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The influence of ethylene glycol on the chemical interaction of PbTe and $Pb_{1-x}Sn_xTe$ crystals with H_2O_2–HBr–ethylene glycol etching compositions

G.P. Malanych[1], V.M. Tomashyk[1], O.S. Lytvyn[1,2]
[1]*V. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine,*
41, prospect Nauky, 03028 Kyiv;
E-mail: galya_malanich@mail.ru
[2]*Borys Grinchenko Kyiv University,*
18/2, Bulvarno-Kudriavska str., 04053 Kyiv

Abstract. The process of cutting, mechanical and chemical treatment of the PbTe and $Pb_{1-x}Sn_xTe$ crystal surface has been studied. The dependences of the chemical-mechanical polishing rate versus dilution of the base polishing etchant H_2O_2–HBr–ethylene glycol by the ethylene glycol have been determined. The surface states after chemical etching have been investigated using electron, metallographic and atomic force microscopy as well as X-ray microanalysis. It has been shown that the surface state is improved after chemical etching. Efficient methods for washing the samples after different types of PbTe and $Pb_{1-x}Sn_xTe$ surface treatment (cutting the crystal, mechanical surface treatment, chemical removing the surface damaged layer) have been developed.

Keywords: chemical etching, lead telluride, solid solutions, dissolution rate, chemical dynamic polishing.

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1. Introduction

Single crystals of PbTe are used as material for substrates when growing the PbTe/$Pb_{1-x}Sn_xTe$ heterostructures that are key components in fabrication of photodetectors and IR diode sources [1]. The quality of detectors and substrates for epitaxy is directly related to the quality of material itself (structural perfection and purity of material) and processes used to produce them (cutting ingots, polishing the crystal surface, and metallic contact deposition). When fabricating detectors and substrates, an important role is played by chemical treatment of the crystal surface of PbTe and $Pb_{1-x}Sn_xTe$ solid solutions. The main task of this chemical treatment is elimination of the disturbed layer that is formed as a result of previous mechanical processing as well as acquisition of the high-clean surfaces maximally structurally perfect and homogeneous in terms of their chemical composition. These problems are successfully solved using liquid-phase etching, in particular, applying the method of chemical-mechanical polishing (CMP). CMP process is realized as a result of the combined effects of the chemical and mechanical factors and is described approximately by the Preston equation [2, 3].

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In most cases, CMP is therefore employed with polishing etchants. During this polishing, the reagents oxidize or dissolve surface layers of the plates, and the polishing member removes mechanically the interaction products and microscopic particles of semiconductor. The material removal, surface quality and geometrical parameters of the plates to a considerable extent depend on the polishing mixture composition, treatment temperature, pressure on the plate and the material of the polishing member. The etchant compositions for CMP must correspond to a number of requirements: to have a required etching rate without formation of insoluble or poorly soluble reaction products; to be inert to the material of the polishing member and equipment and to be not too toxic [4].

Bromine solutions in organic and inorganic solvents are most frequently used for the surface etching of PbTe and $Pb_{1-x}Sn_xTe$ solid solutions. After mechanical lapping of $Pb_{1-x}Sn_xTe$ (100) wafers, cut from a Bridgman grown ingot, 2% Br_2 solution in HBr were used to remove residual lap damage before preferential etching to develop defects and pits [5]. For polishing the PbTe crystals, the solution of 5 vol.% Br_2 + 95 vol.% HBr was used, and etching was carried out for 1 min followed by treatment with 30% KOH ($t \approx 40$ °C) for 20 min and washing in bidistilled water [6].

Etching compositions based on elementary bromine are characterized by high polishing rates. Some problems appear with their preparation and composition control, and their components are highly toxic. Therefore, there is a necessity to search less toxic and more technological etching compositions with low dissolution rates of semiconductor surfaces. More practical and promising are bromine-emerging etchant compositions [7, 8], in which bromine is formed as a result of the redox reaction of etchant components, for example, H_2O_2 and HBr.

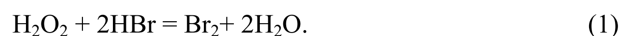
This work is aimed to investigate CMP of PbTe and $Pb_{1-x}Sn_xTe$ single crystal surfaces by bromine-emerging etchant compositions based on aqueous solutions of H_2O_2–HBr–solvent, to determine surface quality after CMP using metallography, AFM and X-ray microanalysis, and to optimize the polishing compositions for formation of high quality surfaces of the semiconductors mentioned above.

