Functional Materials 12, No.2 (2005) © 2005 — Institute for Single Crystals

Chemical etching of CdTe, $Cd_xHg_{1-x}Te$, $Zn_xCd_{1-x}Te$ and Te in the HNO_3–HCl-citric acid

Z.F.Tomashik, Ye.O.Bilevych, P.I.Feichuk, V.M.Tomashik*

V.Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 41 Nauki Ave., Kyiv-28, Ukraine
*Chemistry Department, Yu.Fed'kovych Chernivtsi National University, 17 L. Ukrainki St., Chernivtsi, Ukraine

Received June 27, 2004

The peculiarities of CdTe, $Cd_{1-x}Zn_xTe$, $Cd_xHg_{1-x}Te$ and Te single crystals dissolution in the solutions of HNO_3–HCl-citric acid system are investigated and the surfaces of equal etching rates (Gibbs diagrams) are constructed. The limiting stages of dissolution process and regions of polishing solutions for these semiconductors are determined. Increasing of ZnTe contents in the $Cd_{1-x}Zn_xTe$ solid solutions has been shown to result in a linear increasing of dissolution rate.

Исследованы особенности растворения CdTe, $Cd_{1-x}Zn_xTe$, $Cd_xHg_{1-x}Te$ и Te в растворах системы HNO_3–HCl-лимонная кислота и построены поверхности одинаковых скоростей растворения (диаграммы Гиббса). Определены лимитирующие стадии процесса растворения и области растворов, которые могут использоваться для химического полирования этих полупроводников. Показано, что увеличение содержания ZnTe в составе твердых растворов $Cd_{1-x}Zn_xTe$ приводит к линейному увеличению скорости растворения.

The chemical etching of semiconductors based on the dissolution processes is widely used at the manufacturing of various semiconductor devices. Knowledge of mechanism and kinetic of semiconductor dissolution is the most important condition for a choice of corresponding solution composition for polishing, anisotropic, or selective etching and chemical cutting. The high resolving power of some etchants allows to use them on the different stages of substrate treating, but for this purposes, it is necessary to develop the etchants with corresponding speed of the material removal, attainable surface roughness, and some other parameters [1]. Cadmium telluride and $Cd_xZn_{1-x}Te$ solid solutions are widely used now for manufacturing of X-ray and γ-detectors. $Cd_xZn_{1-x}Te$ solid solutions are also a good substrate material for the epitaxial growing of $Cd_xZn_{1-x}Te$ thin solid films. Therefore, the preparing of good quality surfaces of $Cd_xZn_{1-x}Te$ crystal is of a great importance.

In semiconductor surface treatments, the universal solutions of the bromine-methanol system are used as a rule [2]. However, using of such etchants results in a slight surface oxidization and its contamination with carbon and bromine which remain on the surface even after careful washing [3]. Besides, these etchants contain high toxic components. Hydrochloric acid etchants are widely used for the treatment of II–VI semiconductor compounds. The most numerous etchants of that type have been developed for the cadmium telluride and $Cd_{1-x}Hg_xTe$ solid solutions [3], while chemical etching of $Cd_{1-x}Zn_xTe$ solid solutions is almost not studied. The use of nitric acid as a strong oxidizing agent enriches the CdTe surface in tellurium, tellurium oxide, and probably in cadmium tellurite [5, 6], while hydrobromic acid removes various oxides from

