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## **Polishing etchant compositions for the chemical treatment of the PbTe and Pb<sub>1-x</sub>Sn<sub>x</sub>Te solid solutions single crystals and methods for their processing. Review**

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**Abstract.** The review of works devoted to the use of polishing etchant composition for chemical treatment of the PbTe and Pb<sub>1-x</sub>Sn<sub>x</sub>Te solid solutions single crystals and methods for their processing.

**Keywords:** single crystal, lead telluride, Pb<sub>1-x</sub>Sn<sub>x</sub>Te solid solutions, chemical etching.

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### **1. Chemical polishing the PbTe and Pb<sub>1-x</sub>Sn<sub>x</sub>Te surfaces**

Availability of a disturbed deform layer on the surface of thermoelectric modules that are made from the bulk PbTe by using abrasive technology operations (cutting, mechanical grinding and polishing) reduces their thermoelectric figure of merit (decreases the thermopower, increases thermal conductivity and electrical resistivity) and contributes to their degradation. In addition, the PbTe single crystal is used as a material for substrates at the growth of PbTe/Pb<sub>1-x</sub>Sn<sub>x</sub>Te heterostructures, which are key components in fabrication of photodetectors and IR diodes. Quality of detectors and substrates for epitaxy is directly related to quality of the material itself (structural perfection and purity of the material), and processes used to produce them (cutting the ingots, polishing the crystal surface, and metallic

contact deposition). In manufacturing of detectors and substrates, chemical treatment of the PbTe and Pb<sub>1-x</sub>Sn<sub>x</sub>Te solid solutions surface plays an important role. Its main goal is to remove the surface deformation layer produced by preceding abrasive processing and obtain high-purity chemically homogeneous surfaces as structurally perfect as possible.

For obtaining high-quality polishing and structurally perfect and defectless surfaces of the PbTe and Pb<sub>1-x</sub>Sn<sub>x</sub>Te solid solutions, with simultaneous retaining the needed geometrical parameters, chemical-dynamic polishing (CDP) and chemical-mechanical polishing (CMP) are used [1, 2]. Chemical etching based on the chemical dissolution processes is one of the main technological operations in the chemical treatment of semiconductor single crystals and thin films, which are widely used in manufacturing of different semiconductor devices and integrated circuits. The knowledge of kinetic

behavior, mechanism, and nature of semiconductor dissolution is the most important factors for selection of corresponding solution composition for polishing and chemical cutting. High resolving power of some etchants allow their usage on different phases of the substrate treatment, but for these purposes, it is necessary to develop the etchants corresponding to the removed material, surface roughness, and some other parameters [3]. However, there are technological problems related to technology of treatment and the choice of optimal polishing etchants compositions. Little information on chemical polishing of PbTe and  $Pb_{1-x}Sn_xTe$  that can be practically applied to solve these problems exists in the scientific and technical literature. All etching compositions used for this purpose can be classified as follows: etchants based on bromine or iodine compounds, the so-called bromine (iodine)-containing and bromine (iodine)-emerging, as well as etchants based on other compounds.

## 2. Etchant compositions based on iodine compounds

For chemical etching, composition of etchant solution, its oxidative capacity, and rate of dissolution of interaction products are very essential factors. To select the optimal composition of etchants and research the kinetics of chemical etching of lead chalcogenides, there were performed preliminary studies of samples etching in acid and alkaline solutions with elementary  $I_2$  as oxidant [4]. Lead chalcogenides are not dissolved in HCl and NaOH aqueous solutions in the absence of oxidant, which is probably caused by the nature of covalent chemical bonds in these compounds. Most of the investigated solutions acted on the samples surface at the dissolution forming thin layers or significant sediment, indicating that the rate of dissolution is limited by the etching of oxidation products. The surfaces of lead chalcogenides were clean and shiny only after their treatment in alkaline iodine solutions.

The kinetics of PbSe, PbTe and  $Pb_xSn_{1-x}(Se,Te)$  solid solutions chemical etching in alkaline iodine solutions were investigated in [4]. The 0.015, 0.03, and 0.06 M iodine solutions in 12.5 M NaOH were used for experiments. The samples were preliminary polished with M 14 and M 7 powders and then etched in the mentioned etchant at 60...70 °C. The surface state after etching was monitored with a MIM-7 metallographic microscope. The rate of PbSe and PbTe dissolution in these solutions versus temperature and iodine concentration changed within  $10^{-9}$ ... $10^{-10}$  mol/(cm<sup>2</sup>·s) and increased with mixture stirring. The etchant solution of 0.015 M  $I_2$  in 12.5 M NaOH was the most optimal concerning quality of surface obtained. The surface of PbTe becomes clean and bright after treatment by this etchant, and grain boundaries were exposed on the polished  $Pb_{1-x}Sn_xTe$  surface. It was determined that dissolution of PbTe in this solution under stirring is controlled by the rate of the oxidation with an activation

