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Mass Transmission Regularities in CdTe under Nanosecond Laser Irradiation

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The mechanisms of mass transfer in the In/CdTe system under nanosecond laser pulses are considered in this work. They are caused by nonstationarity, nonequilibrium, physical and geometric nonlinearity, high speed and simultaneity of various physical processes; in particular, by a change in the physical state of a solid body, the generation of elastic and shock waves, significant temperature and stress gradients, defect formation, diffusion, etc. The dominant mechanisms and regularities of indium mass transfer in CdTe under nanosecond laser irradiation of the In-CdTe structure have been established.

Keywords: CdTe, mass transmission, pulsed laser irradiation.

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Introduction

Nowadays, phenomena of high mobility of atoms in crystals under pulsed laser irradiation (PLI) has a great practical importance for solid-phase doping of CdTe by irradiation with laser pulses of the metal-CdTe structure, due to the efficiency, manufacturability, reproducibility and convenience in the choice of parameters in the manufacture of detectors sensitive to X- and gamma-radiation, with low noise and high spectrometric characteristics based on diodes with a sharp p-n transition at shallow depth [1-3].

At the same time, mechanisms of mass transfer process in metal-semiconductor film structures under PLI are currently insufficiently elucidated. First of all, for predication and controlled change of electrical and photoelectric characteristics of semiconductor structures with p-n junction and ohmic and rectifying contacts [1-6], especially based on CdTe, which are used for ionizing radiation detectors [1, 2]. Clarification and analysis of mass transfer mechanisms is necessary to determine the optimal modes of nanosecond laser solid-phase doping CdTe by indium and similar structures of the metal-semiconductor film.

The complexity of mass transfer mechanisms in nanosecond PLI is due to non-stationary, non-equilibrium, physical and geometric nonlinearity, high speed and simultaneity of various physical processes; in in particular, it is a change in the physical state of a solid body, the generation of elastic and shock waves, significant gradients of temperatures and stresses, defect formation, diffusion, etc.

Therefore, it is necessary to establish the dominant mechanisms and patterns of mass transfer of indium in CdTe by nanosecond laser irradiation of the In-CdTe structure.

Experimental data and discussion

For studying mass transfer were used crystals of *p*-CdTe with a size of 5x5x0.5..3 mm^3 and a resistivity of $(2 - 4)\cdot 10^9$ Ohm/cm, orientation (111), compensated by SI. Before applying the indium film, the surface was chemically polished. The In film of a known thickness (30 - 400 nm) was applied by thermal spraying in vacuum at a pressure of 10^{-5} atm.

From the analysis of concentration profile of indium atoms in the monocrystalline CdTe, which is given by the authors [1], it is seen that the depth of penetration of

indium In atoms into the crystal reaches 60 nm from the CdTe surface, with a characteristic peak at a depth of 6 nm, which is explained by the presence of a directed flow of atoms deep into the crystal along x with an average drift velocity $\langle v_x \rangle$ [7, 8]; the presence of a maximum has a threshold character - a maximum formed at

$$\langle v_x \rangle^2 t > 2D \text{ [9, 10]}, \quad (1)$$

where D - the mass transfer coefficient, t - the total time of action of laser radiation, evaporation of the film and relaxation of the temperature gradient and thermoelastic stresses in the diffusion zone. t = 100 ns is determined from the temperature profile of irradiated In-CdTe and is the time of intense mass transfer or the time of existence of forces due to temperature and stress gradients. After 100 ns, the mass transfer processes are virtually frozen and have a relaxing character.

