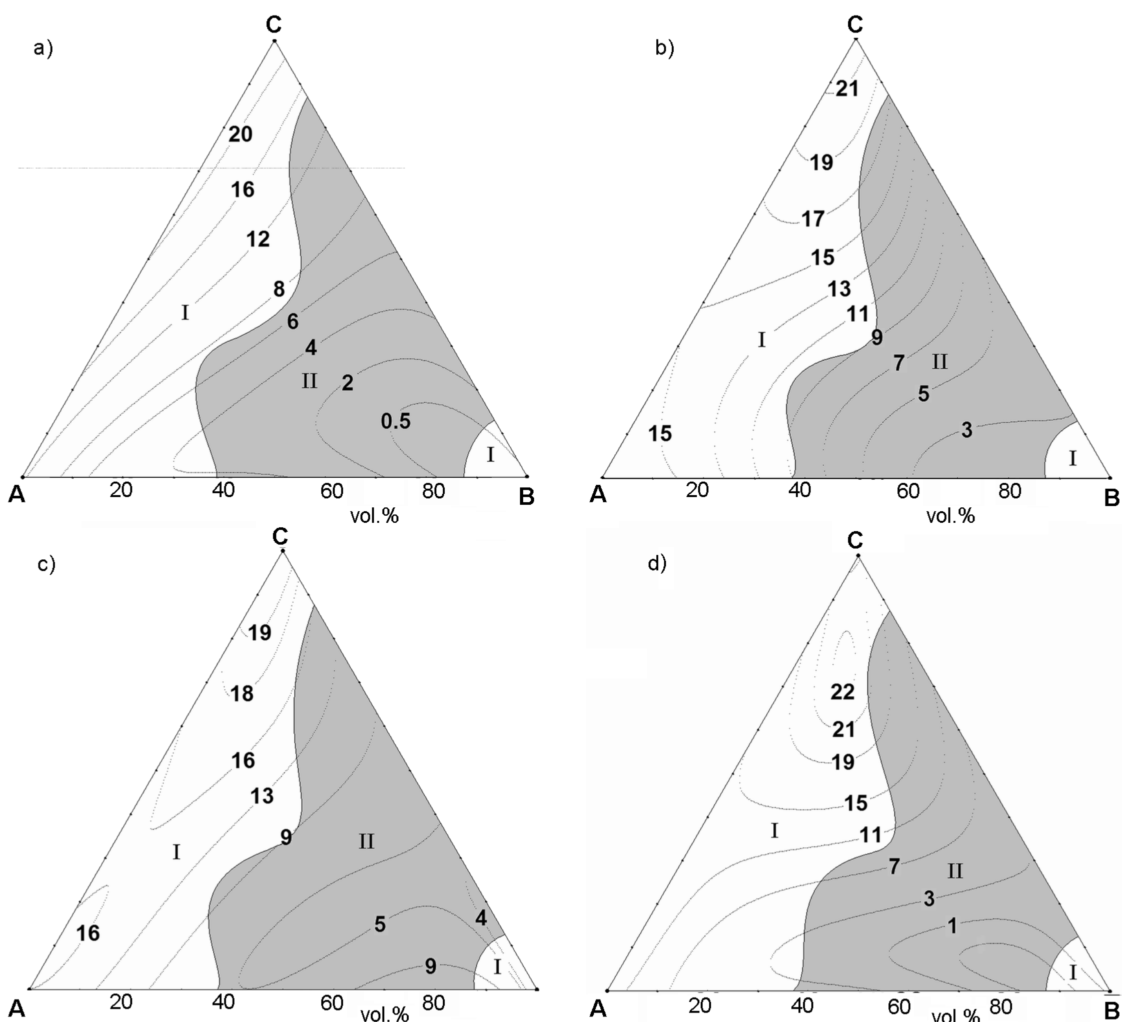
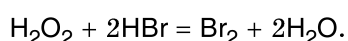