energy of  $E_a = 19.5$  kJ/mol, and  $n_s/n_t \approx 1$  (where  $n_s$  and  $n_t$  are the number of particles per square centimeter of the surface in stirred and unstirred solutions, respectively), *i.e.*, nearly the entire sample surface participates in the dissolution process. The PbTe dissolution rate in stirred solution is half an order of magnitude higher than in unstirred solutions. A partial replacement of lead for tin (8...10 at.%) in PbTe increases the dissolution rate  $1.2 \cdot 10^{-9}$  mol/(cm<sup>2</sup>·s) for PbTe and  $2.8 \cdot 10^{-9}$  mol/(cm<sup>2</sup>·s) for  $Pb_{0.8}Sn_{0.2}Te$  by more than two times and shifts the dissolution process into the transitional region.

An etchant containing NaOH (5 g),  $I_2$  (0.2 g), and  $H_2O$  (10 ml) was also used for PbTe etching [5]. The etching was performed on the PbTe (100) cleavage surface for 5 min under heating up to 95 °C, thereupon the wafers were washed with distilled water and carefully dried using filter paper. As a result of etching, pyramidal etching pits were formed on the samples surface.

As the solvents of elementary iodine can be used not only NaOH, but organic compounds and other substances, too. Practical meaning for being used in the etching compositions at the semiconductor surface is confirmed to such solvents of iodine as HI, KI and some others.

Solutions of  $I_2$  in methanol were used for the chemical-mechanical treatment of  $Pb_{1-x}Sn_xTe$  solid solutions grown by the Czochralski method when forming the laser heterostructures [6]. *p*-type samples with the carrier concentration close to  $5 \cdot 10^{16}$  cm<sup>-3</sup> and dislocation density  $10^7$  cm<sup>-2</sup> were used for the experiments. Wafers of 6.0×6.0×0.4 mm in size and oriented in the direction (100) were polished with alumina powder and after that were etched in an iodine-methanol solution under stirring for 15 s.

Chemical etching of the PbTe and  $Pb_{1-x}Sn_xTe$  solid solutions single crystals were performed using the disk rotating method and iodine solution in dimethylformamide [7]. The dependences of their etching rates versus etchant composition, temperature, stirring speed and the time of solution ageing were studied. The most reasonable application of solutions containing 6 to 18 wt.% of  $I_2$  in DMF is for formation of polishing etching compositions for PbTe and  $Pb_{0.83}Sn_{0.17}Te$  surface treatment.

## 3. Etchants based on bromine compounds (bromine-containing etchant solutions)

Solutions of elemental bromine in organic and inorganic solvents (ethanol, methanol, dimethylformamide, hydrobromic acid, *etc.*) are most frequently used for the surface etching of the PbTe and  $Pb_{1-x}Sn_xTe$  solid solutions. These compositions possess polishing properties, and their etching rate is limited by the diffusion stage of heterogeneous interaction. The reason for this is that the bromine oxidation of the surface layer of the

semiconductors leads to formation of bromides, which are readily soluble in water and various organic solvents. These mixtures are characterized by rather high dissolution rates of PbTe and  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ , and their components are volatile and toxic substances. In particular, in [8] chemical polishing of PbTe samples was spent using etchant containing 5 vol.% of  $\text{Br}_2$  in HBr. The authors investigated the PbTe (100) undoped single crystals of the *n*-type conductivity with the carrier concentration  $n = 3.2 \cdot 10^{17} \text{ cm}^{-3}$  and average density of dislocations  $3.6 \cdot 10^{-5} \text{ cm}^{-2}$ . Before laser irradiation, the samples were first mechanically polished using 1/0 ASM paste, and then they were chemically polished to remove the damaged layer. This solution was also used for chemical etching of PbTe and  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  solid solutions in [9]. When using the bromine etchant solutions in hydrobromic acid, it is essential for obtaining surface quality of PbTe and  $\text{Pb}_x\text{Sn}_{1-x}\text{Te}$  to choose the necessary concentration of bromine and a rate of solution mixing. At the content of  $\text{Br}_2$  in etching mixture less than 1 vol.%, as well as at the decreasing intensity of solution mixing, the samples were covered with a layer of the black interaction products. With addition of water to the etchant, the samples were covered by the yellow film, for which dissolution the authors recommended treatment by boiling 50% solution of NaOH and dilute HCl.

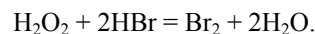
The etchant containing 8 vol.%  $\text{Br}_2$  in HBr was used for chemical etching of  $\text{Pb}_x\text{Sn}_{1-x}\text{Te}$  in [10]. According to the data of Raman spectroscopy, formation of  $\text{TeO}_2$  and Te on the sample surface after chemical etching was observed. Under the subsequent treatment of the samples in boiling 50% NaOH solution and dilute HCl, only Te was detected on the surface. For chemical etching of the PbTe surface, a solution of  $\text{Br}_2:\text{HBr}:\text{H}_2\text{O}$  (volume ratio 1:40:40) can be also used [11].

