

Peculiarities of nanosized relief formation on the $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ single crystals surface using $\text{K}_2\text{Cr}_2\text{O}_7$ -HBr-solvent etchants

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

¹Zhytomyr Franko State University, 40 Velyka Berdychivska Str.,
10008 Zhytomyr, Ukraine

²V.Lashkaryov Institute of Semiconductor Physics, National Academy of
Sciences of Ukraine, 41 Nauky Ave., 03028 Kyiv, Ukraine

Received January 10, 2022

The regularities of chemical-dynamic and chemical-mechanical polishing of the $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ ($x = 0.2$) single crystals surface by bromine-emerging etchants of $\text{K}_2\text{Cr}_2\text{O}_7$ -HBr-solvent have been experimentally established. The dependences "solution concentration — dissolution rate" have been constructed and the concentration limits of polishing solutions have been determined. The effect of the nature of the organic solvent on the rate of dissolution and the quality of the polished surface has been also determined. It was shown that the dissolution process is limited by diffusion stages. It was found that dilution of the base polishing solution by tartaric acid and ethylene glycol leads to the formation of slow polishing etchants with small ($1.5\text{--}18.5 \mu\text{m}\cdot\text{min}^{-1}$) etching rates. The condition and composition of the semiconductor surface after the polishing process have been investigated using metallography, atomic force and scanning electron microscopy. The compositions of polishing etchants and conditions for formation of nanosized relief on the surface of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ single crystals have been optimized.

Keywords: chemical polishing, single crystal, semiconductor, solid solution, surface, etchant.

Особливості формування нанорозмірного рельєфу на поверхні $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ травниками $\text{K}_2\text{Cr}_2\text{O}_7$ -HBr-розчинник. *М.В.Чайка, З.Ф.Томашик, В.М.Томашик, Г.П.Маланич, А.А.Корчовий*

Експериментально встановлено закономірності хіміко-динамічного та хіміко-механічного полірування поверхні монокристалів $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ ($x = 0,2$) бромвиділяючими травниками $\text{K}_2\text{Cr}_2\text{O}_7$ -HBr-розчинник. Побудовано залежності склад розчину і швидкість розчинення та визначено концентраційні межі полірувальних розчинів, виявлено вплив природи органічного компонента на швидкість розчинення, стан полірованої поверхні. Показано, що процес розчинення лімітується дифузійними стадіями. Встановлено, що розведення базового поліруючого розчину тартратною кислотою та етиленгліколем призводить до формування повільних полірувальних травників з невеликими ($1,5\text{--}18,5 \mu\text{м}/\text{хв}$) швидкостями травлення. Методами мікроструктурного аналізу, атомно-силової та скануючої електронної мікроскопії досліджено стан та склад поверхні напівпровідників після процесу полірування. Оптимізовано склади травильних розчинів і режими формування нанорозмірного рельєфу на поверхні монокристалів $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$.

Introduction

$\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ solid solutions are used as the main material in infrared electronics due to their unique physicochemical properties [1]. Nanoscale structures based on these materials are widely used in the creation of infrared photodetectors (Schottky barriers), structures such as *metal — insulator — semiconductor*, photodiodes, injection lasers [2, 3]. Proper selection of etching compositions for both intermediate stages of chemical surface treatment and for final polishing is an important condition for the formation of high-quality, structurally perfect surfaces of semiconductor substrates for the production of working elements of such devices.

Bromine-based mixtures, in particular solutions of Br_2 in CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, DMFA or HBr, are often used to obtain a polished surface of II–VI semiconductors [4]. The main disadvantages of these etchants are instability, high material removal rate, and toxicity of their components. This is the reason to search new, less toxic and more technological etching compositions with low dissolution rates of single crystals under consideration.

Analysis of the literature shows that researchers have developed etching solutions of $\text{K}_2\text{Cr}_2\text{O}_7$ — mineral acid with the addition of various solvents for treatment of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ single crystals surface. Etching compositions based on $\text{K}_2\text{Cr}_2\text{O}_7$ and nitric acid are used for polishing the surface of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$. To remove CdTe layers from the surface of the single crystals under study, an etchant containing 4 g of $\text{K}_2\text{Cr}_2\text{O}_7$ + 10 ml of HNO_3 + 20 ml of H_2O is recommended [5]. The structure and density of etching pits of dissolution of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ crystals [6] and epitaxial films [7, 8] were determined in mixtures of 80 ml H_2O + 10 ml HCl + 20 ml HNO_3 + 8 g $\text{K}_2\text{Cr}_2\text{O}_7$. The results of studies of defect liquation inhomogeneities on the surface of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ solid solutions ($x = 0.210$ – 0.223) were published in [9]. It was found that after chemical polishing with an etchant 12 ml HF + 2 g $\text{K}_2\text{Cr}_2\text{O}_7$ + 15 ml HNO_3 for 40–60 s at $T = 333$ – 338 K, areas with different cadmium content were colored differently. The process of selective etching of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ single crystals using $\text{K}_2\text{Cr}_2\text{O}_7$ – HNO_3 solutions is especially important in the express control of defects in the structure of semiconductors during the production of electronic devices based on them.

