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Chemical etching of CdTe and Cd_{1-x}Zn_xTe solid solutions in the H₂O₂-HJ-tartaric acid solutions

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Kinetics of physico-chemical interaction of CdTe and Cd_xZn_{1-x}Te solid solutions in the H₂O₂-HI-tartaric acid in reproducible hydrodynamics condition has been investigated. The main regularities of chemical etching of these semiconductor materials were determined and surfaces of equal etching rates (Gibbs diagrams) are built. Regions of polishing and unpolishing solutions were determined and etchant compositions for chemical dynamic polishing of CdTe and Cd_xZn_{1-x}Te solid solutions were optimized.

Keywords: polishing, cadmium telluride, solid solution, surface, etching composition, kinetics.

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The most etchant compositions for the treatment of semiconductor compounds consist of oxidant, solvent, complexing agent and viscosity modifiers [1]. The oxidants can be arranged in the next row: H₂O₂ > K₂Cr₂O₇ > Br₂ > HNO₃ > K₃[Fe(CN)₆] according their diminution of standard oxidizing potential E_0 [2].

The etchants where nitric acid is oxidant occur frequently among the etchant compositions for II-VI semiconductor compounds. It is necessary to note that HNO₃ acts as oxidants at the concentrations more than 2M [3]. The solutions of HNO₃ in the mixtures with hydrohalogenic acids are used as well as for the structure and the polishing etching of CdTe, and mostly HF, HCl and HBr are used as hydrohalogenic acid [4,5]. The kinetics and mechanism of CdTe dissolution in the solutions of HCl-HNO₃-H₂O, HF-HNO₃-H₂O and HBr-HNO₃-H₂O systems were investigated by [6-12], and kinetics of Te, CdTe, and Cd_xHg_{1-x}Te dissolution in the solutions of HJ-HNO₃-H₂O system were studied by the authors of [13]. The etchant compositions based on HNO₃ are characterized by the good polishing properties and depending of the used hydrohalogenic acid – by a wide range of etching rates (from 1 to 150 mkm/min).

Hydrogen peroxide has the biggest standard oxidizing potential and the lowest ionization constant among the indicated oxidants [2]. H₂O₂ exhibits weak acid properties in the water solutions and in combination with hydrohalogenic acids one can expect to obtain the etchant compositions for II-VI semiconductor compounds with small etching rates and good polishing properties. Such compositions are widely used for the treatment of III-V semiconductors, and the high quality polishing effect are reached at the treatment using these etchants. The etchants for the InSb, InAs, GaSb and

GaAs treatment, containing H₂O₂, hydrohalogenic acids (HCl, HF) and complexing agents (lactic, tartaric and oxalic acids) are presented by [2]. These etchants facilitate the formation of well dissoluble complex compounds and prevent the formation of hard dissoluble interaction products.

Etchant compositions based on H₂O₂-HF solutions are known for the treatment of II-VI semiconductor compounds. So, the films enriched by tellurium ([Te]/[Cd] = 5) with thickness of 600–800 Å are formed at the treatment of CdTe surfaces by the solutions containing 2 parts of H₂O₂, 3 parts of HF and 1 part of H₂O [14]. The etchant which consists from 2 parts of H₂O₂, 3 parts of HF and 2 parts of H₂O are used for identification of polar planes (111) CdTe and reveal of dislocation density on the surfaces (111) Cd [15,16]. The solution for the detection of structure defects on the surfaces ($\bar{1}\bar{1}\bar{1}$)Te are described in [17]. It contains 0,5 part of H₂O₂, 4 parts of HF and 2 parts of H₂O. Uniform growth steps were determined on the surfaces (110) of Cd_{0,96}Zn_{0,04}Te after the single crystals etching in the solution with composition of 400 ml H₂O₂ + 200 ml HF + 400 ml H₂O [18]. The films that are formed on the surfaces of CdTe and Cd_xHg_{1-x}Te at their treatment in the solutions containing H₂O₂ were investigated by ellipsometric methods [19]. It was determined that oxide which are formed on the CdTe surface is not the mechanical mixture of CdO and TeO₂ but the chemical compound CdTeO₃ or CdTe₂O₅. The etchant that consists from 1 part of H₂O₂, 1 part of HF and 1 part of CH₃COOH is used for the detection of twins, inclusions and dislocation emergences on the CdTe surface [20].