$\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  (100) wafers cut from Bridgman grown ingots were mechanically polished with the solution of 2%  $\text{Br}_2$  in HBr for removing residual lap damage before preferential etching to develop defects and pits [5]. For polishing the PbTe crystals, the solution of 5 vol.%  $\text{Br}_2$  + 95 vol.% HBr was used [12]. Etching was carried out for 1 min followed by treatment with 30% KOH ( $t \sim 40^\circ\text{C}$ ) for 20 min and washing by bidistilled water.  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  [100] wire-like crystals with the diameter from 10 to 60 mm were etched in the mixture containing 10 parts of the (5 vol.%  $\text{Br}_2$  + 95 vol.% HBr) solution and one part of toluene. Toluene contributes to the intensity of dissolution and eliminates formation of oxide film on the sample surface. Polishing was completed by thorough washing with acetone and then with deionized water. After that, the samples were immersed into a 10% HBr solution at the temperature 18...20 °C for 10 to 30 s. With a view to avoid formation of an oxide film, the samples were immediately subjected to contact nickel plating in a solution containing hydrobromic acid and nickel chloride.

Wire-like crystals of the indium doped *p*- and *n*-type  $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$  solid solution obtained by sublimation in silica capillaries with an inner diameter of 10 to 120  $\mu\text{m}$  and the length of about 20 cm were investigated in [14]. The X-ray examination showed that these crystals grew mainly along the crystallographic direction (100); a uniform distribution of indium impurity along their length was observed. Their structure was more perfect than that of bulk crystals grown using a similar method. After chemical-mechanical polishing, the samples were etched with a mixture containing 10 parts of (95% HBr + 5%  $\text{Br}_2$ ) solution and one part of toluene. The use of this etchant for the chemical polishing of indium doped lead-tin telluride wire-like crystals ensures obtaining the mirror-like smooth surfaces without any oxide film. This is due to the fact that the composition of the proposed solution contains toluene governing the intensity of dissolution.

#### **4. Bromine-emerging etchants for chemical-mechanical and chemical-dynamic polishing PbTe and $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ single crystals**

As bromine-containing etchants are often used for chemical treatments of the PbTe and  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  single crystals surface, it is practical to use them as etchant compositions for the chemical treatment of semiconductor materials in liquid active media, in which the halogens are formed as a result of chemical interaction of initial components in the etchant composition [3]. For example, we take  $\text{H}_2\text{O}_2$  as oxidizer and HBr as a halogen-containing compound, and bromine can be formed as a result of the following chemical reaction:



It is necessary to note that hydrogen peroxide has the biggest oxidizing potential and the lowest ionization constant among the used oxidizing agents [2].  $\text{H}_2\text{O}_2$  exhibits weak acidic properties in aqueous solutions and in combination with hydrohalogenic acids can generate etchants for PbTe and based on it solid solutions with small etching rates and good polishing properties.

As an additional solvent, some organic acids, ethylene glycol or dimethylformamide can be used, and the evolving halogens are partly dissolved in them. Moreover, these additional solvents can regulate the halogen generated, decrease the etching rate, and facilitate dissolution of the forming surface reaction products. Recently, for chemical polishing of PbTe and  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$  solid solutions single crystals, as the etchants there were developed promising new solutions based on  $\text{H}_2\text{O}_2$ -HBr system, where bromine is released as a result of interaction of the initial components and dissolved in an excess hydrobromic acid. The bromine emerging

etching compositions are more convenient for practical aims. These solutions are more stable in time, in comparison with bromine-containing solutions, because the concentration of the active component – bromine – which is formed changes slowly. Also, the bromides formed during oxidation of the crystal surface layers promote transition of dissolution process into the diffusion region. In these bromine-emerging etchants, the kinetics of chemical dissolution of PbTe and  $Pb_{1-x}Sn_xTe$  semiconductor crystals was studied. Bridgman-grown PbTe and the  $Pb_{0.83}Sn_{0.17}Te$  and  $Pb_{0.8}Sn_{0.2}Te$  (II) solid solutions single crystals and also vapor-grown  $Pb_{0.8}Sn_{0.2}Te$  (I) single crystals (the samples of dimensions  $5.0 \times 7.0 \times 1.5$  mm were used) [15-25]. The peculiarities of chemical-dynamic polishing of PbTe and  $Pb_{1-x}Sn_xTe$  crystals in  $H_2O_2$ -HBr (44 %) etchant compositions were studied, and it was ascertained that the increase of Sn content in the  $Pb_{1-x}Sn_xTe$  solid solutions leads to a slight increase of the etching rate, but the regions of polishing solutions were without changes [15]. The most attractive polishing solutions for the chemical-dynamic polishing of the single crystals are those containing 2 to 8 vol.%  $H_2O_2$  in HBr, with the etching rates 3.8 to 17.2  $\mu\text{m}/\text{min}$ .

