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The influence of growing in a hydrogen atmosphere on the micromechanical properties of $Cd_{1-x}Zn_xTe$ single crystals

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The paper investigates the influence of a hydrogen atmosphere during the growth of $Cd_{1-x}Zn_xTe$ (CZT) crystals on their microhardness and fracture resistance. We found that the micro-hardness of crystals grown in hydrogen is higher, compared to samples obtained in an inert environment, which is likely related to better ordering of bonds and a reduction in structural defects density. An increase in fracture resistance was observed along with the increase in micro-hardness, indicating a reduction in the number of defects in the crystal lattice. The identified patterns are explained by the passivation of electrically active defects by hydrogen, which contributes to reducing the number of structural disruptions and restoring covalent bonds in the crystal lattice. The obtained results are important for improving the technologies for growing semiconductor materials for detector purposes with controlled mechanical properties.

Keywords: CdZnTe, crystal growth, hydrogen treatment, micro-hardness, brittleness, hydrogen passivation.

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Introduction

Monocrystals of CdTe and $Cd_{1-x}Zn_xTe$ (CZT) are among the key semiconductor materials that are widely used in high-tech industries. Their unique electronic and optical properties make them promising for the development of solar cells, radiation detectors, laser devices, and sensor systems. In the context of increasing demand for efficient and environmentally safe materials, research and improvement of CdTe and its derivatives acquire strategic significance [1].

CdTe and CZT are widely used in the creation of high-energy X-ray and gamma-ray detectors [2], infrared sensors, and next-generation photonics devices [3-5]. Due to the high atomic mass of Cd and Te, the material effectively absorbs hard radiation, making it ideal for applications in medical diagnostics, non-destructive testing of materials, as well as in research of space [6]. CZT detectors have a high resolution and can operate at room temperatures, giving them an advantage over traditional scintillation detectors. CdTe and its compounds, particularly CdZnTe and HgCdTe, are widely used in laser systems and optoelectronics due to the ability to tune the bandgap, making these materials suitable for operation in the infrared (IR) and visible spectral ranges.

The high operational characteristics of such devices directly depend on the mechanical stability and micromechanical properties of the crystalline material. In work [7], the authors studied thermal stresses at the contact/CZT interface that lead to degradation of mechanical bonding, changes in electrical properties, and a reduction in detector stability. The results presented in work [8] show how qualitative thermo-mechanical surface treatment of CZT affects the sensitivity, stability, and efficiency of X-ray and γ-ray detectors.

The features of crystal growth and the effectiveness of post-growth treatment are largely determined by the mechanical characteristics of the starting materials. In particular, the compound CdTe is characterized by relatively low hardness – 50-60 kg/mm^2 according to Vickers [9, 10], which significantly complicates its mechanical processing. During cutting or polishing, the risk of defects arising increases, which can negatively affect the electronic and optical properties of the material. Additionally, the grown crystals often contain twins or cracks [11], which are caused both by mechanical stresses, especially from the walls of the growth ampoule, and by the difference in thermal expansion coefficients of the

components of CdTe.

One of the methods for reducing defectiveness and improving the properties of $Cd_{1-x}Zn_xTe$ monocrystals is their doping and thermal treatment. Doping CZT monocrystals with various chemical elements enables the controlled alteration of their physical and mechanical properties, including hardness, resistance to plastic deformation, resistance to micro-crack formation, as well as reducing the overall defectiveness of the crystal lattice [12]. Traditionally, directed doping is used to form the material with specified parameters, or post-growth technological operations, such as high-temperature annealing in vapours of the components (Cd or Zn) [13, 14].

In the work [15], the authors investigated the microhardness of CdTe single crystals doped with chlorine and iodine over a wide range of doping concentrations. For CdTe:I crystals, a gradual strengthening was observed with an increasing content of the dopant, whereas for CdTe:Cl crystals, the concentration dependence of hardness exhibited non-monotonic behaviour. The authors explain the dependence of hardness on the doping level considering the model of heavily doped inhomogeneous semiconductors, as well as the limited solubility of the dopant in CdTe. A correlation was found between the values of microhardness, defect structure (dislocation density, second phase precipitation), and optical transparency of CdTe crystals doped with halogens.