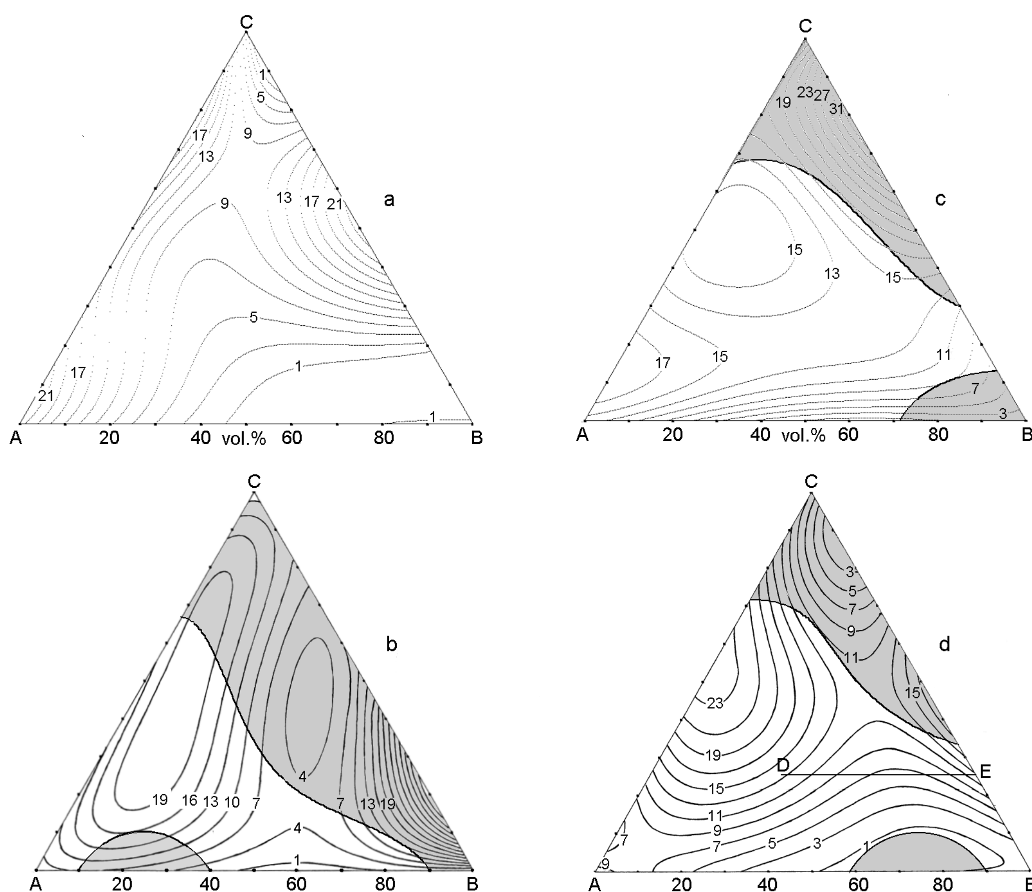


Fig. 1. The surfaces of equal etching rates (μm/min) of Te (a), $Cd_{0.2}Hg_{0.8}Te$ (b), $Cd_{0.97}Zn_{0.03}Te$ (c) and CdTe (d) in the HNO_3–HCl-citric acid system solutions. The ratio of HNO_3:HCl:citric acid in A, B and C tops is (in vol. %): A — 10:90:0; B — 20:20:60; C — 90:10:0.

surface. Citric acid reduces the etching rate because of its high viscosity and low ionization constant [7], which is important at the etching of thin films. The washing of Cd^{2+} and Hg^{2+} ions out of the surface takes place at the etching of CdTe and HgTe in solutions of HNO_3–HCl–H_2O system following by Te^{2-} to Te^0 and Te^{4+} oxidation [2]. The Te film on the surface is formed at the etching in the solutions enriched in hydrochloric acid. After the etching in the solutions on HNO_3 basis, the $CdTeO_3$ compound is formed at the surface [9]. To improve the surface properties of $Cd_{1-x}Zn_xTe$ solid solution single crystals (decreasing of roughness, reduction of surface impurity concentration, deviation from stoichiometry, and the possibility of etching rate variation) we investigated the HNO_3–HCl-citric acid solutions as the etchants.