The surface of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ (100) with $x = 0.226$ after chemical etching have been studied by X-ray photoelectron spectroscopy in [10]. The surface of the crystals was treated in several stages: first, it was successively degreased in an ultrasonic bath with trichloroethane, acetone and methanol, and then dried in a warm nitrogen flow. To form a polished surface of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$, the etching process was performed with the following solution: 4 g of $\text{K}_2\text{Cr}_2\text{O}_7$ + 10 ml of H_2SO_4 + 20 ml of H_2O for 10 s, then the formed TeO_2 was removed with the solution ($\text{Na}_2\text{S}_2\text{O}_3:\text{NaOH}:\text{H}_2\text{O}$) ~ 1:1:1 at 85°C for 10 s. It was found that Cr passivates the polished surface of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ (110) and prevents the loss of Hg; the depth of the dissolved cadmium layer was 21 ?.

Etchants based on $\text{K}_2\text{Cr}_2\text{O}_7$ are widely applied for many technological purposes, but most of them have some disadvantages. The formation of a tellurium film on the polished surface due to the chemical interaction of CdTe with an etchant a disadvantage of mixtures diluted with H_2SO_4 [10]. It was found that solutions based on HNO_3 are characterized by high polishing rates (up to $50 \mu\text{m}\cdot\text{min}^{-1}$) and selectivity of their action [6]. Bromine-emerging solutions, in which bromine is released as a result of the interaction of the initial components of the etchant, are more practical for chemical treatment of semiconductors. Mixtures based on the $\text{K}_2\text{Cr}_2\text{O}_7$ –HBr system are especially promising. Earlier we found [11] that aqueous solutions $\text{K}_2\text{Cr}_2\text{O}_7$ –HBr, which contain 20–50 vol. % $\text{K}_2\text{Cr}_2\text{O}_7$ can be used for chemical polishing the surfaces of CdTe single crystals and $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ and $\text{Cd}_{1-x}\text{Hg}_x\text{Te}$ solid solutions. They have low dissolution rates of the semiconductor material (1 – $7 \mu\text{m}\cdot\text{min}^{-1}$). This facilitates the controlled dissolution of thin layers of material and the surface final treatment of semiconductors.

The purpose of this work is a systematic experimental study of the regularities of chemical-mechanical and chemical-dynamic polishing of $\text{Cd}_{1-x}\text{Hg}_x\text{Te}$ solid solutions by bromine-emerging etchants based on aqueous solutions of $\text{K}_2\text{Cr}_2\text{O}_7$ –HBr-solvent; identification of the influence of the nature of organic solvents when diluting etchants on the rate and quality of the polishing process; study of a polished surface by metallography, atomic force and scanning electron microscopy; development and optimization of the composition of polishing

etchants; creation of the procedure and modes for the formation of a nanoscale relief on the surface of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ single crystals.

2. Experimental

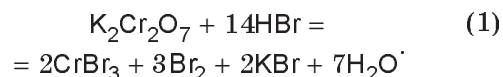
For experimental studies, undoped $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ single crystals grown by the Bridgman method were used. Semiconductor substrates with an area of 0.5 cm^2 and a thickness of 1.5 to 2 mm were cut from the single-crystalline ingots with a diamond wire saw. A deformed layer is formed on the surface of II–VI semiconductors due to intense mechanical impact during cutting [12]. The damaged layer with a thickness of 80 to 100 μm was partially removed by mechanical grinding using abrasive powders of grades M10, M5 and M1 in the form of aqueous suspensions. To remove the surface structurally defective layers formed during cutting and grinding, the samples under study were mechanically polished with ACM grade 7/5, then ACM 3/2 and ACM 1/0 diamond powders with a gradually decreasing abrasive grain size. This made it possible to significantly minimize surface deformation. The process was carried out on a polishing machine, which was constantly cleaned of waste, powder residues and suspensions.

An important stage of surface treatment of semiconductor plates during the production of working elements of the devices is the inter-operative cleaning. The process is aimed to remove contaminants from the surface after each stage of mechanical treatment: cutting, grinding and mechanical polishing. Residues of abrasive powders, particles of material and other contaminants were removed according to the developed technological scheme [13]: washing ($\text{H}_2\text{O dist.} + \text{surfactant}$) \rightarrow washing ($\text{H}_2\text{O dist.}$) \rightarrow degreasing (*acetone*, $\text{C}_2\text{H}_5\text{OH}$) \rightarrow drying (*dry air flow*).

