Study of cadmium-zinc-tellurium crystals growing processes and substrates manufacturing on their base

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Presented are the research results of cadmium-zinc-tellurium crystals no less than 60 mm in diameter growing by vertical Bridgman method (VBM) under conditions of spontaneous melt crystallization at the initial stage of a solid phase formation. It has been established that discontinuity of protective coating on an ampoule internal surface leads to a drop in the single-crystal wafers yield. Use of a glass-carbon tube for eliminating melt contacts with quartz walls of the ampoule has allowed to improve structural perfection of the grown crystals. Defined are the processes realization conditions which can guarantee obtaining of ingots with a volume of monocrystalline area, suitable for manufacturing substrates with the surface orientation parallel to crystallographic planes (111) and (211) no less than 50 mm in diameter with homogeneous distribution of dislocations and of density no more than $8\cdot10^4$ cm^{-2}, without low-angle boundaries. Values of optical transmission coefficient in a spectral range from 2.5 to 20 µm comprise no less than 60%. There was fulfilled an optimization of substrate plates mechanical polishing modes for different choices of polishing pad material with the use of suspensions based on aluminium, ceric and silicon oxides of diverse grain. The best results have been achieved in case of suspensions based on aluminium oxide. Surface roughness of substrate plates, estimated by an arithmetical mean deviation of a profile (R_a) is of the order of 4.5 nm for Al_2O_3 with a 0.05-µm grain and of 6 nm for Al_2O_3 with a 0.3-µm grain, while an average scratch depth doesn't exceed 18 and 40 nm, respectively. Deviation from flatness of profile of substrate plates up to 50 mm in diameter comes to ~0.5 µm after mechanical and the subsequent chemical mechanical polishing. Examination of surface areas of the plates by infrared microscopy has revealed a complete elimination of damages caused by mechanical polishing after stripping of 10–15 µm by chemical mechanical method.

Key words: cadmium-zinc-tellurium, vertical Bridgman method, spontaneous crystallization, substrate, mechanical polishing.

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Introduction

The cadmium-zinc-tellurium ($Cd_{1-y}Zn_yTe$) solid solutions are of considerable use as a substrate material for epitaxial growing photosensitive cadmium-mercury-tellurium ($Cd_xHg_{1-x}Te$) layers, which are the main material for producing modern photodetectors of infrared (IR) spectrum range [1, 2]. In making focal plane arrays with a great number of elements and minimal number of defective pixels, required are the heterostructures of large areas with high structural perfection of layers and specified geometrics, which in most cases are determined by structural perfection and finish quality of the substrate material surface. In producing $Cd_xHg_{1-x}Te$ focal plane arrays with light-struck on underside, one of the most important parameter is the value of $Cd_{1-y}Zn_yTe$ optical transmission coefficient within the range of 2.5–20.0 µm, which should be more than 55% at room temperature.

The main method of growing $Cd_{1-y}Zn_yTe$ crystals are several varieties of the vertical oriented crystallization method in Bridgman configuration without seeding, that is in conditions of spontaneous melt crystallization [3–5]. At the same time, such structural defects as grain boundaries, twinning boundaries and dislocations are forming during the crystal growing process, limiting dimensions of monocrystalline areas in the ingot, suitable for substrates

production. Formation of defective structure of crystals is connected both with peculiarities of the melt solidification under conditions of its spontaneous crystallization at the start time, and with interaction between solid phase and walls of growing container.

Structural perfection of crystals is a necessary but by no means sufficient condition for making high-quality substrates for carrying out epitaxial processes. State of substrate surfaces determine in many respects growth mechanisms of epitaxial layers as well as conditions of forming structural defects in them [6, 7]. Therefore, their flank finish (microrelief with minimal roughness, surface finish) and guaranteeing the required plates geometrics (surface flatness and parallelism of wafer sides) are of great importance aside from the structural characteristics of substrates [8]. As a result of escalating requirements for extension of a substrate in addition to a necessity of increasing dimensions and monocrystalline part in the grown crystals, the need to make alterations into substrate manufacturing operations is also arising. First of all, this relates to mechanical polishing (MP) of plates, the main task of which is ensuring the required flatness of plates over the whole area and minimizing of defects introduced by previous treatments, as well as the surface preparing to a final chemical mechanical polishing (CMP).

