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Chemical-mechanical polishing of CdTe, $Zn_xCd_{1-x}Te$ and $Cd_xHg_{1-x}Te$ single crystal surfaces by $K_2Cr_2O_7$–HBr–solvent etchants

M.V.Chayka[1,2]***, Z.F.Tomashyk***[2]***, V.M.Tomashyk***[2]***,***
G.P.Malanych[2]***, A.A.Korchovyi***[2]

[1]Zhytomyr Franko State University, 40 Velyka Berdychivska Str., 10008 Zhytomyr, Ukraine
[2]V.Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41 Nauky Ave., 03028 Kyiv, Ukraine

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Chemical-mechanical polishing (CMP) of the CdTe single crystals and $Zn_xCd_{1-x}Te$, $Cd_xHg_{1-x}Te$ solid solutions surfaces by bromine-emerging etching compositions based on aqueous solutions of $K_2Cr_2O_7$–HBr–$C_4H_6O_6$ and $K_2Cr_2O_7$–HBr–ethylene glycol has been investigated for the first time. The dependences of the chemical-mechanical polishing rate on the dilution of the base polishing etchant for tartaric acid, ethylene glycol and glycerol have been established. The effect of the nature of the viscous organic solvent on the polishing rate and the quality of the polished surface of the single crystals has been determined. The surface condition after CMP has been investigated using metallographic analysis and atomic force microscopy. The polishing etchant compositions and conditions of conducting the process of CMP for forming a high-quality polished surface of CdTe, $Zn_xCd_{1-x}Te$ and $Cd_xHg_{1-x}Te$ single crystals have been optimized.
Keywords: chemical-mechanical polishing, cadmium telluride, solid solutions, etchant, single crystal, dissolution rate.

Впервые экспериментально исследован процесс химико-механического полирования (ХМП) поверхности монокристаллов CdTe и твердых растворов $Zn_xCd_{1-x}Te$ и $Cd_xHg_{1-x}Te$ бромвыделяющими травителями на основе водных растворов $K_2Cr_2O_7$–HBr–$C_4H_6O_6$ и $K_2Cr_2O_7$–HBr–этиленгликоль. Установлены зависимости скоростей ХМП от разведения базовых полирующих травителей винной кислотой, этиленгликолем и глицерином. Определено влияние природы вязкого органического растворителя на скорость полировки и качество полированной поверхности монокристаллов. Исследовано состояние поверхности после ХМП методами металлографического анализа и атомно-силовой микроскопии. Оптимизированы составы полирующих травителей и режимы проведения процесса ХМП для формирования высококачественной поверхности монокристаллов CdTe, $Zn_xCd_{1-x}Te$ и $Cd_xHg_{1-x}Te$.

Хіміко-механічне полірування монокристалів CdTe, $Zn_xCd_{1-x}Te$ та $Cd_xHg_{1-x}Te$ травниками $K_2Cr_2O_7$–HBr–розчинник. *М.В.Чайка, З.Ф.Томашик, В.М.Томашик, Г.П.Маланич, А.А.Корчовий.*

Вперше експериментально досліджено процес хіміко-механічного полірування (ХМП) поверхні монокристалів CdTe і твердих розчинів $Zn_xCd_{1-x}Te$ та $Cd_xHg_{1-x}Te$ бромвиділяючими травниками на основі водних розчинів $K_2Cr_2O_7$–HBr–$C_4H_6O_6$ та $K_2Cr_2O_7$–HBr–етиленгліколь. Встановлено залежності швидкостей ХМП від розведення базових поліруючих травників тартратною кислотою, етиленгліколем та гліцерином. Визначено вплив природи віязкого органічного розчинника на швидкість полірування і якість полірованої поверхні монокристалів. Досліджено стан поверхні після ХМП методами металографічного аналізу та атомно-силової мікроскопії. Оптимізовано склади поліруючих травників і режими проведення процесу ХМП для формування високоякісної поверхні монокристалів CdTe, $Zn_xCd_{1-x}Te$ і $Cd_xHg_{1-x}Te$.