Fig. 1. Concentration dependences (T = 293 K and γ = 86 min^{-1}) of the etching rate (μm/min): (a) — ZnSe (I), (b) — ZnSe (II), (c) — ZnSe(Al), (d) — ZnSe(Te) at a volume ratio H_2O_2:HBr:EG on vertexes of **ABC**: **A** — 10:90:0, **B** — 10:10:80, **C** — 16:84:0 (I — polishing and II — unpolishing regions).



$$H_2O_2 + 2HBr = Br_2 + 2H_2O.$$

For CMP samples we have developed polishing composition (in vol. %): 10 H_2O_2:10HBr:80EG, which is characterized by high polishing ability and small etching rates ($V \approx 13$ μm/min). The CMP process of wafers was carried out for 5 min at T = 298 K using a glass polisher, covered with cambric tissue. We were developed the washing method after chemical polishing, the samples were washed by 0.01 M aqueous $Na_2S_2O_3$ solution, with distilled water and isopropyl alcohol using ultrasound at T = *308 K*.

The CDP process was performed by kinetics dissolution investigation setup using the method of rotating disk. The crystals on glass substrates were rotated in etchant with speed rotation of 86 min^{-1} at 298 K for 2 min. The glass substrates were held in fluoroplastic disk. After each operation of chemical etching samples were washed by the method developed by us, and then dried in a stream of dry air.

Concentration dependences of etching rate of doped and undoped ZnSe were studied using the method of mathematical simulation of the experiment on the simplex. The phase diagrams of "*etchant composition – etching rate*" were constructed.

The crystal dissolution rates were registered by reducing its thickness before and after etching with an electronic indicator TESA DIGICO 400 with an accuracy of ±0.2 mm.

Investigation of morphology of ZnSe surface after different stages of mechanical and chemical treatments were carried out

