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State of $Cd_{1-x}Zn_xTe$ and $Cd_{1-x}Mn_xTe$ surface depending on treatment type

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Abstract. The morphology and composition of $Cd_{1-x}Zn_xTe$ and $Cd_{1-x}Mn_xTe$ solid solutions surfaces after different types of surface treatment were investigated. Chemical etching of the surfaces and polishing by diamond pastes cause change of surface stoichiometry and contamination of surface layer by carbon and etchant components. Potentiometer studies were carried out to study the processes that take place on the interface "semiconductor-electrolyte". A prediction of phase composition of oxide films on $Cd_{1-x}Zn_xTe$ and $Cd_{1-x}Mn_xTe$ surfaces was made and a mechanism of their dissolution was determined. It was found that chemico-mechanical polishing by alkaline colloidal silica compositions is an optimal surface treatment procedure. Chemico-mechanical polishing with this mixture gives a uniform surface without essential change of surface stoichiometry and fouling of the surface layer by etchant components.

Keywords: $Cd_{1-x}Zn_xTe$, $Cd_{1-x}Mn_xTe$, semiconductor, surface, morphology, etchant.

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High-quality structure-perfect semiconductor surfaces which are uniform on chemical composition and purity are very important in production of semiconductor devices . Polishing with an etchant is one of the most widely used methods of semiconductor surface treatment. At present the etchants on $K_2Cr_2O_7$, CrO_3 and bromine base give the best results of surface polishing. But chemical etching with $K_2Cr_2O_7$ and CrO_3 etchants results in considerable enrichment of cadmium telluride surface by chromium ions, which can be explained by high absorptive ability of $Cr_2O_7^{2-}$ ions on cadmium telluride surface [1, 2]. Oxidation mechanisms of these etching processes were not sufficiently studied.

The use of the etchants with bromine results in change of surfaces stoichiometry and in enrichment of cadmium telluride surface by bromine ions [3]. A formation of elementary tellurium and tellurium dioxide islands was observed in [4, 5]. An etching mechanism of CdTe surface by etchants with bromine was studied in [5,6] were the presence of elementary tellurium on the surface was reported. So, the use of these etchants do not give a possibility to obtain the surface with minimal contamination with etchant elements. Further studies are needed to work out an optimal surface treatment procedure which causes minimal changes in crystals surface.

The purpose of the paper is to determine the etchants composition and an optimal treatment procedure for the $Cd_{1-x}Zn_xTe$ and $Cd_{1-x}Mn_xTe$ surfaces. Solution of the problem is possible if only using wide spectra of chemico-physical methods to study the mechanisms and kinetics of the processes that take place at the interface "semiconductor-electrolyte".

The studies were carried out on the CdTe, $Cd_{1-x}Zn_xTe$ ($0.02 \le x < 0.2$) and $Cd_{1-x}Mn_xTe$ ($0.02 \le x < 0.55$) single crystals grown by the Bridgman technique. Cutting the crystal into wafers was made by tungsten wire (∅ 0.2 mm) with abrasive water suspension of ∅10 μm; mechanical lapping – with free abrasives of ∅10 μm and ∅5 μm; mechanic polishing – with diamond pastes with grain size less than 1 μm. The depth of structure changes has been controlled using two-crystal X-ray spectrometer by subsequent etching the wafers surface [7]. Local distribution of structure defects of thin surface layers was studied by X-ray method with the use of skew asymmetric diffraction geometry with a small critical angle of total internal reflection [8]. The morphology and element composition of the surfaces were studied by an electron raster microscope and X-ray microanalyzer Camscan 4DV.

The studies were carried out after different types of surface treatment: polishing with abrasive pastes; etch-

