PHYSICS AND CHEMISTRY OF SOLID STATE
V. 23, No. 2 (2022) pp. 322-327
Section: Chemistry
DOI: 10.15330/pcss.23.2.322-327

Vasyl Stefanyk Precarpathian National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 23, № 2 (2022) С. 322-327
Хімічні науки

PACS 81.65Ps ISSN 1729-4428

V.G. Ivanitska, P.M. Fochuk

Polishing of CdTe, Cd(Zn)Te, Cd(Mn)Te Single Crystals by Iodine in Dimethylformamide

Yuriy Fedkovych Chernivtsi National University, Chernivtsi, Ukraine, v.ivanitska@chnu.edu.ua

The process of chemical-mechanical polishing of CdTe (110), $Cd_{0,9}Zn_{0,1}Te$ (110) та $Cd_{0.95}Mn_{0.05}Te$ (110) surface by etchants, based on solutions of the I_2–dimethylformamide system, has been studied. Ethylene glycol and lactic acid were used as modifying components. The dependences of chemical-mechanical polishing rates on the content of ethylene glycol and lactic acid in the composition of the basic solution have been studied. The technological stability of the developed etchants has been determined. Qualitative characteristics of the surface are established by atomic force microscopy and non-contact profilographic analysis. Based on the obtained results, the compositions of etching solutions and technological modes of chemical-mechanical treatment of CdTe, $Cd_{0,9}Zn_{0,1}Te$ and $Cd_{0.95}Mn_{0.05}Te$ single crystals were optimized. Etchants modified with an organic component are promising for use in the semiconductor materials technology in the case when the main goal is to obtain high-quality, clean from contaminants and impurities, structurally perfect surface.

Key words: CdTe solid solutions, single crystal, etching rate, chemical-mechanical polishing, dimethylformamide, iodine.

Received 4 February 2022; Accepted 27 May 2022.

Introduction

Semiconductor compounds CdTe, Cd(Zn)Te, Cd(Mn)Te are characterized by a number of properties that determine their dominant role in modern technology of electronic devices. These semiconductors are widely used in the manufacture of solar cells, ionizing radiation detectors, operating elements of infrared and nonlinear optics. The electronic and structural properties of semiconductor surfaces and interfaces result from the existence of surface and interface states [1, 2]. Therefore, high-quality operation of such devices depends not only on the semiconductor physical-chemical characteristics, but also on the chemical composition, structural perfection and geometry of its surface, which makes extremely high demands on its quality.

The main methods of surface treatment and preparation in the technology of semiconductor materials are traditionally its chemical etching and chemical-mechanical polishing. These methods involve the use of certain chemicals that can react with the semiconductor surface to form soluble interaction products. They are used both at certain stages of the technological process of manufacturing materials and structures, and for various researches, aimed at studying the surface properties of semiconductors, which ultimately determine the quality of work, made of their devices.

The etchants compositions, used in semiconductor materials technology, often include halogens or their compounds. Etchants, based on bromine, dissolved in methanol or other organic solvents, traditionally have been used for chemical surface treatment of compounds $A^{III}B^{V}$ and $A^{II}B^{VI}$. After etching with such solutions, due to the bromine high oxidizing ability, the stoichiometry of the surface layer of semiconductors is often disturbed. Sometimes poorly soluble, difficult-to-remove interaction products are formed on the surface. Bromine-based etchants are characterized by a high rate of interaction with the semiconductor surface, which makes it impossible to use them in the processing of thin films. In addition, such etchants are unstable due to the high bromine volatility and quite toxic.

Iodine-based etchants have some advantages over bromine-based etchants and find applications in semiconductor material technology. The HI-treatment effects lead to improved power conversion efficiency in CdTe solar cells [3]. Solutions of iodine in propanol [4, 5], methanol, dimethylformamide [6, 7] and other organic solvents, due to the lower iodine oxidizing ability, are characterized by low dissolution rates of the semiconductor material, are less volatile, more stable over time and are not inferior in polishing properties to bromine-based solutions. Low dissolution rates of semiconductor crystals make it possible to use iodine-based solutions in the process of chemical-mechanical polishing of CdTe and its solid solutions.

