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Chemical dynamic polishing CdTe and $Cd_xHg_{1-x}Te$ single crystals by using solutions of H_2O_2–HCl–tartaric acid system

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Abstract. Dissolution of CdTe and $Cd_xHg_{1-x}Te$ single crystals in solutions of H_2O_2–HCl–tartaric 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: dissolution, etchant, cadmium telluride, solid solutions, semiconductor materials.

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1. Introduction

A chemical treatment of CdTe and $Cd_xHg_{1-x}Te$ strongly influences on the surface properties and their quality, which is of great importance in manufacturing the devices based on above-mentioned semiconductor materials. To develop the optimum conditions of the surface chemical treatment and determine the optimum ratio of etching composition components, it is necessary, first of all, to know the main peculiarities of the dissolution kinetics [1].

Due to its strong oxidizing ability, hydrogen peroxide is rather often used as one of the components of different etching compositions for the chemical treatment of II-VI semiconductor compounds. According to the data, obtained by the non-destructive ellipsometry methods, films of the ternary compounds $CdTeO_3$ or Cd_2TeO_5, with exception of mechanical mixtures containing CdO and TeO_2, are formed most probably on the surface of CdTe and $Cd_xHg_{1-x}Te$ as the result of the chemical etching in water solutions of H_2O_2 [2]. It turned out that solubility of oxidation products strongly depends on the acidity, i.e., one control the film composition when changing the pH value.

Water solutions of H_2O_2 were used for CdTe surface passivation [3]. The composition of the forming surface layers was investigated by the methods of Auger-electron microscopy, X-ray photoelectron spectroscopy and secondary ionic mass spectrometry. It was determined that two regions exist in the surface layer composition. One of these regions is formed at the interface substrate/solution, and another one occurs inside the substrate. The profile of Cd distribution along the film thickness is indicative of Cd "washing out" as a result of its diffusion to the interface, and degree of cadmium depletion is determined by the value of the applied potential.

Etching compositions with hydrogen peroxide and hydrochloric acid are widely used in technological procedures for the chemical treatment of III-V semiconductor compounds. Thus, current-voltage characteristics of *n*- and *p*-type GaAs with the hole concentration 10^{18} cm^{-3} at the electrochemical etching in the solutions H_2O_2–HCl at room temperature were investigated in [4]. A mathematic model and an inspection method for the electrochemical dissolution of GaAs single crystals were also proposed using the results of this investigation.

Our analysis of the literature data shows that the etching compositions based on the solutions of H_2O_2–HCl system for the treatment of II-VI semiconductor compounds have not been used up to date. Although according to our previous investigations, they are perspective and could be a groundwork to create a wide range of etchants for the chemical treatment (for example, polishing, passivation and so on) of the above-mentioned material surfaces.

The aim of this work was to experimentally investigate chemical interaction of H_2O_2–HCl–tartaric acid ($C_4H_6O_6$) solutions with cadmium telluride and $Cd_xHg_{1-x}Te$ solid solutions, determination of concentration and temperature dependences on the dissolution rate *v* and its dependence on etchant mixing as well as optimization of the etchant compositions and technological procedures for the surface modification of the above-mentioned semiconductor materials based on the obtained experimental data.