Another way to improve the properties of CZT single crystals is hydrogen treatment, which can be technologically implemented through hydrogen implantation or by processing the crystal in a gas discharge of a hydrogen atmosphere [16, 17]. However, the mechanisms of the influence of the hydrogen atmosphere on the micromechanical behaviour of single crystals remain insufficiently studied, highlighting the need for such research.

I. Experimental part

This work presents the results of a study on the micromechanical properties of CdZnTe monocrystals with 10% Zn content, which were grown by sublimation in a hydrogen atmosphere [18], compared to similar crystals grown in a vacuum.

The crystals were grown in a hydrogen atmosphere in quartz ampoules, which were filled with charge material to about two-thirds of their volume. Before loading the charge, the ampoules were rinsed with a mixture of hydrochloric and nitric acids, and then rinsed several times with distilled water. The supply of hydrogen into the ampoule was carried out simultaneously with the evacuation of air by a fore vacuum pump to a pressure of approximately 10^{-3} Torr. That is, after creating a vacuum in the ampoule to the specified level, hydrogen was introduced into it. The cycle of evacuation and hydrogen introduction was repeated three times to purify the atmosphere.

In the process of crystallization, hydrogen prevents oxidation of the initial substance or the surface of the crystals at high temperatures. Additionally, it is able to reduce the content of excess components. In particular, in compounds A2B6 (CdTe, ZnTe, CdZnTe), the formation of tellurium oxide (TeO_2) is possible, which negatively affects the crystal structure. Hydrogen reduces these oxides to elemental tellurium or facilitates their removal from the surface. This, in turn, affects the structural and mechanical properties of the grown single crystals.

The Cd1-xZnxTe monocrystals were grown at a temperature of about 980°C with a growth rate of 0.3-0.4 mm/h. The temperature gradient at the crystallization front was 5°C/cm. Thanks to the low growth rate, energetically favourable conditions for the incorporation of atoms after their adsorption on the crystal faces are ensured.

The process of obtaining monocrystals included two main stages:

– synthesis of the solid solution CdZnTe from the starting components of the given composition and doping;

– direct crystal growth from the gas phase.

Growing from the gas phase leads to a purification effect of the grown ingot, as heavy impurities and components of the crucible materials do not vaporize.

Such separation primarily allows for the selection of conditions to obtain a homogeneous mixture, and at the second stage – to provide conditions for obtaining monocrystals of appropriate sizes, compositions, and with the minimum possible number of structural and linear defects and dislocation density.

For the study of microhardness, we used samples in the form of flat-parallel plates with a thickness of 3-5 mm obtained by chipping from the ingot, which consisted of a single monocrystalline block.

Microhardness measurements were carried out using the Vickers method with loads on the indenter ranging from 5 to 150 g. The duration of load holding in all cases was 15 s.

The micro-hardness value was determined using the formula.

$$H_V = 1{,}8544 \cdot \frac{P}{d_c^2},\ \text{(MPa)} \qquad (1)$$

where P is the load on the indenter (N); d_c is the average value of the diagonal of the imprint (m).

With each load, 10-15 impressions of the indenter were measured and the average value of the diagonal dimensions was determined.

At higher loads, cracks were observed along the diagonals of the impressions on some samples, indicating the brittleness of the material. To assess this, we determined the fracture brittleness coefficient (crack resistance) using the formula [19]:

$$K_c = 0{,}0089 \cdot \left(\frac{E}{H}\right)^{2/5} \cdot \frac{P}{a\sqrt{l}} \cdot \left[MPa \cdot m^{1/2}\right], \qquad (2)$$

where E is the Young's modulus (for CdTe – 52 GPa, ZnTe – 64 GPa), taking into account the percentage content of Zn we will take 53.5 GPa; H is the microhardness according to Vickers; l is the length of the crack; a is half the length of the diagonal of the imprint.