It was found [6, 7] that using the various concentrations of HBr (35, 40, 44, and 48%) in the etching compositions  $H_2O_2$ -HBr does not substantially influence the etching rate of the PbTe and  $Pb_{1-x}Sn_xTe$  crystal. However, the concentration range of polishing solutions was enlarged, and quality of polishing was improved when using more concentrated hydrobromic acid. It was shown that, for formation of the polishing etchants for the chemical-dynamic treatment, it is best to use 48% HBr; based on it etching compositions have average etching rates 1.0 to 17.0  $\mu\text{m}/\text{min}$  and good polishing properties within the concentration range of 2 to 10 vol.%  $H_2O_2$  in HBr. It was also developed a scheme of chemical surface treatment which includes cleaning the wafers with organic solvents, etching, and final washing in solutions that readily dissolve both residual etchant compositions and chemical reaction products.

It was also investigated the chemical-mechanical polishing PbTe and  $Pb_{1-x}Sn_xTe$  wafers surface with using  $H_2O_2$ -HBr/ethylene glycol (EG) solutions, which ensured etching rates within the range 0.5 to 80.0  $\mu\text{m}/\text{min}$  [18]. Using the same components, it is possible to form polishing etching mixtures with the required etching rates and to apply them in various purposes. So, etchants with a material removal rate of more than 26...80  $\mu\text{m}/\text{min}$  are suitable for removal of the layer damaged by abrasive machining from the PbTe and  $Pb_{1-x}Sn_xTe$  solid solutions surface as well as for rapid and controlled thinning the wafers. Etchants with polishing rates 10 to 15  $\mu\text{m}/\text{min}$  can be used for the controllable thinning the plates to the given thickness, at the same time the flatness is retained. Polishing compositions with the  $v_{pol} = 0.5...5.0$   $\mu\text{m}/\text{min}$  may be used for the controllable removal of thin layers from the single crystals PbTe and  $Pb_{1-x}Sn_xTe$  surface by using the CMP method. The authors emphasize that this

approach allows reducing the duration of semiconductor chemical treatment and simplifies washing the plates, as in all cases the etchants are composed of the same components taken in various ratios. The surface of the PbTe and  $Pb_{1-x}Sn_xTe$  samples after polishing was studied by microstructural analysis, X-ray diffraction and electron microscopy.

The method of high quality polishing PbTe and  $Pb_{1-x}Sn_xTe$  single crystals surfaces includes their mechanical grinding and CMP the semiconductor wafers by the etchant with the next ratio of components (vol.%) (4...8)  $H_2O_2$ :(72...76) HBr:(the rest) ethylene glycol for 2 to 3 min. After that, additional chemical-dynamic polishing was carried out with the etchant of the compositions (vol.):(2...10)  $H_2O_2$ :(48...98) HBr:(0...50) ethylene glycol for 2 to 3 min.

The chemical etching of PbTe and  $Pb_{1-x}Sn_xTe$  solid solutions single crystals by bromine emerging etchants in the following system  $H_2O_2$ -HBr-EG [20],  $H_2O_2$ -HBr- $CH_3COOH$  [21],  $H_2O_2$ -HBr- $C_4H_6O_6$  [22],  $H_2O_2$ -HBr- $C_2H_2O_4$  [23],  $H_2O_2$ -HBr- $C_3H_6O_3$  [24] and  $H_2O_2$ -HBr- $C_6H_8O_7$  [25] has been also studied. The diagrams "etchant composition – etching rate of semiconductor" for the  $H_2O_2$ -HBr-organic acid systems, in which the bromine-evolving etchants are formed, were constructed using mathematical simulation of the experiment. These diagrams are useful for the comparison of different etchant compositions by their etching rates and selection of the best etchant for the given semiconductor. These diagrams also show the concentration regions of polishing and nonpolishing solutions. It has been ascertained that the etching rates of the abovementioned single crystals in these solutions are relatively low ( $1.5 \leq V_{pol} \leq 18.0$   $\mu\text{m}/\text{min}$ ), and dissolution in the polishing solutions proceeds according to the diffusion mechanism. The present results demonstrate that, during dissolution of the semiconductor materials under consideration in the solutions, even slight changes in the etch rate are accompanied by a decrease in the dimensions of polishing solutions in the following order: PbTe  $\approx$   $Pb_{0.83}Sn_{0.17}Te \rightarrow Pb_{0.8}Sn_{0.2}Te$  [20-22, 24, 25]. The regions of polishing solutions for all crystals have been shown to be essentially identical in dimensions and position: 2...10 vol.%  $H_2O_2$ :48...98 vol.% HBr:0...50 vol.%  $C_2H_2O_4$  [23]. So, bromine evolving etching compositions based on hydrogen peroxide, hydrobromic acid and organic component (ethylene glycol acetate, tartaric, oxalic, lactic and citric acid), which are characterized by good polishing properties, could be proposed for the chemical treatment of PbTe and  $Pb_{1-x}Sn_xTe$  single crystals. High quality of the obtained surfaces has been demonstrated by microstructural analysis and scanning electron microscopy of the PbTe and  $Pb_{1-x}Sn_xTe$  solid solutions surface after the chemical-dynamic treatment.