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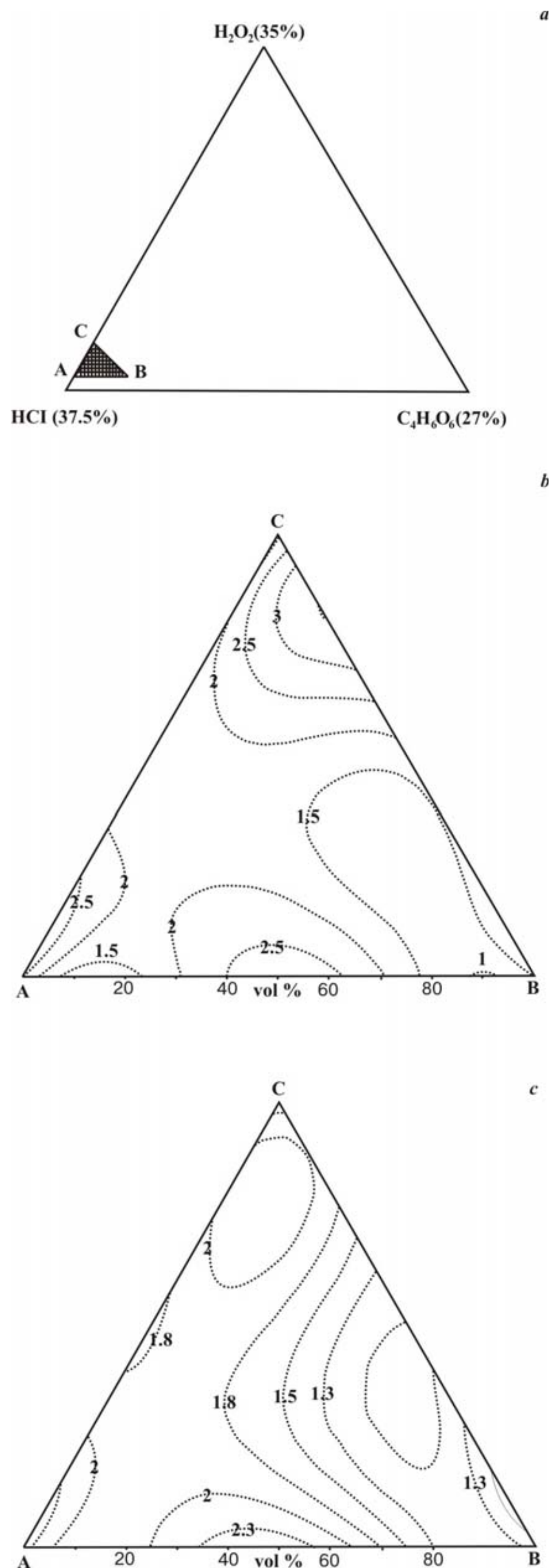

Fig. 1. Concentration dependences of the CdTe and $Cd_{0.22}Hg_{0.78}Te$ etching rates (T = 291…297 K and γ = 86 min^{-1}) in the solutions of H_2O_2–HCl–$C_4H_6O_6$ (b, c) at the volume ratio of H_2O_2 : HCl : $C_4H_6O_6$ in the A, B, C vertexes (a): A – 5 : 95 : 0; B – 5 : 75 : 20; C – 11 : 89 : 0.

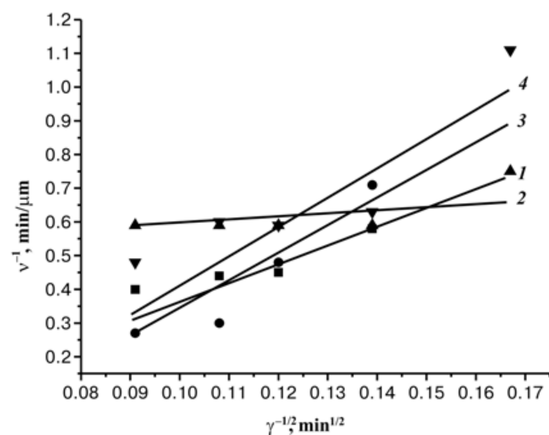

Fig. 2. Dependences of the CdTe (1, 2) and $Cd_{0.22}Hg_{0.78}Te$ (3, 4) etching rates on the speed of disc rotation in the solutions, containing (in vol. %) 6.5 H_2O_2 + 78.5 HCl + 15 $C_4H_6O_6$ (1, 3) and 8 H_2O_2 + 87 HCl + 5 $C_4H_6O_6$ (2, 4).