2. Experimental

In our experiments, the Bridgman-grown single crystals of PbTe and $Pb_{0.83}Sn_{0.17}Te$ and $Pb_{0.8}Sn_{0.2}Te$ (II) solid solutions as well as vapor-grown $Pb_{0.8}Sn_{0.2}Te$ (I) single crystals were used. The ingots were sliced into wafers 5×7×1.5 mm in dimensions by using a diamond wire saw. The authors [9] have found that the depth of the damaged layer for PbTe semiconductor monocrystalline wafers is about 120 μm after diamond wheels cutting, and it doesn't depend on the nature of samples. It should be noted that the damaged layer thickness is almost independent from the surface crystallographic orientation of the plates. The cutting-induced surface deformation layer was partially removed by mechanical grinding with aqueous suspensions of M10 to M5 abrasive powders. The polishing process was carried out on a glass polisher, and working side plate was polished for 2 min with an aqueous suspension of M10 abrasive, and then – M5 abrasive. To remove the surface contamination produced on the wafer surface at the cutting and grinding stages, the wafers were rinsed in warm distilled water containing surfactants, rinsed several times with distilled water, and then dried in flowing dry air. The damaged layer depth of semiconductor wafers after polishing with abrasive powder was amounted for M10 – 11…32 μm, and for M5 – 7…26 μm [10]. The elimination rate of the surface layer is different and depends on the nature of materials and abrasive grit (Table).

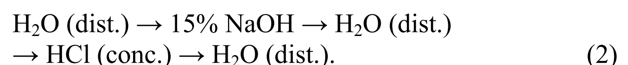
The unprocessed side of the wafers prepared in such manner was then glued with picein to silica substrates. The residual picein was removed from the surface of the specimens and substrates by rinsing with organic solvents: acetone, toluene, and ethanol. Next, the cutting- and grinding-induced surface deformed layer was removed from the surface of all the crystals by CMP [8] using a bromine-emerging H_2O_2–HBr–ethylene glycol etchant at the dissolution rate ≈170 μm/min. The CMP process was performed at $T = 293…295$ K on a glass wheel covered with cloth. The etchant was constantly fed at the rate 2…3 mL/min.

Etchants were prepared using aqueous solutions of 48% HBr, 35% H_2O_2, and ethylene glycol (EG). All the chemicals were of extra pure or reagent grade. The starting chemicals were mixed in appropriate volume ratios (that is, the etchant composition was expressed as a volume percent). All solutions were aged before the etching and were allowed to stand for 120 min to provide the reaction between the given etchant components:



$$H_2O_2 + 2HBr = Br_2 + 2H_2O. \quad (1)$$

After chemical etching, the wafers were rapidly withdrawn from the etchant and at once rinsed to fully remove the residual etchant and reaction products from the surface. According to the proposed technique, the rinsing process comprised several steps (30 s in each solution), as represented by the following scheme:



$$H_2O \text{ (dist.)} \rightarrow 15\%\ NaOH \rightarrow H_2O \text{ (dist.)} \rightarrow HCl \text{ (conc.)} \rightarrow H_2O \text{ (dist.)}. \quad (2)$$

After rinsing, the samples were dried in flowing dry air.

The dissolution rate was determined via the decrease in wafer thickness by using a 1 MIGP multiturn timer with the accuracy of ±0.5 μm. Four samples were dissolved simultaneously, and the deviation in thickness measurements did not exceed 5%. The surface microstructure of the PbTe samples and $Pb_{1-x}Sn_xTe$ solid solutions after various abrasive and chemical treatment

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steps was studied using optical microscopy and electron probe microanalysis. Surfaces were examined in white light on the MIM-7 metallurgical microscope fitted with an eTREK DCM800 digital video camera (8 Mpix) and JEOL JCM-5000 NeoScope benchtop scanning electron microscope. The quality of polished surfaces was assessed by atomic force microscopy (AFM) by using intermittent contact mode imaging with the NanoScope IIIa Dimension 3000TM scanning probe microscope (Digital Instruments, USA). The elemental composition of the wafer surfaces was determined using scanning electron microscopy being based on Zeiss EVO 50 XVP equipped with an INCA450 energy dispersive X-ray spectrometer system, which included an INCAPentaFET×3 detector and HKL Channel-5 backscattered electron diffraction system (Oxford Instruments).