Polishing etchant that can be used for the PbTe and  $Pb_{1-x}Sn_xTe$  single crystals surface treatment of semiconductor and their conditions of use are summarized in Table.

**Polishing etchant for the chemical treatment of the semiconductor PbTe and Pb<sub>1-x</sub>Sn<sub>x</sub>Te surface**

№	Semiconductor	Etchant composition	Conditions	Comments	Ref.
1	PbTe	2% Br <sub>2</sub> -CH <sub>3</sub> OH	The sample was post-processed with 0.25 μm diamond powder and 0.03 μm silica suspension polishing, etching τ = 2 min.	Polishing	[26]
2	PbTe	40 P K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (saturated solution) – 9 P HNO <sub>3</sub> (conc.)	Mechanical polishing samples Al <sub>2</sub> O <sub>3</sub> (0.25 μm); washing: water, methanol	Polishing	[27]
3	PbTe	100 ml H <sub>3</sub> PO <sub>4</sub> (88%) – 10 g H <sub>2</sub> CrO <sub>4</sub>	90...105 °C, 4...6 min, 6...20 V, 3 A/cm <sup>2</sup>	Electropolishing	[28]
4	PbTe	20 g KOH – 35 ml glycerol – 20 ml C <sub>2</sub> H <sub>5</sub> OH – 45 ml H <sub>2</sub> O	25 °C, 5...15 min, 6 V, 0.2 A/cm <sup>2</sup> mixing the electrolyte magnetic stirrer (75...200 min <sup>-1</sup> ), anode slow rotation around the vertical axis (4 min <sup>-1</sup> ). Washing: water → HNO <sub>3</sub> (1:10) → water for 2-3 s	Electropolishing. Cathode – platinum	[28]
5	PbTe, Pb <sub>0.73</sub> Sn <sub>0.17</sub> Te	I <sub>2</sub> -DMF	Etchants for CDP. Optimal conditions: t <sub>CDP</sub> ≈ 25 °C, τ ≈ 2...3 min. Washing: H <sub>2</sub> O → 15% NaOH → H <sub>2</sub> O → HCl (conc.) → H <sub>2</sub> O for 30 s	Mirror-like surface. V <sub>CDP</sub> ranges from 3.5 up to 15.0 μm/min. The process dissolution is limited by the diffusion stages.	[7]
6	PbTe, PbSe	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (saturated solution) – 11.7 N HCl 1:1		Dissolution rate ranges from 5·10 <sup>-8</sup> to 1·10 <sup>-8</sup> mol/cm <sup>2</sup> ·s. Dissolution occurs in the transition region, dominated diffusion.	[4]
7	PbTe, PbSe	16 N HNO <sub>3</sub> –CH <sub>3</sub> COOH 4:1		Polishing brilliant surfaces	[4]
8	PbTe, PbSe, Pb <sub>x</sub> Sn <sub>1-x</sub> (Se, Te)	0.015 (0.03, 0.06) M I <sub>2</sub> in 12.5 M NaOH	Optimal conditions for PbSe and PbTe: 0.015 mol. I <sub>2</sub> in 12.5 M NaOH. Dissolution PbTe limited by the speed of oxidation and the entire surface is etched sample.	Formed clean and shiny surface of lead chalcogenides. Dissolution rate ranges from 10 <sup>-9</sup> to 10 <sup>-10</sup> mol/cm <sup>2</sup> ·s	[4]
9	PbTe	NH <sub>4</sub> OH–H <sub>2</sub> O <sub>2</sub>	The samples were mechanically polished with alumina, degreased with trichloroethylene, and rinsed with acetone, ethanol, and deionized water in turn prior to chemical treatments.	Polishing	[29]
10	PbTe	0.8 m/l K <sub>3</sub> [Fe(CN) <sub>6</sub> ]– 0.6–0.05 m/l NaOH– 100 g/l glycerol	The mechanical polishing with diamond (grain sizes 6; 3; 1 μm) or alumina. As special cleaning with trichlorethylene, acetone, ethanol and high purified water. The sample preservation was carried out in air or under high purified water followed by vacuum at 1.3·10 <sup>-6</sup> Pa.	Chemical-mechanical polishing	[30]
11	PbTe; Pb <sub>1-x</sub> Sn <sub>x</sub> Te 0.1 ≤ x ≤ 0.125	I <sub>2</sub> -CH <sub>3</sub> OH	Etchants for CMP	Mirror-like surface. Single crystals grown by the Czochralski pulling method	[6]
12	PbTe, Pb <sub>1-x</sub> Sn <sub>x</sub> Te x ≤ 0.03	6 P Br <sub>2</sub> – 100 P conc. HBr	Room temperature. With continuous agitation etchant	Polishing surfaces. Speed polishing ≈ 20 μm/min	[31]
13	PbTe; Pb <sub>1-x</sub> Sn <sub>x</sub> Te x = 0.2; 0.17	35% H <sub>2</sub> O <sub>2</sub> :40, 44, 48% HBr	Etchants for CDP. Optimal conditions: t <sub>CDP</sub> ≈ 20...25°C, τ ≈ 3...5 min, the rotation speed of disc γ = 86 rpm. Washing: H <sub>2</sub> O → 15 % NaOH → H <sub>2</sub> O → HCl (conc.) → H <sub>2</sub> O for 30 s	Mirror-like surface. Dissolution rate V <sub>CDP</sub> ranges from 4.0 up to 17.0 μm/min. The process dissolution is limited by the diffusion stages.	[15, 16, 17]