Before finishing polishing, the damaged layer with a thickness of 80 to 100 μm , formed during cutting and grinding, was removed from the $\text{Cd}_{1-x}\text{Hg}_x\text{Te}$ surface with an etchant based on $\text{HNO}_3\text{--HBr--C}_4\text{H}_6\text{O}_6$ ($V_{pol} = 35 \mu\text{m}\cdot\text{min}^{-1}$); and chemical-mechanical polishing (CMP) with a developed universal etchant based on $\text{K}_2\text{Cr}_2\text{O}_7\text{--HBr--ethylene glycol}$ ($V_{pol} = 7 \mu\text{m}\cdot\text{min}^{-1}$) was carried out. The process of CMP allows obtaining a better surface compared to mechanical polishing with an abrasive [12, 14]. The surface polished by the CMP method is

characterized by an ideal structure, a high degree of purity and homogeneous properties. The process of chemical dissolution of surface layers of semiconductors is due to active components of the etching solution, while the polisher mechanically removes the products of their interaction and the remains of the semiconductor material. For the CMP process, a glass polishing machine covered with batiste was used. The etching solution was continuously dripped onto the polisher by a drip method from a dropping funnel with a built-in dispenser at a rate of 2–3 $\text{ml}\cdot\text{min}^{-1}$ at 293 K.

Etching mixtures were prepared before starting measurements according to the method proposed in [15] using 40 % HBr (high purity), 10.9 % aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$, 27 % tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$), glycerol (GL) and ethylene glycol (EG) (all reagents were high purity). Before the etching, all the solutions were kept for two hours to establish the equilibrium of the chemical reaction:



The patterns of dissolution of $\text{Cd}_{1-x}\text{Hg}_x\text{Te}$ solid solutions in etching compositions based on $\text{K}_2\text{Cr}_2\text{O}_7\text{--HBr}$ solutions were investigated under reproducible hydrodynamic conditions using a rotating disc and a device for chemical-dynamic polishing (CDP) at $T = 285\text{--}301 \text{ K}$ and the disc rotation speed $\gamma = 82 \text{ min}^{-1}$ [4].

The dissolution rate was determined from the decrease in the thickness of the plates before and after polishing using a 1-MIGP time indicator with an accuracy of $\pm 0.5 \mu\text{m}$. Four samples fixed in a fluoroplastic holder were simultaneously polished. In this case, all single crystals were in the same plane and dissolved uniformly, which made it possible to avoid the turbulent flow of the etchant. The CDP process was carried out for 3–5 min, and the error in determining the dissolution rate was 0.1–0.3 $\mu\text{m}\cdot\text{min}^{-1}$.

The surface microstructure of the plate after polishing was studied in white light using a metallographic microscope MIM-7 with a digital video camcorder eTREK DCM800 (8 Mpix, magnification from 25 \times to 1600 \times). The surface micro-profiles and the main roughness parameters of $\text{Cd}_{1-x}\text{Hg}_x\text{Te}$ single crystals were studied using a HOMMEL-ETAMIC W5 profilometer by the mechanical contact method at a base length of 0.25 mm (tracing length of

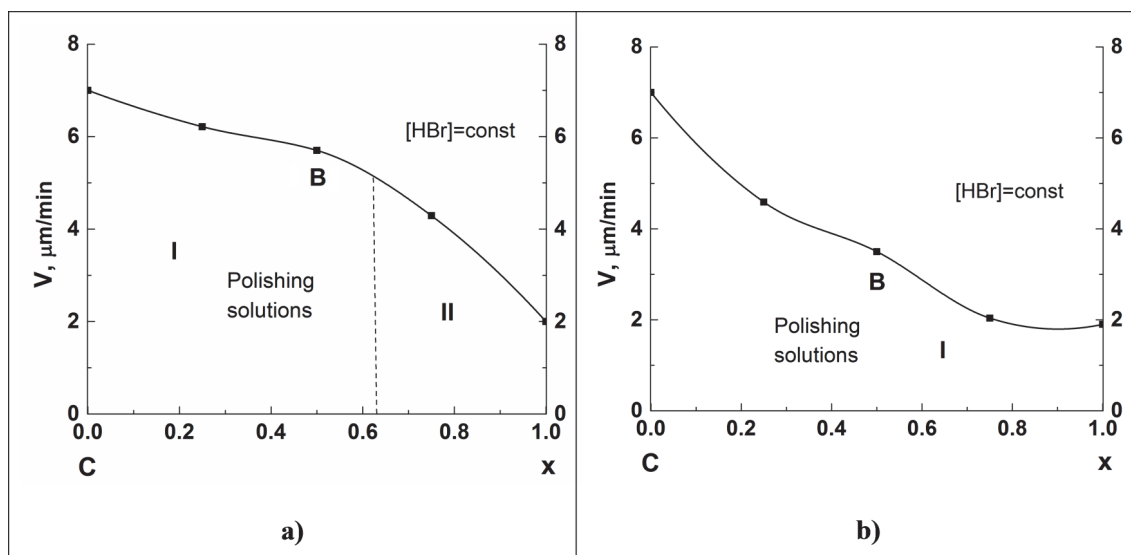


Fig. 1. Dependences of the chemical dissolution rate ($\mu\text{m}\cdot\text{min}^{-1}$) ($T = 294\text{ K}$, $\gamma = 82\text{ min}^{-1}$) of $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ single crystals on the composition of etchants at a volume ratio of components (a) $\text{K}_2\text{Cr}_2\text{O}_7\text{-HBr-C}_4\text{H}_6\text{O}_6$ and (b) $\text{K}_2\text{Cr}_2\text{O}_7\text{-HBr-EG}$ in C and x , respectively: — 50:50:0; x — 20:50:30 (I — polishing and II — unpolishing etchants).

