Computational versus experimental methods on laser processing of binary semiconducting systems

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Abstract

A computational model of pulsed laser-induced phase transitions in binary semiconducting systems is presented. The nonequilibrium phase change processes due to the high velocities of the interface are modeled using the concept of Wilson-Frenkel interface response function and nonequilibrium segregation coefficients are also considered. In the computational experiments, two real experimental situations are simulated, the first being the irradiation of a 150 nm Si_{50}Ge_{50} alloy on 500 nm SOS (silicon on substrate) by Q-switched ruby laser (694 nm, 30 ns FWHM), the second the irradiation of the system of 25 nm of amorphous Ge and 210 nm polycrystalline silicon on quartz substrate by XeCl excimer laser (308 nm, 27 ns FWHM). The comparison of computational results with experimental data shows reasonable agreement if we take account of the uncertainties both in the measurements and in the input data of the model.

1 Introduction

The increasing use of III-V and II-VI semiconductors and of variety of semiconducting alloys in the semiconductor device technology has caused the necessity to decrease thermal load during the production process, because the semiconductor properties are often seriously damaged at temperatures above 300°C. Laser processing has been widely studied as a possible approach to localizing the heat treatment into the thin layer of a processed material for a limited period of time.
Laser treatment has proved its worth as an effective tool to affect the initial structure and microstructure of the irradiated sample and their evolution on the short length scales (1μm–1nm) to create unusual phase combination or metastable phases, chemical modification and high stress or stress gradients. The laser melting and resolidification allows the formation of alloys at a concentration much higher than the maximum solid solubility. Moreover, for some impurities segregation is suppressed and complete solute trapping occurs while other impurities show intermediate segregation between the equilibrium value and complete trapping.

In the mathematical models of binary systems undergoing melting and solidification, two main phenomenological approaches are generally distinguished. The first of them generalizes the classical Stefan formulation (see, e.g., Atkin and Crain [1]), the other approach formulates the balances globally over the whole region occupied by the system (see, e.g., Alexiades and Solomon [2]) and uses a mushy-zone concept. Our treatment belongs to the first of the above types and we model the phase interface as a discontinuity surface.

For multicomponent systems in both approaches, an equilibrium phase diagram is employed most often to determine the actual position of the phase interface. Laser technologies, however, involve solidification processes that are far from equilibrium (as shown, e.g., by Černý, Šášík, Lukeš and Cháb in [3]). Therefore, nonequilibrium models of phase change processes are to be employed, which utilize the concept of an interface response function mostly.

In one-component systems, the interface response function is formulated as a relation between the velocity of the interface and its temperature. In two-component systems, the interface response function is more complicated due to the effect of concentration changes. However, both experimental and theoretical treatments have been developed which make it possible to determine the segregation coefficient as a function of the course of the process: the growth rate and undercooling. Kinetic phase diagrams that are obtained in this way are then employed in modeling phase transitions in these systems, and the mutual relationship between the velocity of the interface and both its temperature and concentration is then described by the interface response function.

In this paper, we will utilize the basic ideas of modeling binary alloy melting and solidification induced by pulsed lasers that were formulated by Černý and Přikryl in [4], [5]. The computational experiments done with two real experimental situations will be presented, and the results will be compared with the available experimental data.

2 Experimental situation

We will consider two real experimental situations involving pulsed laser irradiation of binary semiconducting alloys. The first of them was presented by
Thompson et al. in [6], where the irradiation of a 150 nm Si$_{50}$Ge$_{50}$ alloy on 500 nm SOS (silicon on substrate) by Q-switched ruby laser at wavelength of 694 nm with a 30 ns FWHM pulse duration is studied. The second one is taken from Slaoui et al. [7], where the system of 25 nm of amorphous Ge and 210 nm polycrystalline silicon on quartz substrate was irradiated by an XeCl excimer laser (308 nm, 27 ns FWHM) with energy densities ranging from 0.1 to 0.7 J/cm$^2$. We will briefly describe our computational models of these real experiments and then compare the data obtained.

3 Physical and mathematical model

We consider a binary alloy, consisting of components $A, B$, that is irradiated by a pulsed laser. The pulse width is within the nanosecond range and thus is long enough so that a thermal model not taking the relaxation times into account be employed. On the other hand, the phase transitions in the binary systems under consideration are still fast enough so that we have to assume that they have nonequilibrium character.

In modeling the nonequilibrium phase transitions in a binary system, we employ the model which we have formulated recently [5]. The model comprises the balance equations of internal energy of the system, the mass balances of a component of the mixture in the solid, in the liquid and at the solid/liquid phase interface, and uses the interface response function instead of the condition of local thermodynamic equilibrium common in the Stefan-like problems. Together with the interface response function, nonequilibrium segregation coefficient is also considered due to the high velocities of the interface in the laser induced phase change problems. We give a brief overview of the basic equations here only and refer the interested reader to [4] and [5] for a more detailed exposition.