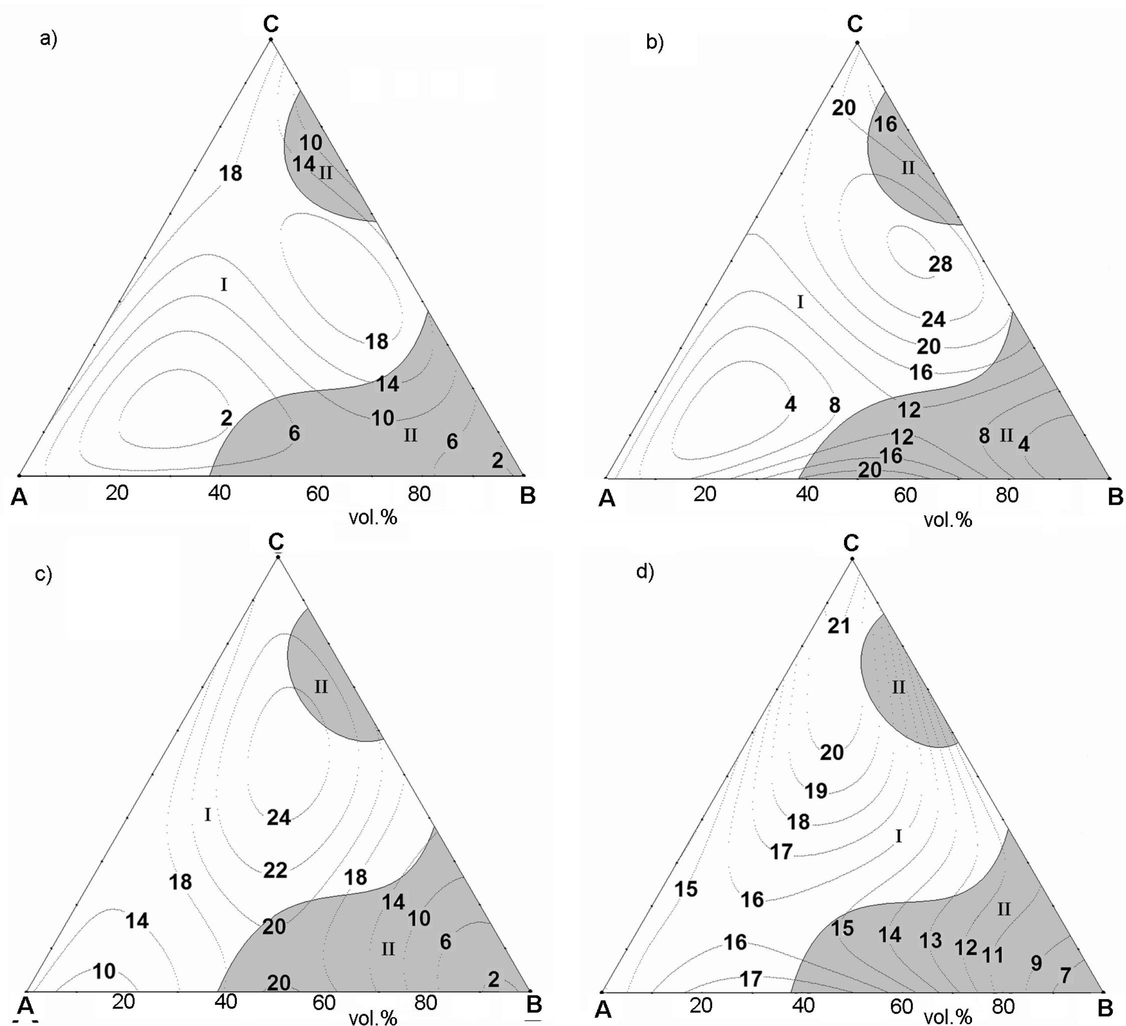


Fig. 2. Concentration dependences (T = 293 K and γ = 86 min^{-1}) of the etching rate (μm/min): (a) — ZnSe (I), (b) — ZnSe (II), (c) — ZnSe(Al), (d) — ZnSe(Te) at a volume ratio H_2O_2–HBr–$C_2H_2O_4$ on vertexes of **ABC**: **A** — 10:90:0, **B** — 10:10:80, **C** — 16:84:0 (I — polishing and II — unpolishing regions).

using a desktop electron microscope JEOL JCM-5000 NeoScope with increasing ×10,000.

Photoluminescence (PL) spectra were performed using spectrometer MDR-23 (spectral range 200–1000 nm) coupled with FEU-100 photomultiplier with excitation by a 405 nm DPSS-laser. For low-temperature measurements UTREKS K.41 liquid helium system of cryostatting was used.

3. Results and discussion

When we study the CDP peculiarities of undoped and doped ZnSe crystals in H_2O_2–HBr solutions it was found that the most perspective for creation of polishing etchants with average speeds removal of material (12–22 μm/min) are solutions containing 10–16 vol. % H_2O_2 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 our experiments the concentration ranges of solutions, bounded by a triangle **ABC**, were selected, where the volume components ratio H_2O_2:HBr:EG ($C_2H_2O_4$) on tops is correspondingly (in vol. %): **A** — 10:90:0, **B** — 10:10:80, **C** — 16:84:0.

The phase diagrams of "*etchant composition — etching rate*" from the research of etching rate dependences of undoped and doped ZnSe on the etching compositions H_2O_2–HBr–EG (Fig. 1) and H_2O_2–HBr–$C_2H_2O_4$ (Fig. 2) were constructed and the concentration limits of polishing (region I)