In order to improve the basic technological characteristics of etchants, a viscous component is often added to their composition in addition to the oxidant [8]. This modification makes it possible the further reduction rate of interaction of the etchants with the semiconductor surface both in the process of chemical etching and in the process of chemical-mechanical polishing.

The aim of this work is to study the effect of the viscous component, such as ethylene glycol (EG) and lactic acid (LA), on the technological characteristics of the etching composition, formed on the basis of iodine solution in dimethylformamide (DMFA). The main result of the study should be the development and optimization of the compositions of polishing etchants based on the I_2–DMFA–EG, I_2–DMFA–LA etching systems, as well as the improvement of technological modes of chemical-mechanical polishing of the CdTe, Cd(Zn)Te and Cd(Mn)Te surfaces.

I. Materials and methods

Single crystal samples of CdTe, $Cd_{0,9}Zn_{0,1}Te$ and $Cd_{0.95}Mn_{0.05}Te$ CdTe ($8\times8\times2$ mm^2), cut from ingots grown by the Bridgman method, were used for the study. All samples were oriented in the crystallographic direction [110]. Pre-treatment of the samples included stages of grinding and mechanical polishing. In order to remove a surface layer, disturbed by mechanical treatment, the samples were chemically etched in a 3 % solution of bromine in methanol.

In the etchants we used crystalline iodine (I_2), dimethylformamide (C_3H_7ON), ethylene glycol (CH_2OHCH_2OH), lactic acid ($C_3H_6O_3$) of chemical purity grade. The process of chemical-mechanical polishing was performed on a glass polisher using chemical-resistant material "Pillon". The 15 % solution of iodine in DMFA as a basic solution (BS) was used [3]. After chemical treatment, the samples were washed with 1 M aqueous sodium thiosulfate solution and then three times with distilled water.

To study the effect of the viscous component on the process of chemical-mechanical polishing, EG and LA were gradually added to the base solution.

The dissolution rate of the semiconductor was determined by decreasing of the thickness of the plates using an ICh-10 clock indicator. The surface of the single crystals after treatment was fixed by a Leitz/Wetzlar microscope with a built-in MD-CP 250 camcorder with a magnification (8× to 16×). The quality of polishing was determined by the method of optical measurement of surface roughness on the non-contact 3D surface profiler "New View 5022S" *(Zygo)* and by the method of atomic force microscopy (AFM).

II. Results and discussion

Experimental studies, related to the etching of CdTe samples of different crystallographic orientation by the I_2–DMFA etching system [3], have shown that the highest quality surface can be obtained using a solution, containing 15 wt % of iodine in DMFA. Therefore, this composition was chosen as the basic solution for studying the effect of the viscous component on the process of chemical-mechanical polishing. The content of EG and LA in the etchant composition varied from 0 to 80 % (by volume).

The etching rate of CdTe in the basic solution (I_2–DMFA) was 8 μm/min [3]. When applying a mechanical component in the process of polishing the samples, the rate of their dissolution increased in 5 - 10 times depending on the pressure on the plate. Under the conditions of our experiment, the rate of chemical-mechanical polishing of the studied samples in a I_2–DMFA solution was 38 - 43 μm/min. The addition of an organic component to the etching composition caused a gradual decrease in the rate of chemical-mechanical polishing to 5 - 8 μm/min in the case of ethylene glycol and 3 - 4 μm/min in the case of lactic acid. The dependence of chemical-mechanical polishing rate of CdTe, $Cd_{0,9}Zn_{0,1}Te$ and $Cd_{0.95}Mn_{0.05}Te$ on the content of ethylene glycol and lactic acid in basic solution is shown in Fig. 1.

As can be seen from the Fig. 1, the concentration dependences of the rate of CdTe, $Cd_{0,9}Zn_{0,1}Te$ and $Cd_{0.95}Mn_{0.05}Te$ surfaces using solutions containing EG and LA are similar. The addition of EG and LA to basic solution significantly slows down the dissolution rate of all test samples, but when using lactic acid, this effect was more noticeable. The addition of 30 vol.% viscous component in basic solution in both cases slows down the interaction more than twice, although a further decrease in the etching rate with increasing content of EG and LA is not so rapid. Therefore, the positive effect of the addition of a viscosity modifier on the reduction of the semiconductor dissolution rate over the entire concentration range (from 0 to 80 % by volume of the organic component) was confirmed. At the same time, the effect of etchants dilution on the quality of the resulting surface was not so clear. It is shown that increasing the content of EG and LA in the etchants composition to 40 vol. % leads not only to a significant reduction in the rate of chemical-mechanical polishing, but also to improve the quality characteristics of the semiconductor surface. The sample surface, treated with solutions containing EG and LA more than 40 vol. %, has poorer quality, which was confirmed by measurements of surface roughness on the Zygo profiler (Fig. 2).

