

Influence of the Degree of Atomic Hydrogen Passivation of Electrically Active Centers in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ on the Resolution of Optical Recording of Images with n - p - i - m Nanostructures

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An electrostatic-deformation model of atomic hydrogen passivation of electrically active centers of the type of compression defects in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ semiconductors is proposed. It is found that the effect of increasing passivation of electrically active centers in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ occurs when the concentration of atomic hydrogen N_H does not exceed the concentration of acceptors N_A ($N_H \leq N_A$), and weakening of the passivation effect is observed when the concentration of atomic hydrogen N_H is much higher than the concentration of acceptors N_A ($N_H \geq N_A$). The expression for the resolution R of optical-registering metal-dielectric-semiconductor nanostructures $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($0 \leq x \leq 1$) is obtained and the resolution value for nonpassivated as well as for passivated in the hydrogen atmosphere semiconductor material $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$ is calculated, which is $R_1 = 6682$ and $R_2 = 17423$, respectively. A method for expanding the spectral range of optical information recording based on n - p - i - m nanostructures by changing the composition ($0 \leq x \leq 1$) of the solid solution $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ is proposed.

Keywords: $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ single crystal, Resolution, Passivation, Deformation, Electrostatic-deformation interaction.

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1. INTRODUCTION

Semiconductors CdTe, ZnTe and solid solutions based on them ($\text{Cd}_{1-x}\text{Zn}_x\text{Te}$) are of great interest from a technological point of view due to their use in optoelectronics. These materials are suitable for photorefraction, electro-optical modulators fabrication, γ -ray and X-ray detectors and elements for optical recording media on n - p - i - m nanostructures [1-3].

The presence of electrically active centers (vacancies, internodal atoms, acceptor and donor impurities) in such single crystals due to the thermodynamic features of their growth leads to a violation of the symmetry of chemical bonds and thus to the formation of impurity energy levels in the band gap of the semiconductor, the position and structure of which lead to a decrease in the recording detector charge.

Equally important is the value of the dark current, which is determined by the concentration of electrically active centers (EAC), because the dark current is the main source of electronic noise and is responsible for reducing the energy resolution. Both bulk and surface outflow currents contribute to the dark current. One of the methods to reduce the level of defects and improve the optical and electrical properties of CdTe ($\text{Cd}_{1-x}\text{Zn}_x\text{Te}$) samples, to reduce the bulk outflow current and improve the effect of image recording on optical-recording semiconductor nanostructures of the n - p - i - m form is hydrogen passivation of EAC in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, which is a working element in optical recording semiconductor devices. Such passivation was technologically carried out as a result of hydrogen implantation or crystal treatment in the hydrogen atmosphere discharge [4].

2. MODEL OF ATOMIC HYDROGEN PASSIVATION OF ELECTRICALLY ACTIVE CENTERS IN $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$

Existing models of passivation (chemical reaction and electrostatic methods) do not cover cases where doping donor or acceptor impurities and hydrogen atoms in the crystal matrix create inhomogeneous deformation of the crystal lattice. In addition to the electrostatic interaction between ionized hydrogen atoms H^+ (or neutral H^0) and acceptors, there is also interaction through the deformation field. This is especially the case when the ionic (covalent) radius of the substitute alloying impurity differs from the ionic radius of the matrix atom. The deformation component of the passivation mechanism will change the annealing conditions of the semiconductor crystal. The theory of elastic interaction of defects is considered in detail in a number of works [5, 7].

