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DETERMINATION OF THE STRUCTURAL STATE AND STABILITY OF THE LASER CRYSTALLIZED $Cd_{1-x}Mn_xTe$ CRYSTAL SURFACE

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Abstract. *The modified surface layers of the $Cd_{1-x}Mn_xTe$ crystals were obtained by the laser recrystallization of the crystal surface with the use of millisecond and nanosecond impulse ruby lasers. The determination and diagnostics of the layer structural state were performed by the study of the electron channeling patterns in the SEM. The AFM studies showed that mechanically stable contact regions within the CdTe crystal – Cu film system can be formed, depending on the laser energy density and beam defocusing. On the base of the ellipsometric studies, it was found that while irradiating the $Cd_{1-x}Mn_xTe$ crystal surface, the refractive index of the oxide film on the modified surface changes depending on the laser beam energy density, which can be interpreted as the formation of the oxides of the different chemical composition.*

Keywords: $Cd_{1-x}Mn_xTe$ crystal, surface, laser, thin film

OKREŚLENIE POSTACI STRUKTURALNEJ ORAZ STABILNOŚCI POWIERZCHNI KRYSZTAŁU $Cd_{1-x}Mn_xTe$ KRYSTALIZOWANEJ LASEREM

Streszczenie. *Zmodyfikowane warstwy wierzchnie kryształów $Cd_{1-x}Mn_xTe$ zostały uzyskane metodą laserowej rekrystalizacji powierzchni kryształu przy wykorzystaniu impulsów milisekundowych i nanosekundowych laserów rubinowych. Określenie i diagnostyka strukturalnej postaci powierzchni zostały wykonane metodą badania struktury kanałów elektronu SEM. Badania AFM wykazały, że mogą zostać wytworzone obszary mechanicznie stabilnego obszaru kontaktowego kryształ CdTe – powłoka Cu, w zależności od skupienia energii laserowej oraz zdekoncentrowania wiązki. Na podstawie pomiarów elipsometrycznych odkryto, że podczas napromieniowywania powierzchni kryształu $Cd_{1-x}Mn_xTe$, wskaźnik refrakcyjny powłoki tlenku na powierzchni zmodyfikowanej ulega zmianie w zależności od skupienia energii wiązki laserowej, co może być interpretowane, jako powstawanie tlenków o różnym składzie chemicznym.*

Słowa kluczowe: kryształ $Cd_{1-x}Mn_xTe$, powierzchnia, laser, cienka powłoka

Introduction

Development and optimization of non-cooled X- and gamma-ray detectors based on the wide band gap $Cd_{1-x}Mn_xTe$ crystals is an important problem of micro- and nanoelectronics [1, 4, 10]. For this purpose, the method of photonic correction of crystallographic and electrophysical characteristics using a laser is used to modify and nanostructure the surface of semiconductors [3, 9]. Laser recrystallization of the $Cd_{1-x}Mn_xTe$ crystal surface with the formation of a laser-modified layer can be used to form active structures and contact places. It is known that the introduction of the Mn atoms into the CdTe crystal stabilizes the $Cd_{1-x}Mn_xTe$ alloy lattice [5, 8]. In this case, the homogeneous and structurally stable alloys are formed with the Mn concentrations up to x = 0.4.

Laser treatment of the $Cd_{1-x}Mn_xTe$ crystals is accompanied by the structural changes in the modified surface layer, which are determined by the laser radiation absorption processes depending on the composition x [2, 6]. When the crystal is transparent for a given laser wavelength, the deposition of a metal film over the surface is very effective for laser melting [2]. An important question here is the degree of structural perfection of the laser-modified layer undergoing the action of the laser irradiation of different intensity and wavelength. The control of the laser recrystallized $Cd_{1-x}Mn_xTe$ crystal surface can be carried out by the scanning atomic force and electron microscopy. Great possibilities of the scanning electron microscopy to determine the structural imperfections of semiconductor crystals are more clearly recognized in the case of the correlation of the electron probe characteristics and the crystal lattice parameters. In the scanning electron microscope at high beam current values and optimal scanning angles, crystal contrast patterns are observed, which contain information about the crystal surface inhomogeneities.

Structure diagnostics of the laser crystallized $Cd_{1-x}Mn_xTe$ crystal surface can be performed by using complex studies in the atomic force and in scanning electron microscopes. The high resolution of the vertical dimensions of the structural imperfections and the statistics in the AFM are complemented by the better lateral resolution in the SEM. It is natural to add the ellipsometric study of the surface films to the AFM and SEM results. Ellipsometry is characterized by the non-destructive action, high sensitivity and a variety of informative features for determination of the optical characteristics and composition of the films [7]. The structural and morphological transformations of the recrystallized surface as a result of the laser treatment are correlated with the change of the ellipsometric parameters. In this paper we propose the method for study the structural state and stability of the modified $Cd_{1-x}Mn_xTe$ crystal surface by using the AFM, SEM and ellipsometric data. The relevance of these studies is related to the search of new opportunities for the development of high-sensitivity radiation sensors based on this material.