The surface roughness of $Cd_{0.95}Mn_{0.05}Te$ sample, which was polished with a basic solution and solutions of I_2–DMFA, containing up to 40 vol. % of the viscous component, was in the range of 10 - 25 nm (Fig. 2a). Chemical-mechanical polishing of samples with solutions

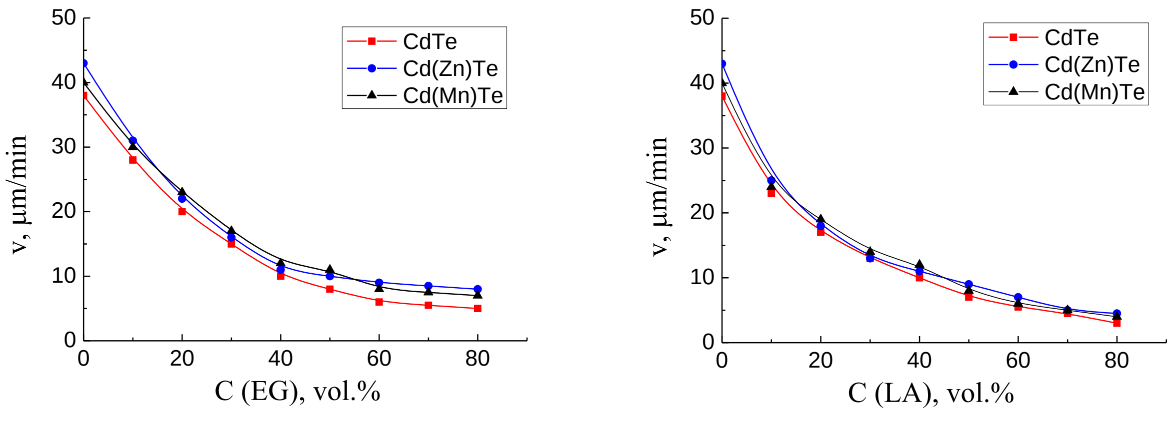
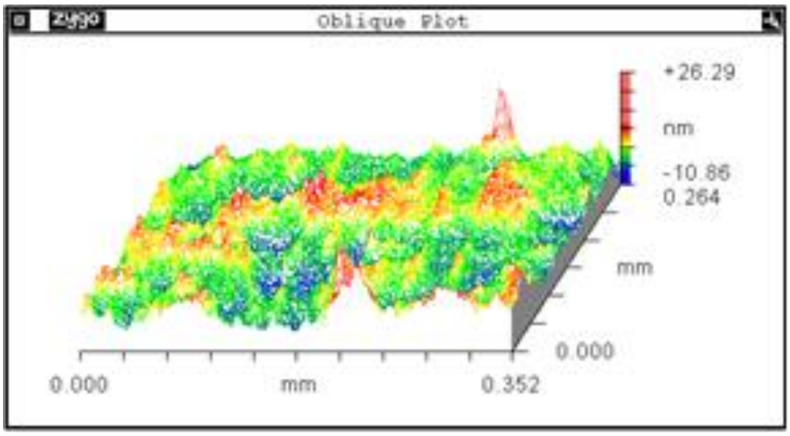
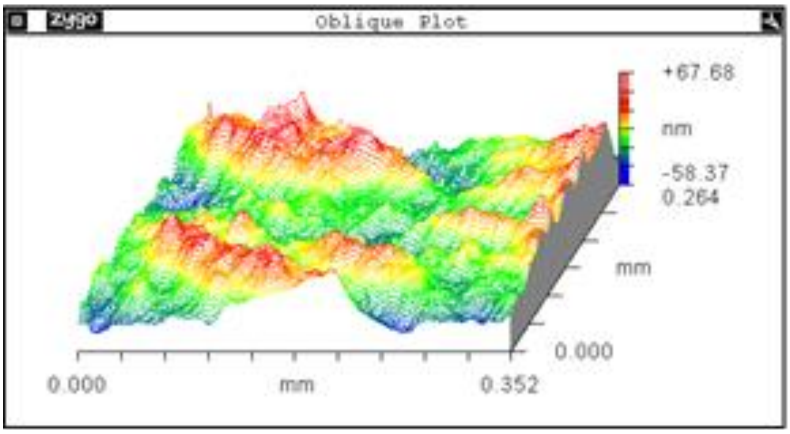