The task of this paper is investigating the $Cd_{1-y}Zn_yTe$ ($y = 0.03 - 0.04$) crystals no less than 60 mm in diameter growing conditions and development of procedure, which can guarantee an increase of monocrystalline part on decreasing density of extended defects, obtaining plates with diameter of working area no less than 50 mm without low-angle boundaries and with dislocations density no more than $1.0 \cdot 10^5$ cm^{-2}, as well as optimizing MP modes, study on profiles of substrate surfaces after MP operation, estimating surface roughness parameters and minimizing damages, introduced to the surface areas during MP.

Experiment procedure

The $Cd_{1-y}Zn_yTe$ crystals growth has been realized by vertical Bridgman method in a sealed quartz ampoule under conditions of non-saturated cadmium vapor pressure. To avoid the melt contacts with quartz on the interior surface of the growing ampoule, a protective silicon-carbon coating has been formed [9]. Polycrystalline bulk synthesis has been carried out by direct alloying of cadmium, zinc and tellurium with purity of 6–7 N, whereupon the ampoule has been evacuated up to the residual gases pressure of no more than $1 \cdot 10^{-5}$ Pa and sealed. Starting polycrystalline bulk synthesis and crystal growing has been fulfilled in the same quartz ampoule. Fixed melt composition in the course of synthesis and growing process has been supported by making non-saturated cadmium vapor pressure in an unconfined space, for which purpose excess cadmium relative to a stoichiometric ratio has been fed into container at the loading stage [10]. An excess cadmium charge has been calculated in accordance with the Mendeleev – Clapeyron equation; the cadmium-zinc-tellurium melt crystallization temperature has been set equal to 1098 °C; cadmium vapor pressure has been specified within the range of $0.65–0.7 \cdot 10^{-5}$ Pa. Deviation from a stoichiometric ratio has been varied, on basis of the phase diagram data [10], in the range from $1 \cdot 10^{-4}$ cadmium atomic fraction to $5 \cdot 10^{-3}$ excess tellurium atomic fraction.

In order to provide a local melt-quartz contact area, in the bottom part of the ampoule a hole with diameter of 3–5 mm is made in protective coating for the melt supercooling value decreasing at the starting point of crystallization [11]. At that, melt solidification at initial stage of the VBM process took place under conditions of spontaneous crystallization.

During VBM, container with synthesized starting bulk has been placed into isothermal zone, heated up to complete melting and held for 2–3 h. The melt overheating value exceeded a liquidus temperature has not been more than 10 degrees. Monitoring thermocouple has been attached to the bottom of container. The presented in Fig. 1 cooling curve has been drawn in accordance with continuously logged indications of the monitoring thermocouple.

At the initial stage of crystallization bottom of container has been cooled at the rate of 1–5 deg/h until a temperature excursion registration by the monitoring thermocouple on the bottom of container, which corresponds with a calorific effect of the melt crystallization. Temperature difference between liquidus and bottom end of container at the moment of recording a calorific effect of the melt crystallization has been taken as a melt supercooling value. As a rule, supercooling value is a random one and isn't reproducible from process to process. With a supercooling value more than 5 degrees, crystallization rate can reach values at which multiple grain boundaries, "growing" twins, pores and cracks formation in the volume of resulting solid phase is possible. Experimentally it is established that the optimum value of the logged supercooling should not exceed 4–5 degrees.