1. Research methods

To study the laser modification of the surface, the samples were made in the form of the plates with a thickness ~ (1–1.3 mm) from the CdTe and $Cd_{1-x}Mn_xTe$ crystals grown by the Bridgman method. The final stage of the surface treatment was the polishing on the diamond pastes and washing in benzene and alcohol. The laser treatment of the samples was carried out by a defocused beam of the millisecond optical generator on the ruby (wavelength $\lambda = 0.694$ µm, pulse duration $\tau = 1.2$ ms), as well as using the nanosecond ruby laser (pulse duration $\tau = 70$ ns). The laser radiation was directed to the diaphragm, which selects the most homogeneous part of the beam. By using projection lens, an image of the diaphragm in the form of the laser spot with a diameter ~3–4 mm was formed on the sample. The studies of the morphology and surface structure of the CdTe and $Cd_{1-x}Mn_xTe$ crystals, before and after the laser treatment, were carried out by application of ~~using~~ TESCAN VEGA-3 scanning electron microscope with the EDS block for the microanalysis of the chemical composition. The SEM data on the morphology of the laser-modified epitaxial layers were complemented with the atomic force microscopy studies using the NT-206 setup. The scans were obtained in the contact mode by using the CSC38/AL probe. In the scan area, the number of points per matrix was 256×256, the load on the probe was 10–12 units. The optical characteristics of the films on the CdTe and $Cd_{1-x}Mn_xTe$ crystal surface were determined by using the laser ellipsometer (wavelength $\lambda = 632.8$ nm) with the incidence angle of the beam within 45–85°. The parameters of the surface films were calculated using the model of “a transparent dielectric thin film – an absorbing substrate”.

2. Experimental results and discussion

The processes of laser recrystallization of the $Cd_{1-x}Mn_xTe$ crystal surface were studied using the nanosecond ruby laser with the wavelength $\lambda = 0.694$ µm and pulse duration $\tau = 70$ ns. The laser-induced melting of the crystal surface, followed by the rapid crystallization, leads to the structural transformations in the nonequilibrium $Cd_{1-x}Mn_xTe$ solid phase system. At the same time, within the area of the laser exposure, a variety of defects is generated, some of which can be relaxed, and the rest are fixed in the solid laser-epitaxial layer. The determination and control of the structural imperfections in the $Cd_{1-x}Mn_xTe$ after the laser treatment was performed by the SEM in order to the carried out photonic correction of the recrystallized epitaxial layer properties. It was found that the CdTe and $Cd_{1-x}Mn_xTe$ crystals show structural features that promote observation of the electron channeling pattern in the crystal contrast mode. The pictures of the crossed strips and lines arising during the anomalous absorption of electrons contain information about the state and stability of the crystalline structure of the layers (Fig. 1). The local fields of the thermoelastic stresses and deformations are observed in the form of the curved lines and a number of bands in the visual area of the raster (Fig. 1a).

