Chemical treatment of $Cd_{1-x}Mn_xTe$ single crystals with H_2O_2–HI–citric acid aqueous solutions

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Abstract. The process of CdTe and $Cd_{1-x}Mn_xTe$ dissolution in 30 % H_2O_2–HI–citric acid solutions under reproducible hydrodynamic conditions has been studied. The equal dissolution rate surfaces (Gibbs diagrams) have been plotted. Limiting stages of the semiconductor dissolution process have been determined. Regions of polishing, selective and unpolishing solutions in the mentioned system have been ascertained. The influence of Mn concentrations in solid solutions on the etching rate and quality has been established.

1. Introduction

Progress in electronics and IR devices demands more semiconductors and more detailed research of materials used for their elemental base development. CdTe and solid solutions based on it are widely used in radiation and X-ray detectors, IR devices and solar cells manufacture [1, 2]. That's why formation of single crystal surfaces of high quality is of great importance.

Most etchant compositions are elaborated for cadmium telluride polishing, anisotropic and selective etching and chemical cutting. But chemical treatment of $Cd_{1-x}Mn_xTe$ solid solutions is still rare [3, 4]. That's why complex researches of the process in semiconductors with different active environment are needed to elaborate new etching compositions and for modification of II-VI semiconductor material surfaces.

The process in $Cd_{1-x}Mn_xTe$ dissolutions in iodine containing organic solvents was researched in [3, 4]. The diffusion mechanism of chemical-dynamic polishing (CDP) with the rate 1.5 to 11 μm/min was ascertained. When iodine is educed from iodine acid in the process of its oxidation, an etching composition similar to iodine solutions in iodine acid is formed with the rate 11 to 16.5 μm/min for $Cd_{1-x}Mn_xTe$ solid solutions [5]. In [6], the dependence of the dissolution rate in H_2O_2–HI–tartaric acid etchants of $Cd_{1-x}Mn_xTe$

solid solutions was studied. The higher is the Mn content in solid solutions, the higher is the etching rate and the better is quality of the polished surface, and the polishing process goes with the rate 5 to 16 μm/min in accord with the diffusion mechanism. The authors [7] studied the CdTe and $Cd_{1-x}Mn_xTe$ polishing processes in H_2O_2–HI–lactic acid under hydrodynamic conditions. It was found that increasing the Mn content in solid solutions leads to a higher rate of semiconductor compounds etching and enlarged range of etching compositions with the polishing rate 4 to 15 μm/min.

2. Methods of the experiment

The kinetics of CdTe and $Cd_{1-x}Mn_xTe$ single crystals dissolution in 30% H_2O_2–HI–citric acid aqueous solutions was studied under reproducible hydrodynamic conditions by using the method of the rotating disk and appropriate device for its practical implementation – installation for CDP. During interaction of hydrogen peroxide with iodine acid, free iodine is educed, which oxidizes semiconductors material, and citric acid facilitates formation of aqueous solutions of complex compounds:

$$H_2O_2 + 2HI = I_2 + 2H_2O. \tag{1}$$
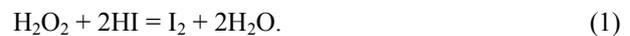
For the investigations, we cut from the ingots the wafers with the dimensions [~5×7×(1.4-2.0) mm]. The wafers surfaces were polished before being etched by the aqueous suspensions of M10, M5 and M1 abrasive powders one after another, then the 50…100-μm layer, damaged during mechanical processing, was taken off using the etching composition that was used for dissolving. The samples were attached to silica substrates with pizzeine and mounted into the rotating disc holder. The dissolution rate was measured by reducing the sample thickness with a watch indicator 2 MIGI with the accuracy within ±0.5 μm. The etching time was chosen so that the process provided dissolution of at least 10…15 μm of material. Three samples were dissolved simultaneously. The difference in semiconductor thickness didn't exceed 5% for each semiconductor. The samples were rinsed first with 0.5 M sodium thiosulphate solution, then with distilled water, and finally they were dried in the stream of dry air.

To prepare etching compositions, 30% H_2O_2, 43% HI and 27% citric acid were used. Before etching, all the solutions were kept in thermostat for 60…90 min to reach a chemical balance between etching solution components.