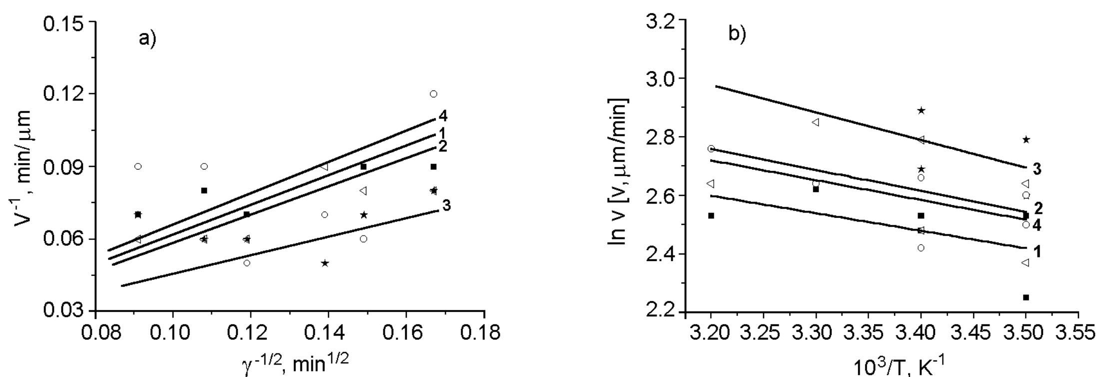


Fig. 3. Dependences of the dissolution rate (μm/min) vs the speed rotation at 293 K (a) and the temperature at $\gamma = 86\ min^{-1}$ (b) of the crystal surfaces of *1* — ZnSe (I), *2* — ZnSe (II), *3* — ZnSe(Al) and *4* — ZnSe(Te) in the solution containing (vol. %):11.5 H_2O_2: 48.5HBr:40$C_2H_2O_4$.

and unpolishing (region II) solutions were found.

As can be seen from Fig. 1 the minimal dissolution rates of ZnSe (I), ZnSe (II), ZnSe(Al), ZnSe(Te) semiconductor crystals were observed in the etching solutions, which enriched with EG solution (near vertex **B** in the **ABC** triangle) and the maximum dissolution rates were observed in the compositions with a maximum content of hydrogen peroxide (the vertex **C**). The diagrams are similar and characterized by a similar location of the etching rate contours, as well as the size and location of the region polishing solutions. It suggests that both undoped and doped crystals of zinc selenide have similar mechanisms of interaction with H_2O_2–HBr–EG etching compositions.

It was shown, that the polishing solutions contain (in vol. %) (10–16) H_2O_2:(58–90)HBr:(0–30)EG, and the optimal CDP rates value for undoped material is 4.3–23.3 and 4.5–23.3 μm/min for doped ones.

In the case of H_2O_2–HBr–$C_2H_2O_4$ etching compositions, the etching was performed at 298 K and $\gamma = 86\ min^{-1}$. As shown in Fig. 2 the minimal dissolution rates of ZnSe (I), ZnSe (II), ZnSe(Al), ZnSe(Te) semiconductor crystals were also observed in the etching solutions, which enriched with oxalic acid solution (the vertex **B** in a triangle **ABC**) and the maximum dissolution rates were observed in compositions with a maximum content of hydrogen peroxide (the vertex **C**). The obtained diagrams are also similar and characterized by a similar location of the etching rates contour, as well as the size and location of the region polishing solutions. It is allowed us to suppose that both undoped and doped crystals of zinc selenide have the similar mechanisms of interaction with H_2O_2–HBr–$C_2H_2O_4$ etching compositions. In the case of $C_2H_2O_4$ as the third component, the range of polishing solutions with medium etching rates is (in vol. %) (10–16)H_2O_2:(38–90)HBr: (0–49)$C_2H_2O_4$ at V_{CDP} = 7.3–23.3 μm/min for undoped material, and 11–22.3 μm/min for the doped samples.

The developed scheme and washing method of the undoped and doped ZnSe after etching solutions of H_2O_2–HBr–EG are effective for crystals cleaning after CDP by H_2O_2–HBr–$C_2H_2O_4$ solutions.

The study of dependences of the dissolution rate (V) on temperature and rotation speed (γ) were performed in polishing solutions (in vol. %): 10H_2O_2:70HBr:20EG and 11.5H_2O_2:48.5HBr:40$C_2H_2O_4$. As an exam-

Table. Apparent activation energy (E_a) and logarithm of pre-exponential multiplier ($\ln C_E$) of ZnSe chemical dissolution in the H_2O_2–HBr-organic solvent solutions