The dissolution of CdTe, Te, $Cd_{1-x}Zn_xTe$ and $Cd_xHg_{1-x}Te$ in HNO_3–HCl-citric acid solutions was studied in this work under reproducible hydrodynamic conditions using a rotating disk. The experiments were carried out using the single crystal wafers with the surface area of about 0.5 cm^2 and thickness of 1.5–2 mm were cut out of ingots. The ingots were grown by Bridgman or modified Bridgman method (HPB) under argon pressure $P_{Ar} = 100$ atm at the growth rate of 2.3 mm/h. Prior to the etching, the wafers were mechanically polished, and the surface layer of 50 to 80 μm was removed by etchant of the same composition that was subsequently used to study the etching process. The samples were fixed to quartz substrates using pizzeine or BF-2 glue and then mounted in a Teflon holder allowing measurements in the rotating disk mode (with the rotation rate ranging from 36 to 120 rpm). The etching rate was determined from the wafer thickness reduction using ICh-1 indicator. Two or three samples were etched simultaneously with differences in the measured thickness not exceeding 5 %. All etchants were allowed to stand for 40–80 min before etching to ascertain the equi-

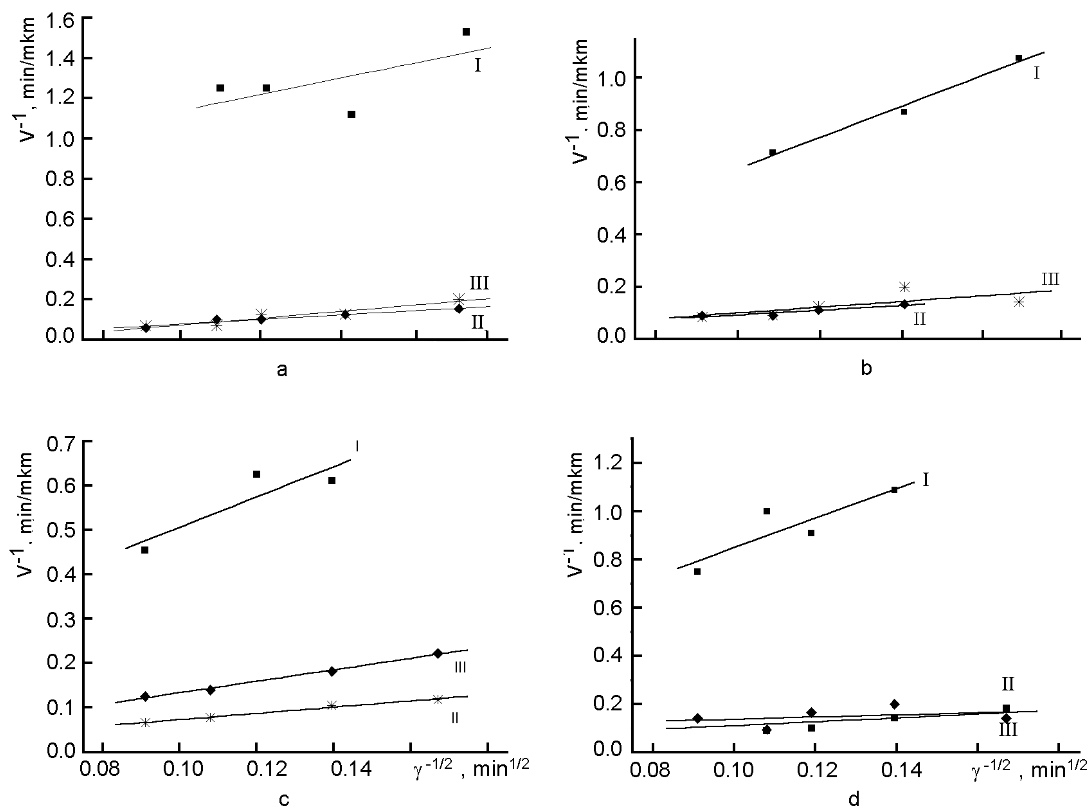
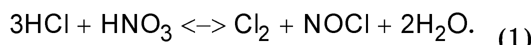