II. Results and their discussion

The results of determining the dependence of the micro-hardness of the studied samples on the load applied to the indenter are presented in Fig. 1. As can be seen, the microhardness of CdZnTe monocrystals grown in a hydrogen atmosphere at an indenter load of 20 g is approximately 930 MPa, which is significantly higher than the microhardness of monocrystals grown in a vacuum, which is 610 MPa. It was also noted that in the latter, microcracks were observed in the indentation area already at indenter loads of 15-20 g, while in the samples of CdZnTe monocrystals grown in a hydrogen atmosphere, such cracks were not observed even at loads of up to 120 g. This indicates that the CdZnTe monocrystals grown in a hydrogen atmosphere have a high crack resistance threshold, which is a positive result in terms of the mechanical stability of structural and functional elements made from them.

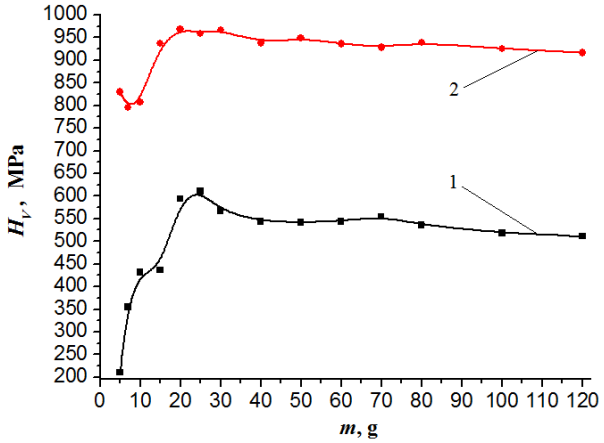

Fig. 1. Microhardness of CdZnTe monocrystals grown by sublimation: 1 – in vacuum; 2 – in hydrogen atmosphere.

Fig. 2 shows a microphotograph of the surface of the sample obtained using a scanning electron microscope, displaying cracks under a load of 100 g on the indenter.

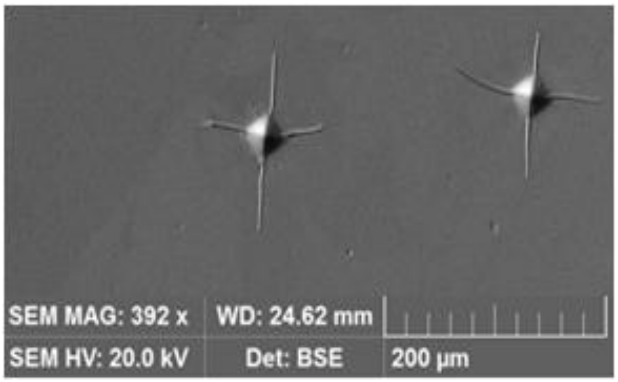

Fig. 2. Microcracks on the output sample of CdZnTe.

Based on the sizes of the diagonal of the imprint and the microcracks using formula (2), the crack resistance coefficient of CdZnTe samples grown in a vacuum was evaluated. Under a load of 100 g, it is approximately 0.39 MPa·$m^{1/2}$.

We will try to explain the behavior of the micromechanical properties of the studied crystals based on the following reasoning. In ordinary metals and ionic crystals, the bond is delocalized and micro-hardness is determined by external factors (the presence of impurities, grain boundaries, etc.). In contrast, in covalent crystals, the chemical bond is localized in electron pairs, and therefore the mechanical microhardness mainly has an internal nature [20-23]. The authors of works [20, 21, 23] argue that in covalent crystals, microhardness is largely determined by their band structure. In particular, in work [21], the microhardness of the covalent crystal is considered as the total resistance exerted by the indenter due to the interatomic bonds, wherein the contribution of each bond is determined by its ability to resist deformation, and their number per unit area is proportional to the concentration of valence electrons. Based on this, the microhardness of covalent crystals can be estimated using the formula:

$$H = A \cdot \left(\frac{N_e}{2}\right)^{2/3} \cdot E_g, \qquad (3)$$

where A is the proportionality coefficient, N_e is the concentration of valence electrons, E_g is double the value of the band gap (the breaking of one bond is equivalent to the transition of two electrons into the conduction band or to an impurity level).