Semiconductor	E_a, kJ/mol	$\ln C_E$
	H_2O_2–HBr–EG	
ZnSe (I)	7.6±1.5	5.5±0.6
ZnSe (II)	8.1±6.3	6.0±2.5
ZnSe(Al)	8.2±3.5	6.0±1.4
ZnSe(Te)	7.0±1.3	5.3±0.5
	H_2O_2–HBr–$C_2H_2O_4$	
ZnSe (I)	5.0±3.7	4.5±1.5
ZnSe (II)	6.0±5.7	5.1±2.3
ZnSe(Al)	5.9±4.2	0.3±1.7
ZnSe(Te)	5.7±3.2	4.9±1.3

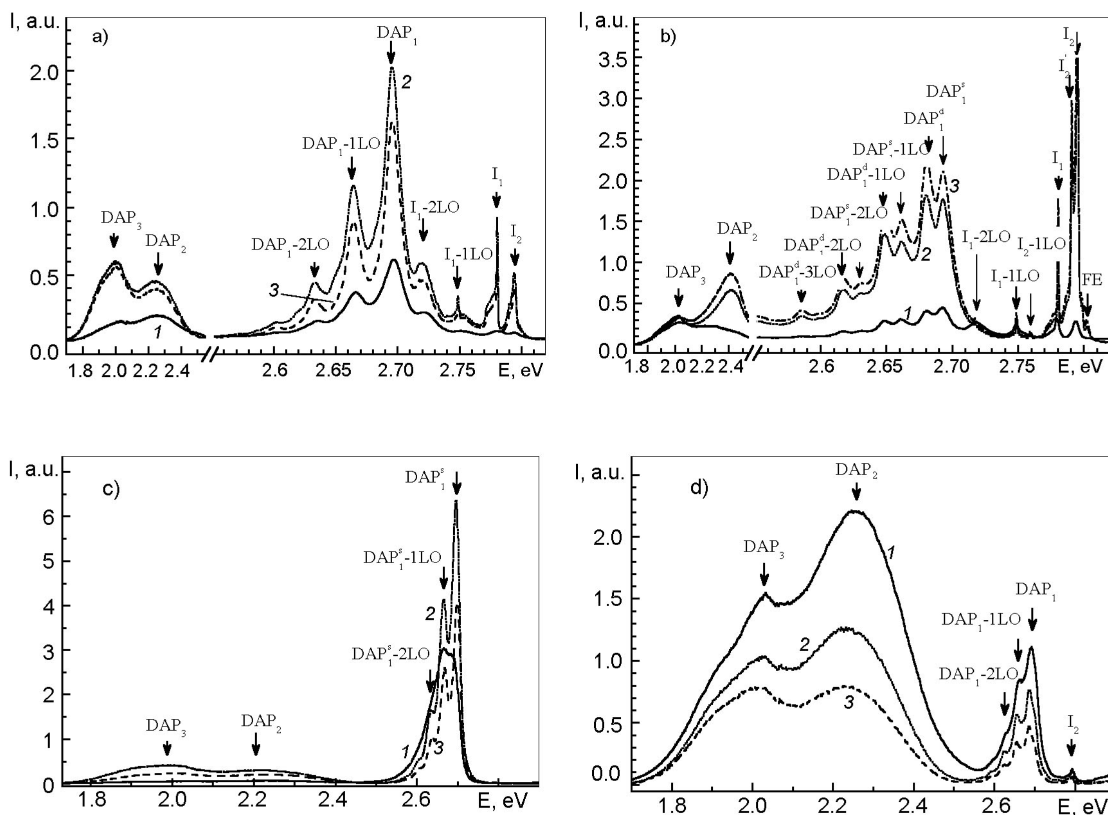


Fig. 4. Low-temperature (T = 5 K) photoluminescence spectra of (a) — ZnSe (I), (b) — ZnSe (II), (c) — ZnSe(Al), (d) — ZnSe(Te) after: *1* — mechanical polishing, *2* — CDP by H_2O_2–HBr–EG (dotted line), *3* — CDP by H_2O_2–HBr–$C_2H_2O_4$ (dashed line).

