# COMPUTATIONAL ANALYSIS OF MELTING, SOLIDIFICATION AND EVAPORATION OF PULSED LASER IRRADIATED CdZnTe

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**Abstract**

Melting, evaporation and solidification of CdZnTe induced by two types of lasers, namely Nd:YAG laser (16 ns FWHM pulse duration, 266 nm wavelength) and ruby laser (80 ns FWHM, 694 nm) are studied by a computational analysis. The temperature and concentration fields, and the positions and velocities of both solid/liquid and liquid/vapor interfaces are calculated as functions of the laser energy density. Contrary to the basic semiconductors such as silicon or germanium, the effect of evaporation is found to dominate the laser irradiation process already in the range of relatively low laser energy densities.

**Key words:** CdZnTe, pulsed laser, melting, evaporation, solidification, computational analysis

## 1 Introduction

In modeling rapid phase change processes in II-VI semiconductors, only several attempts have been done until now. Scepanovic and Jevtic [1] modeled the nonequilibrium segregation in HgCdTe induced by Nd:YAG laser irradiation. However, the heat and mass transfer processes were treated separately in their analysis and, moreover, the thermal equilibrium model was employed in calculating the temperature fields. A more advanced model was formulated and applied for CdZnTe by Přikryl, Segeth and Černý [2]. This model took coupled heat and mass transport into account, and due to the high velocities of the interface the nonequilibrium phase change processes were considered. The concept of the Wilson-Frenkel interface response function was adopted in the modeling process, and nonequilibrium segregation coefficients were used. The model from [2] has been further improved by Přikryl, Gatskevich and Černý [3] lately, who besides the nonequilibrium melting and solidification of II-VI binary alloys modeled also the evaporation from the surface.

In this paper, the model by Přikryl, Gatskevich and Černý [3] is used in a computational analysis of melting, solidification and evaporation processes induced by pulsed laser irradiation of CdZnTe pseudobinary alloy.

## 2 Mathematical model

The model of nonequilibrium melting, evaporation and solidification of II-VI binary alloys formulated by Přikryl, Gatskevich and Černý [3] presents an extension of the model by Přikryl, Segeth and Černý [2]. Therefore, we will not repeat the model in full detail here and will concentrate on the inclusion of the evaporation processes into the model instead, which means the formulation of conditions on the liquid/vapor interface, i.e., the surface of the specimen.

The first necessary condition at the liquid/vapor interface $Z_0(t)$ is the balance equation of internal energy. Assuming evaporation into vacuum, it can be derived using the common rules of the discontinuity surface theory (see e.g. [4]) in the form

$$\rho_\mathrm{l} L_\mathrm{v} \frac{\mathrm{d}Z_0}{\mathrm{d}t} = K_\mathrm{l} \left( \frac{\partial T_\mathrm{l}}{\partial x} \right)_{x=Z_0(t)_+} - \epsilon \sigma_\mathrm{SB} (T_{Z_0}^4 - T_\mathrm{e}^4), \tag{1}$$

where $\rho_\mathrm{l}$ is the density of the liquid, $L_\mathrm{v}$ the latent heat of evaporation, $K_\mathrm{l}$ the thermal conductivity of the liquid, $T_\mathrm{l}$ the temperature of the liquid, $\epsilon$ the emissivity from the liquid surface, $\sigma_\mathrm{SB}$ the Stefan-Boltzmann constant, $T_{Z_0}$ the temperature of the liquid/vapor interface, and $T_\mathrm{e}$ the temperature of the surroundings.

The second necessary equation is the interface response function, which can be generally expressed as

$$\frac{\mathrm{d}Z_0(t)}{\mathrm{d}t} = f(T, C_\mathrm{A,l}), \tag{2}$$

where the function $f(t)$ describes the evaporation kinetics at the sample surface, $T$ is the interface temperature, and $C_\mathrm{A,l}$ is the concentration of the component A of the binary mixture on the liquid surface of the sample.

In the case of evaporation into vacuum, the mass flux $j_\mathrm{v}$ of the vapor can be expressed according to the kinetic theory of gases [5] in the form

$$j_\mathrm{v} = \frac{1}{4} \rho_\mathrm{v} \bar{v} = \frac{1}{4} \rho_\mathrm{v} \sqrt{\frac{8 R_\mathrm{g} T}{\pi M}}, \tag{3}$$

where $\rho_\mathrm{v}$ is the density of the gas, $\bar{v}$ the arithmetical average velocity of molecules, $T$ the absolute temperature, $R_\mathrm{g}$ the universal gas constant, and $M$ the molar mass of the gas.