3. Results and discussion

Correct selection of etchant compositions that are used at the abrasive chemical treatment for CMP is an important condition for obtaining high quality polished surfaces of semiconductor materials. When using the base polishing etchant to form polishing compositions for CMP, it was taken into account that the rate of material removal at the expense of mechanical component action should be several times higher than that of chemical dynamic polishing (CDP). It was shown that in the concentration regions of the H_2O_2–HBr–EG system (in vol.%) (2–10) H_2O_2:(48–98) HBr:(0–50) EG the polishing compositions for CDP of the PbTe and $Pb_{1-x}Sn_xTe$ are formed [7]. A base solution (*B*) with a composition in the EG enriched region was therefore selected from the investigated range. The rate of CDP of the PbTe and $Pb_{1-x}Sn_xTe$ in this etchant is equal to ≈7 µm/min. But when using CMP, the polishing rate increased and reached 170 µm/min (Fig. 1). Some quantity of the viscous component was added to the base solution *B* to diminish the polishing rate and to improve the surface properties. It is clear from Fig. 1 that the increase of added EG quantity to etchant *B* leads to a decrease in the CMP rate of the PbTe and $Pb_{1-x}Sn_xTe$ monocrystalline plate. Using the dependences from Fig. 1, it is possible to select a required CMP rate within the region from 20 to 170 µm/min by changing the ratio of base etchant *B* to EG.

One of the advantages of the developed polishing compositions except for the low polishing rates is their pH that is equal to 6–7. It allows us to avoid interaction of the etchants with the surface of the polishing member. This factor has a great importance as in the majority of cases the etchants can destroy the material of the polishing member due their high acidity or alkalinity and introduce additional impurities on the surfaces of semiconductor plates. It should be noted that the semiconductor surface after CMP in etchants containing from 0 up to 60 vol.% of EG acquired high quality. Further dilution of the stock solution (70 vol.% of EG) deteriorated the surface quality: a white translucent film appeared on the surface.

Using the methods of metallographic analysis and electron microscopy, the sample surfaces were compared after cutting, polishing and CMP to assess the impact of etching processes on surface quality of semiconductor crystals, in particular, on reducing the damaged layer. The microstructure of the PbTe and $Pb_{1-x}Sn_xTe$ solid solution surfaces after their treatment according to the developed method is characterized by a high quality and good mirror brightness.

Analysis of the obtained results shows that at the same improvement of lead telluride surface there is a clear difference between topography after mechanical treatment (Figs. 2a and 2b), which reveals the surface traces after string cutting, scratches from abrasive grains and microcracks of surface even after its treatment with polishing etchant (Fig. 2c) (different size of microroughnesses and surface nature).

Table. The elimination rate of the PbTe and $Pb_{1-x}Sn_xTe$ single crystal surfaces layer during mechanical treatment with free abrasives.

Semiconductor	The rate of surface layer elimination, µm/min	
	M 10	M 5
PbTe	~ 60.0	~ 13.5
$Pb_{0.83}Sn_{0.17}Te$	~ 80.0	~ 20.0
$Pb_{0.8}Sn_{0.2}Te$ (II)	~ 95.0	~ 24.0
$Pb_{0.8}Sn_{0.2}Te$ (II)	~ 68.5	~ 21.0

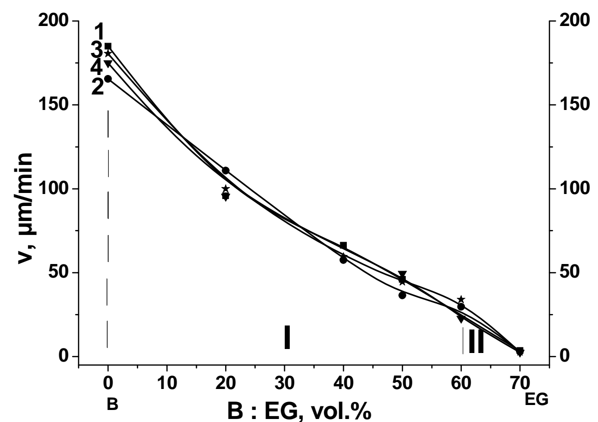

Fig. 1. Dependences of the CMP rate of the PbTe (1), $Pb_{0.83}Sn_{0.17}Te$ (2), $Pb_{0.8}Sn_{0.2}Te$ (I) (3) and $Pb_{0.8}Sn_{0.2}Te$ (II) (4) versus volume ratio of base etchant *B* (H_2O_2–HBr–EG) and viscous organic component – ethylene glycol (I – polishing and II – unpolishing solutions).

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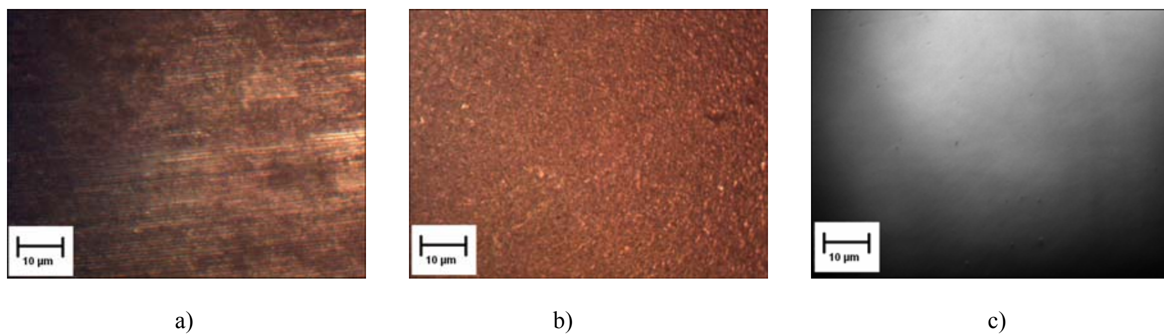