If there has been logged the melt supercooling value of more than 5 degrees, container with a resulting two-phase mixture has been heated for the purpose of the charge

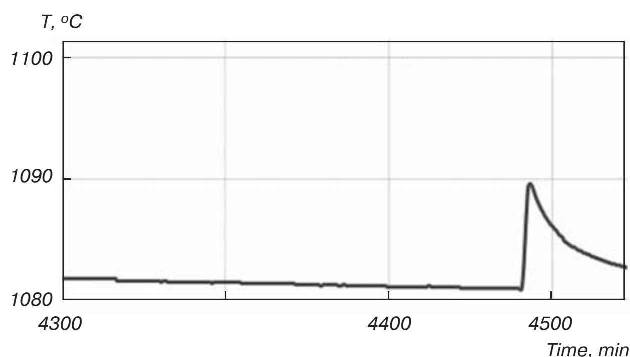


Fig. 1. Fragment of thermogram of the $Cd_{1-y}Zn_yTe$ crystal VBM growing process

repeated meltdown, then held in isothermal conditions and again cooled with the previous rate of temperature changes. In the overwhelming majority of cases such a repeated procedure had provided the optimum melt supercooling values.

With the VBM process completed, the grown ingot annealing has been implemented for no less than 24 h, during which the solid phase composition is set to a definite index within the homogeneity area limits with the object of achieving the desired electrophysical and optical characteristics. Next has been followed the ingot cooling with a 45–50 deg/h rate until the temperature of 450–500 ^{o}C and then the cooling has taken place in the mode of natural cooling down of a heat block of the unit.

Plates with the surface crystallographic orientation (111) and (211) have been cut out of monocrystalline parts of the grown crystals and given the two-sided polishing by aluminium oxide powder with a 10-μm grain. MP of the plates has been carried out on a Logitech LP50 (UK) grinding and polishing unit. As a pad plan there has been used a glass disk on which the following polishing clothes has been glued: VerduTex (Buehler, Germany) silk polishing cloth of medium harshness and Veltex (Buehler, Germany) soft synthetic cloth with short nap. Speed of disk rotation has amounted to 60–70 rpm. Samples have been glued on a plane-sided glass face-plate, which has been held in a special holder by vacuum pencil. Nanodispersed aqueous suspensions based on ceric oxide (Buehler, Germany) and silicon oxide (Alfa Aesar, UK), aqueous suspensions based on aluminium oxide (Buehler, Germany) of various grains (0.3 and 0.05 μm) have been used as abrasives. CMP has been carried out on a Multipol-1 (USA) retrofitted machine tool with feeding pickling solution based on bromine, hydrobromic acid and glycol. Measuring roughness of substrates surface and scratch depth as well as checking geometrics has been implemented on a Sensofar PLμ 2300 (Spain) non-contact optical profilometer, which combines confocal and interferometric measurement techniques. Examination of near-surface layers of the $Cd_{1-y}Zn_yTe$ substrates after MP and CMP has been conducted on an Olympus BX 51 (Japan) infrared microscope in the mode of transmitted light with the wave-length working range from 0.75 to 1.20 μm. Structural perfection has been investigated by selective etching on oriented $Cd_{1-y}Zn_yTe$ plates on a (111)A plane in the mixture of hydrofluoric acid and 50% aqueous solution of chromium (VI) oxide in the ratio 2:3 by volume [12] with the consequent measuring density of dislocations. Spectra of optical transmission have been registered at room temperature on a Tensor 27 (Bruker, Germany) Fourier-transform spectrometer within the spectral range from диапазоне 2.5 to 20.0 μm.