From the equation of state for an ideal gas the density of vapor is given by

$$\rho_\mathrm{v} = \frac{p_\mathrm{v} M}{R_\mathrm{g} T}. \tag{4}$$

Substituting (4) into (3), we get the mass flux in the form

$$j_\mathrm{v} = \sqrt{\frac{M}{2\pi R_\mathrm{g} T}} \cdot p_\mathrm{v}. \tag{5}$$

The equilibrium vapor pressure $p_\mathrm{eq}$ for the temperatures between the melting and boiling point can be written [6] as

$$p_\mathrm{eq} = T^C \cdot 10^{-\frac{A}{T} + B}, \tag{6}$$

where the parameters $A$, $B$, $C$ are functions of $C_{\mathrm{A,l}}$. Denoting

$$X = \sqrt{\frac{M}{2\pi R_{\mathrm{g}}}} \tag{7}$$

and substituting (6) and (7) into (5) we get

$$j_{\mathrm{v}} = X \cdot T^{C-0.5} \cdot 10^{-\frac{A}{T}+B}. \tag{8}$$

On the other hand, the mass flux due to evaporation from the surface of the sample can be expressed in terms of interface velocity as

$$j_{\mathrm{v}} = \rho_{\mathrm{l}} \frac{\mathrm{d}Z_0(t)}{\mathrm{d}t}, \tag{9}$$

where $\rho_{\mathrm{l}}$ is the density of the liquid. Comparing (9) and (8) we finally arrive to the dependence of the interface velocity on temperature and concentration

$$\frac{\mathrm{d}Z_0(t)}{\mathrm{d}t} = \frac{X}{\rho_{\mathrm{l}}} \cdot T^{C-0.5} \cdot 10^{-\frac{A}{T}+B}. \tag{10}$$

Note that in the nonequilibrium model of evaporation, this relation or another relations of the form (2) replace the local thermodynamic equilibrium condition $T = T_{\mathrm{vap}} = \mathrm{const}$ at the surface of the sample.

## 3 Computer implementation

The computer implementation is done similarly as in [2]. In solving the moving boundary problem we first employ the Landau transformation [7] to map both the liquid and the solid domain onto fixed space intervals $[0, 1]$. Then, to discretize the nonlinear fixed-domain initial-boundary value problem obtained we use the Galerkin finite element method. The interface conditions with the exception of the kinetic conditions are incorporated into the global nonlinear system of FEM equations that are solved at each time step iteratively in an inner iterative cycle of the algorithm used. The kinetic conditions are to be satisfied in an outer iterative procedure at each time step. The iterations are performed using the successive approximation method with underrelaxation.

## 4 Computational simulations

The computational analysis was carried out for the problem of melting, evaporation and solidification of CdZnTe induced by Nd:YAG laser (16 ns FWHM, 266 nm) and ruby laser (80 ns FWHM, 694 nm). The initial content of zinc in the CdZnTe pseudo-binary was assumed to be 4% in all calculations. The energy density of the laser pulse varied from 0.01 $\mathrm{Jcm}^{-2}$ to 0.30 $\mathrm{Jcm}^{-2}$ for the Nd:YAG laser and from 0.1 $\mathrm{Jcm}^{-2}$ to 0.70 $\mathrm{Jcm}^{-2}$ for the ruby laser. The shape of the laser pulses employed in the computations was obtained by experimental measurements. The thermodynamic parameters of CdZnTe were taken from [8], the optical parameters from [9].

In the numerical simulations, the temperature and concentration fields and the positions and velocities of both solid/liquid and liquid/vapor interfaces were calculated. As the inclusion of evaporation was the main new feature of the applied model we will concentrate on evaporation-related effects.

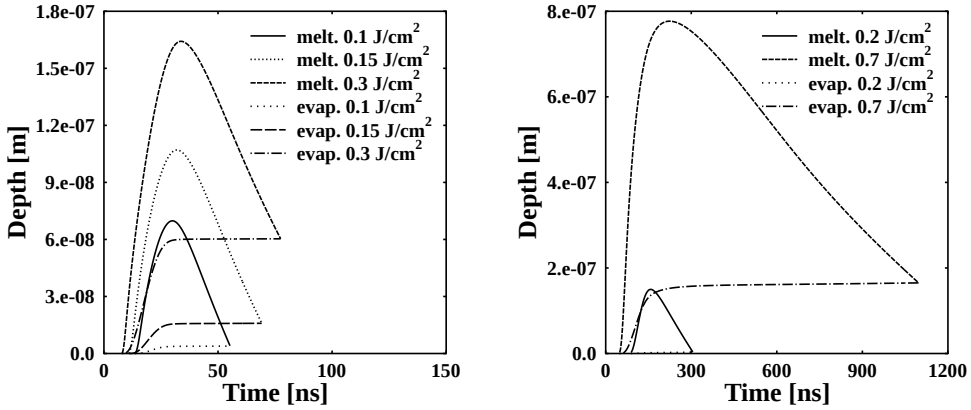


Fig. 1 Melting and evaporation depths as functions of the laser energy density and time: a) Nd:YAG laser, b) ruby laser