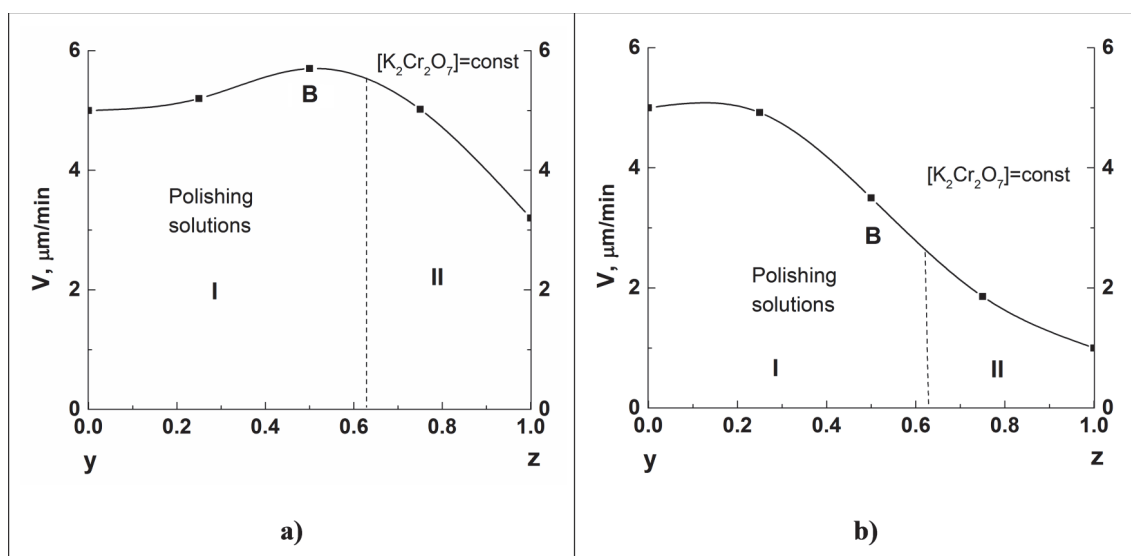


Fig. 2. Dependence of the chemical dissolution rate ($\mu\text{m}\cdot\text{min}^{-1}$) ($T = 294\text{ K}$, $\gamma = 82\text{ min}^{-1}$) of $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ single crystals on the composition of etchants at a volume ratio of components (a) $\text{K}_2\text{Cr}_2\text{O}_7\text{-HBr-C}_4\text{H}_6\text{O}_6$ and (b) $\text{K}_2\text{Cr}_2\text{O}_7\text{-HBr-EG}$ in y , z respectively: y — 35:65:0; z — 35:35:30 (I — polishing and II — unpolishing etchants).

1.5 mm and tracing rate of $0.15\ \mu\text{m}\cdot\text{min}^{-1}$), which allows determination of the microroughness height $\geq 5\text{ nm}$ (DIN 4772, class 1, accuracy 3 %). The quality of polished surfaces was assessed by atomic force microscopy (AFM) using the intermittent contact mode imaging on a NanoScope IIIa Dimension 3000TM scanning probe microscope (Digital Instruments, USA). The measurements were carried out in the central zone of the samples using NanoWorld silicon probes with a

nominal probe tip radius to 10 nm, at a resonant frequency of 320 kHz and a console roughness of 42 nm. The elemental composition of the surfaces of the $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ single crystals was determined using a scanning electron microscope with a 2 nm resolution on a Zeiss EVO 50XVP equipped with an INCAPentaFETx3 energy dispersive X-ray spectrometer system for elemental analysis with an accuracy of $\sim 0.1\%$. Images of the surfaces were obtained at ac-