Results and discussion

Under conditions of the melt spontaneous crystallization on the walls of a growing container, dimensions and number of nucleating centers of a solid are determined by the melt supercooling value. Experimentally was established that in case of the melt — silicon-carbon coating contact, melt supercooling usually amounts from 10 to 15 degrees and can achieve 40 degrees depending on a system cooling rate. A hole with diameter of 3–5 mm in protective coating of the bottom part introduced to the growing ampoule design makes a local area of melt-quartz contact, for which the maximum cooling value rarely exceeds 5 degrees [13]. That allowed to control an initial stage of melt solidification and to affect the number and dimensions of the forming grains of a solid phase. At the same time, research of structural perfection of the crystals grown in ampoules with protective silicon-carbon coating has showed that defect structure of crystals considerably depends on the state of surface and integrity of protective film of the ampoule sidewalls. In the absence of surface damages on the coating before the growing process, then after that, in a number of cases, gaps of size from 20 to 50 μm on the coating surface have appeared [14]. At points of a protective coating uniformity defects, quartz has been wet by melt and crystallized ingot has adhered to internal wall of the ampoule. Resulting significant additional stresses have been accompanied by high level of defects in the crystal, which essentially reduce the yield percentage of monocrystalline plates.

In order to reduce defects of the crystal structure, the “melt – protective coating of an ampoule sidewall” contact has been replaced by the “melt – glass-carbon” one. For that purpose, as before, a protective silicon-carbon coating has been applied over internal face of the quartz ampoule, and a hole with diameter of 3–5 mm has been formed at the bottom. Then a glass-carbon tube has been placed into the ampoule and a quartz cover with pipe has been welded on for evacuating and following sealing-in of container. Using such a construction has allowed to surely isolate the melt from quartz sidewall and at the same time to control the melt supercooling at the initial stage of a solid phase formation.

Grown samples of $Cd_{1-y}Zn_yTe$ crystals have been investigated with the goal of studying structural and optical properties, which define their further suitability for substrates manufacturing. Density of dislocations in crystals has been controlled by pattern of selective etching of plates cut in parallel to crystallographic plane (111). Nature of the etching pits allocation is pictures Fig. 2, *a*. Density of dislocations in the grown crystals didn’t exceed $8\cdot10^4$ cm^{-2}. Typical spectrum of the optical transmitting of plates cut from the obtained ingots is shown in Fig. 2, *b*. The measured values of the optical transmission coefficient in a spectral range from 2.5 μm (4000 cm^{-1}) to 20 μm (500 cm^{-1}) have come to an amount no less than 60%.

Quality of MP, namely flatness of plates and morphology of their surfaces is affected by great number of factors, such as: speed of rotation of plan pad and plates under polishing; load on plates; suspension composition and speed of its feed; type of a pad material. In the present paper, a

research has been carried out to select an optimum combination of expendable components: an abrasive of polishing powder and pad material for MP of $Cd_{1-y}Zn_yTe$ substrate wafers, all other factors being the same. Quality of MP of the plates has been estimated by the following parameters: an arithmetical mean deviation of a profile (R_a), a root mean square (rms), depth of single scratches as well as rates of material removal. Results of the study are represented in the Table.

At mechanical polishing of $Cd_{1-y}Zn_yTe$ plates by a suspension based on a CeO_2 nanodispersed powder, chaotically located hollows of depth up to 300 nm and of diameter up to 50 µm are appearing on the surface. Polishing of plates by a SiO_2-based nanodispersed suspension, in spite of low R_a values, cause an appearance of single scratches of depth up to 250 nm, which to all appearances results from their coagulation to larger formations in the polishing suspension. During the research process it has been also revealed that the Veltex cloth is partly abrading after a few polishing operations, bringing to a nap height nonuniformity over area of the pad and to deterioration of surface flatness, namely to slopes of peripheral face of substrates occurance. Thus, the best results of $Cd_{1-y}Zn_yTe$ plates mechanical polishing have been