The interaction energy $V^{(\alpha,\alpha')}(\vec{r})$ (α, α' characterize the type of impurities) is determined by two components: electrostatic $V_{\text{el-st}}^{(\alpha,\alpha')}(\vec{r})$ (within the screened electrostatic potential) and elastic $V_{\text{def}}^{(\alpha,\alpha')}(\vec{r})$ (within the deformation potential [8]):

$$V^{(\alpha,\alpha')}(\vec{r}) = V_{\text{el-st}}^{(\alpha,\alpha')}(\vec{r}) + V_{\text{def}}^{(\alpha,\alpha')}(\vec{r}), \quad (1)$$

where

$$V_{\text{el-st}}^{(\alpha,\alpha')}(\vec{r}) = - \frac{Ze^2 \exp\left[-r/\sqrt{\frac{k_0 T \epsilon \epsilon_0}{e^2(N_A + N_H)}}\right]}{4\pi\epsilon\epsilon_0 r}, \quad (2)$$

where e is the electron charge, T is the temperature of the crystal, k_b is the Boltzmann constant, ε is the relative dielectric constant of the material $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, N_A and N_H are the concentrations of acceptors and hydrogen atoms, respectively.

The energy of elastic interaction between acceptor (α) and hydrogen (α') impurities with centers at points t, t' is determined by the free energy difference $F_{t\alpha t'\alpha'}$ of the crystal in the presence of two interacting defects at points t, t' and components of free energies $F_{t\alpha}$ and $F_{t'\alpha'}$ of the crystal with two isolated defects [8]:

$$V_{t,t'}^{(\alpha,\alpha')}(\vec{r}) = F_{t\alpha t'\alpha'} - F_{t\alpha} - F_{t'\alpha'} \quad (3)$$

In the harmonic approximation, the values of $F_{t\alpha t'\alpha'}$ or $F_{t\alpha}$ are defined as the difference of free energies $F - F_0$ of the crystal both with defects and without them, respectively.

At large distances r between defects, the energy of their interaction decreases as $1/r^3$ and strongly depends on the orientation of the vector \vec{r} . For a pair of cubic symmetry defects in weakly anisotropic crystals, we write the expression for the energy of elastic interaction of two defects $E_{\alpha\alpha'}(r)$

$$E_{\alpha\alpha'}(r) \equiv V_{def}^{(\alpha,\alpha')}(\vec{r}) = -\frac{1}{24\pi} C_{44} \left(1 + 2 \frac{C_{12}}{C_{11}} \right) \times \quad (4)$$

$$\times \xi \Delta V_A \Delta V_H \frac{1}{r^3} \left(3 - 5 \sum_{x=1}^3 \bar{n}_{rx}^4 \right)$$

where $\bar{n}_r = \frac{\vec{r}}{r}$, $\xi = \frac{C_{11} - C_{12} - 2C_{44}}{C_{44}}$ is the parameter of elastic anisotropy of a cubic crystal, T is the crystal temperature, C_{ij} ($i, j = 1-4$) are the elastic constants, $\Delta V_A, \Delta V_H$ are the changes in the crystal lattice volume in the presence of acceptor and atomic hydrogen impurities, respectively. For crystallographic directions [100], [110], [111], (4) takes values of $-2, 1/2, 4/3$, respectively, i.e., at $\xi < 0$ the same defects placed along the [100] axis are attracted by the deformation interaction, while along the [110] or [111] axis they are repelled. Therefore, the elastic interaction leads to the predominant orientation of pairs of distant identical point defects in the crystallographic direction [100]. The equilibrium distance between the acceptor and atomic hydrogen impurities was determined from the condition of minimum energy $V^{(\alpha,\alpha')}(\vec{r})$ (1).

3. BINDING ENERGY OF ELECTRICALLY ACTIVE CENTERS WITH ATOMIC HYDROGEN

In semiconductor $\text{Cd}_{1-x}\text{Zn}_x\text{Te}:\text{H}$ crystals grown in a hydrogen atmosphere or sustained in a gas hydrogen discharge, electrically neutral complexes arise, one of the components of which is acceptor vacancy V_{Cd}^- or

V_{Cd}^{2-} where hydrogen acts as a donor. In particular, as shown by calculations performed in [9], by the ab initio method in p -type material hydrogen is in a positively charged state neutralizing holes, while in n -type material hydrogen captures electrons compensating for the action of donors. That is, hydrogen forms complexes, which consist of vacancies of cadmium, hydrogen and other acceptor impurities passivating them. The reduction of the defect level and the improvement of the optical and electrical properties of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ samples as a result of annealing in a hydrogen atmosphere or hydrogen implantation were confirmed experimentally in [10].