The samples microstructure was researched with a universal Zeiss Jenatach-inspection microscope with video camera with 25…1600 magnification and Leitz/laborlux 12HL one with Leica DFC 3200 video camera with 50…1500 magnification. The maximum diameter for observation was 200…250 μm. The plate surface microrelief and structure after etching were measured using the mechanic contact method with the DECTAK 3030 auto II profile meter.

3. Results and the discussion

Earlier [8], similar investigations were made, but most of the proposed solutions couldn't be used for polishing
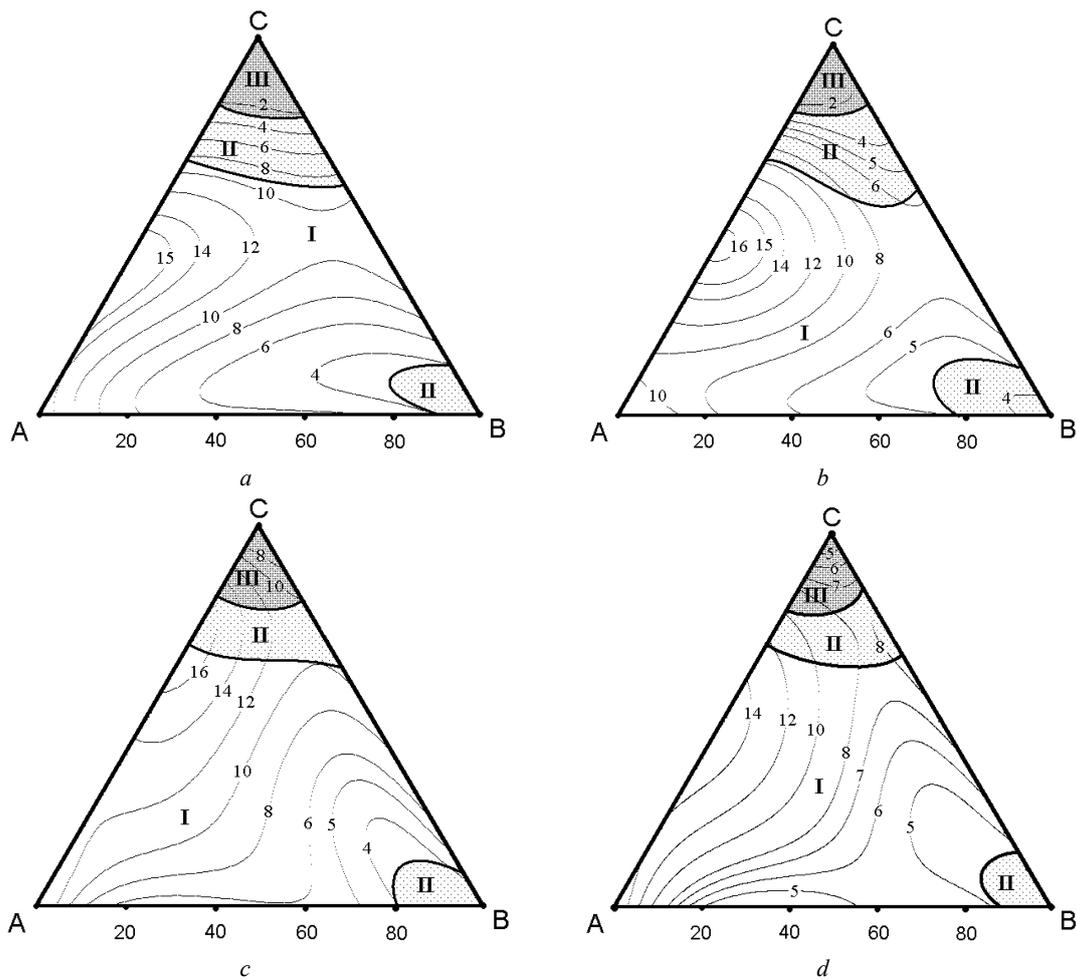
Fig. 1. The equal etching rate surfaces (μm/min) of CdTe (*a*), $Cd_{0.7}Mn_{0.3}Te$ (*b*), $Cd_{0.57}Mn_{0.43}Te$ (*c*) and $Cd_{0.5}Mn_{0.5}Te$ (*d*) (*T* = 297 K, γ = 82 min⁻¹) in the aqueous solutions of the HI–H_2O_2–citric acid system in the ABC region and the regions of polishing (I), selective (II) and unpolishing solutions (III) at the volume ratio of H_2O_2:HI:citric acid in the A, B, C vertexes: A – 2:98:0; B – 2:38:60; C –10:90:0.