Literature data about using the H₂O₂-HJ solutions as the etchants for the treatment of II-VI semiconductor

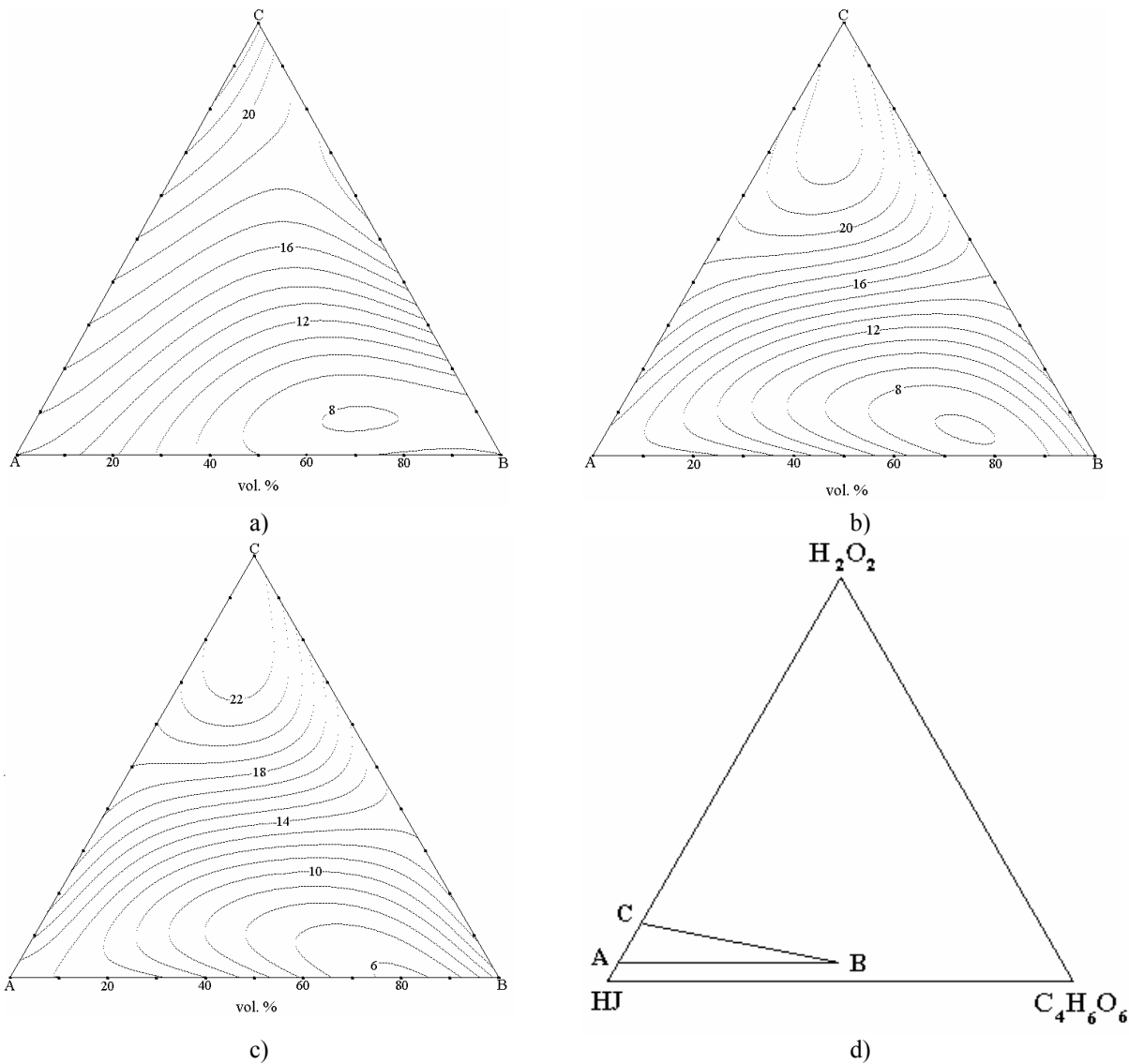


Fig. 1. The surfaces of equal etching rates (mkm/min) of CdTe (a), Cd_{0.96}Zn_{0.04}Te (b) and Cd_{0.8}Zn_{0.2}Te (c) in the solutions of the H₂O₂-HJ-tartaric acid system within the concentration interval A – B – C (d) (the ratio of 35 % H₂O₂ : 55 % HJ : 27 % tartaric acid in A, B and C tops is (in vol. %): A – 5:95:0; B – 5:45:50; C – 15:85:0).

compounds are absent since such solutions are some technologic interest as HJ has high viscosity. Therefore it is possible to obtain the etchants with small etching rates and to improve the quality of polishing surfaces.

The objective of this paper is to investigate the kinetics and mechanism of dissolution of CdTe and Cd_xZn_{1-x}Te solid solutions in the solutions of the H₂O₂-HJ-tartaric acid system as such solutions are perspective for the development of polishing and selective etchant compositions.

Single crystals of CdTe and Cd_{0.8}Zn_{0.2}Te and Cd_{0.96}Zn_{0.04}Te solid solutions were used for investigations. The wafers whose areas were about 0,5 cm² and thickness of 1,5 to 2 mm were previously mechanically polished using abrasive dust M-5 and ungreased by acetone. After mechanically grinding the wafers were attached on the quartz substrate by the inactive side. The violated at the cutting, grinding and chemico-mechanical polishing layer with thickness of 50