The depth of energy levels of complexes can be estimated from the ratio

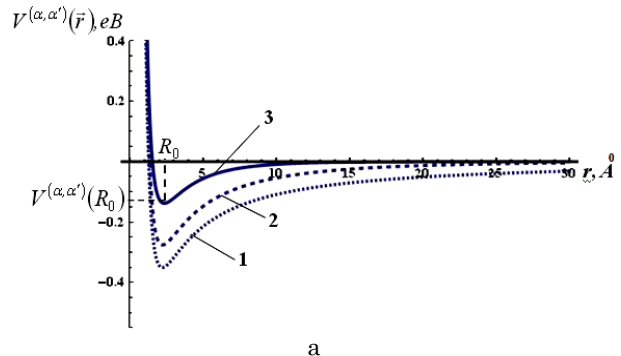
$$E_{(V_{Cd}^- H^+)} = E_{V_{Cd}^-} - |V^{(\alpha,\alpha')}(R_0)| \quad (5)$$

The second term of this formula, $|V^{(\alpha,\alpha')}(R_0)|$, describes the shift of energy levels of vacancies V_{Cd}^{2-} or V_{Cd}^- due to the presence of a charged acceptor at the equilibrium distance R_0 from ionized hydrogen taking into account their deformation interaction, which is confirmed by experimental data of photoluminescence spectra [11].

Fig. 1 shows the numerical calculations of the coordinate dependence of the interaction energy between a negatively charged vacancy and a positively charged hydrogen complex $(V_{Cd}^- - H^+)^0$ at different values of hydrogen concentration ($N_H = 10^{16} - 10^{20} \text{ cm}^{-3}$) and a fixed value of acceptor concentration ($N_A = 10^{17} \text{ cm}^{-3}$) at $T = 300 \text{ K}$.

The equilibrium distance R_0 between these point defects being a function of the hydrogen concentration (N_H), acceptor concentration (N_A) and anisotropy parameter ξ was determined from the condition of minimum energy, i.e. $\left. \frac{dV(\vec{r})}{dr} \right|_{r=R_0} = 0$.

As can be seen from Fig. 1, at small distances between the acceptor V_{Cd}^- and the hydrogen ion H^+ ($0 < r \ll R_0$), the deformation component is dominated in the repulsive force between these defects, because at $r \rightarrow 0$ this component increases much faster than the electrostatic



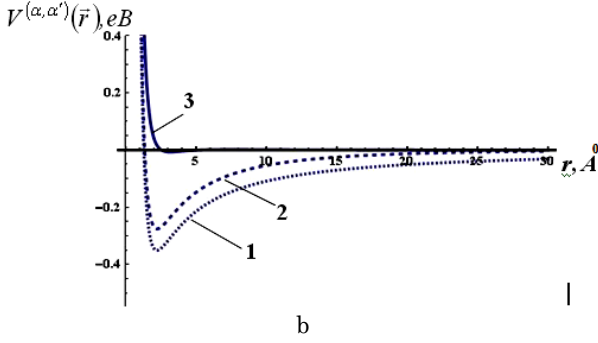


Fig. 1 – Numerical calculations of the coordinate dependence of the complex $(V_{Cd^-} - H^+)^0$ interaction energy at $T = 300$ K and $N_A = 10^{17} \text{ cm}^{-3}$: a) 1 – $N_A = 10^{16} \text{ cm}^{-3}$; 2 – $N_A = 10^{19} \text{ cm}^{-3}$; 3 – $N_A = 10^{20} \text{ cm}^{-3}$; b) 1 – $N_A = 10^{16} \text{ cm}^{-3}$; 2 – $N_A = 10^{19} \text{ cm}^{-3}$; 3 – $N_A = 5 \cdot 10^{20} \text{ cm}^{-3}$