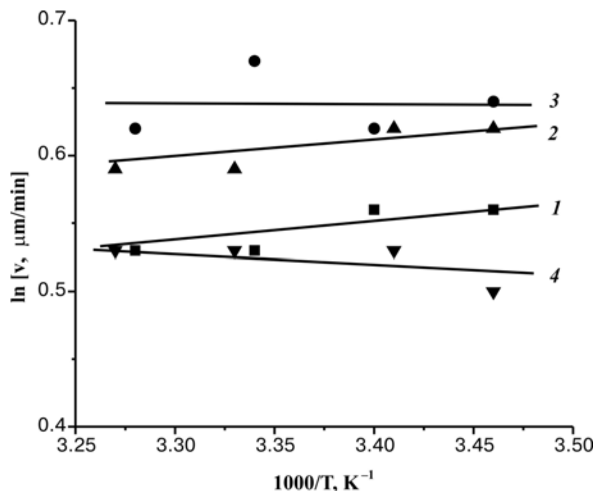

Fig. 3. Temperature dependences of the CdTe and $Cd_{0.22}Hg_{0.78}Te$ etching rates in the same solutions as in Fig. 2.

2. Results and discussion

Chemical dissolution of the semiconductor materials was investigated by determining the etching rate dependences from temperature, rate of solution stirring and etchant composition. Concentration dependence of the CdTe and
$Cd_xHg_{1-x}Te$ etching rate in the above mentioned solutions was determined under reproducible hydrodynamic conditions using a rotating disc and a device for chemical dynamic polishing. The nominally undoped *p*-type CdTe single crystals with the hole concentration $p = 8.5\cdot10^{15}…1.2\cdot10^{16}$ cm^{-3} and their mobility μ_h = 100 $cm^2/(V\cdot s)$ oriented along the direction [110] and also the nominally undoped *p*-type $Cd_{0.22}Hg_{0.78}Te$ solid solution were used for these investigations. The samples under study were

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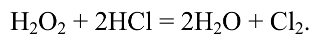
characterized by the surface area of about 0.5 cm^2 and the thickness of 1.5 to 2 mm. Prior to etching, they were mechanically polished using M5 and M1 abrasive powders, polished by diamond paste, and ungreased using acetone. Then the samples were attached to glass substrates using pizzeine and mounted in a Teflon holder allowing measurements in the rotating disc mode (speed of rotation was changed within the interval from 36 to 120 rpm). All samples were washed by distilled water after etching and dried in air.

The dissolution rate was determined by the sample thickness reduction before and after etching using ICh-1 time indicator with precision ±0.5 μm. Two or three samples were etched simultaneously with a difference in the measured thickness not exceeding 5 %.

In the course of the experiments, we used 35 % extra grade water solution of H_2O_2 37.5 % extra grade hydrochloric acid, and 27 % reagent grade water solution of tartaric acid ($C_4H_6O_6$). The prepared solutions were cooled and allowed to stand during 120 min for the chemical interaction of hydrogen peroxide and hydrochloric acid:



$$H_2O_2 + 2HCl = 2H_2O + Cl_2.$$

It is necessary to note that, while preparing initial solutions, the mixture was heated and became yellow, and gas emerged (apparently chlorine).

The microstructure of the surfaces obtained after etching was investigated using the device HMV-2000 for the microhardness measurements with digital camera Nikon Coolpix 880 of the magnification $100^{\times}$ and $500^{\times}$. The obtained microphotographs were processed using Nikon View Vers 3 program.

The diagrams "etchant composition – dissolution rate" of CdTe and $Cd_{0.22}Hg_{0.78}Te$ in the solutions of H_2O_2–HCl–$C_4H_6O_6$ system were built at the room temperature (291…297 K) and speed of disc rotation $\gamma = 86\ min^{-1}$ according to the results of the experimental measurements and using the simplex method of mathematical planning of the experiment (the approach of the fourth degree). The choice of the investigation solution interval (Fig. 1a) was determined by the necessity, first of all, to exclude the passivation regions and the regions with small quantities of one component in another.