Fig. 1. Concentration dependence of the chemical-mechanical polishing rate (μm/min) of CdTe, $Cd_{0,9}Zn_{0,1}Te$ and $Cd_{0.95}Mn_{0.05}Te$ in solutions BS–EG (a), BS–LA (b), (T = 293 K).



a)



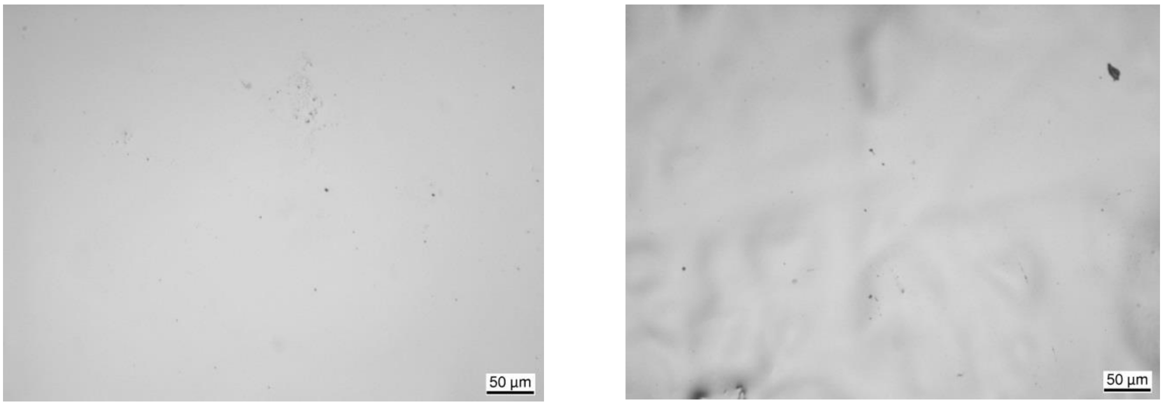
b)

Fig. 2. 3D image of a fragment of the $Cd_{0.95}Mn_{0.05}Te$ surface, treated by I_2–DMFA–EG solutions (30 vol. % EG (a), 60 vol. % EG (b)).

in which the content of EG and LA was more than 40 vol. %, leads to receive the surface with higher values of roughness, the value of rms in this case increased to 40 - 50 nm (Fig. 2b). Similar measurements were carried out for CdTe and $Cd_{0,96}Zn_{0,04}Te$ samples.

In order to optimize the etchant composition for chemical-mechanical polishing of CdTe and its solid solutions, a set of metallographic studies of the samples surface after polishing by I_2–DMFA–EG (LA) etchants was performed (Fig. 3).

The obtained results confirmed the conclusions, made from the analysis of profilographic measurements. It is shown that chemical-mechanical polishing of samples in solution I_2–DMFA with the addition of 30 vol. % EG (Fig. 3a) makes it possible to obtain a high-quality mirror surface, free from dirt, insoluble films and visible defects. Increasing the content of EG in the composition of basic solution to 60 vol. % (Fig. 3b) adversely affects the



a) b)

Fig. 3. The $Cd_{0.95}Mn_{0.05}Te$ surface, chemically-mechanically polished with I_2–DMFA–EG solutions (30 vol. % EG (a), 60 vol. % EG (b)).

polishing properties of the etchants, because the surface of the samples appears relief, visible even to the naked eye.

Satisfactory quality characteristics of the CdTe, $Cd_{0,9}Zn_{0,1}Te$ and $Cd_{0.95}Mn_{0.05}Te$ surface, polished with a modified solutions of iodine in dimethylformamide, the minimum values of interaction rates make it possible to recommend such solutions for chemical-mechanical polishing of semiconductors, if controlled removal of material is required, and also in the process of final polishing of semiconductor materials and thin films.