attraction component of the force. At relatively large distances between these point defects ($R_0 - \delta < r < L$, $\delta \geq 0$), a significant contribution to the resulting force is given by the electrostatic attraction force component. At a distance $R_0(N_H, N_A, \xi)$, the total force is zero, so this distance is the equilibrium position of point defects. Analysis of the graphs shown in Fig. 1 demonstrates that with increasing hydrogen concentration in the range of $10^{16} \text{ cm}^{-3} \leq N_H \leq 5 \cdot 10^{20} \text{ cm}^{-3}$ the binding energy $|V^{(\alpha\alpha')}(R_0)|$ decreases from 353 meV (Fig. 1a, curve 3) to $k_B T$ (Fig. 1b, curve 3), i.e., passivation effect is significantly weakened and the degree of passivation $P = \frac{|V^{(\alpha\alpha')}(R_0)| - k_B T}{|V^{(\alpha\alpha')}(R_0)|}$ goes to zero. As can be seen from

the graphs (Fig. 1), the equilibrium distance R_0 between point defects (hydrogen-acceptor) correlates with the results of [9].

Fig. 2 shows the dependence of the complex $(V_{Cd^-} - H^+)^0$ binding energy on the hydrogen ion concentration N_H at $T = 300$ K and $N_A = 10^{17} \text{ cm}^{-3}$.

Analysis of the complex $|V^{(\alpha\alpha')}(R_0)| = f(N_H)$ binding energy dependence on the concentration shows that in the range of concentrations of atomic hydrogen $10^{14} \text{ cm}^{-3} \leq N_H \leq 10^{16} \text{ cm}^{-3}$ the binding energy of the complex practically does not change, and in the interval $10^{14} \text{ cm}^{-3} \leq N_H \leq 10^{16} \text{ cm}^{-3}$ the binding energy decreases sharply with increasing N_H .

Dependence $|V(R_0)| = f(N_H)$ (Fig. 2) can be approximated by the following polynomial:

$$|V(R_0)| = 0.412 - 3.934 \cdot 10^{-21} N_H + 1.997 \cdot 10^{-41} N_H^2 - 0.0017 \cdot \log(N_H)$$

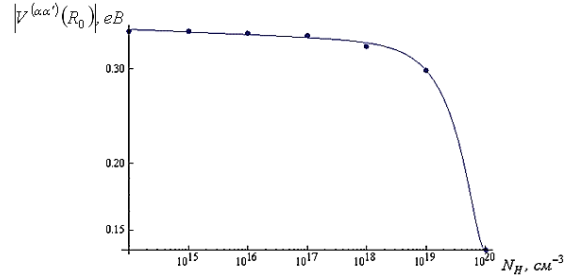


Fig. 2 – Dependence of the complex $(V_{Cd^-} - H^+)^0$ binding energy on the hydrogen ion concentration N_H at $T = 300$ K and $N_A = 10^{17} \text{ cm}^{-3}$

The sharp decrease in the binding energy $|V(R_0)|$ in the interval $10^{18} \text{ cm}^{-3} \leq N_H \leq 10^{20} \text{ cm}^{-3}$ is explained by the predominant action of the repulsive force deformation component.

