State of Cd$_{1-x}$Zn$_x$Te and Cd$_{1-x}$Mn$_x$Te surface depending on treatment type

S.G. Dremlyuzhenko, Z.I. Zakharuk, I.M. Rarenko, V.M. Srtebegev, A.G. Voloshchuk, I.M. Yurijchuk
Chernivtsi National University, 2, Kotsyubynsky str., 58012 Chernivtsi, Ukraine
E-mail: microel@chnu.cv.ua, Phone.: +380 (372) 584875

Abstract. The morphology and composition of Cd$_{1-x}$Zn$_x$Te and Cd$_{1-x}$Mn$_x$Te 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$_x$Te and Cd$_{1-x}$Mn$_x$Te 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$_x$Te, Cd$_{1-x}$Mn$_x$Te, semiconductor, surface, morphology, etchant.

Paper received 24.11.03; accepted for publication 30.03.04.
ing in etchant 1 (HNO₃:H₂O:K₂Cr₂O₇) and etchant 2 (Br (8 %): methanol); chemico-mechanical polishing. The studies of the Cd₁₋ₓZnₓTe and Cd₁₋ₓMnₓTe surface composition after different treatments reveal the presence of carbon and oxygen on the surface. The presence of carbon on the Cd₁₋ₓZnₓTe and Cd₁₋ₓMnₓTe surfaces can be caused by: the contamination of the material by pyrolytic 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. 1a, 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. 1c). 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 Cd₁₋ₓZnₓTe and Cd₁₋ₓMnₓTe 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–H₂O 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–H₂O 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–H₂O 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–H₂O system, because cadmium and zinc are chemically similar elements. More higher zinc activity somewhat restrict the pH interval in which Cd₁₋ₓZnₓTe single crystal surface can be in active state. In the “Cd₁₋ₓZnₓTe–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 HZnO₂⁻ and ZnO₂⁻ ions.

Thermodynamic analysis of redox processes in the Cd₁₋ₓMnₓTe–H₂O system is more complicated as compared to the CdTe–H₂O system. It is caused by the presence of manganese, which can be oxidized to Mn²⁺, Mn³⁺, Mn⁴⁺, Mn⁶⁺ and Mn⁷⁺ 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 ϕ = f(pH) dependencies define the Pourbaix diagram for the Mn–H₂O system. Comparing “equilibrium potential–pH” diagrams for the Mn–H₂O and the CdTe–H₂O systems the prediction of thermodynamic possible reactions in the Cd₁₋ₓMnₓTe–H₂O 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 Cd²⁺, Mn²⁺, Te⁴⁺ 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 Cd₁₋ₓMnₓTe 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 Mn²⁺/Mn and the Cd²⁺/Cd systems the Te⁴⁺/Te system has a positive value of the standard electrode potential ϕ₀ = 0.568 V. So, taking into account the high concentration of free surface electrons, the reduction of the Te⁴⁺ ions and the formation of the elementary tellurium phase on the Cd₁₋ₓMnₓTe 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 H₂TeO₄⁻. However a small increase of the oxidizing potential of the medium (for example, due to the dissolved O₂) produces a conditions for extraction of low soluble H₂TeO₄⁻ phase on the Cd₁₋ₓMnₓTe surface. An increase of Te⁴⁺ and H₂TeO₄⁻ ions concentrations in the Cd₁₋ₓMnₓTe–H₂O system also makes for this process.

In low-acidic, neutral and low-alkaline solutions (pH 5.45…10.45) the Cd₁₋ₓMnₓTe surface is passivated. It is...
caused by the formation of the oxide and hydroxide compounds on the semiconductor surface. Calculated Gibbs free energies of possible Cd$_{1-x}$Mn$_x$Te oxidation products have negative values and decrease in the row: CdO $\rightarrow$ 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$_3$O$_4$ and Mn$_2$O$_3$ with an increase of the oxidative potential. Further increase of pH activates dissolution processes of the film: TeO$_2$ completely dissolves at pH $\geq$ 10.45; Cd(OH)$_2$ $\rightarrow$ Mn(OH)$_2$ at pH $\geq$ 11.17; Mn(OH)$_2$ $\rightarrow$ at pH $\geq$ 11.45. Therefore, one can expect that in high-alkaline medium (pH $\geq$ 11.45) the Cd$_{1-x}$Mn$_x$Te 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;

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.
Table 1. Composition of the matrix and inclusions (in at.%) of Cd$_{1-x}$Zn$_x$Te (0.02 ≤ $x$ < 0.2) and Cd$_{1-x}$Mn$_x$Te surfaces after etching with K$_2$Cr$_2$O$_7$ solution ($M$ – matrix; $I$ – inclusions).

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

Acknowledgements

The financial support of the Civilian Research and Development Foundation (grant UP2-536) and the Science and Technology Center of Ukraine (grant №1440) is gratefully acknowledged.

Reference