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Chemical treatment of monocrystalline cadmium telluride and $Cd_{1-x}Mn_xTe$ solid solutions by H_2O_2–HI–citric acid etchant compositions

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Abstract. Dissolution of CdTe and $Cd_{1-x}Mn_xTe$ single crystals in aqueous solutions of H_2O_2–HI–citric acid system has been studied. The surfaces of equal etching rates were constructed and the limiting stages of the dissolution process were ascertained. Also determined were the concentration limits for the solutions that can be used for chemical polishing the above-mentioned semiconductor materials.

Keywords: cadmium telluride, chemical dissolution, citric acid, semiconductor, etching rate, solid solution.

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1. Introduction

Preparatory treatment of the semiconductor surfaces has a great importance when manufacturing the electronic devices. Chemical etching, which allows to obtain polished defectless surface with given roughness and some other parameters, is often used at the finishing stage of its preparation. Therefore, investigation of the processes that take place on the semiconductor surface during its dissolution, selection of optimal procedures and conditions for chemical treatment and development of the etching-polishing compositions with control of dissolution rates is very actual.

II-VI semiconductor compounds are widely used in electronic engineering. For example, CdTe and solid solutions based on it are used for manufacturing the γ- and X-ray detectors as well as in optoelectronics when fabricating IR devices and solar cells [1, 2]. Formation of perfect surface on monocrystalline substrates made of these semiconductor materials is of a great importance. Predominant quantity of etchant compositions was developed for various treatments (polishing, anisotropic and selective etching, chemical cutting) of cadmium telluride. But the chemical treatment of the $Cd_{1-x}Mn_xTe$ solid solutions was almost not investigated [3, 4-6]. The data that are most frequently met in the literature concern the use of bromine containing and bromine evolving etchant compositions [3, 7]. The crystal surface is oxidized and contaminated by various impurities after this treatment and these etchant compositions are characterized by high dissolution rates.

The mechanism and kinetics of the undoped and germanium doped CdTe dissolution in the aqueous solutions H_2O_2–HI–citric (tartaric) acid systems were investigated in [5]. It was determined that these aqueous solutions in the high concentration region could be used for chemical polishing the mentioned above semiconductor materials. It was shown that doping the CdTe crystals by germanium leads to increasing the etching rate approximately up to 2 μm/min. A small increase of the etching rate takes places when dissolving the $Zn_xCd_{1-x}Te$ and $Cd_xHg_{1-x}Te$ crystals in these solutions [4].

2. Results and discussion

This work is devoted to investigations of kinetics inherent to chemical etching the monocrystalline CdTe and $Cd_xMn_{1-x}Te$ solid solutions in the etchant compositions H_2O_2–HI–citric acid in reproduced hydrodynamic conditions that were obtained using the rotating disc. In these solutions, hydrogen peroxide activates formation of iodine, which is an oxidizing agent, hydroiodic acid dissolves the evolving iodine and the products of surface oxidation, while the citric acid assists in the process of dissolving the oxidation products and in their complexing.

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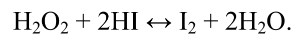
The samples under study were cut from the single crystals and were characterized by the surface area of about 0.5 cm^2 and the thickness of 1.4-2.0 mm. Prior to etching, their surfaces were mechanically polished decreasing step-by-step a diameter of the abrasive grains. Then, the layer disturbed during the mechanical treatment with its thickness from 50 to 100 µm was removed by the same etchant composition, which was used for the experimental investigation. The samples were attached to quartz substrates using pizzeine and mounted in a Teflon holder allowing measurements in the rotating disc mode. The dissolution rate was determined with account of sample thickness reduction before and after the etching process by using a mechanical watch indicator with the precision ± 0.5 µm. Three samples were etched simultaneously with the difference in the measured thickness not exceeding 5 %. The etched samples were initially rinsed by the 0.5 M solution of the sodium thiosulfate and then by the big quantity of distilled water and dried in air.