The transport equations in the particular phases (the index $s$ denotes the solid phase, the index $l$ the liquid phase) can be expressed as follows:

\[
\rho_c \frac{\partial T_1}{\partial t} = \frac{\partial}{\partial x} \left( K_1 \frac{\partial T_1}{\partial x} \right) + (1 - R(t))\alpha_1(x)I_0(t) \exp(-\int_0^x \alpha_1(\eta)d\eta),
\]

\[x \in [0, Z(t)], \quad t > 0, \tag{1}\]

\[
\rho_s \frac{\partial T_s}{\partial t} = \frac{\partial}{\partial x} \left( K_s \frac{\partial T_s}{\partial x} \right) + (1 - R(t))\alpha_s(x)I_0(t) \times
\]

\[\times \exp(-\int_0^{Z(t)} \alpha_1(\eta)d\eta - \int_{Z(t)}^x \alpha_s(\eta)d\eta),
\]

\[x \in [Z(t), D], \quad t > 0, \tag{2}\]

\[
\frac{\partial C_{A,l}}{\partial t} = \frac{\partial}{\partial x} \left( D_1 \frac{\partial C_{A,l}}{\partial x} \right), \quad x \in [0, Z(t)], \quad t > 0, \tag{3}\]
where $T$ is the temperature, $\rho$ the density (assumed to be the same for both the phases), $c$ the specific heat, $K$ the thermal conductivity, $R(t)$ the reflectivity, $\alpha(x)$ the optical absorption coefficient, $I_0(t)$ the power density of the pulse (power per unit area), $Z(t)$ the position of the phase interface between the solid and liquid phase, $D$ the diffusion coefficient, and $C_A$ is the mass concentration of the component $A$.

On the phase interface we formulate the balance equations

$$\rho L_m \frac{dZ}{dt} = -K_1 \left( \frac{\partial T_1}{\partial x} \right)_{x=Z(t)^-} + K_s \left( \frac{\partial T_s}{\partial x} \right)_{x=Z(t)^+},$$

$$(C_{A,1} - C_{A,s}) \frac{dZ}{dt} = -D_1 \left( \frac{\partial C_{A,1}}{\partial x} \right)_{x=Z(t)^-} + D_s \left( \frac{\partial C_{A,s}}{\partial x} \right)_{x=Z(t)^+},$$

where $L_m$ is the latent heat of fusion, and employ the kinetic phase diagram by introducing the nonequilibrium segregation coefficient $k(T_z, C_z, dZ/dt)$ into the model. Moreover, we employ the Wilson-Frenkel interface response function

$$\frac{dZ}{dt} = f \nu \left[ 1 - \exp \left( -\frac{\Delta G}{k_B T_Z} \right) \right],$$

where

$$\Delta G = \Delta \mu_A C_{A,1,2} + \Delta \mu_B C_{B,1,2},$$

$T_Z$, $C_Z$ are the temperature and the concentration at the interface, $\Delta G$, $\Delta \mu$ are the changes of the Gibbs energy and of the chemical potential due to the phase transition, $k_B$ is the Boltzmann constant and $f, \nu$ are frequency factors.

The initial and boundary conditions are formulated in a way common for the models of laser processing [3]:

$$T(x, 0) = T_0 = \text{const.}, \quad x \in [0, D],$$

$$Z(0) = 0,$$

$$T(D, t) = T_0, \quad t > 0,$$

$$\frac{\partial T(0,t)}{\partial x} = 0, \quad t > 0,$$

$$C_A(x, 0) = C_0(x), \quad x \in [0, D],$$

$$\frac{\partial C_A(0,t)}{\partial x} = 0, \quad t > 0,$$

$$\frac{\partial C_A(D,t)}{\partial x} = 0, \quad t > 0.$$
4 Computational implementation

In solving the moving boundary problem formulated in Sec. 3 we employed a front-fixing technique and used the Landau transformations

\[ \xi = \frac{x}{Z(t)}, \quad x \in [0, Z(t)], \]

in the liquid and

\[ \xi = \frac{x - Z(t)}{D - Z(t)}, \quad x \in [Z(t), D], \]

in the solid.

The fixed-domain initial-boundary value problem obtained after the transformation was solved by the Galerkin finite element method. The space and time discretization was performed in a common way using linear basis functions, and thus a system of nonlinear algebraic equations for temperatures and concentrations to be solved at every time step of length \( \Delta t \) was obtained. The iteration algorithm used to solve the Stefan-like problem under consideration was based on the successive approximation approach with underrelaxation. The interface balance conditions were incorporated in the right-hand side of the system of algebraic equations, the interface values of temperature and concentrations being coupled through the phase diagram. The interface response function was used as the convergence condition in the iteration procedure. The details of the computational algorithm can be found in [5].