ple the graphic etching rates dependence on the speed rotation of the disk are presented in Fig. 3, which are constructed in the coordinates $\upsilon^{-1} \sim \gamma^{-1/2}$ at γ = 36–120 min^{-1} (T = 298 K), and on the temperature in the coordinates $\ln\upsilon \sim 1/T$ in range of T = 283–308 K (at γ = 86 min^{-1}). As shown in Fig. 3a, the straight lines *1–4* can be extrapolated to the origin of coordinate, and this shows that the interaction processes of ZnSe (I), ZnSe (II), ZnSe(Al), ZnSe(Te) with H_2O_2–HBr–$C_2H_2O_4$ solutions are limited by diffusion stages [2]. The values of apparent activation energy (E_a) and logarithm of pre-exponential multiplier ($\ln C_E$), which are defined from the results of the temperature dependences of the etching rate (Fig. 3b), are confirmed the limitation of the dissolution by diffusion stages, because for all studied materials E_a value not exceed 35 kJ/mol (Table).

The excitonic PL lines and boundary luminescence could be distinctly shown in the spectra of low-temperature PL (T = 5 K). The specified PL regions are very sensitive to nonradiative losses at ZnSe crystal surface. Therefore, the low-temperature PL is very important for studying the surface after appropriate treatments (grinding, polishing, and etching). The mechanical polishing of semiconductor crystals leads to a significant weakening of PL intensity for the both undoped and doped ZnSe samples, which is due to nonradiative losses by new centers introducing of defective light diffusion surface with a significant thickness of the damaged layer.

In Fig. 4 the low-temperature PL spectra of ZnSe crystals after mechanical polishing and after their treatment by H_2O_2–HBr–EG and H_2O_2–HBr–$C_2H_2O_4$ etching compositions are shown. Chemical polishing of the undoped ZnSe (Fig. 4a,b) leads to significant increasing in the intensity of all PL bands, and thus to an increase of the integral PL intensity. For ZnSe(Al) crystals the treatment by H_2O_2–HBr–EG and H_2O_2–HBr–$C_2H_2O_4$ solutions provides only a slight in-