In our case, the thin film In is evaporated during PLI, we can use the diffusion model from an infinitely thin layer and, taking into account the kinetics of the process of penetration of In atoms into CdTe at $C(x,0) = C_0\delta(x)$in depth, the concentration profile can be described by expressions from [11]:

$$C(x,t) = \frac{C_0}{2\sqrt{\pi D t}}\left[exp\left(-\frac{(x-\langle v_x \rangle t)^2}{4Dt}\right) + exp\left(-\frac{(x+\langle v_x \rangle t)^2}{4Dt}\right)\right] \quad (2)$$

or [7]:

$$C(x,t) = \frac{C_0}{2\sqrt{\pi D t}} exp\left(-\frac{(x-\langle v_x \rangle t)^2}{4Dt}\right) - \frac{C_0 \langle v_x \rangle}{4D} exp\left(\frac{\langle v_x \rangle x}{D}\right) erfc\left(\frac{x+\langle v_x \rangle t}{2\sqrt{Dt}}\right) \quad (3)$$

where C_0 - the initial concentration of In atoms on the surface (x = 0), $\delta(x)$ - the delta function.

We have calculated theoretically the temperature of the metal surface and correspondingly, the In-CdTe interface in accordance to the process of interaction of a powerful light flux with a thin film of absorbing material (metal) on the substrate. The calculations were performed for the range of In film thicknesses of 30 -400 nm.

The heating temperature of the surface of a thin film with a thickness of h ($h \geq \delta$ is the depth of the skin layer) on the substrate under pulsed laser irradiation in the visible and near-IR range of light at $E/\tau < 10^8$ J/(s·cm^2) (when the thermal destruction mechanism is valid) is defined by the expression [9]:

$$\Delta T(t) = \frac{E}{\tau}\frac{A\sqrt{a_2 t}}{\chi_2}\left\{\frac{2}{\sqrt{\pi}} + \gamma v\left[exp\left(\frac{1}{\gamma^2 v^2}\right) erfc\left(\frac{1}{\gamma v}\right) - 1\right]\right\} \quad (4)$$

where A = 1 - R, a is a thermal diffusivity index and χ is a thermal conductivity index, herewith $v = \frac{\chi_1\sqrt{a_2}}{\chi_2\sqrt{a_1}}$ and $\gamma = \frac{h}{\sqrt{a_1 t}}$. In our case index "1" refers to In film and "2" to CdTe. Here $t \leq \tau$.

The value $\gamma \cdot v$ is actually the ratio of the volumetric heat capacities of the film and the heated layer of the substrate and determines the heating rate of the film, the depth of heat diffusion $\sqrt{a_1 t}$ (or heated by thermal conductivity layer) is 1 μm for In at t = 20 ns. The depths of the skin layer $\delta = \lambda/2\pi\kappa$ for In at the absorption index κ = 6 (λ = 0.694 μm) and κ = 2.8 (λ = 0.248 μm) are equal 18.4 nm and 14 nm, respectively.

The temperature of the film in its thickness can be considered roughly the same (with an accuracy of ~ 10 %) after a time $t_0 \approx 10h^2/a_1$ from the beginning of the pulse. For In film with a thickness of 300 - 400 nm, $t_0 \approx 90 - 160$ ns. According to expression (4), the maximum temperature of the indium film with h = 300 nm at E = 100 mJ/cm^2 is 130 ºC (for R = 0.9) and 522 ºC (for R = 0.6). For h = 30 nm T = 254 ºC (R = 0.9) and 1010 ºC (R = 0.6), respectively. This is less than the melting point of CdTe T_{melt} = 1067 ºC therefore the diffusion processes (mass transfer) in CdTe occur in the solid phase. T_{melt} of In = 157 ºC. Note that when $E_{incident}$ = 16 mJ/cm^2 and R = 0.6… 0.8, indium melting does not occur, but changes in the I–V characteristics indicate about mass transfer.

Let us analyze the simulation results presented by authors [4, 6] for two typical irradiation modes of E = 80 and 150 mJ/cm^2 values. Heating occurs up to 1 μm. The temperature gradient in the film is almost absent, and in the CdTe substrate it is significant: at h_{In} = 30 nm dT/dx is $25 \cdot 10^9$ K/m at E = 150 mJ/cm^2 and $18 \cdot 10^9$ K/m at E = 80 mJ/cm^2. dT/dx decreases with increasing of film thickness.