Fig. 2. Dependences of the CdTe (a), $Cd_{0.97}Zn_{0.03}Te$ (b), Te (c) and $Cd_{0.2}Hg_{0.8}Te$ (d) dissolution rates on the mixing rate for the solutions I (15 vol.% HNO_3 + 55 vol.% HCl + 30 vol. % citric acid), II (25 vol.% HNO_3 + 75 vol.% HCl) and III (32.5 vol.% HNO_3 + 52.5 vol.% HCl + 30 vol. % citric acid).

librium in the chemical reaction which take place between the etchant components:



$$3HCl + HNO_3 \leftrightarrow Cl_2 + NOCl + 2H_2O. \quad (1)$$

The solutions were prepared using 70 % special purity grade HNO_3, 34 % reagent grade HCl, and 20 % reagent grade citric acid.

The etching process is characterized quantitatively by the sample dissolution rate. Fig. 1 shows the diagrams of the Te, CdTe, $Cd_{0.2}Hg_{0.8}Te$, and $Cd_{0.97}Zn_{0.03}Te$ single crystals etching rates (μm/min) vs the HNO_3–HCl-citric acid etchant composition. These diagrams were constructed using the simplex method of the experiment mathematical planning [7] at 22°C and disk rotating rate 86 min^{-1}. It is seen from this Figure that the surfaces of equal etching rates (Gibbs diagrams) of the above semiconductors in the investigated solutions are similar, probably due to similarity of their etching mechanism. The obtained dissolution rates are relatively low (not exceeding 30 μm/min). This allows us to conclude that there is a large region of polishing solutions for such materials in the HNO_3–HCl-citric acid system. In Fig. 1, the non-polishing solution areas for CdTe, $Cd_{0.2}Hg_{0.8}Te$, and $Cd_{0.97}Zn_{0.03}Te$ are dashed and the polishing ones (not dashed) are located mainly in the lower part of these diagrams.

For some solutions of the HNO_3–HCl-citric acid system, the dependences of the dissolution rate (v) on the disk rotation rate (γ) are plotted as v^{-1} vs $\gamma^{-1/2}$ (Fig. 2). The curves of this type may elucidate the character of the dissolution processes [1, 2], as the dissolution rate can be expressed by the equation:

$$v^{-1} = 1/kC_0 + (a/DC_0)\gamma^{-1/2}, \quad (2)$$

where k is the reaction rate constant; C_0, the active component concentration; D, diffusivity in the solution; and a, a constant. When the process is diffusion-limited, the curve should pass the coordinate origin as far as $k >> 0$ and the first term of the equation (2) is equal zero. A larger role of the surface (chemical) reaction in the entire dissolution process results in a smaller slope