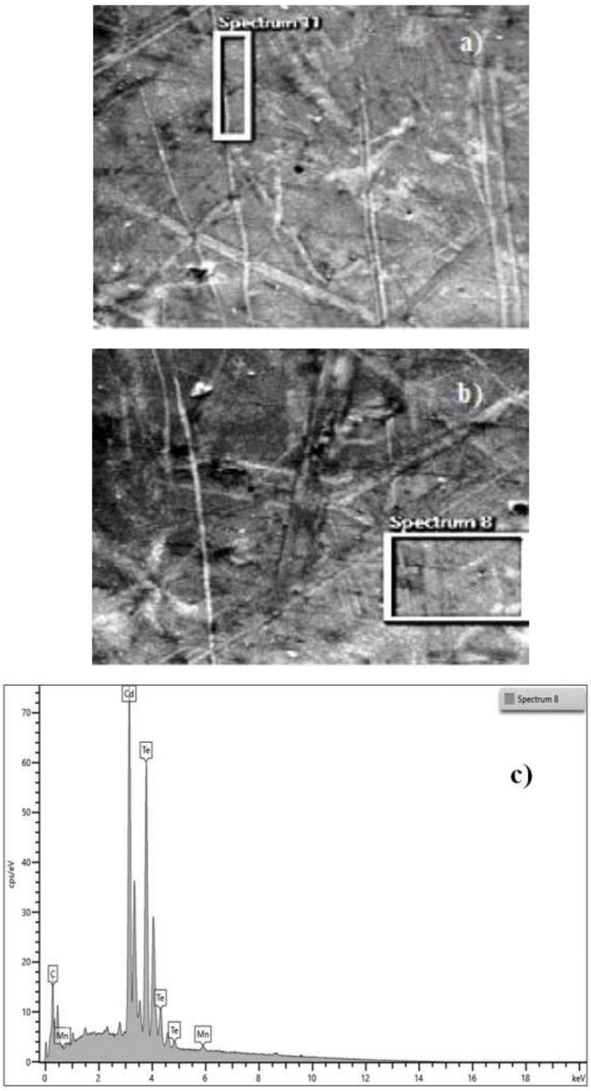

Fig. 1. Electron channeling patterns and EDS spectra (c) in the $Cd_{0.96}Mn_{0.04}Te$ crystals after irradiation by a ruby laser with the energy density: a) E = 0.15 J/cm²; b) E = 0.21 J/cm² (study in SEM)

The optimal modes of the laser treatment made it possible to obtain a better pattern of electron channeling with a large number of straight stripes and lines, which indicates the perfection of the laser epitaxial $Cd_{0.96}Mn_{0.04}Te$ layer (Fig. 1a). It should be noted that the electron channeling patterns for the laser-modified layers do not appear to be as symmetrical and geometrically correct as compared to the bulk single crystals. Further studies of the crystalline contrast on the films and layers, which are significantly non-equilibrium systems, are need to be compared to the single crystals. In our study, the shape of the channeling patterns (typical patterns are presented in Fig. 1) for the $Cd_{1-x}Mn_xTe$ layers was used to determine the optimal laser treatment modes. The EDS chemical composition analysis of the most perfect $Cd_{0.96}Mn_{0.04}Te$ layers showed the accordance of the spectra to the chemical composition of the $Cd_{0.96}Mn_{0.04}Te$ base crystal (Fig. 1c), which indicates that there is no significant evaporation of the components at the optimal laser treatment mode.

The presence of the carbon in the EDS spectrum can be explained by the fact, that on the surface of the base $Cd_{0.96}Mn_{0.04}Te$ crystal after mechanical treatment and washing with organic solvents the organic films remain, which decompose under the action of the laser beam. It is possible to get rid of these residues by the ion-plasma etching of the crystal surface in an argon atmosphere just before laser treatment.

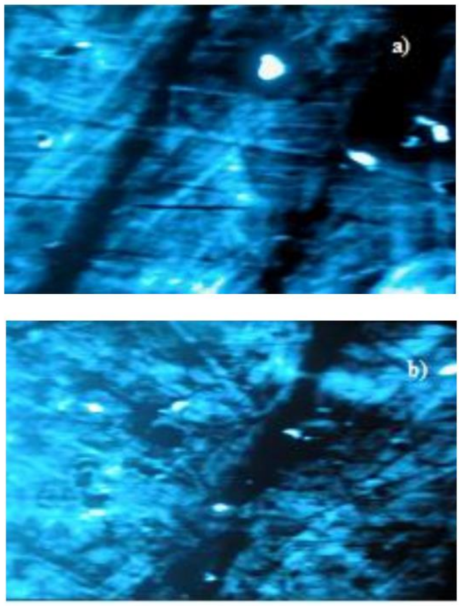

Fig. 2. Electron channeling patterns in the $Cd_{0.9}Mn_{0.1}Te$ crystals after irradiation by a ruby laser with the energy density: a) E = 7 J/cm²; b) E = 12 J/cm² (study in SEM)

We also present the electron channeling patterns of the $Cd_{1-x}Mn_xTe$ ($x = 0.1$–0.45) crystal irradiated by the millisecond ruby laser ($\tau = 1.2$ ms, $\lambda = 0.694$ µm). For the compositions $x \leq 0.2$ the depth of the surface melting, depending on the energy density, is $h = 5$–14 µm. The correlation of the structure perfection of the laser-epitaxial layer with the crystal contrast patterns is observed for the millisecond laser irradiation as well as for the nanosecond laser irradiation (Fig. 2).

For example, the laser-modified $Cd_{0.9}Mn_{0.1}Te$ layer after the irradiation of the laser with the energy density $E = 7$ J/cm² gives a better symmetrical and clear picture of the lines and bands (Fig. 2a) than in the case of more destructive energy $E = 12$ J/cm² (Fig. 2b). In both cases, the inclusions of the light and dark contrast regions, depending on the chemical composition, are detected in the electron channeling pictures (Fig. 2). Accordingly, they can be identified as the inclusions of Te and Cd, since the atomic number contrast in the SEM is brighter for the heavy element and darker for the relatively light element.