4. RESOLUTION OF OPTICAL RECORDING PASSIVATED WORKING ELEMENTS IN SEMICONDUCTOR $Cd_{1-x}Zn_xTe$ NANOSTRUCTURES

To date, as high-speed optical recording media, there have been proposed media based on MIS structures with a thin nanoscale layer of thallium dielectric (Tl) with a thickness of 2-5 nm, (M(Tl)S-nanostructure) [12], where

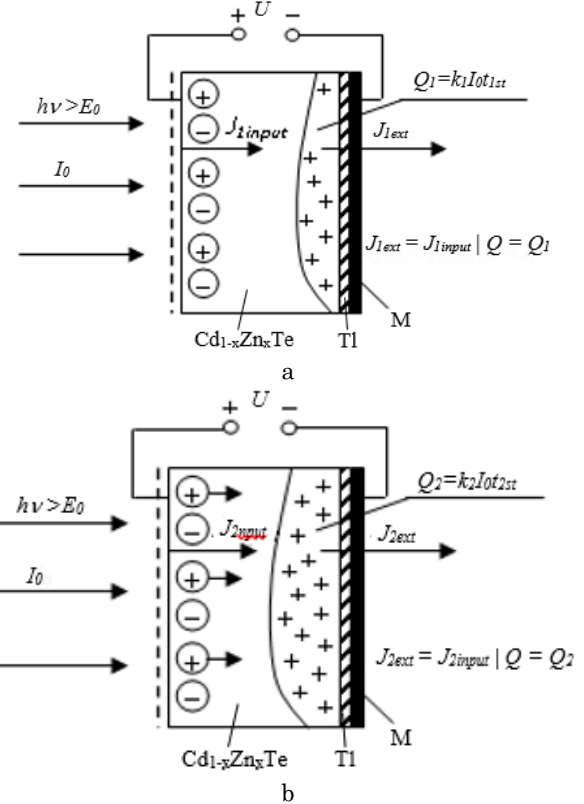


Fig. 3 – Scheme of optical recording of information on metal-dielectric-semiconductor CdTe ($Cd_{1-x}Zn_xTe$) structures with a nanometer layer of dielectric, Tl – dielectric thallium, M – metal: a) non-passivated (CdTe, $Cd_{1-x}Zn_xTe$), b) passivated (CdTe:H, $Cd_{1-x}Zn_xTe:H$).

high-resistance cadmium telluride (CdTe) with a resistivity of 10^7 - 10^8 Ohm-cm (Fig. 3a) is used as a semiconductor element.

One way to obtain high-resistance single crystals is to grow or anneal them in a hydrogen atmosphere (CdTe:H) what in turn leads to the passivation of electrically active centers (vacancies, internodal atoms), i.e., to a decrease in their concentration. Then, under the action of light on the working semiconductor element (CdTe:H) the concentration of free charge carriers in it increases, i.e., the detecting charge on the electrodes Q_2 increases (Fig. 3b) compared to the charge Q_1 , which occurs when light hits the non-passivated CdTe semiconductor element (Fig. 3a).

To fabricate optical recording media on semiconductor nanostructures for recording and processing high-resolution images, it is necessary that the illumination profile is ideally described by a step function. However, the real profile of the light intensity $I_0(x, y)$ near the given boundary of the element is a non-monotonic function [13], which is due to the wave properties of light.

The charge Q formed in the crystal by quanta of absorbing reading light and collected on the electrodes due to the passage of the charge $q(z)$ is determined from the expression [12]

$$Q = \frac{1}{L} \int_0^L q(z) dz, \quad (6)$$

where L is the length of the monocrystal.

When the structure is illuminated by reading light from the negative electrode side, the charge is transferred through the monocrystal by electrons, and its value $q(z)$ will decrease with time according to the law

$$q(z, x) = e\beta k(\lambda)\tau SL \frac{I_0 e^{-\frac{x^2}{r_0^2} - kz}}{E_g} e^{-\frac{t}{\tau}}, \quad (7)$$

where β is the quantum yield (number of excited electrons per absorbing photon); $k(\lambda)$ is the absorption coefficient; c is the speed of light in vacuum; I_0 is the light intensity on the crystal surface ($z=0$); τ is the lifetime of carriers; r_0 is the radius of the illuminated area ($r_0 \approx 5 \mu\text{m}$); S is the area of the single crystal (XOY plane) on which monochromatic light of length λ falls in the direction of the OZ axis.