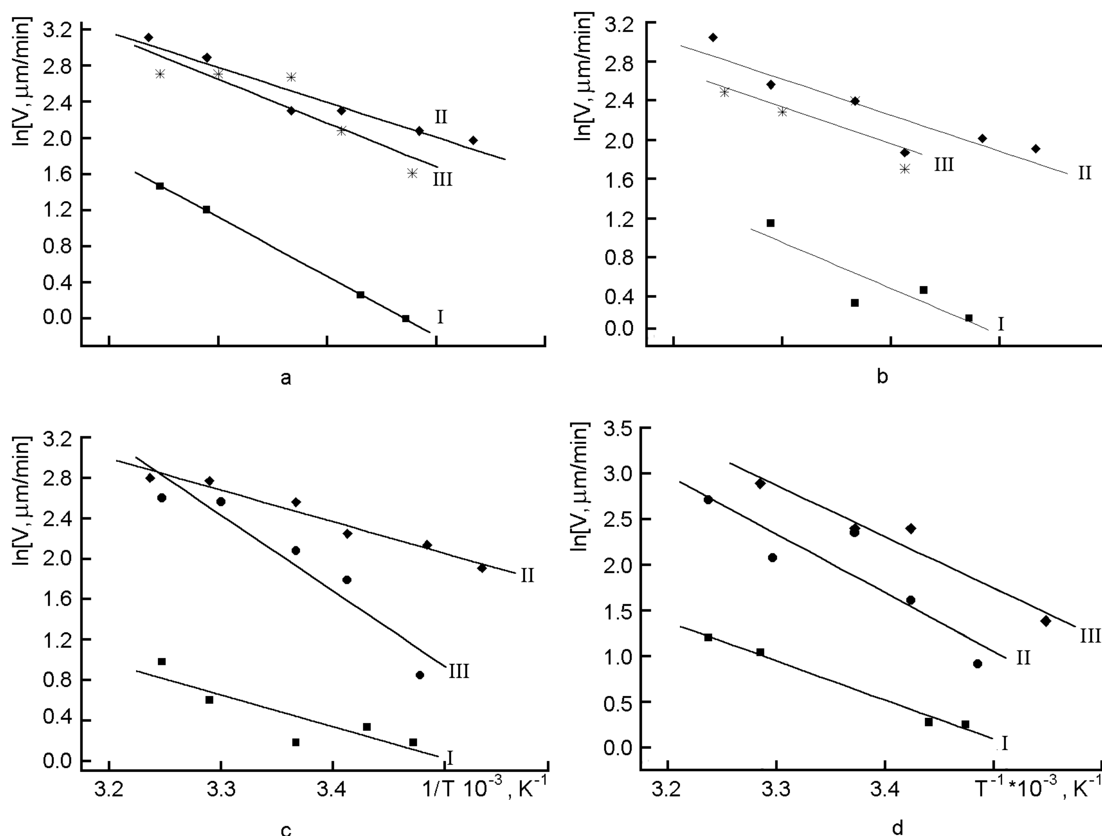


Fig. 3. Temperature dependences of the CdTe (a), $Cd_{0.97}Zn_{0.03}Te$ (b), Te (c) and $Cd_{0.2}Hg_{0.8}Te$ (d) dissolution rates for the same solutions as in the Fig. 2.

of the line. In the case when the process of dissolving is limited by the rate of the chemical reaction, the line becomes parallel to the X-axis as in this case the second term of the equation (2) is equal zero. When the process has a combined mechanism, the line or its extrapolation cuts off a certain portion of the Y axis, the length thereof allows to calculate the constant of the overall chemical reaction.

Fig. 2 shows that the dissolution of $Cd_{0.97}Zn_{0.03}Te$ and $Cd_{0.2}Hg_{0.8}Te$ solid solutions, CdTe (except for solution I), and Te (in the II and III solutions) is a diffusion-limited process, since the corresponding lines can be extrapolated in the coordinate origin. The temperature dependences of dissolution rates for CdTe, $Cd_{0.97}Zn_{0.03}Te$, $Cd_{0.2}Hg_{0.8}Te$ and Te in the same solutions are presented in Fig. 3. It can be seen that the dissolution process of the $Cd_{0.97}Zn_{0.03}Te$ solid solution, CdTe (except for solution I), Te (except for solution II), and $Cd_{0.2}Hg_{0.8}Te$ solid solution (in the solution I) is really diffusion-limited, since the apparent activation energy of the overall process (E_a) does not exceed 40 kJ/mol (see Table). The activation energy of CdTe dissolution in the solution I, Te dissolution in the solution II,

Table. The apparent activation energy (kJ/mol) of CdTe, $Cd_{0.97}Zn_{0.03}Te$, Te, and $Cd_{0.2}Hg_{0.8}Te$ dissolution in the solutions I (15 vol.% HNO_3 + 55 vol.% HCl + 30 vol. % citric acid), II (25 vol.% HNO_3 + 75 vol.% HCl) and III (32.5 vol.% HNO_3 + 52.5 vol.% HCl + 30 vol. % citric acid)

	CdTe	$Cd_{0.97}Zn_{0.03}Te$	Te	$Cd_{0.2}Hg_{0.8}Te$
Solution I	54.5	39.0	26.1	40.0
Solution II	40.4	31.1	62.3	59.8
Solution III	32.3	30.5	26.1	52.4

and $Cd_{0.2}Hg_{0.8}Te$ dissolution in the solutions II and III exceeds 40 kJ/mol, thus, these dissolution processes are limited by the combined stages.