to 80 mkm was removed from their surfaces before investigation of dissolution kinetics with the etchant of the same composition as that subsequently used for studies of the etching process.

The wafer dissolution was realized in the unit of chemical dynamic polishing which allowed to carry out experiments in the rotating disk mode. The etching rate was determined by the wafer thickness reduction using ICh-1 watch indicator to within ± 0.5 mkm. Two or three samples were etched simultaneously, with differences in the measured thickness exceeding 5 %. After etching all wafers were rinsed at first by the 1 M water solution of Na₂S₂O₃, then by the distilled water and dried on the air.

The solutions were prepared using 35 % extra-grade H₂O₂, 55 % reagent-grade HJ and water solution of tartaric acid (C₄H₆O₆). Before etching, all solutions were allowed to stand for 120 min to achieve the equilibrium. The chemical reaction takes place in such solutions with formation of iodine:



Depending from the $[\text{HJ}]/[\text{H}_2\text{O}_2]$ ratio in the solution iodine can either dissolve in the excess of HJ forming the etchant compositions like the solutions of J₂ in HJ, or coexists with excess of hydrogen peroxide. Chemical interaction according reaction (1) runs practically completely at the containing in the mixture 19,1 vol.% hydrogen peroxide if we use the initial components of mentioned concentrations. At the lower H₂O₂ contents in the solutions, e.g. at the excess of HJ, forming iodine practically completely dissolves in the hydroiodic acid.