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ing in etchant 1 (HNO_3:H_2O:$K_2Cr_2O_7$) and etchant 2 (Br (8 %): methanol); chemico-mechanical polishing. The studies of the $Cd_{1-x}Zn_xTe$ and $Cd_{1-x}Mn_xTe$ surface composition after different treatments reveal the presence of carbon and oxygen on the surface. The presence of carbon on the $Cd_{1-x}Zn_xTe$ and $Cd_{1-x}Mn_xTe$ surfaces can be caused by: the contamination of the material by pirolytic coating of quarts container in which the crystal was grown; the chafing of carbon while cutting the samples by corundum abrasive; the contamination while lapping and polishing with abrasive pastes; the contamination of the surface while etching with chemical solutions and washing in organic solvents. The removal of damaged layer after mechanical polishing was achieved by long-term chemical treatment of the surface with polishing etchants. The use of rather long etching time results in breakdown of plainness and emergence of a relief (Fig. 1*a*, *b*). Besides, in these samples the local micro inhomogeneities (<100 μm) were revealed by the X-ray method. In topograms, as a rule, they are surrounded by bright background, which testifies about the existence of tensions around them. Using skew asymmetric X-ray topography we have found that one part of these inhomogeneities are humps and the other are pits. The roughness of the surface is caused by different etching velocity of the matrix and inclusions. The dimension of the inclusions is of 10÷50 μm (Fig. 1*c*). The studies of the element composition of the humps by X-ray microanalyzer have shown that most of the humps have considerable content of tellurium (Table 1). The presence of silicon, aluminium, oxygen, iron, sulphur and others was also detected. Quantitative analysis of the matrix (beyond the inclusions) detects the presence of non-uniformly distributed impurity elements which concentration is up to 1 at. %. The presence of the impurities in the matrix changes the composition of the solid solution.

Chemical etching of the $Cd_{1-x}Zn_xTe$ and $Cd_{1-x}Mn_xTe$ surfaces with bromine-methanol etchants enriches the surface layer by bromine and oxygen into the depth of 13–15 nm, so as in the case of cadmium telluride surface [3].

In order to determine an optimal composition of the etchant it is necessary to study the processes that take place in the system "CdTe–etchant". Electro-potentiometer method is an effective tool for studying the processes on the interface "semiconductor–electrolyte" ("semiconductor–etchant"). One of the possible ways to carry out electro-potentiometer investigation is to determine the dependencies of equilibrium potential on pH (Pourbaix diagram). An analysis of the Pourbaix diagram give a possibility to make a reliable prediction of the phase composition of oxide films on semiconductors surface and to find out a mechanism of their solubility. The analysis of the φ–pH diagram for the CdTe–H_2O system shows that region of thermodynamic stability of cadmium telluride in solid phase spreads through whole studied pH interval. A mechanism of corrosion processes in the CdTe–H_2O system and chemical forms of corrosion products are defined by the values of the oxidative potential of the medium and pH [9]. Proposed procedure for thermodynamic prediction of possible redox reactions in the CdTe–H_2O system may also be used for an analysis of more complex "semiconductor-electrolyte" systems.

Zinc component doesn't considerably change (from thermodynamic point of view) the possible oxidative processes in the CdTe–H_2O system, because cadmium and zinc are chemically similar elements. More higher zinc activity somewhat restrict the pH interval in which $Cd_{1-x}Zn_xTe$ single crystal surface can be in active state. In the "$Cd_{1-x}Zn_xTe$–aqueous solution" system a formation of insoluble $Zn(OH)_2$ phase, which passivate a semiconductor surface, is possible at pH = 6.13, whereas a formation of $Cd(OH)_2$ – at pH = 6.9. Zinc hydroxide is thermodynamically stable in 6.13…12.37 pH interval and dissolve at higher values of pH forming $HZnO_2^-$ and ZnO_2^{2-} ions.

Thermodynamic analysis of redox processes in the $Cd_{1-x}Mn_xTe$–H_2O system is more complicated as compared to the CdTe–H_2O system. It is caused by the presence of manganese, which can be oxidized to Mn^{2+}, Mn^{3+}, Mn^{4+}, Mn^{6+} and Mn^{7+} forming soluble and insoluble in water compounds. Analysis of the literature reveals more than 30 reactions by which manganese and its components can be oxidized in aqueous solutions. Calculations of the $\varphi = f(\mathrm{pH})$ dependencies define the Pourbaix diagram for the Mn–H_2O system. Comparing "equilibrium potential – pH" diagrams for the Mn–H_2O and the CdTe–H_2O systems the prediction of thermodynamic possible reactions in the $Cd_{1-x}Mn_xTe$–H_2O systems is given and an estimate of the chemical state of the semiconductors surface in aqueous solutions with different pH is made.