Although the covalent bond dominates in the semiconductor CdZnTe, there is also a certain degree of ionic bonding. In this case, a correction is introduced into formula (3) [21]:

$$H = A \cdot \left(\frac{N_e}{2}\right)^{2/3} \cdot \sqrt{E_{g_0}^2 + C^2}, \qquad (4)$$

where E_{g_0} is the contribution from covalent bonding (for semiconductor group IV $E_{g_0} = E_g$), and C is the contribution to microhardness from ionic bonding.

The semiconductor CdZnTe at room temperature has a rather low concentration of intrinsic charge carriers. Therefore, intrinsic defects play a majorole in the kinetic characteristics of this material. A significant concentration of these defects leads to the breaking of covalent bonds, a decrease in the concentration of valence electrons, and, accordingly, a decrease in microhardness. Treatment of the semiconductor material CdZnTe with hydrogen results in the passivation of electrically active defects, such as Cd and Zn vacancies, which are acceptor centers [16]. Due to the electrostatic interaction of ionized acceptors and hydrogen, neutral complexes are formed, which leads to an increase in the concentration of valence electrons Ne and, accordingly, an increase in the microhardness of the crystal. This result qualitatively aligns with the findings of work [16], which studied the effect of hydrogen treatment on the electrical conductivity of CdZnTe semiconductors. This work shows that the treatment of CdZnTe in a hydrogen atmosphere significantly reduces its electrical conductivity due to the passivation of electrically active centers.

Conclusions

The work investigates the influence of growing $Cd_{1-x}Zn_xTe$ ($x = 0.1$) monocrystals on their micromechanical properties in a hydrogen atmosphere. Based on the analysis of experimental data, it has been established that the crystals obtained under these conditions exhibit significantly higher microhardness compared to similar samples grown in vacuum. In particular, under a load of 20 g, the microhardness of samples from the hydrogen atmosphere reaches approximately 930 MPa, while for vacuum-grown samples, it is only about 610 MPa. Moreover, the crystals obtained in a hydrogen atmosphere showed increased crack resistance: microcracks caused by the indenter were not detected until loads exceeded 120 g, whereas in vacuum-grown samples, they appeared already at 15-20 g. This indicates a reduction in material brittleness and suggests an improvement in its mechanical stability.

The increase in microhardness and crack resistance is likely associated with the passivation of electrically active defects by hydrogen, which contributes to a reduction in the number of structural disturbances and the restoration of covalent bonds in the crystal lattice. This, in turn, leads to an increase in the concentration of valence electrons and an improvement in the micromechanical properties according to the models of the microhardness of covalent crystals.

The obtained results indicate the feasibility of using a hydrogen atmosphere when growing CdZnTe single crystals for the creation of detectors, sensors, and optoelectronic devices that require high mechanical reliability and stability.

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Вплив вирощування в атмосфері водню на мікромеханічні властивості монокристалів $Cd_{1-x}Zn_xTe$

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У статті досліджено вплив атмосфери водню під час вирощування кристалів $Cd_{1-x}Zn_xTe$ (CZT) на їхню мікротвердість і тріщиностійкість. Встановлено, що мікротвердість кристалів, вирощених у водні, є вищою порівняно зі зразками, отриманими в інертному середовищі, що, ймовірно, пов'язано з кращою впорядкованістю зв'язків і зменшенням щільності структурних недосконалостей. Одночасно з підвищенням мікротвердості виявлено зростання тріщиностійкості, що свідчить про зменшення кількості дефектів у кристалічній ґратці. Виявлені закономірності пояснено пасивацією електрично-активних дефектів воднем, що сприяє зменшенню кількості структурних порушень та відновленню ковалентного зв'язку в кристалічній ґратці. Отримані результати є важливими для розробки технологій вирощування напівпровідникових матеріалів детекторного призначення з керованими механічними властивостями.

Ключові слова. CdZnTe, ріст кристалів, воднева обробка, мікротвердість, крихкість, пасивація воднем.