The investigated solution region, in which the etching rate is not equal zero and the solutions are homogeneous, is given on the Fig. 1, d. The concentration dependences of CdTe, Cd_{0,96}Zn_{0,04}Te and Cd_{0,8}Zn_{0,2}Te dissolution rate in the solutions of the H₂O₂-HJ-C₄H₆O₆ system (Gibbs diagrams) were built using the simplex method of mathematical planning of experiments and are shown on the Fig. 1, a-c. It is seen that investigated semiconductor materials dissolve in the solutions of given system according of the same mechanism, which is determined apparently by the dissolution of tellurium that forms on the surface of cadmium telluride and based on it solid solutions. Maximum dissolution rate of CdTe, Cd_{0,8}Zn_{0,2}Te and Cd_{0,96}Zn_{0,04}Te in the investigated solutions (Fig. 1, d) is not higher than 23 mkm/min at their enrichment by hydrogen peroxide (C corner of Gibbs triangle). Minimum dissolution rates take place at the dissolution of indicated semiconductor materials in the solutions enriched by tartaric acid (at the B corner of investigated ternary systems). It is necessary to note that minimum dissolution rate of corresponding material decreases and the solution region with minimum dissolution rate shifts gradually to the solutions enriched by tartaric acid at the transition from CdTe to Cd_{0,96}Zn_{0,04}Te and Cd_{0,8}Zn_{0,2}Te solid solutions.

It is interesting that the region of polishing solutions in the system H₂O₂-HJ-tartaric acid changes also at the transition from CdTe to Cd_{0,96}Zn_{0,04}Te and Cd_{0,8}Zn_{0,2}Te solid solutions. So, almost all solutions from the investigated concentration region can be used for the chemical dynamical polishing of CdTe, with the exception of small solution region, situated at the B corner, e.g., enriched by tartaric acid. For the chemical polishing of Cd_{0,96}Zn_{0,04}Te solid solution are available practically all solutions, with the exception of solutions, situated at the AB line, which are enriched by HJ and

tartaric acid simultaneously. The region of polishing solutions increases at the transition to the solid solutions containing 20 mol.% ZnTe, and for the chemical polishing of Cd_{0,8}Zn_{0,2}Te the same solutions that are available for analogous treatment of CdTe can be. This can be determined that apparently small zinc contents in the solid solutions leads to hardening of crystal lattice of Cd_{0,96}Zn_{0,04}Te, e.g. the doping is prevail over the forming solid solution effect. The next increasing of zinc content leads evidently to that main role plays the forming solid solution effect and that causes the enlarged of concentration limits of polishing solution region.

For the solutions containing (in vol. %): 75 HI + 12,5 H₂O₂ + 12,5 C₄H₆O₆ (solution 1) and 82,5 HI + 5 H₂O₂ + 12,5 C₄H₆O₆ (solution 2), the dependences of the dissolution rate (v) on the speed of disk rotation (γ) are plotted as v^{-1} vs $\gamma^{-1/2}$. The building of such dependences gives us the possibility to predetermine the character of the processes that take place at the semiconductor dissolution and to determine the limiting stage [2,21]. It can be seen from obtained dependences that CdTe dissolution both in solution 1, and in solution 2 (Fig. 2, a) is limited by the mixed kinetics as far as corresponding dependences intercept the ordinate. Interaction of the Cd_{0,96}Zn_{0,04}Te solid solution with solution 1 as in previous case is determined by the mixed kinetics, but in the case of solution 2 diffusion limitation takes place as corresponding line from the Fig. 2,b can be extrapolated in the coordinate origin. The dissolution of Cd_{0,8}Zn_{0,2}Te in the both solutions, as in the case of CdTe, is limited by the mixed kinetics as both dependences intercept y-axis.

The temperature dependences of dissolution rate of investigated semiconductor materials in the solutions 1 and 2 at the speed of disk rotation 86 min⁻¹ and temperature 19°C are shown in the Fig.3. The apparent activation energy (E_a) values (Table) were calculated from these curves. As far as E_a is not higher than 30 kJ/mol for all investigated solutions the dissolution of CdTe and Cd_xZn_{1-x}Te solid solutions is determined by the diffusion limitation [22]. Apparently discrepancies between the data obtained at the investigation of temperature dependence of dissolution rate and their dependence from speed of disk rotation (excluding the dissolution of Cd_{0,96}Zn_{0,04}Te solid solution in the solution 2) can be explained by the fact that in the mixed mechanisms the diffusion processes prevail.