In the high acidic medium (pH < – 0.37), all the components (Cd, Mn, Te) dissolve and pass into the solution in the form of Cd^{2+}, Mn^{2+}, Te^{4+} ions. It indicates on uniform dissolution of the semiconductor and gives a possibility to predict (introducing special agents into the solution) the possible effect of the $Cd_{1-x}Mn_xTe$ single crystal surface etching. Mineral or organic acid substances, which form stable complex compounds with above mentioned ions, can be used as a special agents. It is worth to note that unlike the Mn^{2+}/Mn and the Cd^{2+}/Cd systems the Te^{4+}/Te system has a positive value of the standard electrode potential $\varphi°$ =0.568 V. So, taking into account the high concentration of free surface electrons, the reduction of the Te^{4+} ions and the formation of the elementary tellurium phase on the Cd_{1-x}MnxTe single crystals surface is expected.

In the pH interval 0.37…5.45, the mechanism of cadmium and manganese components dissolution does not change, and tellurium oxidizes forming dissoluble $HTeO_2^+$. However a small increase of the oxidizing potential of the medium (for example, due to the dissolved O_2) produces a conditions for extraction of low soluble H_2TeO_4 phase on the $Cd_{1-x}Mn_xTe$ surface. An increase of Te^{4+} and $HTeO_2^+$ ions concentrations in the $Cd_{1-x}Mn_xTe$–H_2O system also makes for this process.

In low-acidic, neutral and low-alkaline solutions (pH 5.45…10.45) the $Cd_{1-x}Mn_xTe$ surface is passivated. It is