The mechanical polishing of plates investigation results

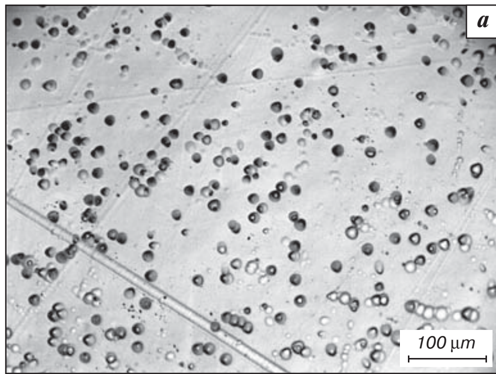
Polishing pad material and abrasive	R_a, nm	rms, nm	Average depth of scratches, nm	Removal rate, µm/min
VelTex, Al_2O_3 (0.05 µm)	3.5	4.5	12.5	1
VelTex, Al_2O_3 (0.3 µm)	3.3	4.2	17	2
VerduTex, Al_2O_3 (0.05 µm)	4.5	5.8	18	2
VerduTex, Al_2O_3 (0.3 µm)	6.0	8.0	40	4
VerduTex, CeO_2	10.0	13.5	52	<1
VerduTex, SiO_2	3.4	4.5	250	<0.5

achieved with the use of VerduTex cloth and Al_2O_3-based polishing suspensions. Removal rates when using polishing suspensions with grain of 0.05 and 0.30 µm differ by a factor of 2, as also is the depth of the nascent surface scratches. However, the following chemical mechanical treatment didn't reveal the essential differences in quality of obtained surface, which allow to choose a 0.3-µm grain suspension owing to the higher rates of material removal.

In Fig. 3 is shown a typical profile of substrate wafers after MP stage with the used of VerduTex cloth and an Al_2O_3-based polishing suspension with a 0.3-µm grain, at that an average deviation from flatness of profile of substrate plates up to 50 mm in diameter comes to ~0.5 µm.

In Fig. 4 are given the typical surface images of $Cd_{1-y}Zn_yTe$ plates (optical image, surface topogram and one of the profiles) after MP with the use of VerduTex cloth and an Al_2O_3-based polishing suspension with a 0.3-µm grain.

In order to estimate defects introduced by MP and to define a durability of the consequent CMP treatment for their complete elimination, studies on determining thickness of a layer disrupted by MP have been



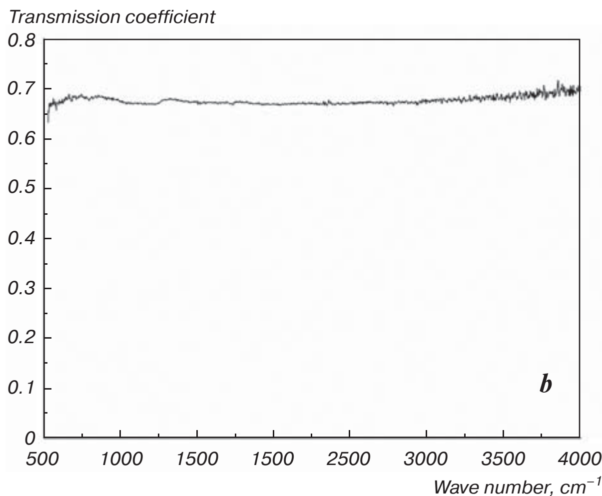


Fig. 2. Etching pits on the $Cd_{1-y}Zn_yTe$ (111) plate surface (*a*) and typical spectrum of the $Cd_{1-y}Zn_yTe$ wafer optical transmission (*b*)