14	PbTe; Pb <sub>1-x</sub> Sn <sub>x</sub> Te x = 0.2; 0.17	35% H <sub>2</sub> O <sub>2</sub> :40% HBr:EG	Etchants for CMP. Optimal conditions: $t_{CMP} \approx 20^\circ\text{C}$ , $\tau \approx 2$ min. Washing: H <sub>2</sub> O → 15 % NaOH → H <sub>2</sub> O → HCl (conc.) → H <sub>2</sub> O for 30 s	Mirror-like surface. Dissolution rate $V_{CMP}$ ranges from 0.5 up to 80.0 $\mu\text{m}/\text{min}$	[18]
15	PbTe; Pb <sub>1-x</sub> Sn <sub>x</sub> Te x = 0.2; 0.17	35% H <sub>2</sub> O <sub>2</sub> :48% HBr:EG	Etchants for CDP. Optimal conditions: $t_{CDP} \approx 25^\circ\text{C}$ , $\tau \approx 2 \dots 3$ min, the rotation speed of disc $\gamma = 86$ rpm. Washing: H <sub>2</sub> O → 15 % NaOH → H <sub>2</sub> O → HCl (conc.) → H <sub>2</sub> O for 30 s	Mirror-like surface. Dissolution rate $V_{CDP}$ ranges from 1.5 up to 18.0 $\mu\text{m}/\text{min}$ . The process dissolution is limited by the diffusion stages.	[19, 20]
16		35% H <sub>2</sub> O <sub>2</sub> :48% HBr:80% acetic acid			[21]
17		35% H <sub>2</sub> O <sub>2</sub> :48% HBr:40% tartaric acid			[22]
18		35% H <sub>2</sub> O <sub>2</sub> :48% HBr:8% oxalic acid			[23]
19		35% H <sub>2</sub> O <sub>2</sub> :48% HBr:80% lactic acid			[24]
20		35% H <sub>2</sub> O <sub>2</sub> :48% HBr:40% citric acid			[25]
21	Pb <sub>x</sub> Sn <sub>1-x</sub> (Se, Te)	4 P NaOH (4 N) – 1 P H <sub>2</sub> O <sub>2</sub> (30%)		Chemical etching	[4]
22	Pb <sub>x</sub> Sn <sub>1-x</sub> (Se, Te)	HNO <sub>3</sub> :H <sub>2</sub> O 1:1		Chemical etching	[4]

**Comments:** EG – ethylene glycol.

## 5. Conclusions

The analysis of literature data shows that for forming the polished surface of the PbTe and Pb<sub>1-x</sub>Sn<sub>x</sub>Te crystals mainly bromine (iodine)-containing etchants have been used, but the physical-chemical interaction of PbTe and Pb<sub>1-x</sub>Sn<sub>x</sub>Te single crystal with the above etchants has been studied not enough.

It was shown that the solutions of Br<sub>2</sub> in HBr, which are characterized by good polishing properties, are mostly used for the surface treatment of PbTe and Pb<sub>1-x</sub>Sn<sub>x</sub>Te semiconductors. However, bromine-containing etchants, along with their good polishing properties, have some disadvantages. Among them, it is necessary to note a significant toxicity of elemental bromine and technological difficulties associated with its practical application. To avoid these limitations, it is better to use bromine evolving etching compositions, in which bromine is formed as a result of chemical interaction of initial components in the etchant composition (H<sub>2</sub>O<sub>2</sub> and HBr); this bromine is dissolved in excess of hydrobromic acid. The kinetic peculiarities of PbTe and Pb<sub>1-x</sub>Sn<sub>x</sub>Te single crystal etching for such etchant have been investigated. The prospects of their use for forming the polished surface of PbTe and Pb<sub>0.83</sub>Sn<sub>0.17</sub>Te and Pb<sub>0.8</sub>Sn<sub>0.2</sub>Te solid solutions single-crystal plates have been shown.