1. Introduction

Such methods of chemical dissolution of single crystals that provide the rate and reliability of obtaining results in conjunction with the relative simplicity and availability of the implementation of operations of surface chemical etching should be used in the manufacture of modern electronics devices to prepare a quality surface of II–VI semiconductor materials [1–3]. These problems are successfully solved by chemical etching of semiconductor wafers, in particular chemical-mechanical polishing (CMP). This method allows obtaining a higher quality surface compared to polishing abrasive [4, 5]. Polished surface of semiconductors is characterized by an ideal structure, high purity and homogeneous physical properties, which obviously is associated with the perfection of the chemical dissolution of the surface using this method. The process of CMP is performing on a polishing member which is made of soft natural or artificial fabrics and the etching solution is dropped onto it at a controlled rate. In this case, the chemical dissolution of the surface layers of the semiconductors is due to the initial reagents of the etching solution, and polishing member mechanically removes the products of their interaction and the residuals of the semiconductor material [6].

It was found in [7] that the CMP of CdTe single crystals and of $Cd_{1-x}Mn_xTe$, $Cd_{1-x}Zn_xTe$ solid solutions surfaces with alkaline solution of colloidal silica gives an oxide layer of minor thickness and a minimal contaminated surface with a composition close to the stoichiometric. In addition, the violation of the plane-parallel surface of the wafers was not found, but if the CMP was performed for more than 25 min, there was an increase in defects and surface oxidation. The authors [8] used bromine-containing etchant Br_2–HBr–ethylene glycol (EG) for the CMP of the surface of $Cd_{1-x}Zn_xTe$ solid solutions, and in [9], chemical etching of this material was carried out with a solution with a volumetric fraction of 0.5 % Br_2 in CH_3OH. The dependence of the rate of $Cd_xHg_{1-x}Te$ chemical dissolution on the concentration of bromine-methanol etchant is published in [10]. Authors have established that the research of the depth inequalities dependence on the composition of the etchant provides an opportunity to find optimal conditions for surface treatment. It has been found that at the first stage of $Cd_xHg_{1-x}Te$ treatment are best carried out in a solution with a high concentration of the active component (about 2.5 vol. % Br_2 in CH_3OH), and the final stage is is necessary to accomplish using low concentration of the active component (0.5 vol. % Br_2 in CH_3OH). Sometimes, instead of methanol, EG or glycerin (GL) is used, which increases the viscosity of solutions for CMP and gives the chance to obtain a smooth and mirror surface with a minimum thickness of the broken layer which does not exceed 1 μm and the surface of the samples becomes crystallographically perfect. The use of solutions with a Br_2 content in CH_3OH less than 0.1–0.2 vol.% leads to the formation of a Te thin layer with the thickness from 10 to 40 Å [10].

However, these bromine-containing etching solutions are aggressive, have high rates of chemical dissolution of the material, and their components are highly toxic. Therefore, there are difficulties in their preparation, control of their composition, and also for this it is necessary to apply special equipment. More practical and promising are bromine-emerging etchants [11–13] in which Br_2 is released when the initial components — HBr and the oxidizing agent (HNO_3, H_2O_2, $K_2Cr_2O_7$ etc.) are interacting. Bromine dissolves in excess of HBr and forms etching compositions that are similar to the composition and properties of Br_2 in HBr solutions.

Analyzing the literature concerning the chemical-mechanical treatment of the surface of II–VI semiconductor compounds [1–13], systematic researches on the use of bromine-emerging etchants based on $K_2Cr_2O_7$ and HBr for CMP of CdTe single crystals and their solid solutions were not found. However, our previous researches have shown the perspective to use of such etchants for CMP of mentioned above semiconductors.

The purpose of this work is to investigate the peculiarities of chemical-mechanical polishing of CdTe single crystals and $Cd_{1-x}Zn_xTe$ and $Cd_xHg_{1-x}Te$ solid solutions with bromine-emerging aqueous solutions based on $K_2Cr_2O_7$–HBr–solvent, revealing the influence of the nature of viscous components for the dilution of the base etchants on the rate and quality of CMP, to investigate the polished surface through atomic force microscopy and to develop and to optimize the composition of polishing etchants, and to create the technique and modes of the CMP of semiconductors.