Fig. 2. Microstructure of PbTe surface (metallographic microscope MIM-7 with digital video camcorder eTREK DCM800 (8 Mpix)): (a) after string cutting, (b) after abrasive polishing M5, (c) after chemical-mechanical polishing with H_2O_2–HBr–EG etchant.

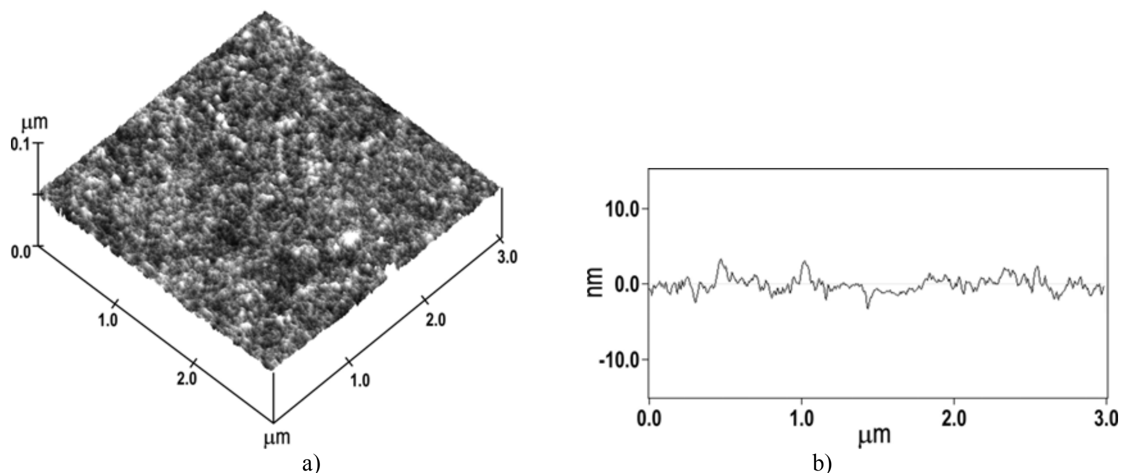

Fig. 3. (a) Three-dimensional AFM image of the PbTe surface after CMP with a H_2O_2–HBr–EG polishing solution, (b) surface roughness profile.

The surface microstructure of the samples under investigation was examined after each abrasive and chemical treatment step (cutting, grinding, CMP) using optical and electron microscopy techniques. AFM characterization was only carried out for polished surfaces with the best microstructure, that is, for the surfaces treated with the most promising etchant mixtures. Fig. 3 shows a three-dimensional AFM image of the surface of the PbTe single crystal after CMP with a bromine-emerging H_2O_2–HBr–EG etchant. The AFM data demonstrate that the average surface roughness R_a of all our samples does not exceed 4 nm. CMP of the surface of the PbTe and $Pb_{1-x}Sn_xTe$ crystals with the proposed etchant mixtures produces a surface microprofile with R_z = 5…11 nm. Thus, one can obtain high-quality polished PbTe and $Pb_{1-x}Sn_xTe$ surfaces with tailored parameters satisfying the requirements (roughness value $R_z \leq$ 40 nm) for polished surfaces of semiconductor materials [4].

Using X-ray microanalysis, we checked the presence of oxygen and carbon, as well as possible contamination with chemical compounds present in the etchant and rinsing solutions. Oxygen was not detected immediately after treatment with polishing etchants but was found after prolonged storage of the samples (for about two months) in air. The absence of Br, Cl, and Na on the surface of the studied samples suggests that an adequate rinsing procedure was used.

4. Conclusion

The CMP process of the PbTe, $Pb_{0,83}Sn_{0,17}Te$ and $Pb_{0,8}Sn_{0,2}Te$ solid solutions surfaces with the H_2O_2–HBr–EG bromine-emerging etchants has been investigated. It has been shown that etchant compositions based on aqueous solutions of the H_2O_2–HBr–solvent systems with ethylene glycol as a solvent completely meet the requirements for CMP etchants. The surface roughness of the single crystals of PbTe and $Pb_{1-x}Sn_xTe$ solid solutions after their treatment by using the CMP method including the developed etchant compositions does not exceed 40 nm. The compositions of the polishing etchants for the various surface treatments of the above semiconductor materials were optimized.

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