## References

- Sangval K. *Etching of Crystals: Theory, Experiment, Application*. North-Holland, 1987.
- Perevoshchikov V.A. Processes of the chemical-dynamic polishing of the semiconductor surfaces. *Vysokochistyye veshchestva*. 1995. **2**. P. 5–29 (in Russian).
- Tomashik V.N., Tomashik Z.F. Chemical treatment of the CdTe and Zn<sub>x</sub>Cd<sub>1-x</sub>Te surfaces. In: *CdTe and Related Compounds; Physics, Defects, Hetero- and Nano-Structures, Crystal Growth, Surfaces and Applications*. Part II. Editors R. Triboulet and P. Siffert. Netherlands, Elsevier, 2010. P. 119–144.
- Orlova G.M., Blinov L.N., Belyakova N.V., Kozharina T.P. Kinetics of lead chalcogenide chemical etching. *Zhurnal Prikladnoi Khimii*. 1975. **48**, No. 9. P. 1945–1949 (in Russian).
- Walker P., Tarn W.H. *Handbook of Metal Etchants*. CRC Press LLC, 1991.
- Tomasetta L.R., Fonstad C.G. Liquid phase epitaxial growth of laser heterostructure in Pb<sub>1-x</sub>Sn<sub>x</sub>Te. *Appl. Phys. Lett.* 1974. **24**, No. 11. P. 567–570.
- Tomashyk Z.F., Tomashyk V.N., Stratiychuk I.B., Malanych G.P., Pavlovich I.I. Specifics of chemical etching of PbTe and Pb<sub>1-x</sub>Sn<sub>x</sub>Te single crystals with I<sub>2</sub>-DMFA solutions. *Russ. J. Inorg. Chem.* 2013. **58**, No. 3. P. 367–371.
- Budzulyak I.M. Transform of structure in double semiconductors in field action laser irradiation. *Fizika Khimiya Tverd. Tila*. 2008. **9**, No. 1. P. 51–57 (in Ukrainian).
- Vasil'eva L.F., Sokolova G.A., Shakhina T.V. Etching behavior of PbTe and Pb<sub>1-x</sub>Sn<sub>x</sub>Te substrate surfaces. *Zavodskaya Laboratoriya*. 1980. **46**, No. 11. P. 1034–1035 (in Russian).
- Kanter Y.O., Shahina T.V. Investigation of Pb<sub>1-x</sub>Sn<sub>x</sub>Te surface composition. *Poverkhnost. Fizika, khimiya, mekhanika*. 1982. **1**. P. 99–102 (in Russian).