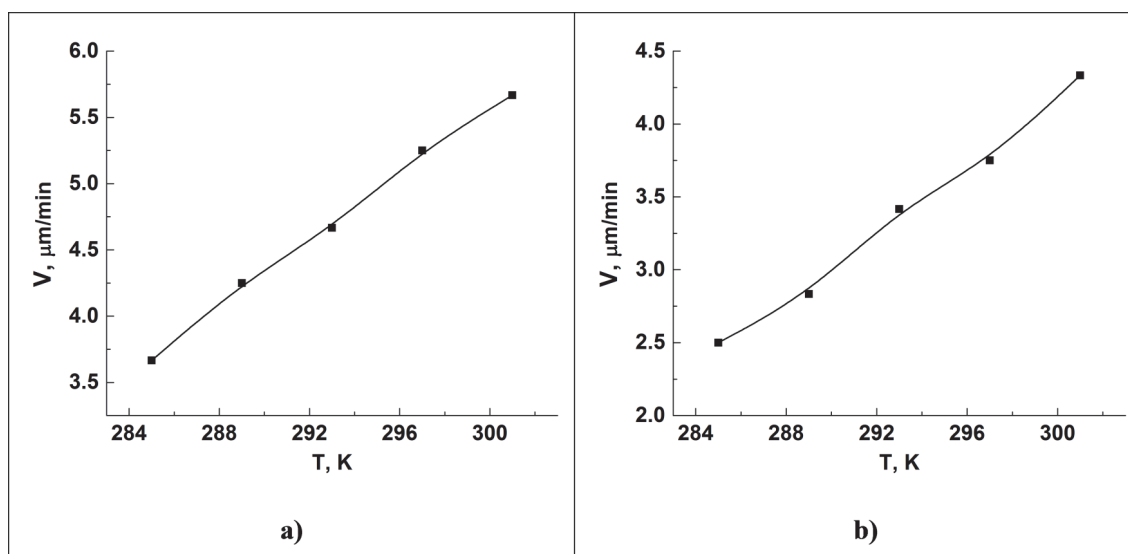


Fig. 3. Dependence of the CDP rate ($\mu\text{m}\cdot\text{min}^{-1}$) of the $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ single crystals versus temperature ($\gamma = 82 \text{ min}^{-1}$) in solution containing (in vol. %) (a) 35 $\text{K}_2\text{Cr}_2\text{O}_7$ + 50HBr + 15 $\text{C}_4\text{H}_6\text{O}_6$ and (b) 35 $\text{K}_2\text{Cr}_2\text{O}_7$ + 50 HBr + 15 EG.

celerating voltages $V = 20 \text{ kV}$, a probe current $I = 40 \text{ pA}$, and magnifications from $5\times$ to $1000000\times$.

3. Results and discussion

Chemical dissolution of semiconductors is accompanied by redox reactions on the surface of single crystals and layers of material removed from it. Etching solutions must have not only good polishing properties, but also the ability of the reagents of these solutions to break the chemical bond in semiconductors and form soluble compounds of the reaction products. It was previously established [11] that the range from 20 to 50 vol. % of $\text{K}_2\text{Cr}_2\text{O}_7$ in HBr is optimal for the adding the third component (27 % solution of tartaric acid, ethylene glycol and glycerol) and excluding from the study the compositions of the $\text{K}_2\text{Cr}_2\text{O}_7$ -HBr solutions that passivate the surface. The introduction of organic acids significantly improves the polishing properties of etchants due to the inhibition of hydrolysis of the reaction products. Addition of a EG or GL solution with high viscosity (5.026 and 22.164 cP, respectively [16]) into bromine-emerging solutions based on $\text{K}_2\text{Cr}_2\text{O}_7$ -HBr allows partial controlling the release of bromine, which is supplied to the surface of the semiconductors under study during CDP. In addition, the dissolution rate of the single crystals can be partly regulated in this way. Figs. 1 and 2 show the concentration dependences of the CDP rate of $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ single crystals in $\text{K}_2\text{Cr}_2\text{O}_7$ -HBr

etching solutions, which were additionally diluted with tartaric acid or ethylene glycol. It was found (Fig. 1) that the rate of additionally diluted with tartaric acid or ethylene glycol. It was found (Fig. 1) that the rate of CDP decreases in the studied range from 7 to $2 \mu\text{m}\cdot\text{min}^{-1}$ when organic solvent was added to etchants with a constant content of HBr. It was shown that solutions with the maximum $\text{K}_2\text{Cr}_2\text{O}_7$ oxidant content have the highest polishing rate. Thin white film is formed on the semiconductor surface during dissolution in etchants with a $\text{C}_4\text{H}_6\text{O}_6$ content of more than 20 vol. % (Fig. 1a). It can be removed with filter paper after the samples have dried, but the surface of the single crystals remains matte with a dull sheen (unpolishing etchants).

Fig. 2 shows the dependence of the chemical dissolution rate of $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ in the solutions with a constant content of oxidant ($\text{K}_2\text{Cr}_2\text{O}_7$) and different contents of HBr and solvent (EG or $\text{C}_4\text{H}_6\text{O}_6$). It was found that the introduction of tartaric acid to the etching composition led to a decrease in the polishing rate from 5 to $3.2 \mu\text{m}\cdot\text{min}^{-1}$ (Fig. 2a), and addition of EG — up to $1 \mu\text{m}\cdot\text{min}^{-1}$ (Fig. 2b). The reason may be not only the good chelating ability of EG and tartaric acid, but also the increasing viscosity of etching compositions. The increase in the viscosity of the solutions partially inhibits the interaction of reagents, which leads to a decrease in the rate of chemical dissolution and deterioration of the polished surface quality of semiconduc-