with a controlled rate. That's why iodine acid oxidizer H_2O_2 of lower concentration was chosen. As a result, we got a low iodine concentration in iodine acid solutions and broader range of solutions for polishing $Cd_{1-x}Mn_xTe$ single crystals with a low rate of dissolution (Fig. 1). CdTe, $Cd_{0.7}Mn_{0.3}Te$, $Cd_{0.53}Mn_{0.47}Te$, $Cd_{0.5}Mn_{0.5}Te$ dissolution rate concentration dependences in H_2O_2–HI–citric acid solutions were constructed using the mathematical simulation of the experiments [9] at $T = 297\pm0.5$ K and the disk rotation speed $\gamma = 82$ min^{-1}. These dependences are characterized by the similar features.

The region of the solutions with polishing properties (I) occupies almost the whole range of the investigated solutions with the polishing rate 4 to 16 μm/min. The maximum etching rate (14…16 μm/min) for $Cd_{1-x}Mn_xTe$ was observed at 6 vol.% of H_2O_2 in the solution. The increase of hydrogen peroxide leads to formation of excess free iodine and thus to surface deterioration – round etching dots are formed on the surface (region II), or it is covered with grey thin coating (region III), and dissolution rates decrease to 2…6 μm/min.

Introduction of citric acid slows down the crystal etching rate. The etchants containing 50 to 60 vol.% of citric acid form round dots on semiconductor surfaces (II). At the increase of the Mn content in the $Cd_{1-x}Mn_xTe$ solid solution up to 30 at.%, the dissolution rate is slower in comparison with cadmium telluride dissolution; and at the Mn content higher than 30 at.%, the etching rates are higher as compared to CdTe dissolution. In all the cases, the increase of Mn in $Cd_{1-x}Mn_xTe$ leads to higher quality of semiconductor surfaces and enlarges the region of solutions with polishing properties, which is, perhaps, related with Mn higher activity (lower electrode potential) and different microhardness of the crystals.

For polishing the mentioned above semiconductors, the solutions of H_2O_2–HI–citric acid with (2…6) H_2O_2: (48…98) HI: (0…50) $C_6H_8O_7$ vol.% ratio can be used.

In order to study the process of dissolution of the investigated semiconductor materials in etching compositions of H_2O_2–HI–citric acid, we performed the kinetic research and plotted the dependences of the dissolution rate (v) in the coordinates $v^{-1} \sim \gamma^{-1/2}$ at $T = 293$ K as well as dependences of the etchant temperature in the coordinates $\ln v - 1/T$ in the polishing solution containing (in vol.%) $4H_2O_2 + 81HI + 15C_6H_8O_7$. As seen from Fig. 2a, for all the investigated materials, the suitable lines can be extrapolated to the origin, which indicates the diffusion mechanism of dissolution inherent to these semiconductors. Investigation of the temperature dependences of the dissolution rate in the mentioned above materials in the same etching solution (Fig. 2b) revealed that the apparent activation energy did not exceed $E_a = 30$ kJ/mol (Table). It confirms the conclusion that the limiting stage in the dissolution process of the investigated semiconductor materials is diffusion [10].
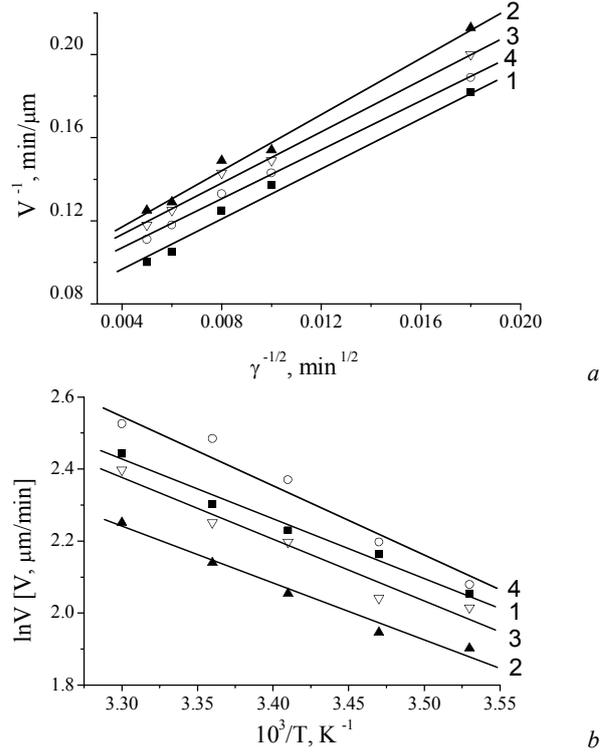