2. Experimental

Undoped single crystals were used for experiments: CdTe, $Zn_{0.1}Cd_{0.9}Te$ and $Cd_{0.2}Hg_{0.8}Te$ grown by the Bridgman method and $Zn_{0.04}Cd_{0.96}Te$ obtained from the gas phase. The samples with 0.5 cm^2 in area and 1.5 to 2 mm thickness were cut from the single-crystalline ingots by a diamond wire saw lubricated with distilled water during the cutting process. Cutting is accompanied by intense mechanical impact on the surface and causes it defectives and a degree of roughness. The disturbed layer formed during the cutting, was partially removed by mechanical grinding using abrasive powders of grades M10, M5 and M1 in the form of aqueous suspensions. The cutting-induced surface deformation layers was removed by mechanical polishing of samples with diamond paste of ASM grade 7/5, followed by ACM 3/2 and ACM 1/0 with the gradually reduced abrasive grain size. After each stage of mechanical treatment for removing from the surface of residues of abrasive powders, material particles and other contaminants, inter-operative cleaning was performed according to the developed technological scheme: washing (H_2O dist. + surfactant) $\rightarrow$ washing (H_2O dist.) $\rightarrow$ degreasing (acetone, C_2H_5OH) $\rightarrow$ drying (dry air flow).

Before the realization CMP, the disturbed surface layers of the samples that were previously smoothed and mechanically polished with thickness from 80 to 100 μm was removed by etchant based on HNO_3–HBr–$C_4H_6O_6$ (at V = 35 μm/min). Plates were washed thoroughly with a 0.25 M solution of $Na_2S_2O_3$ and large amount of distilled water after etching.

The etching mixtures were prepared before starting measurements from 40 % HBr (high purity), 10.9 % aqueous solution of $K_2Cr_2O_7$, 27 % tartaric acid ($C_4H_6O_6$), 20 % glycerol ($C_3H_5(OH)_3$) and EG ($C_2H_4(OH)_2$) (all reagents high grade), and maintained for 2 h to establish the equilibrium of the chemical reaction:

$$K_2Cr_2O_7 + 14HBr = \\ = 2CrBr_3 + 3Br_2\uparrow + 2KBr + 7H_2O. \quad (1)$$

For the CMP, a glass polisher was used, covered with batiste. The main attention was paid to the stable structure of the fabric and its mechanical and chemical durability to the components of the etchant. The polishing mixture were continuously dropped onto the polishing member by a drip method from a dropping funnel with a built-in dispenser at a rate of 2–3 ml/min at T = 293 K. At the end of the etching process, the plates were quickly removed from the etchant and immediately washed in 0.1 M $Na_2S_2O_3$ aqueous solution and distilled water to completely remove from the surface of the residues of the etching mixture. The dissolution rate was determined by the thickness reduction of single crystal before and after CMP using 1-MIGP time indicator with precision ±0.5 μm.

Microstructure of the samples surface after the CMP was investigated at white light using metallographic microscope MIM-7 with 8 Mpix digital video camcorder eTREK DCM 800. The quality of polished surfaces was assessed by atomic force microscopy (AFM) using intermittent contact mode imaging on a NanoScope IIIa Dimension 3000TM scanning probe microscope (Digital Instruments, USA).

3. Results and discussion

The chemical dissolution of the semiconductor surface often requires simultaneous reduction of the plate's thickness to the given size while flatness is retained. The application of the method of chemical-dynamic polishing (CDP) does not always allow obtaining a polished surface with an ideal plane in a macroscale, and in such cases it is better to use the method of CMP. It should be noted that the rate of removal of a layer of semiconductor material from the surface of single crystals by the CMP due to the simultaneous action of the chemical and mechanical components is several times higher than using the etchant of the same composition for the CDP.

Several polishing base solutions (B) (vol. %): B1 = $35K_2Cr_2O_7$–50HBr–15 tartaric acid and B2 = $35K_2Cr_2O_7$–50HBr–15 ethylene glycol, characterized by low rates of CDP and high polishing properties have been developed for experimental research. Immediately before the CMP by the base etchant B1, there was additionally introduced a certain amount of viscosity modifier — $C_4H_6O_6$ (tartaric acid — TA), and the base etchant B2 was gradually diluted with viscous ethylene glycol (EG) or glycerin (GL) for develop slow pol-