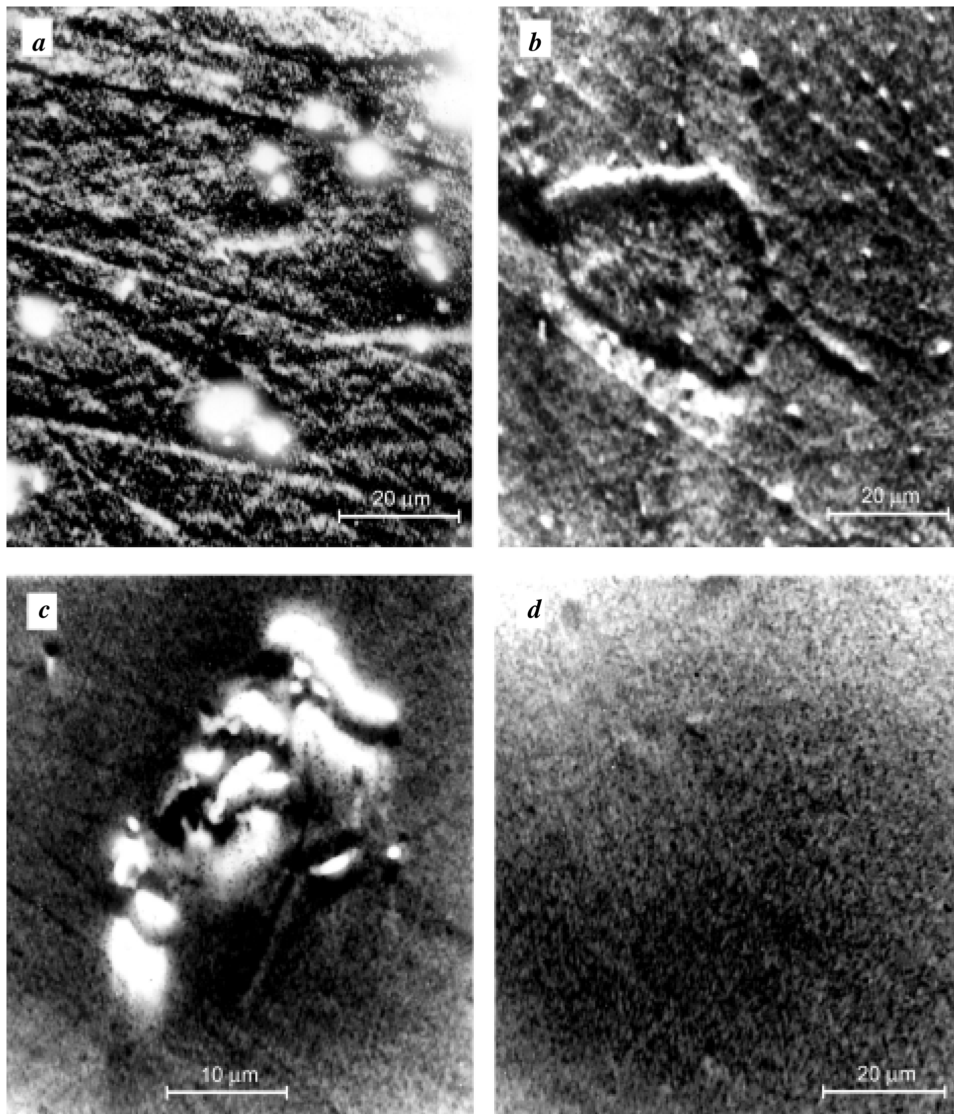

Fig. 1. Scanning electron microscope image of the $Cd_{0.55}Mn_{0.45}Te$ surface: a) after mechanical lapping; b) after etching with bromine methanol solutions; c) inclusions on the surface after etching with bromine methanol solutions; d) after chemico-mechanical polishing with SiO_2 colloidal solution.

caused by the formation of the oxide and hydroxide compounds on the semiconductor surface. Calculated Gibbs free energies of possible $Cd_{1-x}Mn_xTe$ oxidation products have negative values and decrease in the row: $CO\rightarrow \rightarrow TeO_2\rightarrow Cd(OH)_2\rightarrow Mn(OH)_2$. Taking into account the ability of the CdO, TeO_2, $Cd(OH)_2$ to dissolve in alkaline medium, it is possible to predict an enrichment of the passivating films by $Mn(OH)_2$ phase, which transforms into Mn_3O_4 and Mn_2O_3 with an increase of the oxidative potential. Further increase of pH activates dissolution processes of the film: TeO_2 completely dissolves at pH ≥ ≥ 10.45; $Cd(OH)_2$ – at pH ≥ 11.17; $Mn(OH)_2$ – at pH ≥ ≥ 11.45. Therefore, one can expect that in high-alkaline medium (pH ≥ 11.45) the $Cd_{1-x}Mn_xTe$ surface is free from oxides and hydroxides. Calculations show that cadmium, manganese and tellurium oxidation is possible in this conditions. In the result the soluble in water $HCdO_2^-$, $HMnO_2^-$ and TeO_3^{2-} ionic forms are produced.

The analysis of the Pourbaix diagram allows us to conclude:

– dominant action of Te is caused by the fact that the oxidation potential of the reactions, that take place in "semiconductor-electrolyte" system with tellurium component, is greater than the oxidation potentials of cadmium, manganese and zinc;

– according to the thermodynamic analysis a uniform dissolution from the surface takes place in acidic mediums. Polishing etching is possible in the systems which oxidation potential is not less than 0.416 V. The most effective systems are etchants which contain the solvent HNO_3 as an oxidizer;

Table 1. Composition of the matrix and inclusions (in at.%) of $Cd_{1-x}Zn_xTe$ ($0{,}02 \le x < 0{,}2$) and $Cd_{1-x}Mn_xTe$ surfaces after etching with $K_2Cr_2O_7$ solution (*M* – matrix; *I* – inclusions).

N	Sample	Cd	Te	Zn	Mn	Si	Al	Fe	Cr	Cl	S	Na	O
1	CdZnTe (M)	44.8	49.5	4.97					0.69				
2	CdZnTe (M)	44.6	49.6	5.03		0.41			0.11		0.24		
3	CdMnTe (M)	45.9	50.2		3.01	0.18		0.32	0.13	0.22			
4	CdMnTe (M)	46.7	49.7		2.88	0.34	0.19		0.22				
5	CdZnTe (I)	19.0	38.7	1.25				35.3	2.49	2.8	0.38		
6	CdZnTe (I)	8.66	34.0	0.48		37.1	12.7	0.12	3.48	1.24	0.24		
7	CdMnTe (I)	12.8	15.1		1.5	17.0	7.16	0.92		19.1		15.3	11.0
8	CdMnTe (I)	34.4	35.6		3.58	12.2	2.8	2.65		8.67			

– in highly alkaline mediums the substances which electrode potential doesn't exceed the potential of the reaction $Te + 6OH^- = TeO_3^{2-} + 6H^+ + 4e$ ($\varphi° = -0.57$ V) can serve as an oxidizer. There are many substances that meet this condition, but the use of H_2O_2, taking into account the specificity of the medium (pH ≥ 11.45), is more preferred because its decomposition products are reduced in alkaline medium at potentials greater than –0.267 V.