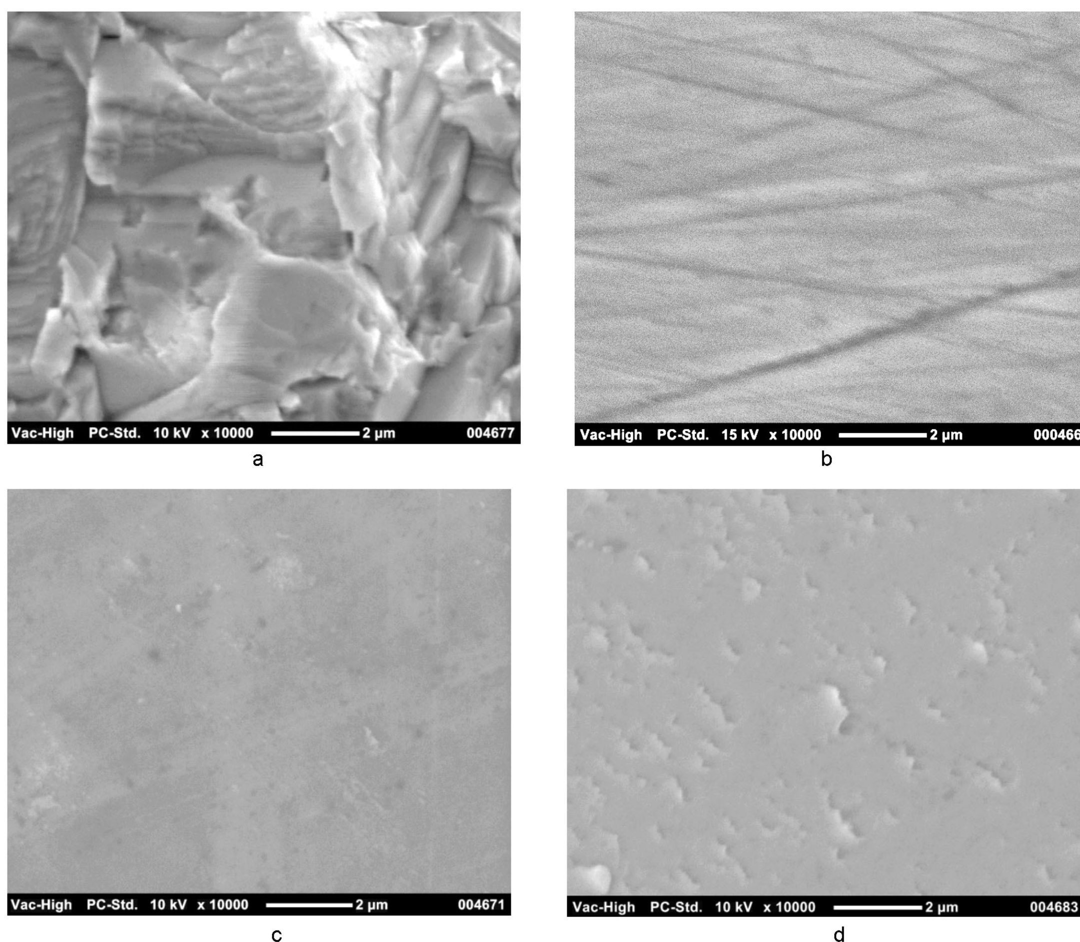


Fig. 5. Surface morphology of ZnSe crystals after different types of treatment: a — cutting, b — mechanical polishing, c — CMP, d — CDP.

crease in the integral PL intensity (by 1.7 times after etching using H_2O_2–HBr–EG solutions) and almost constant the integral PL intensity (for H_2O_2–HBr–$C_2H_2O_4$ solutions) (Fig. 4c). The surface state is significantly improved by reducing the rate of nonradiative recombination after such treatment. But ZnSe(Te) etching using H_2O_2–HBr–EG and H_2O_2–HBr–$C_2H_2O_4$ solutions leads to decreasing of PL intensity approximately twice (Fig. 4d). The above peculiarity may be due to the fact that the treatment of ZnSe crystals by H_2O_2–HBr–EG and H_2O_2–HBr–$C_2H_2O_4$ etching compositions eliminates mainly only point nonradiative recombination centers. The doped ZnSe(Te) and ZnSe(Al) crystals contain more impurity-defect complexes and complex centers formed as a result of mechanical stress, and that, in general, are centers of nonradiative recombination.

A more detailed analysis of the experimental results suggests that the developed etchants are characterized by different polishing ability for the samples with different type of doping impurity. The presence of one or another doping impurity influences on ZnSe dissolution. It is shown that the CMP and CDP processes result into improvement of the surface quality for the investigated materials.

To assess the impact of the etching processes on the surface quality of semiconductor crystals, in particular, to reduce the damaged layer, the microstructure of the samples without treatment and after CMP and CDP were compared (Fig. 5). The results of ZnSe surface electron microscopy after CMP and CDP treatment revealed the high-quality of the polishing surface.

4. Conclusions

The dependences of the dissolution rate of undoped and doped ZnSe on the composition of etchants H_2O_2–HBr–EG and H_2O_2–HBr–$C_2H_2O_4$, their stirring, temperature

and shelf time have been investigated. It is shown that the polishing mixtures are formed in the following ratio of the components (in vol. %): (10–16) H_2O_2: (35–90)HBr: (0–55) EG and (10–16)H_2O_2: (38–90)HBr: (0–49)$C_2H_2O_4$. We have found that the investigated etchants are stable in time and preserve their polishing properties during 24 h after preparing. It was determined that dissolution process of these materials is limited by diffusion stage. This is confirmed by the low values of apparent energy $E_a \leq 8$ kJ/mol (in case of H_2O_2–HBr–EG) and $E_a \leq 6$ kJ/mol (in case of H_2O_2–HBr–$C_2H_2O_4$). The controlled polishing rate of these materials within 12–22 μm/min allows developing polishing etchants for thinning of wafers to the specified sizes. The processes of CMP and CDP lead to an increase of the PL integral intensity for the undoped and doped ZnSe crystals. The high quality of the semiconductors surface after the chemical polishing process was confirmed by using method of electron microscopy.

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