From a technological point of view, one of the defining characteristics of etching solutions is their stability. If the etchant contains a volatile component, then its composition changes uncontrollably over time. Particularly critical changes occur when the volatile component of the etching composition is an oxidant. The change in the etchant composition occurs faster, if the volatility of the ingredient is higher, which makes it impossible to carry out the experiment under stable reproducible conditions and adversely affects the result of chemical treatment of the semiconductor surface.

In order to study the time stability of iodine solutions in dimethylformamide, modified with ethylene glycol and lactic acid, the dependence of the CdTe, $Cd_{0,9}Zn_{0,1}Te$ and $Cd_{0.95}Mn_{0.05}Te$ chemical-mechanical polishing rate and the dependence of surface quality on the solutions storage time were obtained and analyzed. Samples of CdTe, $Cd_{0,9}Zn_{0,1}Te$ and $Cd_{0.95}Mn_{0.05}Te$ were polished by the chemical-mechanical method using I_2–DMFA solutions containing 0, 10, and 30 vol. % EG and LC, aged for 2, 24, 48, 72, 96, 120, 168 and 240 hours after preparation. The dependence of the rate of CdTe chemical-mechanical polishing on the storage time of I_2–DMFA–EG solutions with different contents of the organic component is shown in Fig. 4. When lactic acid was used as a viscosity modifier and for $Cd_{0,9}Zn_{0,1}Te$ and $Cd_{0.95}Mn_{0.05}Te$ samples, the specified dependence was similar.

It has been shown that the storage of I_2–DMFA and I_2–DMFA–EG etchants at room temperature does not cause a critical decrease in the rate of chemical-mechanical polishing of samples. A slight decrease in the polishing rate was observed in the initial period of time, while longer storage of etchants had little effect on the rate of the process. Dependence analysis shows that the addition of an organic component (EG) to the basic solution slightly slows down the degradation rate of the etchant with time. The decrease in the rate of chemical-mechanical polishing when holding the etchant for 48 h. was more noticeable in solutions that did not contain ethylene glycol. The addition of 10 and 30 vol. % EG stabilizes the etchants and minimizes the relative reduction in polishing rate, even at the initial time.

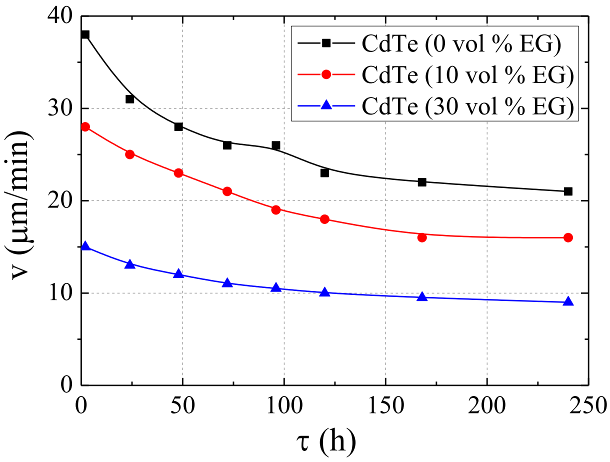


Fig. 4. Dependence of the CdTe chemical-mechanical polishing rate by solutions with EG different contents vs the storage time of the etchant (T = 293 K).

The surface quality of samples polished with I_2–DMFA solutions without and with the addition of EG and LA, aged for different times after preparation was studied by atomic force microscopy. It is shown that storage of etchants for up to 48 hours does not cause loss of their polishing properties. The treated surface remained shiny, without visible defects, the roughness did not exceed 25 nm. AFM image of the CdTe sample, polished with a solution of I_2–DMFA–10 vol. % EG, aged for 48 hours is shown in Fig. 5.