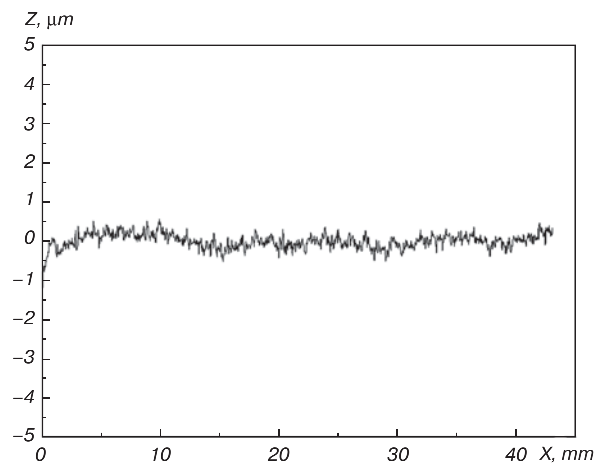


Fig. 3. Typical profile of $Cd_{1-y}Zn_yTe$ substrate wafers after MP

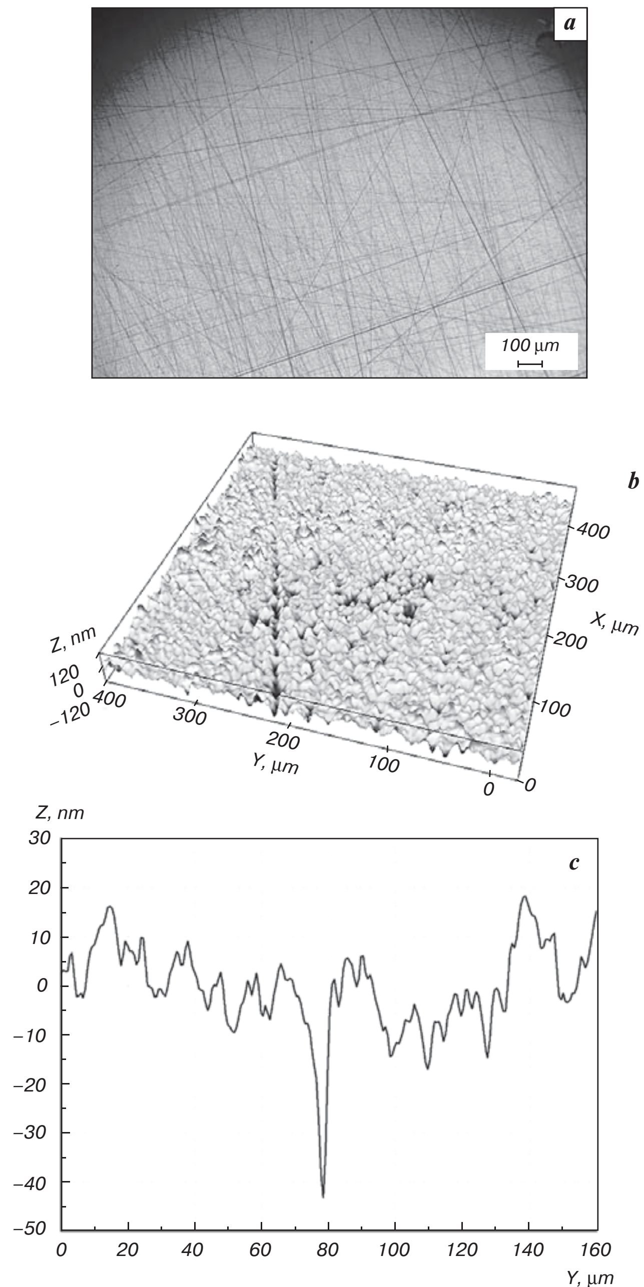


Fig. 4. The $Cd_{1-y}Zn_yTe$ wafers after mechanical polishing:
a — optical image of a plate surface fragment; *b* — topogram of a plate surface fragment; *c* — profile of a scratch