Table.

Apparent activation energy and preexponential factor of CdTe and Cd_{1-x}Zn_xTe dissolution in the H₂O₂-HJ-tartaric acid solutions.

| Semiconductor | E_a , kJ/mol | $\ln c_3$ | E_a , kJ/mol | $\ln c_3$ |
|--|----------------|-----------|----------------|-----------|
| | solution 1 | | solution 2 | |
| CdTe | 16,9 | 9,9 | 15,9 | 8,9 |
| Cd _{0,96} Zn _{0,04} Te | 12,7 | 8,2 | 15,9 | 8,9 |
| Cd _{0,8} Zn _{0,2} Te | 12,5 | 8,1 | 16,6 | 9,3 |

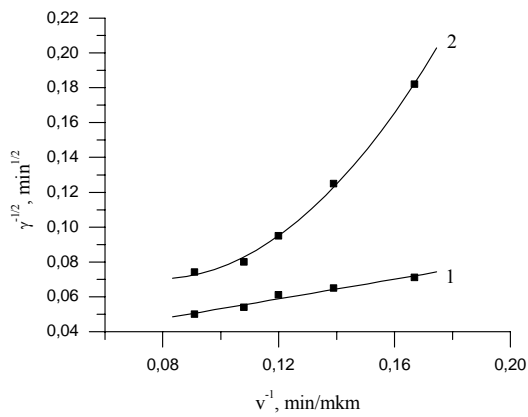
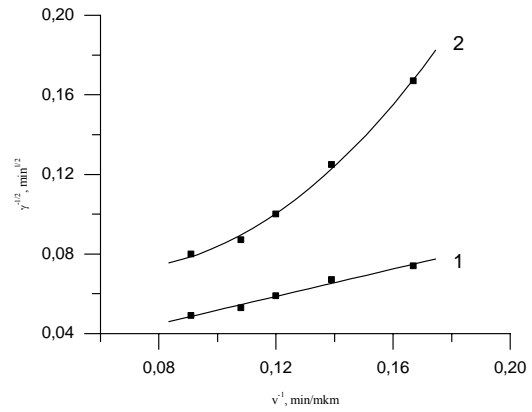
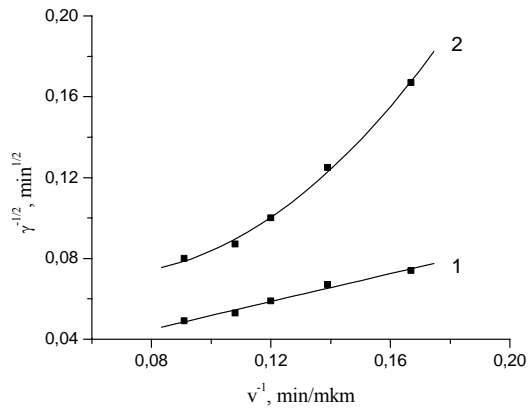


Рис. 2. Зависимость скорости растворения CdTe (а), Cd_{0,96}Zn_{0,04}Te (б) и Cd_{0,8}Zn_{0,2}Te (в) от скорости перемешивания в растворах, содержащих 75 об. % HJ + 12,5 об. % H₂O₂ + 12,5 об. % C₄H₆O₆ (1) и 82,5 об. % HJ + 5 об. % H₂O₂ + 12,5 об. % C₄H₆O₆ (2) (в координатах $v^{-1} - \gamma^{-1/2}$).