These conclusions confirm the right choice of the chemico-mechanical polishing with a solution which consists of fine-dispersed SiO_2, H_2O_2, NaOH, glycerin and monoethanolamin [3] as a final treatment. This is due to the fact that the SiO_2 colloidal powder with 2–20 nm size as an abrasive material doesn't cause essential structural distortion and its hydrophilic character allows to put easily it into water medium and to obtain stable water dispersions. The products of polishing are eliminated from the surface due to high absorption ability of the etchant, caused by large SiO_2 colloidal powder surface with active hydroxo-(OH) and amino-(NH_2) groups. Besides, in order to transfer an etching process into the diffusive region and to remove roughness of the working surface the glycerine is added to the solution. Glycerine addition leads to a decrease of etching velocity and gives a possibility to control and regulate effectively an etching process. Monoethanolamin fixes the dissolution products in the etchants volume.

Hence, chemico-mechanical polishing by colloidal silica compositions does not contaminate the surface layer with etchants components. Besides, this method causes a minimal change of the $Cd_{1-x}Zn_xTe$ and $Cd_{1-x}Mn_xTe$ surface stoichiometry as compared with chemical etching, that was confirmed by investigation of the surface composition. An advantage of this method is also a possibility to obtain a surface free from local micro-inhomogeneities, that are formed on chemical etching (Fig. 1*d*). Moreover, the chemico-mechanical polishing does not brake down the plane-parallelism of the surface. Thus, the use of the chemico-mechanical polishing with colloidal silica compositions allows to obtain a surface, which mostly satisfies the demands, which are required to the optical devices surface.

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Reference

1. R.N. Fesh, P.I. Feichuk, O.E. Panchuk, L.P. Shcherbak, Chemical etching of cadmium telluride single crystals // *Izvestiya AN SSSR, Neorganicheskie Materialy*, **17**(6), pp. 1118-(1981).
2. V.N. Tomachshyk, O.O. Panchuk, Z.F. Tomachshyk, Chemical etching of CdTe with sulphate solution of bichromate potassium // *Neorganicheskie Materialy*, **31**(8), pp.1023-1026 (1995).
3. Z.I. Zakharuk, I.M. Rarenko, O.N. Krylyuk, S.G. Dremluzhenko, Yu.P. Stetsko State of cadmium telluride surface after different treatment, // *Ukrainskiy Chimischeskiy Zhurnal*, **66**(12), pp.97-99 (2000).
4. A.K. Gutakovsky, V.M. Eliseev, R.I. Lyubinskaya, N.V. Lyach, A.S. Mardezhov, I.P. Petrenko, L.D. Pokrovsky, I.V. Sabinina, Yu.G.Sidorov, V.A.Schvets, Study of CdTe sufrace state // *Poverkhnost. Fizika. Chimiya. Mechanika*, N9, pp.80-87 (1988).
5. M.Sh. Komisarchik, L.M. Prokator, Yu.F. Orlov, The mechanism of cadmium selenide etching in alcoholic solution of bromine // *Izvestiya AN SSSR, Neorganicheskie Materialy*, **20**(1), pp.24-27 (1984).
6. I.M. Kotina, L.M. Tukhkonen, G.V. Patsekina, A.V. Shchukarev, G.M.Gusinskii, Study of CdTe etching process in alcoholic solution of bromine // *Semicond. Sci. Technol.*, **13**, pp. 890-894 (1998).
7. V.V. Ratnikov, V.N. Sorokin, V.I. Ivanov-Omskiy, K.E. Mironov, I.A. Gerko, V.K. Erganov, V.M. Merinov, X-ray studies of cadmium telluride single crystals structure perfection // *Pis'ma v JTF*, **14**, pp.1410-1413 (1988).
8. C.A.Kshevetskiy, Yu.P.Stetsko, I.M. Fodchuk, I.V. Melnichuk, V.S. Polyanko, Non-symmetric X-ray topography of single crystals surface layers // *Ukrainskiy Fizicheskiy Zhurnal*, **35**(3), p.444-447 (1990).
9. A.G. Voloshchuk, N.I. Tsypyshchuk, Dependence of equilibrium reaction potentials on pH for CdTe-H_2O system // *Neorganicheskie Materialy*, **38**(11), pp.1320-1323 (2002).