In the course of the experiments, we used 47 % extra grade water solution of H_2O_2, 43 % extra grade hydroiodic acid, and 20 % reagent grade water solution of citric acid ($C_6H_8O_7$). The prepared solutions were cooled and allowed to stand during 60-90 min in a thermostat for the chemical interaction of hydrogen peroxide and hydroiodic acid:



$$H_2O_2 + 2HI \leftrightarrow I_2 + 2H_2O.$$

Depending on the $[HI]/[H_2O_2]$ ratio in the solution, evolving iodine either dissolves in the excess of hydroiodic acid to form an etchant close in its composition and properties to iodine solutions in hydroiodic acid or is present in a free state together with the excess hydrogen peroxide. The sponge substance is formed in the latter case, which is not available for chemical etching [4]. Therefore, to form the etchant compositions the solutions contain no more than 5 vol. % H_2O_2 of the given concentration.

The concentration dependences of the CdTe, $Cd_{0.7}Mn_{0.3}Te$ and $Cd_{0.5}Mn_{0.5}Te$ dissolution rates in the aqueous solutions of the H_2O_2–HI–citric acid system (Fig. 1) were constructed at 297 K and speed of disc rotation γ = 82 min^{-1} using the simplex method of mathematical planning of the experiment (the approach of the fourth degree) [8]. The regions of the solutions that possess polishing, selective and unpolishing properties are also indicated in Fig. 1.