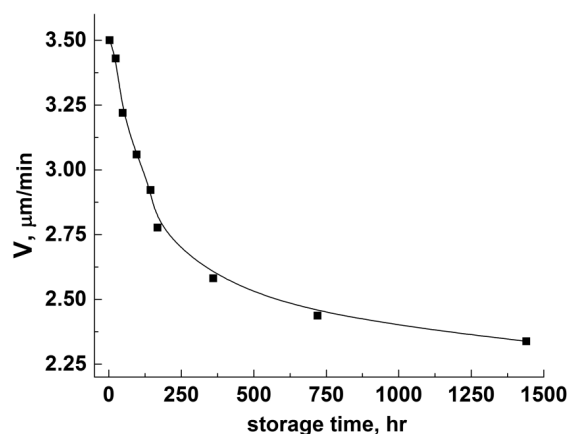


Fig. 4. Dependence of the CMP rate ($\mu\text{m}\cdot\text{min}^{-1}$) of the $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ versus storage time of solution containing (in vol. %) 35 $\text{K}_2\text{Cr}_2\text{O}_7$ + 50 HBr + 15 EG.

tors. In addition, the content of the active component of bromine-containing solutions, HBr, decreases with an increase in the content of the organic solvent in etchants.

It was established that the areas of polishing etchants occupy most of the investigated interval. The CMP treatment of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ solid solutions in such mixtures is carried out at the same rate; the etchant evenly dissolves the thin damaged layers and allows obtaining a high-quality polished surface with a mirror finish.

The dependences of the CMP rate of $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ single crystals on the temperature of the solutions in the temperature range of 285–301 K (at $\gamma = 82 \text{ min}^{-1}$) were studied for the polishing etchants with compositions (in vol. %): 35 $\text{K}_2\text{Cr}_2\text{O}_7$ + 50 HBr + 15 $\text{C}_4\text{H}_6\text{O}_6$ (Fig. 3a) and 35 $\text{K}_2\text{Cr}_2\text{O}_7$ + 50 HBr + 15 EG (Fig. 3b). The optimum temperature for formation of an ultra-smooth polished surface is 294 K. The apparent activation energy (E_a) of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ chemical dissolution was calculated from the temperature dependences of the etching rate. The calculated value of E_a of the process of dissolution semiconductors in solutions diluted with tartaric acid is 19.3 $\text{kJ}\cdot\text{mol}^{-1}$, and in the case of EG – 24.6 $\text{kJ}\cdot\text{mol}^{-1}$, that is, they do not exceed 30 $\text{kJ}\cdot\text{mol}^{-1}$, this indicates on the limiting of the dissolution by diffusion stages [17].

The study of the effect of storage of solutions is an important condition for the choice of polishing etching compositions for CMP of semiconductor surfaces. For this

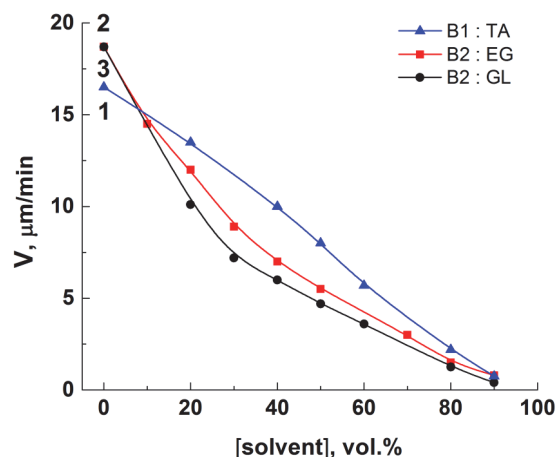


Fig. 5. Dependences of CMP rate of $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ single crystals on the degree of dilution of the base solution **B1** ($\text{K}_2\text{Cr}_2\text{O}_7$ –HBr– $\text{C}_4\text{H}_6\text{O}_6$) with a (1) tartaric acid and base solution **B2** ($\text{K}_2\text{Cr}_2\text{O}_7$ –HBr–EG) by (2) ethylene glycol and (3) glycerin.

purpose, we studied the effect of storage time of polishing etchant composition (vol. %): 35 $\text{K}_2\text{Cr}_2\text{O}_7$ + 50 HBr + 15 EG on the dissolution rate and polishing ability of $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$. It was found (Fig. 4) that the CMP rate proportionally decreased by 0.1–0.2 $\mu\text{m}\cdot\text{day}^{-1}$; and after 7 days it was reduced from 3.5 $\mu\text{m}\cdot\text{min}^{-1}$ to 2.8 $\mu\text{m}\cdot\text{min}^{-1}$. This is probably due to the gradual removal of bromine from the etchant. The polishing rate almost did not decrease for a long time (up to 62 days), because the concentration of bromine did not change. The polishing properties of the solution were retained throughout the entire study period; no films and sediments were formed on the surface of the samples. This indicates the prospect of using the polishing solution for a long time after formation (up to 1440 hours).