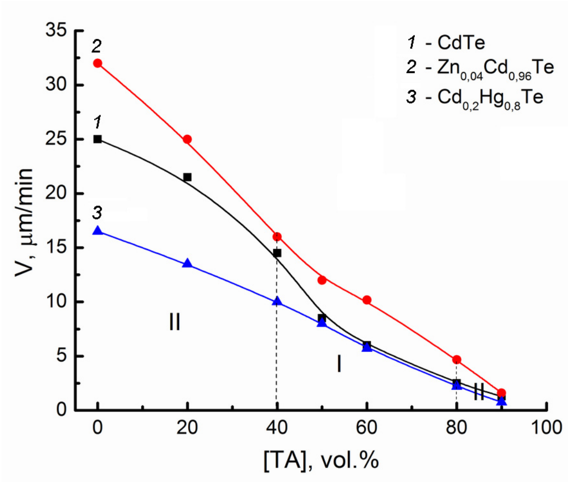

Fig. 1. Dependences of the CMP rate of CdTe (*1*), $Zn_{0.04}Cd_{0.96}Te$ (*2*) and $Cd_{0.2}Hg_{0.8}Te$ (*3*) single crystals versus the tartaric acid content in the basic etchant B1 containing (vol. %): $35K_2Cr_2O_7$–50HBr–$15C_4H_6O_6$ (area I — polishing and II — non-polishing etchants).

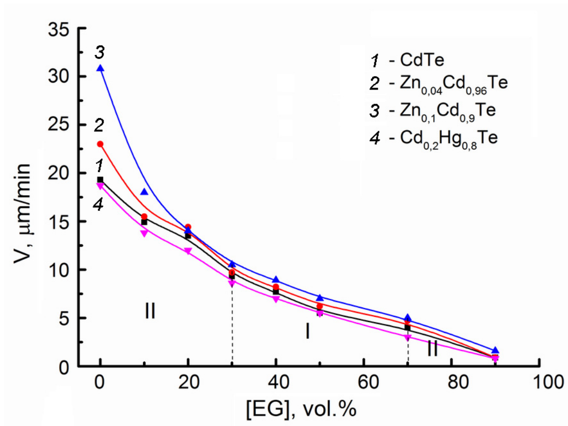

Fig. 2. Dependences of the CMP rate of CdTe (*1*), $Zn_{0.04}Cd_{0.96}Te$ (*2*), $Cd_{0.2}Hg_{0.8}Te$ (*3*) and $Zn_{0.1}Cd_{0.9}Te$ (*4*) single crystals versus the EG content in the basic etchant B2 containing (vol. %): $35K_2Cr_2O_7$–50HBr–15EG (I — polishing and II — non-polishing etchants area).

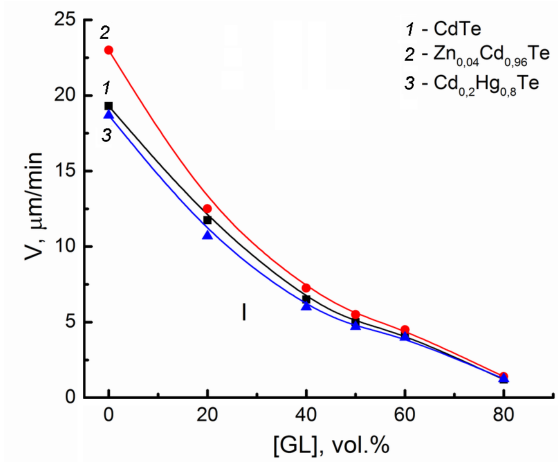

Fig. 3. Dependences of the CMP rate of CdTe (*1*), $Zn_{0.04}Cd_{0.96}Te$ (*2*) and $Cd_{0.2}Hg_{0.8}Te$ (*3*) single crystals versus the glycerol content in the basic etchant B2 containing (vol. %):

ishing mixtures and diminishing the rate of CMP (diminishing the content of the active component) and improving the quality of the etching surface of CdTe, $Zn_xCd_{1-x}Te$ and $Cd_xHg_{1-x}Te$.

We determined that the rate of the CDP in the B1 solution based on $K_2Cr_2O_7$–HBr–$C_4H_6O_6$ for the CdTe is 4.2 µm/min, for $Zn_{0.04}Cd_{0.96}Te$ — 4.7 µm/min and for $Cd_{0.2}Hg_{0.8}Te$ — 5.7 µm/min, and the rate of CMP is much higher and is 25 µm/min, 32 µm/min and 16.5 µm/min, respectively. It was found (Fig. 1) that, with increasing the amount of tartaric acid additionally introduced in B1, the rate of CMP gradually diminishes within the studied etchant solution interval from 16.6 to 0.75 µm/min for $Cd_{0.2}Hg_{0.8}Te$, from 25 to 1.3 µm/min for CdTe and from 32 to 1.6 µm/min for $Zn_{0.04}Cd_{0.96}Te$. It was established that non-polishing solutions are formed in the range of concentrations (0–40 vol. % $C_4H_6O_6$–B1), and the surface of treated single crystals becomes a matt light gray. The surface of all single crystals is polished and acquires a mirror luster, and the rate of CPM is in range of 16–2.2 µm/min with increasing tartaric acid content from 40 to 80 vol. % in the etchants. A thin white film is formed on the surface of semiconductors with increasing the viscous component content in the polishing mixture (up to 90 vol. % of $C_4H_6O_6$).