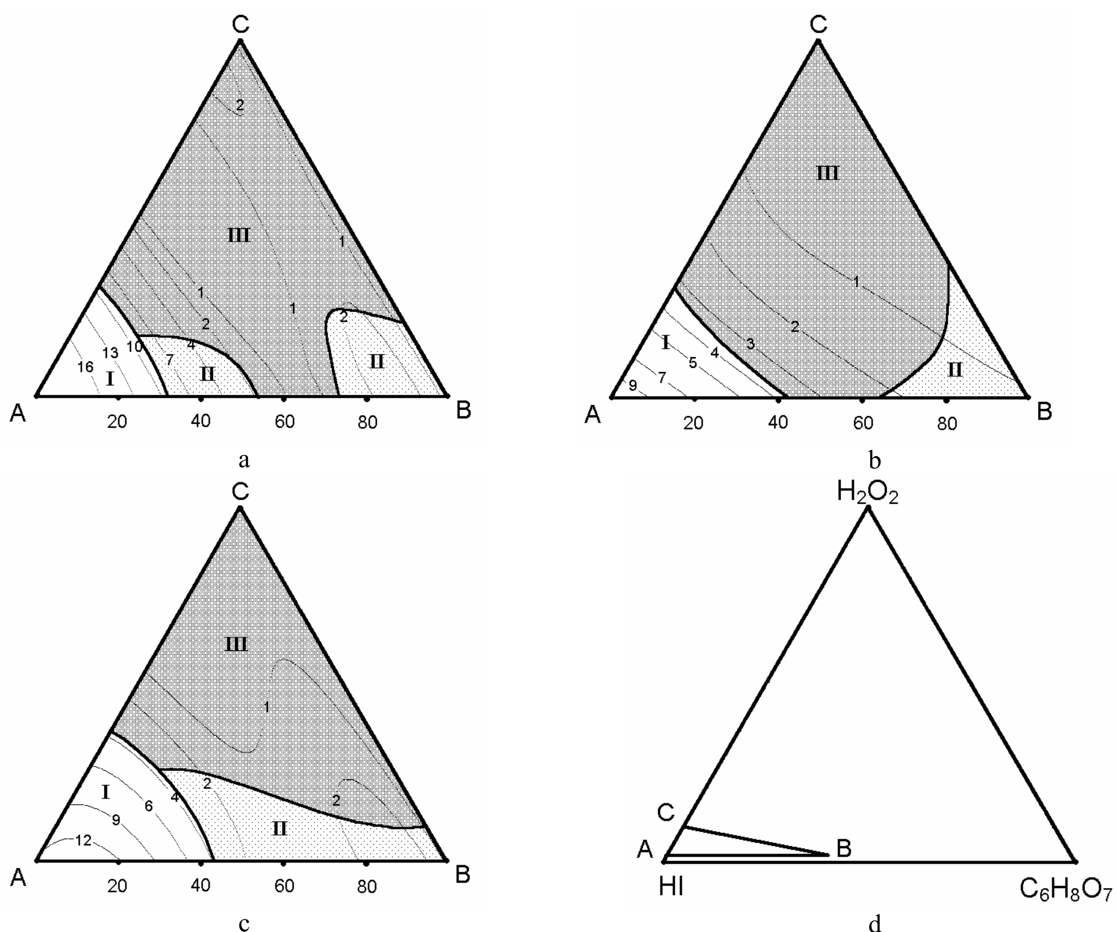


Fig. 1. The equal etching rate surfaces (µm/min) of CdTe (a), $Cd_{0.7}Mn_{0.3}Te$ (b) and $Cd_{0.5}Mn_{0.5}Te$ (c) (T = 297 K, γ = 82 min^{-1}) in the aqueous solutions of the HI–H_2O_2–citric acid system in ABC region and the regions of polishing (I), selective (II) and unpolishing solutions (III) at the volume ratio of HI:H_2O_2:citric acid in the A, B, C vertexes (d): A – 99:1:0; B – 59:1:40; C – 95:5:0.

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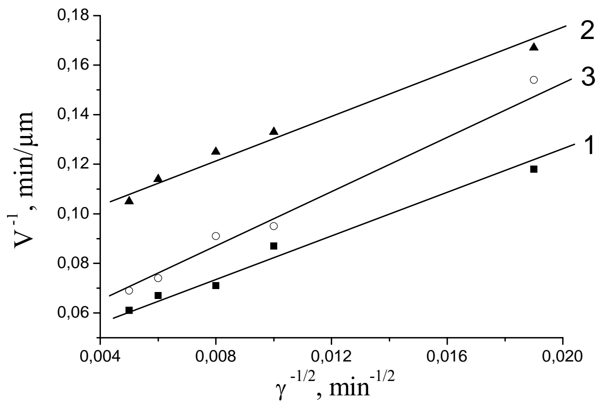

Fig. 2. Dependences of the CdTe (1), $Cd_{0.7}Mn_{0.3}Te$ (2) and $Cd_{0.5}Mn_{0.5}Te$ (3) etching rates on the speed of disc rotation (T = 293 K) in the solution containing 93.75 vol. % HI + 1.25 vol. % H_2O_2 + 5 vol. % $C_6H_8O_7$.

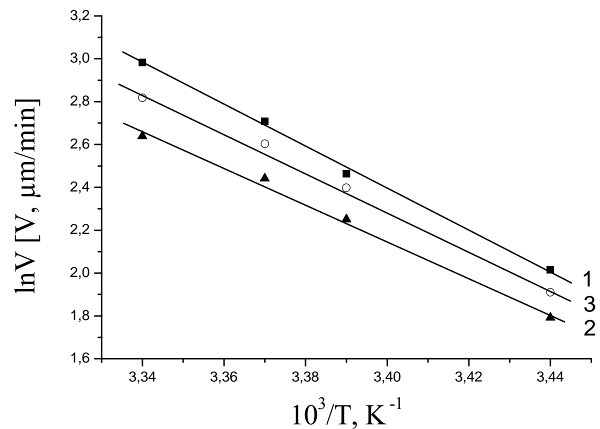

Fig. 3. Temperature dependences of the CdTe (1), $Cd_{0.7}Mn_{0.3}Te$ (2) and $Cd_{0.5}Mn_{0.5}Te$ (3) etching rates (γ = 82 min^{-1}) in the same solutions as in Fig. 2.

The surfaces of equal etching rates of the CdTe and $Cd_{1-x}Mn_xTe$ solid solutions resemble one another and are characterized by small etching rates (down to 16 µm/min). $Cd_{1-x}Mn_xTe$ solid solutions dissolve in the investigated etchant compositions more slowly than CdTe. Increasing the manganese content in the composition of the solid solutions leads to increase in the etching rate and to amelioration of the polished surface quality. The concentration regions of the polishing solutions increases in the following raw: CdTe → $Cd_{0.7}Mn_{0.3}Te$ → $Cd_{0.5}Mn_{0.5}Te$, which is related with higher manganese activity and the less value of its electrode potential.