We also studied the action of the lased on the CdTe crystals with the Cu films deposited from the $CuSO_4$ salt solutions. The melting of the sample surface and formation of the layers with different morphology are observed within the pulse area at laser treatment. This is a result of the redistribution of the energy between the environment, Cu film and CdTe crystal. It was experimentally found that, depending on the energy density and the corresponding defocusing of the laser beam, the relief and surface structure of the CdTe crystal change in different ways.

The surface presents the concentric angular morphology with the radial step-wave formations at irradiation by the laser beam with the density $E = 15$ J/cm^2 (Fig. 3a). Such morphology can be explained by the geometry of the surface wave dissemination in the liquid phase of the melt, which are formed as closed concentric circles. The wave pattern which is formed in the melt is fixed in the solid film after the crystallization process. The processes of copper ablation are observed at the maximum temperature in the center of the light spot of the laser. This leads to the formation of the craters of unequal shape (Fig. 3a).

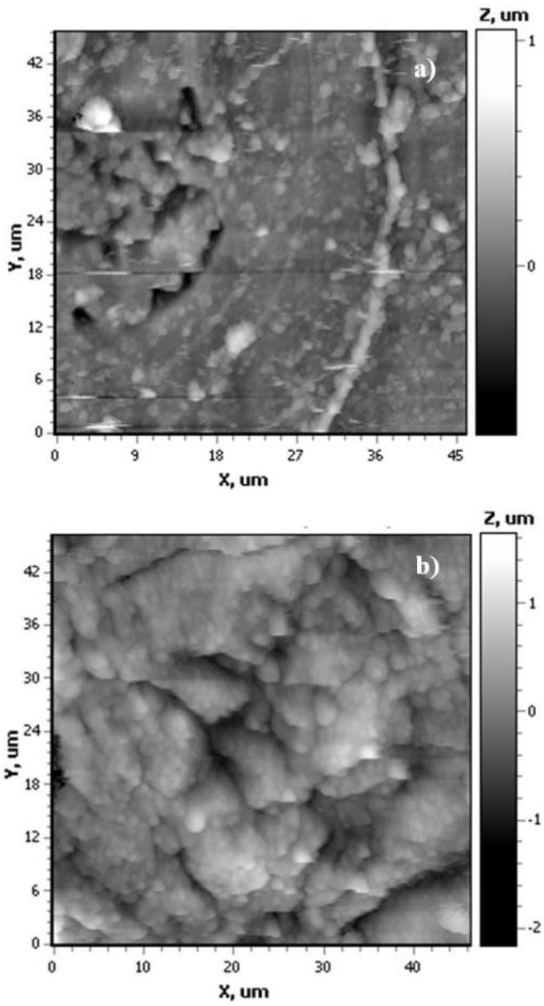

Fig. 3. Morphology of the CdTe crystal surface with the Cu film after the laser irradiation: a) focused beam with the energy density E = 15 J/cm^2 (at the center of the laser spot); b) defocused beam with the energy density E = 9 J/cm^2 (study in AFM)

In the case of the defocused laser beam, the irradiated surface presents humpy morphology (Fig. 3b). Here the Cu film does not contain craters, areas of evaporation of the material, microcracks and other defects. When soldering the electrodes to the regions of the samples with such humpy morphology, good adhesion and hardness at the point of the contact is ensured.

The structure of the grains (crystallites) that formed the Cu film was analyzed. The direction of crystallite growth is determined by the intensity of heat dissipation in the area of the laser spot. The crystallites are preferably in the form of rounded triangles, the size of which decreases slightly from 1–1.3 μm in the middle of the laser spot to 0.5–0.8 μm on the periphery of the laser spot. More elongated crystallites, oriented along the axis of the heat dissipation of the grain, are observed on the periphery of the laser spot. One can visually identify areas of the initial crystallization and recrystallization, which form larger grains, as well as areas of recrystallization with smaller grains of secondary structure. To evaluate the microroughness of the Cu film surface, the parameters R_a and R_q were used, which characterize the surface roughness and are calculated by the AFM software of the NT-206 microscope for each scan image.

In order to diagnose the structural state of the laser-modified $Cd_xMn_{1-x}Te$ crystals, it is necessary to determine the presence of the surface films formed after the crystallization of the molten regions. For this purpose, the ellipsometry method is used, the interpretation of which requires the selection of adequate models of the laser beam reflection process and the simulation of the corresponding nomograms.