The dependences of the CMP rate versus dilution B2 with ethylene glycol and glycerol are similar. It was established (Fig. 2) that when the concentration of EG in B2 increases from 30 to 70 vol. %, the polishing solutions are formed, the surface of the etched single crystals is polished and has a mirror luster, and the rate of the CMP is within (µm/min): 8.6–3.0 for $Cd_{0.2}Hg_{0.8}Te$; 9.3–4.0 for CdTe; 9.7–4.7 for $Zn_{0.04}Cd_{0.96}Te$ and 10.5–5.0 for $Zn_{0.1}Cd_{0.9}Te$. Such etching mixtures can be used for CMP with controlled small rate of chemical dissolution. If the content of the viscosity component is increased up to 90 vol. % EG, the dissolution rate will be significantly reduced to 0.8–1.6 µm/min and a polished surface of lower quality ("metallic shine") is formed.

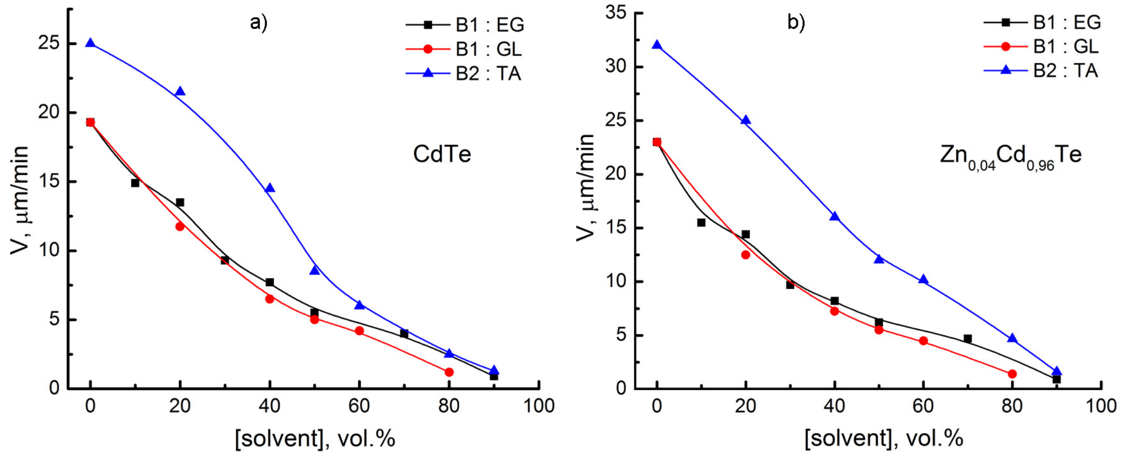

Fig. 4. Dependences of the CMP rate of CdTe (a), and $Zn_{0.04}Cd_{0.96}Te$ (b) single crystals from the dilution of the basic etchant by a viscous organic solvent (tartaric acid, ethylene glycol and glycerol).

Dilution of the B2 solution by glycerol leads to the formation of polishing solutions at all the investigated range (Fig. 3) and allows obtaining a high-quality polished surface with a mirror luster without films and sediments. As can be seen from Fig. 3, the rate of CMP decreases from 18.7 to 1.25 μm/min for $Cd_{0.2}Hg_{0.8}Te$, from 19.3 to 1.2 μm/min for CdTe, and from 2.3 to 1.4 μm/min for $Zn_{0.04}Cd_{0.96}Te$ with retaining high quality polishing if the etchant B2 is diluted by glycerol.

The regularities of the etching rate changing of single crystals and their surface after the CMP have been investigated (Fig. 4) to find out the influence of the nature of the viscosity modifier on the rate of CMP and the character of the chemical dissolution of CdTe single crystals and Zn_xCd_{1-x} solid solutions. It has been established that for all semiconductors the dependences are similar, and V_{CMP} decreases and the quality of the polished surface is improved if the base solution is diluted with such solvents: tartaric acid → ethylene glycol → glycerol.