11. Barros A.S., Abramof E., Rappl P.H.O. Lead telluride *p-n* junctions for infrared detection: Electrical and optical characteristics. *Braz. J. Phys.* 2006. **36**, No. 2A. P. 474–477.
12. Danilova M.G., Sveshnikova L.L., Repinskii S.M. The electrode behavior of lead telluride in alkaline solutions of hydrogen peroxide. *Elektrokimiya*. 1990. **26**, No. 6. P. 788–790 (in Russian).
13. Dyntu M.P., Meglei D.F., Donu S.V. The technique for preparing high-quality contacts on lead tin telluride. *Fizika Khimiya Tverd. Tila*. 2010. **11**, No.3. P. 744–746.
14. Meglei D.F., Dyntu M.P., Donu S.V. Indium impurity effect on growth and structural perfection of lead–tin telluride wire crystals. *Mold. J. Phys. Sci.* 2010. **9**, No. 2. P. 156–158.
15. Tomashyk Z.F., Tomashyk V.M., Stratiychuk I.B., Malanych G.P., Pavlovich I.I. Application of H<sub>2</sub>O<sub>2</sub>–HBr bromine-releasing etchants for chemical polishing of the surface of PbTe and Pb<sub>1–x</sub>Sn<sub>x</sub>Te solid solutions. *Fizika Khimiya Tverd. Tila*. 2012. **12**, No. 4. P. 1007–1012 (in Ukrainian).
16. Malanych G.P., Tomashyk Z.F., Tomashyk V.M., Stratiychuk I.B. Optimization of the bromine emerging etchants for the chemical–dynamic polishing of the PbTe and Pb<sub>1–x</sub>Sn<sub>x</sub>Te solid solutions single crystals. *Metallofizika Noveishie Tekhnol.* 2011. **33**. P. 255–263 (in Ukrainian).
17. Malanych G.P., Tomashyk V.M., Stratiychuk I.B., Tomashyk Z.F. Chemical etching of PbTe and Pb<sub>1–x</sub>Sn<sub>x</sub>Te single crystals by using H<sub>2</sub>O<sub>2</sub>–HBr solutions with different initial HBr concentrations. *Optoelektronika i Poluprovodnikovaya Tekhnika*. 2015. **50**. P. 94–101 (in Ukrainian).
18. Malanych G.P., Tomashyk Z.F., Tomashyk V.M., Stratiychuk I.B., Safryuk N.V., Klad'ko V.P. Chemical–mechanical polishing of single crystals of PbTe and Pb<sub>1–x</sub>Sn<sub>x</sub>Te solid solutions in H<sub>2</sub>O<sub>2</sub>–HBr–ethylene glycol etchants. *Nauk. Visnyk Chernivets'koho Natsional'noho Universitetu, Khim.* 2013. **640**. P. 72–78 (in Ukrainian).
19. *UA Patent 95348*, CI (2014.01) H01L 21/00. Method of formation of polishing surfaces of lead telluride and Pb<sub>1–x</sub>Sn<sub>x</sub>Te solid solutions. G.P. Malanych, V.M. Tomashyk, Z.F. Tomashyk, I.B. Stratiychuk, P.M. Lytvyn, O.S. Lytvyn, O.I. Kopyl. No. u2014 06110. December 25, 2014.
20. Tomashyk Z.F., Malanych G.P., Tomashyk V.N., Stratiychuk I.B., Pashchenko G.A., Kravtsova A.S. Polishing of PbTe and Pb<sub>1–x</sub>Sn<sub>x</sub>Te single crystals with H<sub>2</sub>O<sub>2</sub>–HBr–ethylene glycol bromine-releasing etchants. *Voprosy Khim. Khim. Tekhnol.* 2012. No. 4. P. 120–125 (in Ukrainian).
21. Malanych G.P., Tomashyk Z.F., Tomashyk V.N., Stratiychuk I.B., Lukiyanchuk E.M. Chemical dissolution of PbTe and Pb<sub>1–x</sub>Sn<sub>x</sub>Te solid solutions single crystals in the H<sub>2</sub>O<sub>2</sub>–HBr–acetate acid etching compositions. *Nauk. Visnyk Cherniv. Universitetu, Khimiya*. 2011. **581**. P. 63–69 (in Ukrainian).
22. Malanych G.P., Tomashyk V.N., Stratiychuk I.B., Tomashyk Z.F. Etching behavior of PbTe and Pb<sub>1–x</sub>Sn<sub>x</sub>Te crystal surfaces in aqueous H<sub>2</sub>O<sub>2</sub>–HBr–tartaric acid solutions. *Inorg. Mater.* 2014. **50**, No. 7. P. 661–666.
23. Malanych G.P., Tomashyk V.N., Stratiychuk I.B., Tomashyk Z.F. Polishing of PbTe and Pb<sub>1–x</sub>Sn<sub>x</sub>Te surfaces with H<sub>2</sub>O<sub>2</sub>–HBr–C<sub>2</sub>H<sub>2</sub>O<sub>4</sub> solutions. *Inorg. Mater.* 2015. **51**, No. 1. P. 15–19.
24. Malanych G.P., Tomashyk V.N., Stratiychuk I.B., Tomashyk Z.F. Use of H<sub>2</sub>O<sub>2</sub>–HBr–lactic acid etchants for chemical dissolution of PbTe and Pb<sub>1–x</sub>Sn<sub>x</sub>Te crystals. *Russ. J. Inorg. Chem.* 2015. **60**, No. 9. P. 1143–1147.
25. Malanych G.P., Tomashyk V.N., Stratiychuk I.B., Tomashyk Z.F. Wet chemical etching of PbTe and Pb<sub>1–x</sub>Sn<sub>x</sub>Te crystal surfaces with bromine releasing aqueous H<sub>2</sub>O<sub>2</sub>–HBr–citric acid solutions. *Inorg. Mater.* 2016. **52**, No. 2. P. 136–143.
26. Kim G., Hammig M.D. An investigation of single-crystal PbTe for nuclear radiation detector applications. *Nuclear Science Symposium and Medical Imaging Conference (NSS/MIC), 2011 IEEE*. USA, Michigan. Conf. Publ. 2011. P. 1732–1737.
27. Rolls W., Lee R., Eddington R.J. Preparation and properties of lead-tin-telluride photodiodes. *Solid-State Electronics*. 1970. **13**, No. 1. P. 75–81.
28. Pshenichnov Yu.P. *Revealing the Fine Structure of Crystals: Handbook*. Metallurgiya, Moscow, 1974 (in Russian).
29. Okumura H., Ihara H., Gonda S. XPS analysis of PbTe surfaces prepared by various cleaning procedures. *J. Vac. Sci. Technol.* 1984. **2**, No. 3. P. 1329–1332.
30. Engel A., Gaskov A.M. Auger electron spectroscopy of cut and polished PbTe surfaces. *Cryst. Res. Technol.* 1986. **21**, No. 1. P. K13–K20.
31. Crocker A.J., Wilson M. Microhardness in PbTe and related alloys. *J. Mater. Sci.* 1978. **13**, No. 4. P. 833–842.