To find the solution of the ellipsometric problem for the system consisting of a transparent dielectric thin film on a substrate we applied the graphical-analytical method [7]. The nomograms in the Ψ-Δ ellipsometric parameters were calculated to determine the refractive index of the film and its thickness for the different incidence angles of the laser beam with 632.8 nm wavelength. In Fig. 4, as an example, we present the nomogram calculated for the thin film on the $Cd_xMn_{1-x}Te$ substrate for the incidence angle $\varphi = 50^o$. The solid lines correspond to the constant value of the refractive index of the film and the less bold lines correspond to the constant value of its thickness in nanometers. The input data for the calculations are the refractive index and the absorption coefficient of $Cd_xMn_{1-x}Te$, the wavelength of the radiation, and the refractive index of the environment (air).

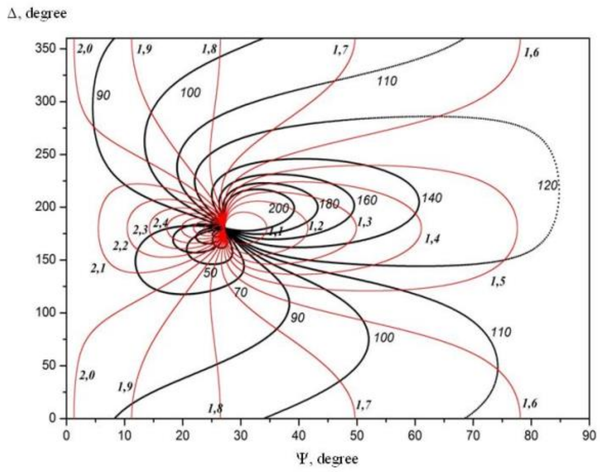

Fig. 4. Calculated nomogram for the determination of the refractive index and thickness of the thin film on the $Cd_xMn_{1-x}Te$ substrate for the incidence angle $\varphi = 50^o$

The refractive index and the thickness of the films were determined using an ellipsometer by measuring the compensation angle of the polarizer and the analyzer at the zero value of the intensity of the reflected laser beam. The main ellipsometric parameters Ψ and Δ were calculated using the experimental values of these angles. It was found that while irradiating the $Cd_{0.9}Mn_{0.1}Te$ surface the different values of the laser beam energy density correspond to the different values of the refractive index of the oxide film on the modified surface (Table 1).

Table 1. The dependence of the refractive index and the corresponding chemical composition of the film on the energy density of the laser

N	Energy density of the laser, J/cm^2	Refractive index	Composition of the film
1	2.5	2.43	CdO
2	5.2	2.45	CdO
3	7.3	2.2	$CdTeO_3$
4	8.4	2.15	$CdTeO_3$
5	9.0	2.1	$CdTeO_3$
6	10.3	1.9	TeO_2
7	11.5	1.8	TeO_2

These changes in the refractive index can be interpreted as the formation of the oxides of different chemical composition. The TeO_2 oxide is unstable among these oxides. The mechanism of formation and growth of the oxide film changes depending on the intensity of the laser action. The formation of the oxides, which are mainly formed from the Cd or Te component, is affected by the evaporation of the volatile component from the region of rapid melting in the $Cd_{0.9}Mn_{0.1}Te$ crystal.

The thickness of the oxide film according to the Ψ-Δ nomograms increase with increasing laser energy density and is within 35–56 nm. Since the oxide films can act as dielectrics or passivators, especially for submicron- and nanoelectronics, the obtained experimental data can be used for the laser correction of the structural phase state of the film layers in the radiation detectors on the base of the $Cd_{1-x}Mn_xTe$ crystals.

3. Conclusion

The processes of the laser recrystallization of the $Cd_{1-x}Mn_xTe$ crystal surface with the use of both millisecond and nanosecondlaser lead to the structural transformations in the $Cd_{1-x}Mn_xTe$ laser epitaxial layer. The analysis of the channeling patterns, which still needs further development with respect to the $Cd_{1-x}Mn_xTe$, can be used as a criterion for the selection of the optimal laser treatment modes. The complex studies using the SEM, AFM, and ellipsometry methods of the laser-modified surface are promising for the determination, diagnostics, and correction of the surface structural phase state in the $Cd_{1-x}Mn_xTe$ based devices.

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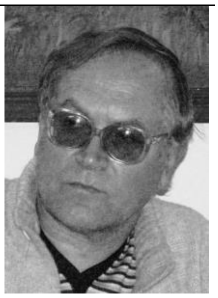

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