Fig. 2. Dependences of the CdTe (*1*), $Cd_{0.7}Mn_{0.3}Te$ (*2*), $Cd_{0.57}Mn_{0.43}Te$ (*3*) and $Cd_{0.5}Mn_{0.5}Te$ (*4*) etching rates on the speed of the disc rotation ($T = 293$ K) (*a*) and temperature ($\gamma = 82$ min^{-1}) (*b*) in the solution containing 4 vol.% H_2O_2 + 81 vol.% HI + 15 vol.% $C_6H_8O_7$.

Using the 46% aqueous solution of hydrogen peroxide as HI oxidizer leads to the limitation of the polishing process by both diffusion and kinetic stages [8] due to saturation of the forming solution with elemental iodine. When diluting the oxidizer by adding H_2O_2, the quantity of iodine decreases and the polishing process goes on due to the diffusion mechanism.

Thus, the results of the experimental researches helped to obtain the etching compositions that can be used for polishing and selective etching of CdTe, $Cd_{0.7}Mn_{0.3}Te$, $Cd_{0.53}Mn_{0.47}Te$ and $Cd_{0.5}Mn_{0.5}Te$ by using the aqueous solutions of the 30% H_2O_2–HI–citric acid system.

Table. Apparent activation energy (E_a) and logarithm of the pre-exponential factor (ln C_E) of the CdTe, $Cd_{0.7}Mn_{0.3}Te$, $Cd_{0.57}Mn_{0.43}Te$ and $Cd_{0.5}Mn_{0.5}Te$ dissolution processes in the etchant composition containing 4 vol.% H_2O_2 + 81 vol.% HI + 15 vol.% citric acid ($\gamma = 82$ min^{-1}).

Semiconductor	E_a, kJ/mol	ln C_E
CdTe	13.36	2.044
$Cd_{0.7}Mn_{0.3}Te$	12.99	2.001
$Cd_{0.57}Mn_{0.43}Te$	14.24	2.200
$Cd_{0.5}Mn_{0.5}Te$	17.22	2.241

4. Conclusion

The physico-chemical interaction of the single crystals of the CdTe and $Cd_{1-x}Mn_xTe$ solid solution with H_2O_2–HI–citric acid etching compositions has been established. Using mathematical simulation, the "*etchant concentration – etching rate*" diagrams have been plotted where the equal rate dissolution surfaces are shown and the solutions with polishing, selective and unpolishing properties are indicated.

It has been found that solutions enriched with iodine acid are characterized by the highest etching rates. Most of the investigated polishing solutions can be used for CDP of CdTe and $Cd_{1-x}Mn_xTe$ solid solutions. The polishing rates are slower and can be controlled. In all the cases, the higher organic acid contents in etching solutions lead to the slower semiconductor dissolution rates (the etching rate diminishes from 16 down to 4 µm/min). It has been shown that all polishing solutions are characterized by the diffusion limitation. The investigated etching compositions of the H_2O_2–HI–citric acid system can be used for $Cd_{1-x}Mn_xTe$ and CdTe single crystals.

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