Substituting formula (7) into formula (6), after integration we obtain

$$Q = \frac{eI_0}{E_g} \beta\tau S e^{-\frac{x^2}{r_0^2}} (e^{-kL} - 1) e^{-\frac{t}{\tau}}, \quad (8)$$

where

$$L = \frac{1}{k(\lambda)}. \quad (9)$$

The time t and the coordinate z of charge carriers in the crystal are related by the relation

$$dt = \frac{dz}{v_{dr.}(z)} = \frac{dz}{\mu E(z)}, \quad (10)$$

where $v_{dr.}$, μ are the drift speed and mobility of charge carriers, respectively; $E(z)$ is the electric field.

From expressions (6), (8), (10) we obtain the ratio for the magnitude of the charge collected on the electrodes of the structure formed by the action of N quanta of light in the plane $Z=0$

$$\frac{Q}{e} = I_0 A e^{-\frac{x^2}{r_0^2}}, \quad (11)$$

where $A = \frac{\beta\tau}{E_g} S (e^{-k(\lambda)L} - 1) e^{-\frac{1}{\mu\tau} \int \frac{dz}{E(z)}}$.

The resolution R_i of optical-recording non-passivated ($i=1$) or passivated ($i=2$) working elements in semiconductor nanostructures is described by the formula

$$R_i = - \frac{\partial \left(\frac{Q}{e} \right) / \partial x}{b} \Bigg|_{x=x_0}, \quad (12)$$

where $b = \frac{1}{I_0} \frac{\partial I}{\partial x}$ is the relative edge gradient of the incident light intensity; x_0 is the coordinate x at which $\partial^2 \left(\frac{Q}{e} \right) / \partial x^2 = 0$ (under this condition the maximum sharp border in the charge distribution is provided).

We will perform a numerical evaluation of the resolution of an optical recording device, the working element of which is a p -type semiconductor material (Cd_{0.8}Zn_{0.2}Te) in two cases: untreated in a hydrogen atmosphere p -type semiconductor material ($i=1$) and treated ($i=2$). For evaluation were used the following parameters: $E_g = 1.53$ eV; $k = 2\sqrt{5} \cdot 10^4 \text{ m}^{-1}$ [13];

$\tau_1 = 10^{-7}$ s; $\mu_1\tau_1 = 2.5 \cdot 10^{-10} \frac{\text{m}^2}{\text{V}}$ [14]; $E_1 = 10^4 \frac{\text{V}}{\text{m}}$ [12];

$I_{01} = 700 \frac{\text{W}}{\text{m}^2}$ [12]; $S = 3 \cdot 10^{-7} \text{ mm}^2$;

$\mu_2\tau_2 = 3.5 \cdot 10^{-10} \frac{\text{m}^2}{\text{V}}$; $E_2 = 0.8 \cdot 10^4 \frac{\text{V}}{\text{m}}$. The evaluation

showed that for untreated semiconductor material in a hydrogen atmosphere, the resolution (the number of grooves per millimeter) is $R_1 = 6682$ and for treated

one $R_2 = 17423$ $\left(\frac{R_2}{R_1} = 2.6 \right)$. Thus, two recording signals

with a resolution of 150 nm and 57 nm, respectively, can be read separately.

The expansion of the spectral range of optical information recording can be carried out by a change in the fraction ($0 \leq x \leq 1$) of zinc atoms in a solid solution of Cd_{1-x}Zn_xTe, which is a working element in semicon-

ductor nanostructures. Thus, by changing the band gap $E_g(x)$, which in the Vegard approximation is described by formula $E_g(x) = xE_g^{\text{ZnTe}} + (1-x)E_g^{\text{CdTe}}$ (E_g^{ZnTe} , E_g^{CdTe} are the band gaps of ZnTe and CdTe, respectively) it is possible to change the spectral wavelength range of the recording optical information within $\lambda(x) = \frac{hc}{xE_g^{\text{ZnTe}} + (1-x)E_g^{\text{CdTe}}}$, where h is the Planck constant and c is the speed of light in vacuum. Then the change in the wavelength of the recording information with a change in the composition x will be expressed by the ratio

$$\frac{d\lambda(x)}{dx} = \frac{hc(E_g^{\text{CdTe}} - E_g^{\text{ZnTe}})}{(xE_g^{\text{ZnTe}} + (1-x)E_g^{\text{CdTe}})^2}.$$