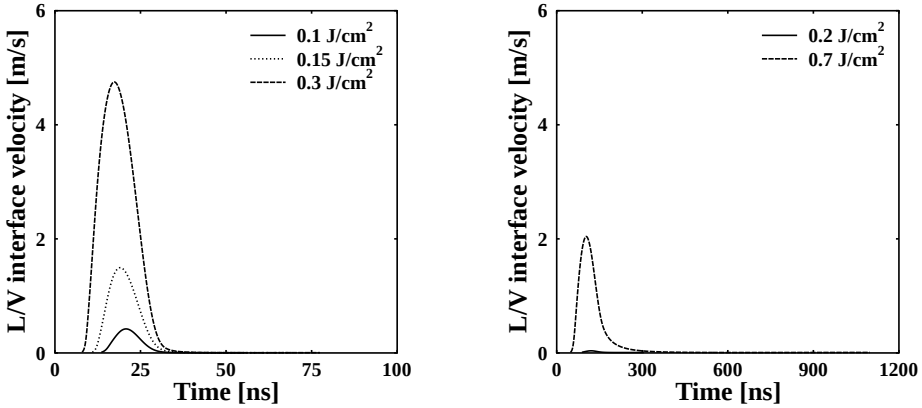


Fig. 2 Liquid/vapor interface velocity as a function of the laser energy density and time: a) Nd:YAG laser, b) ruby laser

Figs. 1a,b show a comparison of melting and evaporation depths. For the Nd:YAG laser, the evaporation depth is found to be very high relatively, the thickness of the evaporated layer being approximately one third of the maximum molten layer thickness for the energy density of the laser of 0.30 $\mathrm{Jcm}^{-2}$. For the ruby laser, the differences between the melting and evaporation depths are relatively lower, which is clearly a consequence of its five times longer pulse duration compared to the Nd:YAG laser.

The comparison of the liquid/vapor interface velocities in Figs. 2a,b with the solid/liquid interface velocities in Figs. 3a,b exhibits similar features. With the energy density of the Nd:YAG laser of 0.30 $\mathrm{Jcm}^{-2}$, the maximum liquid/vapor interface velocity is about one third of the maximum solid/liquid interface velocity, which is quite large relatively. For the ruby laser, the maximum evaporation velocity is for the same maximum melting velocity 2.5 times lower than that for the Nd:YAG laser.

The relatively high values of interface velocities give a clear evidence of the highly

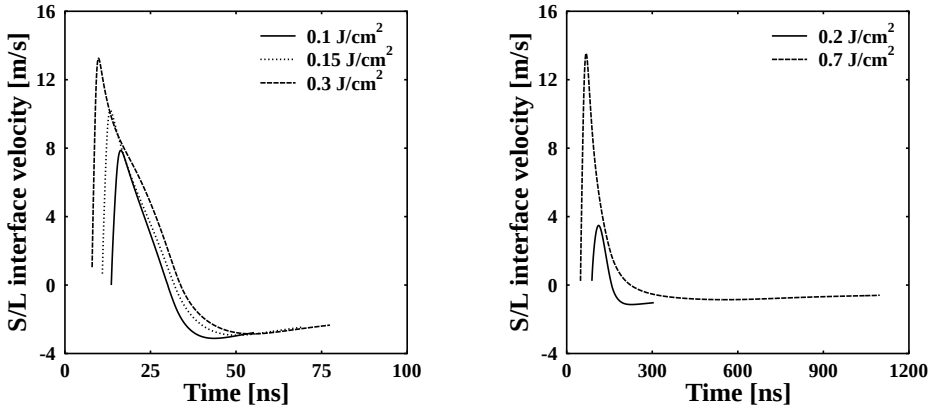


Fig. 3 Solid/liquid interface velocity as a function of the laser energy density and time: a) Nd:YAG laser, b) ruby laser