In the chemical dissolution of semiconductor surfaces, it is often necessary to simultaneously reduce the thickness of the wafer to a given size while maintaining flatness. In such cases it is better to use the method of CMP. The polishing solutions were selected from the two systems $\text{K}_2\text{Cr}_2\text{O}_7$ –HBr–tartaric acid and $\text{K}_2\text{Cr}_2\text{O}_7$ –HBr–EG to study the effect of the nature of the organic component on the rate of CMP and the quality of the polished surface of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ single crystals. These are the base solutions (**B**): **B1** refers to the $\text{K}_2\text{Cr}_2\text{O}_7$ –HBr– $\text{C}_4\text{H}_6\text{O}_6$ system (Fig. 1a, point B1) and **B2** — to $\text{K}_2\text{Cr}_2\text{O}_7$ –HBr–EG (Fig. 1b, point B2), which are characterized by low

Table 1. Roughness parameters of the $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ surface after different stages of treatment. Processing steps

| Processing steps | R_a , nm |
|--|-------------------|
| Cutting string | 4580 ^a |
| Cutting string + grinding by abrasive ASM 10/7 | 3103 ^a |
| Cutting string + grinding by abrasive ASM 10/7 + ASM 5/3 | 1353 ^a |
| Cutting string + grinding by abrasive ASM10/7 + ASM5/3 + ACM1/0 | 430 ^a |
| Cutting string + grinding by abrasive + CDP with etchant compositions $\text{K}_2\text{Cr}_2\text{O}_7$ + HBr + EG | 2.5 ^b |
| Cutting using string + grinding by abrasive + CMP with etchant compositions (vol. %) 50 B2 + 50 GL | 1.9 ^b |

^a — profilometer HOMMEL-ETAMIC W5, ^b — method of AFM

CDP rates (5.7 and $3.5 \mu\text{m}\cdot\text{min}^{-1}$, respectively) and high polishing properties. Before the CMP process, a certain amount of viscosity modifier was added to the **B** to determine the effect of diluting **B** with a viscous component on the state of the polished surface. A certain amount of tartaric acid (TA) was additionally introduced into the etchant **B1**, and ethylene glycol and glycerin were gradually added to the **B2** to reduce the dissolution rate of the semiconductor material and improve the quality of the polished surface.

It was determined that the rate of CDP of the $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ single crystal surface in the **B1** solution is $5.7 \mu\text{m}\cdot\text{min}^{-1}$ (Fig. 1a), and the rate of CMP in this solution is much higher $V_{pol} = 16.5 \mu\text{m}\cdot\text{min}^{-1}$. It has been established (Fig. 5, curve 1) that the dissolution rate gradually decreases to $0.75 \mu\text{m}\cdot\text{min}^{-1}$ with an increase in the content of tartaric acid in the etchant. The surface of single crystals becomes a matt light gray after CMP in solutions containing $\text{C}_4\text{H}_6\text{O}_6$ from 0 to 40 vol. % in **B1**. Polishing solutions are formed in the range of 40–80 vol % $\text{C}_4\text{H}_6\text{O}_6$ in **B1**. The surface of polished single crystals in these solutions is characterized by a mirror luster without films and sediments, and the rate of CMP is in the range of $10\text{--}2 \mu\text{m}\cdot\text{min}^{-1}$.

The polishing effect of the etchant improves with an increase in the viscosity of the solution, which is probably due to a decrease in the rate of CMP as a result of slowing down the removal of dissolution products and delivery of fresh portions of active components of etching compositions into the interface "single crystal — etching solution". It was found (Fig. 5, curve 2) that the use of EG as a viscosity modifier reduces the rate of CMP of the $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$

surface to $0.8 \mu\text{m}\cdot\text{min}^{-1}$ when the EG content in the etchants increases. The ultra-smooth surface with a mirror luster is formed in the range of concentrations 30–70 vol % EG in **B2**, and the rate of CMP decreases from 8.5 to $1.5 \mu\text{m}\cdot\text{min}^{-1}$. Dilution of the **B2** etchant by glycerol leads to the formation of polishing solutions in the entire area under study (Fig. 3) and makes it possible to obtain a high-quality polished surface of the studied single crystals. If the content of the organic component ($\text{C}_4\text{H}_6\text{O}_6$, GL or EG) increases more than 80 vol. % in **B**, a thin white film is formed on the polished surface of the semiconductors.

The surface quality of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ solid solutions after CDP and CMP in $\text{K}_2\text{Cr}_2\text{O}_7\text{--HBr}$ -solvent etchants and the change in the parameters of the surface roughness of $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ after different stages of mechanical and chemical treatment has been studied using the methods of metallography and profilometry, atomic force and scanning electron microscopy (Table 1).

Table 1 shows that each subsequent stages of mechanical treatment reduces the surface roughness $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ from 4580 nm after cutting to 430 nm after grinding with an abrasive. The structure of the sample surface after CDP in the $\text{K}_2\text{Cr}_2\text{O}_7\text{--HBr}\text{--EG}$ polishing solution was studied by AFM. It was found that the arithmetic mean surface roughness of the $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ substrate after chemical treatment is $R_a = 2.5$ nm (the analysis area is $3 \times 3 \mu\text{m}$). The surfaceroughness (*rms*) of $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ crystals after CDP with $\text{K}_2\text{Cr}_2\text{O}_7\text{--HBr}\text{--EG}$ aqueous solutions is 4.3 nm according to profilometry.