The surface of the samples, polished with solutions aged for more than 48 hours, was also shiny and without visible defects. However, it should be noted that its roughness slightly increases. This can be caused by a decrease of oxidant content in the etchants composition, which leads to a weakening of the chemical component and strengthening of the mechanical component in the polishing process. The surface of the samples polished with solutions, aged more than 48 h, in some cases had a

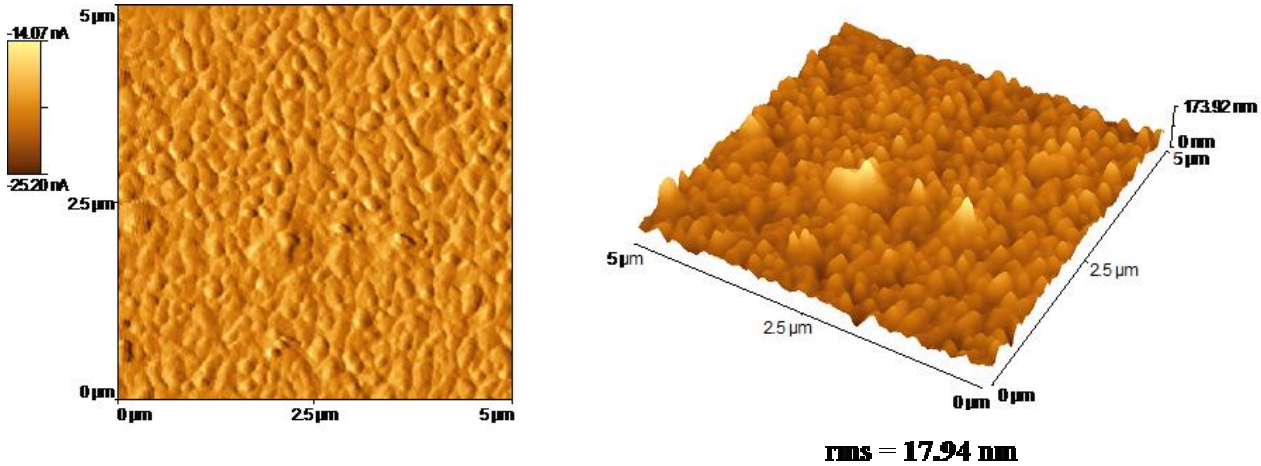


Fig. 5. AFM image of the CdTe surface, polished in a I_2–DMFA–10 vol. % EG solution.

roughness up to 50 nm.

Thus, solutions of iodine in dimethylformamide, modified with ethylene glycol and lactic acid, were characterized by low dissolution rates of the semiconductor material and stability over time. Such etchants were more environmentally friendly compared to other halogen-containing and halogen-emerging solutions, which were traditionally used for surface treatment of $A^{II}B^{VI}$ semiconductor compounds. The elaborated etching compositions can be recommended for chemical-mechanical polishing of the surface of cadmium telluride and its solid solutions in the case when the purpose of processing is the controlled removal of thin layers of material and obtaining a polished surface of high quality.

Conclusions

A series of new compositions of solutions for chemical-mechanical polishing of CdTe, $Cd_{0,9}Zn_{0,1}Te$ and $Cd_{0.95}Mn_{0.05}Te$ has been developed on the basis of the I_2–DMFA etching composition. Solutions modified with ethylene glycol and lactic acids are characterized by low rates of interaction with the semiconductors surface. It was shown that the addition of the organic component into the polishing solution of the I_2–DMFA system can significantly reduce the dissolution rate of the semiconductor while maintaining high quality characteristics of the treated surface. Iodine solutions in dimethylformamide, modified with ethyleneglycol and lactic acid, didn't lose their polishing properties during storage, which indicated their satisfactory technological characteristics. Optimized compositions of etching solutions can be recommended for chemical-mechanical polishing of CdTe and its solid solutions, if it is necessary to remove thin layers of material in a controlled manner, finish processing of wafers and thin films to achieve nanometer roughness of their surface.

Acknowledgement

The authors thank the Ministry of Education and Science of Ukraine for financial support in the framework of project №0121U112421.

Ivanitska V.G. – Candidate of Chemical Sciences, Associate Professor of the Department of General Chemistry and Chemical Materials Science;
Fochuk P.M. - Doctor of Chemical Sciences, Professor of the Department of General Chemistry and Chemical Materials Science.

[1] W. Mönch, Semiconductor Surfaces and Interfaces (Springer Series on Surface Sciences, (Springer Berlin, Heidelberg, 2001); https://doi.org/10.1007/978-3-662-04459-9.