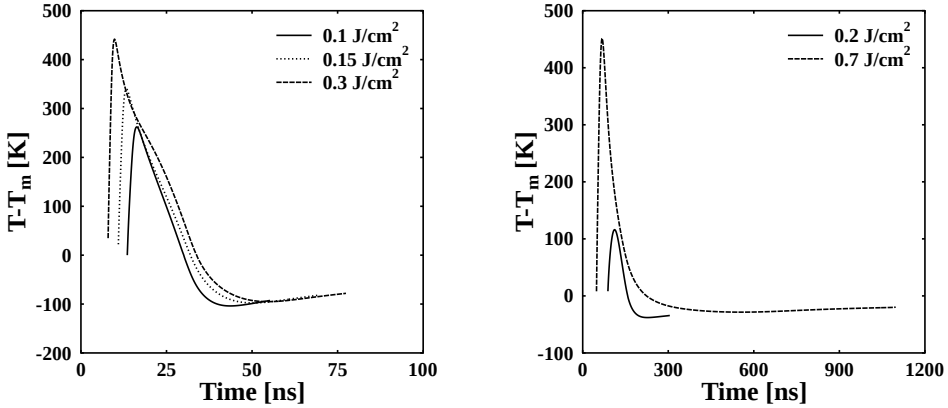


Fig. 4 Overheating/undercooling of the solid/liquid interface as a function of the laser energy density and time ($T$ is the temperature at the solid/liquid interface, $T_{\mathrm{m}}$ the equilibrium melting temperature): a) Nd:YAG laser, b) ruby laser

nonequilibrium character of the phase change processes in the studied experimental situation. This is well illustrated by the high values of overheating and undercooling of the solid/liquid interface in Figs. 4a,b.

## 5 Conclusions

The computational analysis of melting, evaporation and solidification of CdZnTe induced by Nd:YAG and ruby lasers carried out in this paper clearly demonstrated the remarkable effect of evaporation in the laser irradiation process. The evaporation was found (contrary to the basic semiconductors such as silicon or germanium)—if combined with the relatively low thermal conductivity of CdZnTe in both the solid and the liquid phase—to dominate the process already in the range of laser energy densities that would not be considered for Si or Ge as very high.

Concerning the applicability of the model, it should be noted that it assumes no decomposition in the liquid phase in the higher temperature range that was observed for some II-VI materials experimentally. Therefore, the prediction capabilities of the model will certainly be better for temperatures close to the melting point than for a temperature say 1000°C above the melting point. Nevertheless, also in this form the model can be quite useful for the experimentalist because, in addition to the classical output data, as the temperature and concentration fields and the position and velocity of the solid/liquid interface, it is able to provide the data for evaporation depths and evaporation velocities that can reveal the limits for the laser energy density of the incident laser from the point of view of the surface damage.

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## References

[1] Scepanovic, M., Jevtic, M., Numerical simulation of laser-induced mercury diffusion in HgCdTe using nonconstant segregation coefficients. *Phys. Stat. Sol. (a)*, **147**, pp. 379–387, 1995.

[2] Přikryl, P., Segeth, K., Černý, R., Computational modeling of pulsed laser-induced phase change processes in II-VI semiconductors. *Proc. of Heat Transfer VII*, eds. B. Sunden, C.A. Brebbia, WIT Press: Southampton, pp. 205–214, 2002.

[3] Přikryl, P., Gatskevich, E., Černý, R., Computational solution of a two-phase moving boundary problem with two moving interfaces in pulsed laser processing of semiconductors. *Proc. of Moving Boundaries 2003*, Santa Fe, November 4-6, 2003, to appear.

[4] Bayazitoglu, Y., Černý, R., Nonequilibrium evaporation of molten-metal drops in an alternating magnetic field. *Int. J. Heat Mass Trans.*, **36**, pp. 3449–3458, 1993.

[5] Kennard, E.A., *Kinetic Theory of Gases*, McGraw-Hill: New York 1938.

[6] Roth, A., *Vacuum Technology*, Amsterdam: North-Holland, 1976.

[7] Landau, H., Heat conduction in a melting solid. *Quart. of Applied Math.*, **8**, pp. 81–94, 1950.

[8] Černý, R., Kalbáč, A., Přikryl, P., Computational modeling of CdZnTe crystal growth from the melt. *Computational Materials Science*, **17**, pp. 34–60, 2000.

[9] Kim, C.C., Daraselia, M., Garland, J.W., Sivananthan, S., Temperature dependence of the optical properties of CdTe. *Phys. Rev. B*, **56**, pp. 4786–4797, 1997.