5 Numerical simulations vs. experimental data

In the computational models of the experimental situations of Sec. 2, we applied the thermodynamic and optical parameters of the crystalline and liquid silicon, amorphous and liquid germanium, and the Si-Ge system that were analyzed and surveyed in [8]. In the practical calculations, we have simulated the temperature and concentration fields in both solid and liquid phases, and the position and velocity of the solid/liquid interface. In this way, we have obtained results directly comparable with the experimental data.

First, we have done the calculations corresponding to the experimental conditions of Thompson et al. [6]. The main results are summarized in Figs. 1–5. Figure 1 shows the surface temperatures as functions of time and energy density. The characteristic delays in the decreasing parts of the curves indicate that the melt remains a rather long time in an undercooled state while the solid/liquid interface moves with a near constant velocity. This is also supported by Fig. 2, where the solid/liquid interface velocity is presented.

Figure 3 shows that the molten layer thickness vs. time curves are developing in a similar way until the laser energy is high enough for the
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Figure 1: Surface temperature as a function of the laser energy density and time for the experimental situation according to [6].

Figure 2: Solid/liquid interface velocity as a function of the laser energy density and time for the experimental situation according to [6].

Figure 3: Molten layer thickness as a function of the laser energy density and time for the experimental situation according to [6].

Figure 4: Solid mass concentration of Si on the solid/liquid interface as a function of the laser energy density and time for the experimental situation according to [6].
melt front to reach the SOS substrate. This occurs at approximately 0.92 J/cm². Then, the character of the decreasing parts of the curves is changed, which is apparently related to the changes in the composition at the melt front that affect its velocity significantly. This is documented in Fig. 4, where the time development of the solid concentration at the interface is depicted. Figure 5 shows the melt duration as a function of the energy density. The delay on the curve beginning at approximately 0.80 J/cm² can again be attributed to the fact that the front is approaching the SOS substrate.

The comparison of computational results with the experimental data by Thompson et al. [6] could be done for the energy density 1.0 J/cm² only because no other data were presented in [6]. From these results it follows that our model was able to reproduce relatively very well the surface melt duration (174 ns in our model and around 180 ns in [6]). On the other hand, the agreement in maximum molten layer thickness was worse (180 nm in our model contrary to about 250 nm in [6]), whereas the front velocities predicted by our model achieved an excellent agreement in the maximum value (both about 3.5 m/s) but the plateau values differed significantly (about 1 m/s in our model but 2 m/s in [6]). However, taking into account the uncertainties both in calibrating the TRC data which served for the calculations of melt depths and front velocities by Thompson et al. [6] and in the thermal conductivity values of the Si-Ge alloy used in our model, also this agreement can be found satisfactory.

In the second part of our calculations, we have simulated the experimental conditions by Slaoui et al. [7]. The results are summarized in Figs. 6–10.
Surface temperatures in Fig. 6 exhibit similar features as those in Fig. 1, i.e., the delays in the decreasing parts of the curves. Contrary to the previous experimental situation, the delays are more apparent in the range of higher energy densities where the effect of alloying the original surface Ge layer is more pronounced.

Figure 7 shows that certain delays appear in the initial parts of the melt depth vs. time curves. This may be explained as a consequence of the fact that the melt front approached the Si substrate, and the velocity of the front was suddenly reduced because of the higher melting temperature of silicon compared to germanium. This is evidenced more clearly in Fig. 8 where the interface velocity as a function of the energy density and time is presented.

Slaoui et al. [7] measured surface melt duration and final molar Ge concentration in their experimental work. Figures 9 and 10 present a comparison of our experimental results with those obtained in [7]. We can see that our melt durations are slightly lower than those given by Slaoui et al. but the differences are less than 20%, which can be considered a reasonable agreement taking account of the uncertainties in the values of the thermal conductivities of the Si-Ge alloy used in our model. Concerning the final molar concentrations, we achieved a very good agreement for 0.60 J/cm², where the differences were less than 20%, but the agreement for other laser energy densities was worse. However, if we consider the uncertainties in both the experimental measurements of concentration profiles, which particularly in the parts close to the sample surface have significantly lower precision, and in the input data of our model, particularly in the parame-

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**Figure 7:** Molten layer thickness as a function of the laser energy density and time for the experimental situation according to [7].

**Figure 8:** Solid/liquid interface velocity as a function of the laser energy density and time for the experimental situation according to [7].
6 Conclusion

The computational model of pulsed laser-induced phase-change processes in binary semiconducting systems presented in this paper was found to reproduce reasonably well the characteristic data that can be obtained from the experimental measurements. The differences up to 20% observed for the most of compared quantities can be considered reasonable if the uncertainties in both the experimental data and the material parameters entering the computational model are taken into account.

It is worth noting in conclusion that it is rarely an easy task to gather all the necessary material data for the model to describe the real experimental situation adequately. A good model can describe the real experiment qualitatively well but to achieve a satisfactory quantitative agreement the quality of the model input data is at least as important as the quality of the model itself.

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References