The results of AFM studying the surface $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ (Fig. 6) after CMP with 50 B2 + 50 EG etchants (vol. %) confirm the high

Table 2. Results X-ray microscopy evaluation for $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ samples after different surface of treatment

| Surface treatments | Concentrations of elements (at. %) | | | | | |
|--|------------------------------------|-------|-------|----|----|---|
| | (Cd + Hg)/Te | C | O | Cr | Br | S |
| string cutting | 1.03 | 32.01 | 11.72 | – | – | – |
| grinding by abrasive ASM 1/0 | 1.01 | 46.98 | – | – | – | – |
| CDP with B2 (9 months in isopropanol) | 1.01 | 25.07 | 9.50 | – | – | – |
| CMP with 50 B2 + 50 GL (2 hours in air) | 1.00 | – | – | – | – | – |

quality of chemical treatment and the effectiveness of our method for forming a nanoscale relief on the $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ surface. The roughness parameters of the $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ ($R_a = 1.9$ nm, $rms = 2.3$ nm) meet the requirements [18] for super-smooth polished surfaces of semiconductor materials in production and do not exceed $R_a < 10$ nm.

The elemental composition of the surface layers of $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ after polishing with the developed etchants was studied using scanning electron microscopy (Table 2). This method was used to control the concentrations of matrix elements (Cd + Hg, Te) as well as probable contamination with compounds that were part of the etchants and mixtures used for washing the semiconductor materials under study.

Table 2 shows that the ratio $[\text{Cd} + \text{Hg}]/[\text{Te}]$ on the $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ surface is stoichiometric. This indicates the same dissolution of matrix elements with etchants based on $\text{K}_2\text{Cr}_2\text{O}_7\text{--HBr}\text{--EG}$ aqueous solutions. The absence of Br, Cr, S and K on the surface of the samples confirms the high efficiency of the developed method for washing single crystals after CDP and CMP.

As a result of the obtained experimental data, it was established that to obtain a high-quality polished surface of $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ single crystals, the process of chemical-dynamic polishing should be carried out at 294 K and the rate of disc rotation $\gamma = 82$ min^{-1} . Upon completion of polishing, it is recommended to immediately wash the samples in 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ to remove unreacted residues of the etchant from the surface and then in a large amount of distilled water and dry in a flow of dry air [19]. It has been established that the simultaneous action of the chemical and mechanical components in CMP increases the dissolution rate of the single crystals under study in comparison with CDP. It was determined that by introducing different amounts of solvents to the composition of

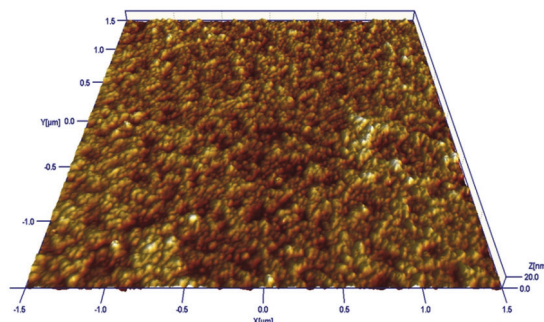


Fig. 6. AFM-images of the $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ surface after CMP with etchant composition (vol. %) 50 BB2 + 50 EG.

base solutions it is possible to regulate the rate of the polishing and obtain etchants with the required range of dissolution rates of the materials under study. The developed mixtures are characterized by high polishing ability ($R_a < 10$ nm) and can be used for controllable removing thin layer to the given thickness. For finishing treatment with the formation of high-quality polished surface with nanometer roughness and chemical treatment of thin films, the etchants with $V_{pol} = 1\text{--}5$ $\mu\text{m}\cdot\text{min}^{-1}$ could be recommend.

4. Conclusions

For chemical-mechanical and chemical-dynamic polishing of the surface of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ ($x = 0.2$) solid solutions by the etching, the compositions based on aqueous solutions of $\text{K}_2\text{Cr}_2\text{O}_7\text{--HBr}\text{--tartaric acid}$ and $\text{K}_2\text{Cr}_2\text{O}_7\text{--HBr}\text{--ethylene glycol}$ have been studied and the concentration limits of the polishing solutions have been determined. It was established that the addition of an organic solvent leads to the formation of polishing etchants with low rates of CDP (2–7 $\mu\text{m}\cdot\text{min}^{-1}$) and CMP (1.5–18.5 $\mu\text{m}\cdot\text{min}^{-1}$). The surface state of the single crystals after different stages of mechanical and chemical treatment has been studied using the methods of metallography and profilometry,

atomic force and scanning electron microscopy. Optimized compositions of slow polishing etchants, developed modes for process of CDP and CMP and the operation of an effective method for washing the polished samples after chemical treatment could be recommended for controlled bringing the thickness of the plates to the specified dimensions, finishing chemical treatment of films and formation of nanosized relief on the surface of $\text{Cd}_{1-x}\text{Hg}_x\text{Te}$ single crystals.

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