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# Nanodimensional formations on the CdTe and $Zn_xCd_{1-x}Te$ surfaces at chemical etching

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Aperiodic nanodimensional needle-shaped formations have been shown to appear on the polished surfaces of undoped CdTe and $Cd_{1-x}Zn_xTe$ single crystals at one- and two-stage chemical treatment including consecutive procedures of chemical-mechanical and chemical-dynamic polishing using the optimized polishing etchant compositions $H_2O_2$–HBr-glycol and $H_2O_2$–HBr-lactic acid as well as the appropriate interstage rinsing. The dimensions of these nano-needles vary from 10 to 80 nm, depending on the semiconductor nature, chemical treatment methods and polishing etchant composition.

Показано, что в результате одно- и двустадийной химической обработки поверхности монокристаллов нелегированного CdTe и твердых растворов $Cd_{1-x}Zn_xTe$, которая состоит из последовательных операций химико-механического и химико-динамического полирования оптимизированными полирующими травильными смесями $H_2O_2$–HBr-этиленгликоль и $H_2O_2$–HBr-молочная кислота, а также соответствующих межоперационных промывок, на полированной поверхности формируются непериодические наноразмерные игольчатые образования. В зависимости от природы полупроводника, методов химической обработки и состава полирующих травильных композиций размер наноиголок изменяется в пределах от 10 до 80 нм.

The semiconductor single crystals of cadmium telluride and $Zn_xCd_{1-x}Te$ solid solutions are widely used in the manufacturing of working elements for various modern microelectronics devices. To obtain the high-quality polished surface, of a great importance is the proper selection of etchant compositions being used at intermediate stages of abrasive-chemical treatment for chemical-mechanical and chemical-dynamic polishing. Bromine-containing mixtures are most often used for chemical treatment of the II–VI semiconductor surfaces [1, 2]. In most cases, the polishing action of the etchant composition is intensified as the solution viscosity increases. This could be explained by decreasing etching rate due to slowed elimination of the dissolution products and arrival of the fresh etchant portions to the crystal/solution interface. Therefore, it is expedient to use glycol and lactic acid in the etchant compositions based on $H_2O_2$–HBr. These solvents increase somewhat the viscosity of the etchant compositions thus resulting in decrease of the semiconductor material dissolution rate in such solutions, increase of the polishing solution regions as well as in the surface quality improvement after the etching.

The chemical-dynamic polishing of undoped and doped CdTe and $Zn_xCd_{1-x}Te$ solid solutions with the etchant compositions $H_2O_2$–HBr-glycol is described in [3, 4] where the concentration ranges of polishing solutions have been determined and the etching mechanism investigated. It has been established that the etching rates of the above-mentioned single crystals in such solutions are relatively low ($0.3 \le \upsilon \le 20$ μm/min), and the dissolution in the polishing solutions proceeds according to diffusion mechanism. As the zinc content in the $Zn_xCd_{1-x}Te$ solid solutions increases, an insignificant etching rate increase occurs, but the concentration ranges of the polishing solutions do not change essentially [4]. The investigations of the chemical-mechanical and chemical-dynamic polishing of the single crystals of undoped and doped CdTe and $Zn_xCd_{1-x}Te$ solid solutions with the $H_2O_2$–HBr–$C_3H_6O_3$ etchant compositions have shown that the polishing solutions occupy almost the whole studied concentration range and the etching rate is 1.0–16.8 μm/min for CdTe, 1.0–17.8 μm/min for $Zn_{0.04}Cd_{0.96}Te$ and 2.3–22.5 μm/min for $Zn_{0.2}Cd_{0.8}Te$ [5, 6]. The goal of this work is to study the single crystal surfaces of undoped CdTe and $Zn_xCd_{1-x}Te$ solid solutions treated with the $H_2O_2$–HBr–glycol and $H_2O_2$–HBr–$C_3H_6O_3$ polishing etching compositions.

The etchant compositions based on aqueous solutions of $H_2O_2$–HBr–$C_3H_6O_3$ and $H_2O_2$–HBr–glycol systems optimized by us before [3–6] were used for the chemical polishing of CdTe and $Cd_{1-x}Zn_xTe$ solid solutions. The surface treatment was realized under reproducible hydrodynamic conditions at 290–295 K and the disc rotation speed of the 86 $min^{-1}$. The chemical-dynamic polishing setup was used for these experiments. The investigations were carried out using the 1.5–2 mm thick single crystal plates of about 0.5 $cm^2$ area cut out of the [110] oriented p-CdTe ingots, as well as of $Cd_{0.96}Zn_{0.04}Te$ and $Cd_{0.8}Zn_{0.2}Te$ solid solutions. 40 % HBr (special purity grade), 35 % $H_2O_2$, 80 % lactic acid and glycol (all reagents chemical purity grade) were used to prepare the etching compositions. All solutions were aged before the etching during two hours till the full stopping of the gassing due to the reaction between the initial etchant components: $H_2O_2 + 2HBr = Br_2 + 2H_2O$.