Maximum dissolution rates of the CdTe and $Cd_{1-x}Mn_xTe$ solid solutions (9-16 µm/min) occur in the solutions enriched by hydroiodic acid (**A** angle of the ABC triangle). The etchant compositions enriched by H_2O_2 and citric acid (**C** and **B** angles of the ABC triangle) are characterized by the minimum dissolution rates, which can be explained by passivation of CdTe, $Cd_{0.7}Mn_{0.3}Te$ and $Cd_{0.5}Mn_{0.5}Te$ as well as by the appearance of the grey film-like deposit on the etched surfaces. This deposit can be simply eliminated by the polishing etchant compositions of the H_2O_2–HI–citric acid system. The etchant compositions which could be used for polishing the mentioned above semiconductor materials are given in Table 1.

Table 1. Aqueous solutions of the HI–H_2O_2–citric acid system, which can be used for surface polishing the CdTe and $Cd_{1-x}Mn_xTe$ solid solutions (T = 297 K, γ = 82 min^{-1}).

Semiconductor	Solution composition (vol. %)
CdTe	87-99 HI : 1-3 H_2O_2 : 0-12 $C_6H_8O_7$
$Cd_{0.7}Mn_{0.3}Te$	84-99 HI : 1-3 H_2O_2 : 0-16 $C_6H_8O_7$
$Cd_{0.5}Mn_{0.5}Te$	82-99 HI : 1-3 H_2O_2 : 0-18 $C_6H_8O_7$

For the solution of the H_2O_2–HI–$C_7H_8O_6$ system with the best polishing properties, the dependences of the dissolution rate v for mentioned above semiconductor materials on the speed of disc rotation γ are plotted as v^{-1} *vs* $\gamma^{-1/2}$ (Fig. 2). Behavior of these dependences gave us the possibility to determine which stage, diffusion or kinetic, is limiting in the course of heterogeneous semiconductor dissolution. The dissolution rate can be described by the equation $v^{-1} = 1/kC_0 + a/DC_0\gamma^{-1/2}$, where k is a constant of the reaction rate, C_0 – concentration of active component, D – diffusion coefficient of this component in solution, a is a constant [1, 2]. At the diffusion limiting stage, the dependence $v^{-1} = f(\gamma^{-1/2})$ passes through the coordinate origin. For the kinetic limitation of the dissolution rate, this dependence is described by the straight line parallel to x-coordinate. It can be seen from Fig. 2 that the chemical polishing the CdTe, $Cd_{0.7}Mn_{0.3}Te$ and $Cd_{0.5}Mn_{0.5}Te$ semiconductor materials occurs according to a complex mechanism with a dominance of kinetic stages, as a section on y-coordinate is cut off.

Temperature dependences of the dissolution rate of these semiconductors in the same etchant composition are indicative of the kinetic limiting stages (Fig. 3), as the determined apparent activation energy (E_a) of the chemical polishing process is higher than 40 kJ/mol (Table 2).

Table 2. Apparent activation energy (E_a) and logarithm of the pre-exponential factor ($\ln C_E$) of CdTe, $Cd_{0.7}Mn_{0.3}Te$ and $Cd_{0.5}Mn_{0.5}Te$ dissolution processes in the etchant composition, containing 93.75 vol. % H_2O_2, 1.25 vol. % HI and 5 vol. % citric acid (γ = 82 min^{-1}).

Semiconductor	E_a, kJ/mol	$\ln C_E$
CdTe	86.77	3.63
$Cd_{0.7}Mn_{0.3}Te$	76.66	3.51
$Cd_{0.5}Mn_{0.5}Te$	82.13	3.58

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3. Conclusion

The nature of chemical dissolution of the CdTe and $Cd_{1-x}Mn_xTe$ solid solutions in aqueous solutions of HI–H_2O_2–citric acid system were investigated under reproducible hydrodynamic conditions by using a rotating disk. The diagrams of equal etching rates were built using the experimental results and simplex mathematic planning of experiments at room temperature and the speed of disc rotation 82 min^{-1}. The limiting stages of the dissolution processes were also determined. It was shown that for chemical polishing the above mentioned semiconductor materials, the solutions with a low content of hydrogen peroxide can be used. It was established that the $Cd_{1-x}Mn_xTe$ solid solutions are etched more slowly than CdTe, and increase of the manganese content in their composition leads to respective increase of the dissolution rate and the region of polishing etchant compositions in the HI–H_2O_2–citric acid system.

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