[2] A. Vilan and D. Cahen, Chem. Rev., Chemical Modification of Semiconductor Surfaces for Molecular Electronics 117(5), 4624, (2017); https://doi.org/10.1021/acs.chemrev.6b00746.

[3] R.A. Awni, D.-B. Li, C.R. Grice, Z. Song, M.A. Razooqi, A.B. Phillips, S.S. Bista, P. J. Roland, F.K. Alfadhili, R.J. Ellingson, M.J. Heben, J.V. Li and Y. Yan, Solar RRL, The Effects of Hydrogen Iodide Back Surface Treatment on CdTe Solar Cells 3(3), 1800304 (2019); https://doi.org/10.1002/solr.201800304.

[4] J.M. Kurley, M.G. Panthani, R.W. Crisp, S.U. Nanayakkara, G.F. Pach, M.O. Reese, M.H. Hudson, D.S. Dolzhnikov, V. Tanygin, J.M. Luther, and D.V. Talapin, *Transparent Ohmic Contacts for Solution-Processed, Ultrathin CdTe Solar Cells,* ACS Energy Lett. *2*(1), 270, (2017); https://doi.org/10.1021/acsenergylett.6b00587.

[5] E. Bastola, F.K. Alfadhili, A.B. Phillips, M.J. Heben, R.J. Ellingson, Wet chemical etching of cadmium telluride photovoltaics for enhanced open-circuit voltage, fill factor, and power conversion efficiency, J. Mater. Research 34(34), 3988 (2019); https://doi.org/10.1557/jmr.2019.363.

[6] Z.F. Tomashik, V.G. Ivanitskaya, V.N. Tomashik, P.I. Feichuk, and L.P. Shcherbak, Effect of Surface Orientation on the Chemical Etching of CdTe Single Crystals with Iodine in Dimethylformamide, Russian J. Inorgan. Chem. 50(11), 1651 (2005).

[7] V.G. Ivanits'ka, P. Moravec, J. Franc, V.M. Tomashik, Z.F. Tomashik, K. Masek, P.S. Chukhnenko, P. Hoschl, J. Ulrich, J. Electron. Mater., Chemical Polishing of CdTe and CdZnTe in Iodine–Methanol Etching Solutions 40(8), 1802, (2011); https://doi.org/10.1007/s11664-011-1649-2.

[8] M. Chayka, Z. Tomashyk, V. Tomashyk, G. Malanych, A. Korchovyi, Appl. Nanosci., Formation of nanosized relief on the CdTe single crystals surface by bromine-emerging etchants 12, 603, (2022); https://doi.org/10.1007/s13204-021-01716-8.

В.Г. Іваніцька, П.М. Фочук

Полірування монокристалів CdTe, Cd(Zn)Te, Cd(Mn)Te розчинами йоду у диметилформаміді

Чернівецький національний університет імені Юрія Федьковича, Чернівці, Україна, v.ivanitska@chnu.edu.ua

Вивчено процес хіміко-механічного полірування поверхні CdTe (110), $Cd_{0,9}Zn_{0,1}Te$ (110) та $Cd_{0.95}Mn_{0.05}Te$ (110) травниками на основі розчинів системи I_2–диметилформамід. В якості модифікуючих компонентів використано етиленгліколь та лактатну кислоту. Досліджено залежності швидкостей хіміко-механічного полірування від вмісту етиленгліколю та лактатної кислоти у складі базового розчину, а також визначено технологічну стабільність розроблених травників. Якісні характеристики поверхні встановлені методом атомно-силової мікроскопії та безконтактного профілографічного аналізу. На основі одержаних результатів оптимізовано склади травильних розчинів та технологічні режими проведення хіміко-механічної обробки монокристалів CdTe, $Cd_{0,9}Zn_{0,1}Te$, $Cd_{0.95}Mn_{0.05}Te$. Модифіковані органічним компонентом травники є перспективними для використання у технології напівпровідникових матеріалів у тому випадку, коли основною метою є одержання високоякісної, чистої від забруднень і сторонніх домішок, структурно-досконалої поверхні.

Ключові слова: CdTe, тверді розчини, монокристал, швидкість травлення, хіміко-механічне полірування, диметилформамід, йод.