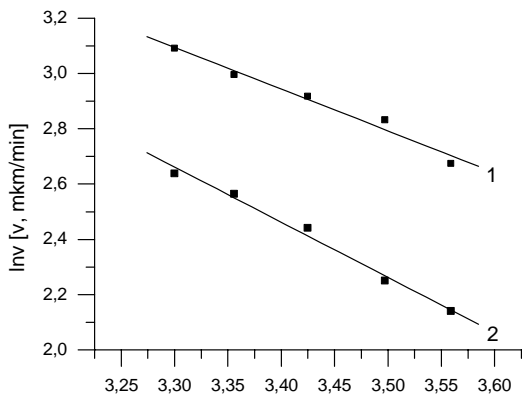
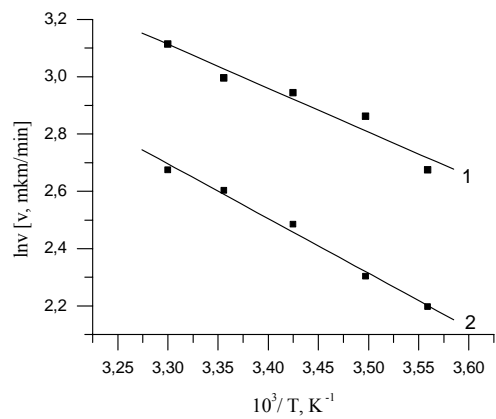
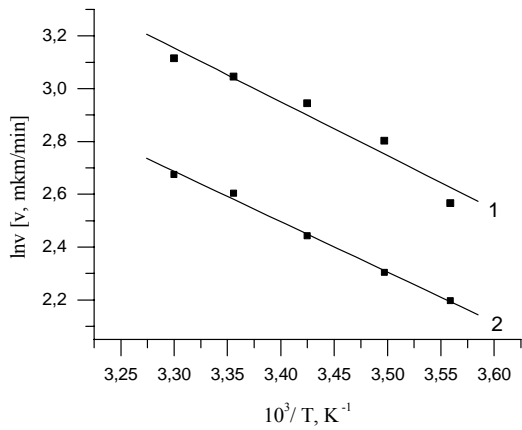


Рис. 3. Температурная зависимость скорости растворения CdTe (а), Cd_{0,96}Zn_{0,04}Te (б) и Cd_{0,8}Zn_{0,2}Te (в) в растворах, содержащих 75 об. % HJ + 12,5 об. % H₂O₂ + 12,5 об. % C₄H₆O₆ (1) и 82,5 об. % HJ + 5 об. % H₂O₂ + 12,5 об. % C₄H₆O₆ (2).

Thus, the mechanism and kinetics of physico-chemical interaction of CdTe and Cd_xZn_{1-x}Te solid solutions with the solutions of H₂O₂-HI-tartaric acid system is investigated in reproducible hydrodynamic conditions and the main regularities of the chemical etching of these semiconductor materials are determined. The surfaces of equal etching rates (Gibbs diagrams) were constructed and the regions of polishing and unpolishing solutions were determined. The etchant

compositions for the chemical dynamical polishing of CdTe and Cd_xZn_{1-x}Te solid solutions with different zinc content were optimized.

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Хімічне травлення CdTe та твердих розчинів Cd_{1-x}Zn_xTe в розчинах H₂O₂-HJ-винна кислота

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У відтворюваних гідродинамічних умовах досліджено механізм та кінетику фізико-хімічної взаємодії CdTe і твердих розчинів Cd_xZn_{1-x}Te в розчинах H₂O₂-HJ-винна кислота. Визначено основні закономірності хімічного травлення вказаних напівпровідникових матеріалів і побудовано поверхні однакових швидкостей травлення (діаграми Гіббса). Встановлено також області існування поліруючих та неполіруючих розчинів і оптимізовано склади травників для хіміко-динамічного полірування CdTe і твердих розчинів Cd_xZn_{1-x}Te з різним вмістом цинку.

Ключові слова: травлення, телурид кадмію, твердий розчин, поверхня, травильна композиція, кінетика, механізм.