This dependence could be associated with a decrease in the ionization constant in the solvent series and an increase in the kinematic viscosity of organic solvents. Therefore, the bromine diffusion which is released in the etching composition occurs uniformly. Increasing of the viscosity of the etching mixtures, leads to the formation of shiny surface with smoothing her with minimal contact between the polishing fabric and the treated sample. There is also a regularity of the chemical dissolution change rate of CdTe and $Zn_xCd_{1-x}Te$ single crystals from solid solutions composition: in all etchants, the rate of CMP increases and the quality of the polished surface improves with increasing content of Zn in the solid solutions.

Metallographic analysis of the CdTe and $Zn_xCd_{1-x}Te$ surfaces showed that after the CMP treatment with B2 solution, the quality of the polished surface is the best (metallographic microscope MIM-7 with 8 Mpix digital video camcorder eTREK DCM 800). Therefore, AFM studies were conducted only for samples treated with etchants at different ratios B2:organic solvent (EG, GL).

2D AFM-images for the samples of CdTe single crystals after CMP treatment using different etchants compositions are given (Fig. 5). Figure 5a illustrates AFM-image of the CdTe sample after CMP treatment with etchant compositions (vol. %): 30 B2/70 EG, taken on the edge of the polishing region (Fig. 2). Figure 5b and 5c illustrates the surface images of the CdTe after CMP polishing etchants with the same composition but with different organic components. In all cases a polished surface is formed with the roughness parameters according to the requirements for the polished surface in the production of semiconductor materials (R_a < 10 nm) [14]. It should be noted that the use of glycerin as an organic solvent in the CMP processing of the CdTe semiconductor wafers contributes to the formation of a super-smooth polished surface with R_a < 1 nm (Fig. 5c).

The results of the surface morphology investigation of the CdTe sample after the CMP in which the glycerin was used (Fig. 5c) demonstrated that the surface is densely packed with round-shaped grains of 20–30 nm in