In PLI, these gradients move from the surface to the depth of the crystal over time, which stimulates thermo- and pressure diffusion. According to these calculations of the heating kinetics, the melting thresholds of indium and CdTe under irradiation of In/CdTe were established. The In film begins to melt at E_{absor} = 5 mJ/cm^2 for thickness of 30 nm, E_{absor} = 8 mJ/cm^2 at h_{In} = 100 nm and E_{absor} = 16 mJ/cm^2 at h_{In} = 400 nm. CdTe begins to melt (1365 K) at approximately E_{absor} = 40 mJ/cm^2 for a thickness of In h_{In} = 30 nm, at E_{absor} = 50 mJ/cm^2 for a thickness h_{In} = 100 nm and at E_{absor} = 100 mJ/cm^2 for h_{In} = 400 nm.

The substrate is 10 times less in the molten state than the film. The film is in the molten state for more than 1 -10 μs (Fig. 1), while the substrate is 10 and hundreds of nanoseconds.

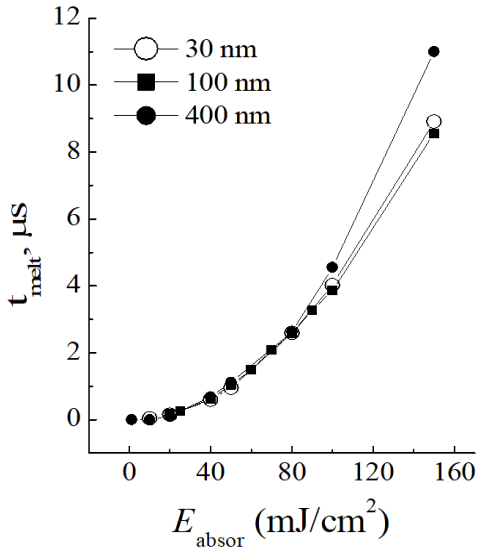

Fig. 1. Dependence of lifetime of melt on In/CdTe surface on energy density.

The lifetime of the Indium film in the molten state at E_{absor} = 40 mJ/cm^2 is 590 ns, 620 ns and 680 ns at film thicknesses h_{In} = 30, 100, 400 nm, respectively; and at 100 mJ/cm^2 it is 4020 ns, 3870 ns and 4560 ns at film thicknesses h_{In} = 30, 100, 400 nm. Figure 2 shows that at E = 40 mJ/cm^2 the maximum temperature is T_{max} = 1610 K at a thickness of In 30 nm, T_{max} = 1200 K for a thickness of 100 nm and T_{max} = 660 K for a thickness of 400 nm.

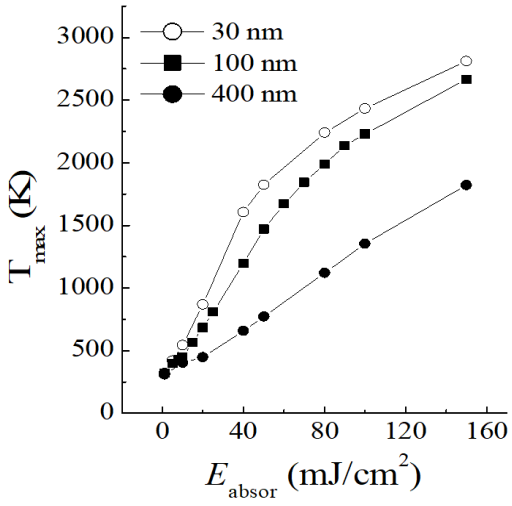

Fig. 2. Dependence of the maximum temperature on In/CdTe surface on energy density.

The value of the evaporated indium layer at 100 mJ/cm^2 under laser ablation is estimated by expression (5) [12], which is ~ 50…120 nm in the calculation.

$$x(t) = \frac{3\mu_{In}\bar{v}_{In}^3}{\lambda_{In}} t\ exp\left[-\frac{\lambda_{In}k_{CdTe}\sqrt{\pi}}{2IAR\sqrt{a_{CdTe}t}}\right] \qquad (5)$$

The value of the evaporated indium layer at 100 mJ/cm^2 under laser ablation is estimated by expression (5) [12], which is ~ 50…120 nm in the calculation.