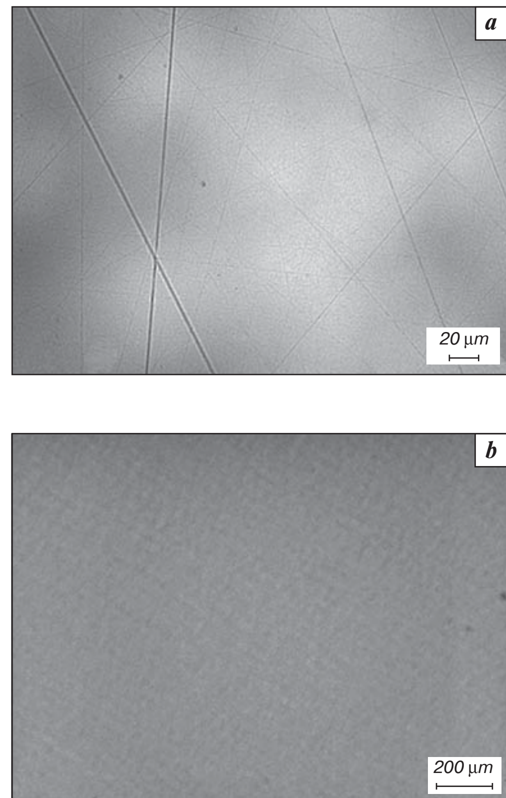


Fig. 5. Image of a $Cd_{1-y}Zn_yTe$ wafer surface observed in the IR microscope:
a — after MP; *b* — after the subsequent CMP

fulfilled by a layer by layer etching of plates, which have shown that size of the disrupted layer has amounted to ~10–15 µm.

State examination of the near-surface layers of the $Cd_{1-y}Zn_yTe$ substrates after MP has been conducted by IR-microscopy technique which is based on the difference in infrared emission absorption by defective areas of material and their surrounding matrix and which allows to examine internal structure of plates. Traces of MP treatment can be observed on the surface of plates in the form of dark stripes when studying the near-surface area. Fig. 5 contains images of the same are of a $Cd_{1-y}Zn_yTe$ plate surface observed in an IR microscope after MP (Fig. 5, *a*) and after the subsequent removal of 10 µm from the surface by CMP method (Fig. 5, *b*). It is shown that all the defects introduced by MP can be eliminated by removal of 10–15 µm from the surface by CMP method.

Conclusion

Growing process for $Cd_{1-y}Zn_yTe$ *crystals no less than 60 mm in diameter has been developed and optimized. Design of a quartz container with insert of glass-carbon tube has been developed and tested. Selected are technological modes which guarantee growing of ingots with a monocrystalline area suitable for allocating plates with orientation parallel to (111) and (211) plane and with diameter of working area no less than 50 mm. Metallographic research points out to the absence of cellular substructures and high uniformity of dislocation etching pits distribution throughout the surface of obtained plates. Density of dislocations in the grown crystals doesn't exceed* $8\cdot10^4$ cm^{-2}. *Measured values of an optical transmission coefficient within the spectral range from 2.5 to 20* µm *for the plates cut from obtained ingots has came to an amount not less than 60%.*

Research of $Cd_{1-y}Zn_yTe$ *substrate wafers mechanical polishing has been carried out. The best results have been achieved in case of using a VerduTex cloth and* Al_2O_3*-based polishing suspensions of various grains (0.30 and 0.05* µm*).*

Surface roughness of substrate wafers, estimated by an arithmetical mean deviation of a profile (R_a), is of the order of 4.5 nm for Al_2O_3 (0.05 μm) and of 6 nm for Al_2O_3 (0.3 μm), while an average scratch depth doesn't exceed 18 and 40 nm, respectively. Removal rates on application of polishing suspensions with grains of 0.05 and 0.3 μm differ by a factor of 2, as also is the depth of the nascent surface scratches. The following chemical mechanical treatment didn't reveal the essential differences in quality of obtained surface, which allowed to choose a 0.3-μm grain suspension owing to the higher rates of material removal. It is established that deviation from flatness of profile of substrate plates up to 50 mm in diameter comes to ~0.5 μm after mechanical and the subsequent chemical mechanical polishing. Examination of surface areas of the plates by infrared microscopy has revealed a complete elimination of damages caused by mechanical polishing after stripping of 10—15 μm by chemical mechanical method.

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