The samples were glued by the nonworking side to quartz substrates and placed into the Teflon holder of the chemical-dynamic polishing unit. Before the etching, the damaged layer of 50 to 100 μm thickness was removed from the plate surfaces previously grounded and mechanically polished, using the same etchant composition in which the next studies were carried out. The chemical-mechanical polishing of the semiconductors was realized onto the cover by a cambric tissue glass polishing pad. The etching polishing solution was supplied at a controlled rate. After the chemical-mechanical and chemical-dynamic polishing, the samples were rinsed with 0.01 M $Na_2S_2O_3$ solution, water, isopropanol, and methanol. A 3D Surface Profiler NewView 5022S at 1500× magnification was used to obtain the surface image in white light, examine its microstructure and measure its roughness after some proposed variants of the chemical treatments at various technological regimes.

As a result of the experimental studies, it has been determined that the microstructure of the CdTe and $Zn_{0.04}Cd_{0.96}Te$ and $Zn_{0.2}Cd_{0.8}Te$ solid solutions surfaces treated using the developed technological procedures are characterized by high quality and high luster. The roughness ($R_z$) does not exceed 0.05 μm, thus meeting the requirements to the surface preparation in the manufacturing of various semiconductor devices. However, a more detailed study of the formed polished CdTe and $Zn_xCd_{1-x}Te$ surfaces has shown that in most cases, the polished surfaces are not perfectly smooth.

In Fig., shown are the surface microstructure of the $Zn_{0.04}Cd_{0.96}Te$ solid solution after two-stage treatment, including chemical-mechanical and chemical-dynamic polishing with the $H_2O_2$–HBr–glycol polishing etchant compositions (a, b, c), as well as similar pictures for nominally undoped CdTe (110) polished the $H_2O_2$–HBr–$C_3H_6O_3$ polishing etchant composition (d, e) and for $Zn_{0.2}Cd_{0.8}Te$ solid solution (f) after the corresponding interstage rinsing. It is evident that the obtained CdTe, $Zn_{0.04}Cd_{0.96}Te$ and $Zn_{0.2}Cd_{0.8}Te$ surfaces are characterized by a high luster and high polishing quality. However, aperiodic nano-sized needle-shaped formations are revealed on the polished surfaces, which appeared in the course of chemical polishing. The size of these nanoneedles varies between 10 and 80 nm, depending from the semiconductor, chemical treatment methods and the polishing etching composition. It follows from the surface roughness analyze that the arithmetic average profile deviation $R_a$ for the undoped CdTe and $Cd_{1-x}Zn_xTe$ solid solutions single crystals after the chemical two-stage treatment, including chemical-mechanical and chemical-dynamic polishing with the $H_2O_2$–HBr–glycol and $H_2O_2$–HBr–$C_3H_6O_3$ polishing etching compositions, varies within limits of 11 to 30 nm, and the inregularity profile height is of 8 to 50 nm.