5. CONCLUSIONS

Therefore, the amplification of the effect of atomic hydrogen passivation of electrically active centers such as compressing type defects in CdTe, $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ semiconductors occurs if the concentration of atomic hydrogen N_H does not exceed the concentration of acceptors N_A , and in the case $N_H \gg N_A$ the degree of pas-

sivation $P = \frac{|V^{(aa')}(R_0)| - k_B T}{|V^{(aa')}(R_0)|}$ goes to zero.

The resolution of optical image recording on $n-p-i-m$ nanostructures is also related to the concentration of atomic hydrogen N_H : if this concentration does not exceed the concentration of acceptors, the passivation by atomic hydrogen of electrically active centers such as compressing or stretching type defects leads to an increase in the resolution, while in the case $N_H > N_A$ – to its decrease.

From the obtained expression for the resolution of optical-recording nanostructures of metal-dielectric-semiconductor $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($0 \leq x \leq 1$) it follows that for the non-passivated semiconductor material $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$ the resolution is $R_1 = 6682$, and for the passivated one in a hydrogen atmosphere $R_2 = 17423$

$\left(\frac{R_2}{R_1} = 2.6\right)$, i.e., it is possible to read separately two recording signals with a minimum wavelength interval of 150 nm and 57 nm, respectively.

By changing the composition of the solid solution $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ as a working semiconductor element in $n-p-i-m$ nanostructures, it is possible to expand the spectral range of optical information recording.

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Вплив ступеня пасивації електрично-активних центрів у $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ атомарним воднем на роздільну здатність оптичного запису зображень на n - p - i - m наноструктурахВ.Б. Британ¹, Р.М. Пелешак², Ю.О. Угрин¹, М.Я. Сенета¹, О.Х. Тадеуш³¹ Дрогобицький державний педагогічний університет імені Івана Франка, вул. І. Франка, 24, 82100 Дрогобич, Україна² Національний університет «Львівська політехніка», вул. С. Бандери 12, 79013 Львів, Україна³ Південноукраїнський національний педагогічний університет імені К.Д. Ушинського, вул. Старопортофранківська, 26, 65000 Одеса, Україна

У роботі запропоновано електростатично-деформаційну модель пасивації атомарним воднем електрично-активних центрів виду дефектів стиску (розтягу) у напівпровідниках $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$. Встановлено, що ефект підсилення пасивації електрично-активних центрів у $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ має місце у випадку коли концентрація атомарного водню N_H не перевищує концентрацію акцепторів N_A ($N_H \leq N_A$), а послаблення ефекту пасивації спостерігається коли концентрація атомарного водню N_H є набагато більшою за концентрацію акцепторів N_A ($N_H \geq N_A$). Отримано вираз для роздільної здатності R_i оптично-реєструючих наноструктур метал-діелектрик-напівпровідник $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($0 \leq x \leq 1$) та розраховано значення роздільної здатності для непасивованого напівпровідникового матеріалу $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{Te}$ та для пасивованого в атмосфері водню, яке становить $R_1 = 6682$ та $R_2 = 17423$ відповідно. Запропоновано спосіб розширення спектрального діапазону запису оптичної інформації на основі n - p - i - m наноструктур за допомогою зміни складу ($0 \leq x \leq 1$) твердого розчину $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$.

Ключові слова: Монокристал $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, Роздільна здатність, Пасивація, Деформація, Електростатично-деформаційна взаємодія.