In our case $\bar{v}_{In}$ is an average speed of sound in In, 1400 m/s; μ is a molar weight of In, 117 g/mol; R is a gas constant; A = 1 – R – absorption coefficient; I = intensity of the laser pulse; $\lambda_{In} = \eta \cdot \mu/\rho$, where η is a heat of vaporization per volume unit of indium film substance, ρ is a density; k = thermal conductivity index and a = heat conduction.

The thickness of the molten indium layer, calculated according to expression (6) [13], at T at $E_{incident}$ = 100 mJ/cm^2, is equal to $x_{melt} \approx$ 130 nm.

$$X_{melt} = \frac{a_{liq.}}{V} ln\left(1 + \frac{C_{liq.}\rho_{liq.}(T_{vap.} - T_{melt}}{C_m\rho_m(T_{melt} - T_0) + \rho_m Q_{melt}}\right), \qquad (6)$$

where, a_{liq} is the thermal diffusivity index of indium in the liquid state (thermal conductivity is equal to 87 J/(m·K·s); C_{sol} and C_{liq} are specific heat capacities of indium in solid and liquid states, C_{sol} = 234,461 J/(kg·K); ρ_{sol}, ρ_{liq} are densities in solid and liquid state (7310 and 7030 kg/m^3 respectively); V is the speed of movement of the phase boundary solid-liquid at PLI (~ 2 m/s); T_{vap}, T_{melt}, T_0 - evaporation, melting and initial temperatures (T_{vap} = 2024 °C) and Q_{melt} - specific melting heat indium, equal to 28,400 J/kg.

It was found experimentally that in the case of h = 30 nm the film completely disappeared due to diffusion, melting and ablation, as in [3], but melting of the near-surface CdTe layer does not occur, the temperature is below T_{melt} of CdTe. With an increase of PLI energy, at some E the near-surface CdTe layer melts and the phase mixing mechanism may appear [14], which in the melt zone will affect the mechanisms of mass transfer of In to CdTe in the solid state. The laser plasma observed by us arises due to avalanche ionization of the formed vapors at optical breakdown during ablation - fast evaporation of indium atoms from a surface. It should be noted that during ablation and formation of laser plasma, such additional channels of energy distribution of the laser pulse as the energy of evaporated atoms, plasma absorption at the time and after breakdown are added [15]; but due to the high evaporation temperature of indium (3000 K) and the high heat of evaporation, these effects are neglected.

Despite the complete ablation of the In film with a thickness of 30 nm, by the time of its disappearance, some atoms penetrate far into the CdTe in the solid phase, which indirectly indicates a significant speed of the mass transfer process.

Conclusions

Experimental studies and theoretical calculations have shown that, depending on the thickness of the Indium film and the energy density of the laser irradiation, both liquid-phase diffusion of In into CdTe and solid-phase diffusion will occur. Melting will significantly affect the mechanisms of mass transfer of In to CdTe.

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Механізми масопереносу в CdTe при дії наносекундних лазерних імпульсів

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В даній роботі розглянуто механізми масопереносу в системи In/CdTe при наносекундному імпульсному лазерному опроміненні, які обумовлена нестаціонарністю, нерівноважністю, фізичною та геометричною нелінійністю, високою швидкістю і одночасністю протікання різних фізичних процесів; зокрема це зміна агрегатного стану твердого тіла, генерація пружних та ударних хвиль, значних градієнтів температур і напруг, дефектоутворення, дифузія та ін. Встановлено домінуючі механізми та закономірності масопереносу індію в CdTe при наносекундному лазерному опроміненні структури In-CdTe.

Ключові слова: CdTe, імпульсне лазерне опромінення, масоперенесення.