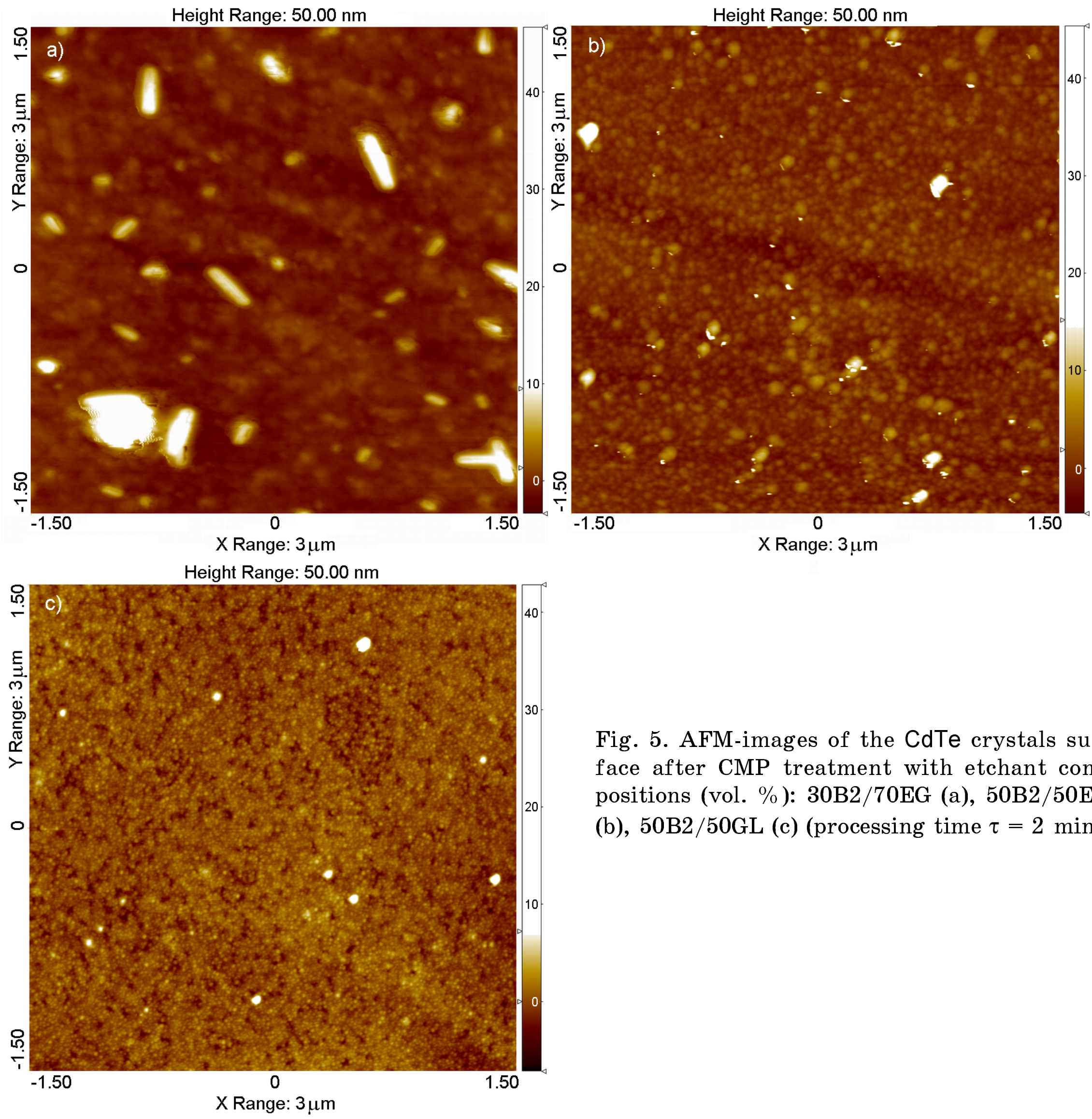

Fig. 5. AFM-images of the CdTe crystals surface after CMP treatment with etchant compositions (vol. %): 30B2/70EG (a), 50B2/50EG (b), 50B2/50GL (c) (processing time τ = 2 min).

size, also, pores with a depth of 4–10 nm and a diameter of 30–40 nm are present. The mean square roughness of a fragment of such a surface is equal to 0.59 nm (see Table).

Table gives the parameters of the surface (real surface area, mean square roughness) of the CdTe samples after CMP treatment at dilution of the basic etchant using different organic solvent (ethylene glycol and glycerin).

On the basis of the obtained experimental data, it was determined that by introducing different amounts of viscosity modifier to the composition of etching solutions it is possible to regulate the rate of the CMP of the mention above semiconductors. Thus, using the same reagents one can obtain polishing etchant compositions with the necessary spectrum of dissolution rates for

Table. Surface parameters of the CdTe single crystals after CMP treatment with polishing etchant compositions B2 (vol. %: $35K_2Cr_2O_7$–50HBr–15EG)/organic solvent

Etchant composition, vol. %	Roughness parameters for a 3×3 µm^2 surface fragment	
	Real surface area, mm^2	Mean square roughness R_a, nm
30B2/70EG	9.11128	6.13
50B2/50EG	9.12549	2.12
50B2/50GL	9.02388	0.59

various technological purposes. Etching solutions with rate of CMP greater than 20 µm/min can be used to quickly removing damaged layers as a result of mechanical grinding and rapidly reducing the thickness of the plate. Etchants with etch rates from

10 μm/min to 20 μm/min can be used for controllable thinning of the plates to the given thickness while flatness is retained and with rates of CMP less than 10 μm/min can be used to removing thin layers of material, chemical processing of films, and finishing polishing. Therefore, this method allows reducing the duration of semiconductors chemical treatment and simplifying the washing stages of polished plates, since in all cases the etchant compositions are composed of the same components taken in various ratios.

4. Conclusions

The chemical-mechanical polishing of the surface of CdTe single crystals and solid solutions of $Zn_xCd_{1-x}Te$, $Cd_xHg_{1-x}Te$ by the etchants based on aqueous solutions of $K_2Cr_2O_7$–HBr–$C_4H_6O_6$ and $K_2Cr_2O_7$–HBr–ethylene glycol has been investigated. It was established that by introducing into the composition of basic solutions of different amounts of viscosity modifiers, it is possible to regulate the rate of CMP of the semiconductors and to receive etching solutions with a wide spectrum of etching rates (0.8–32.0 μm/min). New slow bromine-emerging etchants have been developed, which have high polishing properties and low rates of chemical dissolution. The structural perfection and quality of the polished surface have been investigated by atomic force microscopy. Optimized compositions of polishing etchants and technological modes for treatment of the surface can be used for controlled removal of layers, chemical treatment of films and finishing polishing of the surface of CdTe, $Zn_xCd_{1-x}Te$ and $Cd_xHg_{1-x}Te$.

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