To verify the obtained experimental results, we investigated the dependence of the dissolution rates of CdTe and $Cd_{1-x}Zn_xTe$ solid solutions with different x in the HNO_3–HCl-citric acid solutions along the line DE in Fig. 1,d. The CdTe, $Cd_{1-x}Zn_xTe$ solid solutions single crystals at $x = 0.025$, 0.04 and 0.1, respectively, obtained by the ordinary Bridgman method and by HPB were used. According to the results obtained, the dissolution rates of all investigated materials pass through a minimum present on the surfaces of equal etching rates in the CdTe and $Cd_{0.97}Zn_{0.03}Te$ cases (Fig. 1, c, d). The dependence of the dissolution rate of $Cd_{1-x}Zn_xTe$ single crystals in the HNO_3–HCl–-citric acid system solutions vs ZnTe content indicates that increasing ZnTe content in the $Cd_{1-x}Zn_xTe$ solid solutions results in a linear increase of dissolution rate. For the completeness of investigation, the stoichiometry of surface layers and their contamination with the components of etchant composition and the products of chemical interaction is to be studied further.

Thus, the surfaces of equal etching rates (Gibbs diagrams) for CdTe, $Cd_{1-x}Zn_xTe$ and $Cd_xHg_{1-x}Te$ solid solutions, and Te single crystals in the solutions of HNO_3–HCl-citric acid system have been constructed basing on the kinetic investigation of these materials dissolution. The regions of the polishing solutions composition have been determined. It has been found that increasing of ZnTe content in the $Cd_{1-x}Zn_xTe$ solid solutions results in a linear increase of dissolution rate.

References

1. B.D.Luft, V.A.Perevoshchikov, L.N.Vozmilova et al., Physico-Chemical Methods for Treatment of Semiconductor Surfaces, Radio i Svyaz', Moscow (1982) [in Russian].
2. V.N.Tomashik, Z.F.Tomashik, *Neorg. Mater.*, **33**, 1451 (1997).
3. M.Hage-Ali, R.Stuck, A.N.Saxena, P.Siffert, *Appl. Phys.*, **19**, 25 (1979).
4. V.A.Perevoshchikov, *Vysokochistye Veshchestva*, No.2, 5 (1995).
5. R.N.Zitter, *Surf. Sci.*, **28**, 335 (1971).
6. P.Gaugash, A.G.Milnes, *J. Electrochem. Soc.*, **128**, 924 (1981).
7. R.D.Feldman, R.L.Opila, P.M.Bardenbaugh, *J. Vac. Sci. Technol.*, **A3**, 1988 (1985).
8. V.N.Tomashik, A.A.Sava, Z.F.Tomashik, I.B.Mizetskaya, *Izv. AN SSSR. Neorg. Mater.*, **24**, 730 (1988).
9. V.N.Tomashik, A.A.Sava, *Izv. AN SSSR. Neorg. Mater.*, **26**, 1189 (1990).

Хімічне травлення CdTe, $Cd_xHg_{1-x}Te$, $Zn_xCd_{1-x}Te$ та Te у розчинах HNO_3–HCl-лимонна кислота

З.Ф.Томашик, Є.О.Білевич, П.І.Фейчук, В.М.Томашик

Досліджено особливості розчинення монокристалів CdTe, $Cd_{1-x}Zn_xTe$ $Cd_xHg_{1-x}Te$ та Te в розчинах системи HNO_3–HCl-лимонна кислота та побудовано поверхні однакових швидкостей розчинення (діаграми Гіббса). Визначено лімітуючі стадії процесу розчинення та області розчинів, що можуть використовуватися для хімічного полірування цих напівпровідників. Показано, що збільшення вмісту ZnTe у складі твердих розчинів $Cd_{1-x}Zn_xTe$ приводить до лінійного збільшення швидкості розчинення.