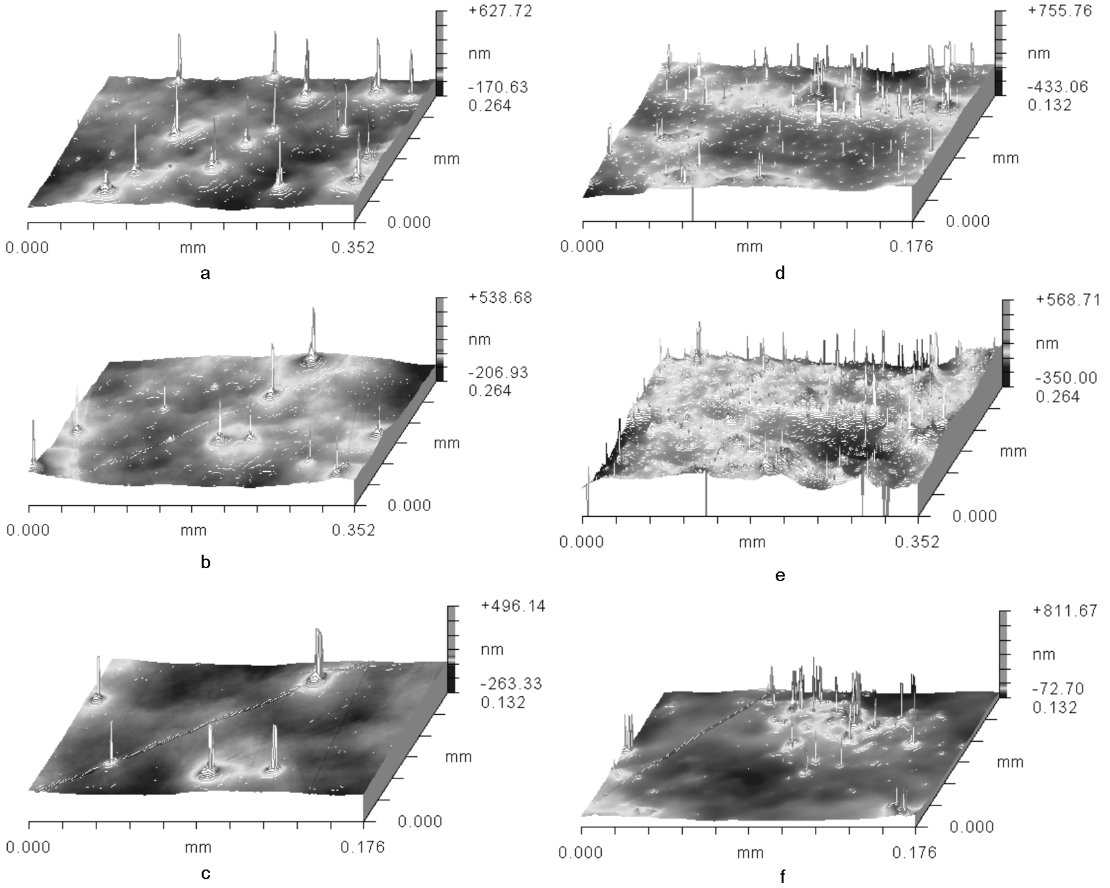

Fig. Surface microstructure after treatment with polishing etchant compositions: $H_2O_2$–HBr–glycol for $Zn_{0.04}Cd_{0.96}Te$ (a, b, c) and $H_2O_2$–HBr–$C_3H_6O_3$ for CdTe (d, e) and $Zn_{0.2}Cd_{0.8}Te$ (f).

The phase and elementary compositions of such needle-shaped formations have not been studied in this work. However, it is possible to suppose that these formations must be enriched in tellurium, since the cadmium telluride dissolution in the acid solvents is limited, as a rule, by the dissolution of tellurium sublattice [7]. Obviously, such aperiodic nanosized needle-shaped formations could appear also in the course of chemical surface polishing of other semiconductors. This should be taken into account at the chemical polishing, since their presence could influence the physical properties of the formed metal/semiconductor contacts and at the manufacturing of the device working elements.

Thus, aperiodic nanosized needle-shaped formations have been revealed on surfaces of CdTe and $Cd_{1-x}Zn_xTe$ solid solutions treated by chemical surface polishing using two-stage method including chemical-mechanical and chemical-dynamic polishing with $H_2O_2$–HBr–glycol and $H_2O_2$–HBr–$C_3H_6O_3$ etching compositions. Taking into account the miniaturization of the modern semiconductor devices, such nanosized needle-shaped formations could influence the physical properties of the working elements in such devices.

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# Нанорозмірні утворення на поверхнях CdTe та $Zn_xCd_{1-x}Te$ при хімічному травленні

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Показано, що в результаті одно- і двостадійної хімічної обробки поверхні монокристалів нелегованого CdTe та твердих розчинів $Cd_{1-x}Zn_xTe$, яка складається із послідовних операцій хіміко-механічного та хіміко-динамічного полірування оптимізованими полірувальними травильними сумішами $H_2O_2$–HBr–етиленгліколь та $H_2O_2$–HBr-молочна кислота ($C_3H_6O_3$), а також відповідних міжопераційних промивок, на полірованій поверхні формуються неперіодичні нанорозмірні голчасті утворення. В залежності від природи напівпровідника, методів хімічної обробки та складу полірувальних травильних композицій розмір наноголок варіює у межах від 10 до 80 нм.