Fig. 1b shows that the maximum dissolution rate of CdTe (3.3 μm/min) in the solutions of H_2O_2–HCl–$C_4H_6O_6$ occurs at the volume ratio of the components with above mentioned concentrations in the etching composition H_2O_2 : HCl : $C_4H_6O_6$ = 9.5 : 85.5 : 5, i.e., in the solutions enriched by hydrochloric acid. The minimum dissolution rate (1.4 μm/min) is observed at the component ratio in the etching composition H_2O_2 : HCl : $C_4H_6O_6$ = 6.5 : 83.5 : 10, i.e., in the solutions with the greatest quantity of the tartaric acid, when the dissolution rate decreases almost to zero during the following increase of the tartaric acid quantity in the etchant.

The maximum dissolution rate of $Cd_{0.22}Hg_{0.78}Te$ (2.4 μm/min) in the etching compositions of H_2O_2–HCl–$C_4H_6O_6$ system (Fig. 1c) occurs in two cases: at the ratio of the etchant components H_2O_2 : HCl : $C_4H_6O_6$ = 5 : 95 : 0 and 5 : 85 : 10. The minimum dissolution rate (1.2 μm/min) is observed at the component ratio in the etching composition H_2O_2 : HCl : $C_4H_6O_6$ = 6.5 : 83.5 : 10, when the rate decreases abruptly with increasing the tartaric acid contents.

It is necessary to note that, with an increase of $C_4H_6O_6$ content in the water solution, there is a possibility to significantly decrease the polishing rate of above-mentioned semiconductor materials.

For some solutions of H_2O_2–HCl–$C_4H_6O_6$ system (at the ratios of the components H_2O_2 : HCl : $C_4H_6O_6$ = 6.5 : 78.5 : 15 and 8 : 87 : 5), the dependences of the dissolution rate v for cadmium telluride and $Cd_{0.22}Hg_{0.78}Te$ solid solution on the speed of disc rotation γ are plotted as v^{-1} *vs* $\gamma^{-1/2}$ (Fig. 2). As the result of the experiments performed, it was determined that for the compositions of polishing regions such dependences could be extrapolated to the coordinate origin (Fig. 2, the lines 1, 3, and 4), which is indicative of the diffusion limitation in this dissolution process. For the solution of the unpolishing region, such dependences is described by the line that is almost parallel to the abscissa (Fig. 2, the line 2). This points to the kinetic limitations of the dissolution process [5, 6].

The experimental results, obtained while studying the etching rate dependences on the speed of disc rotation, can not be approved by the temperature dependences of the etching rates. As can be seen from Fig. 3, the dissolution rates of CdTe and $Cd_{0.22}Hg_{0.78}Te$ solid solutions, in the solutions used for these experiments are practically temperature independent. This can be explained by the surface passivation processes that do not result in increasing the etching rate with the temperature increase. Therefore, it is not possible to determine the apparent activation energy to approve the mechanism of the above-mentioned semiconductor material dissolution in the solutions of H_2O_2–HCl–$C_4H_6O_6$ system.

It is necessary to note that, when treating the CdTe and $Cd_{0.22}Hg_{0.78}Te$ single crystals surfaces by the etching compositions from the interval of H_2O_2–HCl–$C_4H_6O_6$ system solutions (Fig. 1a), in all the cases, one can obtain well polished surfaces, CdTe being dissolved a little quicker than $Cd_{0.22}Hg_{0.78}Te$ solid solution.

3. Conclusions

The kinetics and mechanism of chemical dissolution of CdTe and $Cd_xHg_{1-x}Te$ in solutions of H_2O_2–HCl–$C_4H_6O_6$ system were investigated under reproducible hydrodynamic conditions using a rotating disk. The diagrams "etchant composition – dissolution rate" were built using the experimental results and simplex mathematic planning of experiments at room

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temperature and speed of disc rotation 86 min^{-1}. There were determined the concentration limits of the solutions that can be used for chemical polishing the above mentioned semiconductor materials.

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