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A computational model of phase changes in the Ni-Si system with chemical reactions

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Abstract

A computational model describing pulsed-laser induced chemical reactions in the thin nickel film – silicon system undergoing phase changes is formulated in the paper. The implementation of the model is performed using the finite element method. The moving boundary problem describing the behavior of the sample is solved by a front-fixing method combined with the successive approximation approach. The implementation of the model is discussed and typical results of numerical experiments are presented. A comparison with preliminary experimental results shows that the model can predict the behaviour of the studied system quite satisfactorily.

1 Physical model

We consider the following experimental situation: A thin nickel film is deposited on the mono-Si substrate by an evaporation technique and the system then undergoes pulsed laser irradiation. Due to the increasing temperature, a solid-state chemical reaction is initiated on the Ni/Si interface.

Following the classical theory of solid-state reactions [1] and previous experimental work with Ni silicides [2,3], we suppose that the chemical reactions in the solid-state Ni-Si system are driven by diffusion effects. In

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the diffusion process, we assume that only a part of diffusing atoms can be trapped in the lattice of the majority compound to form a silicide, whereas the remaining atoms diffuse further. The diffusion effects are always coupled with heat transfer since the material parameters are functions of both temperature and concentration. Also, the chemical-reaction production terms appear both in heat and mass balance equations. Therefore, a coupled heat and mass transfer problem is to be solved.

The pulsed-laser induced chemical reactions in the Ni-Si system are modelled as follows. In accordance with [2,3] we assume that for $T < T_{\mathrm{cr1}}$ the predominant chemical reaction is $2\,\mathrm{Ni} + \mathrm{Si} \rightarrow \mathrm{Ni_2Si}$ and the only silicide formed is $\mathrm{Ni_2Si}$.

When $T > T_{\mathrm{cr1}}$ but still $T < T_{\mathrm{cr2}}$, we suppose that only NiSi is formed, either by $\mathrm{Ni_2Si} + \mathrm{Si} \rightarrow 2\,\mathrm{NiSi}$ or directly as $\mathrm{Ni} + \mathrm{Si} \rightarrow \mathrm{NiSi}$. Since the heat necessary for the former reaction is approximately 4–5 times lower than that for the latter (see [4]), it is apparent that for the formation of NiSi the first of the above mechanisms will be dominant.

After the temperature reaches T_{cr2}, we assume that only $\mathrm{NiSi_2}$ is formed, either as $\mathrm{NiSi} + \mathrm{Si} \rightarrow \mathrm{NiSi_2}$ or $\mathrm{Ni} + 2\,\mathrm{Si} \rightarrow \mathrm{NiSi_2}$, eventually also as $\mathrm{Ni_2Si} + 3\,\mathrm{Si} \rightarrow 2\,\mathrm{NiSi_2}$ since there may still remain some $\mathrm{Ni_2Si}$ due to the rapidity of the process. The first mechanism is dominating again because the heat necessary for this reaction is almost 20 times lower than that for a direct formation of $\mathrm{NiSi_2}$ from Ni and Si and approximately 4 times lower than that for the third of the above reactions.

With the decrease of laser energy absorbed in the sample later in the pulse, temperature begins to decrease and the conditions for silicide formation change again. In accordance with [5] we suppose that $\mathrm{NiSi_2}$ remains unchanged and no reverse reaction resulting in a formation of silicon-less-rich silicides can occur. However, Ni and Si still diffuse in the system and either NiSi or $\mathrm{Ni_2Si}$, depending on the temperature, can be formed by a similar mechanism as above.

To summarize our considerations, the final structure of the surface layer may be quite complicated and consist generally of all three silicides, $\mathrm{Ni_2Si}$, NiSi and $\mathrm{NiSi_2}$, together with some free Si atoms diffusing for instance on the grain boundaries.

We have been working under the solid-state conditions, until now. In general, a chemically reacting system can undergo phase changes as well. Also here, we solve a coupled heat and mass transfer problem, naturally with different material parameters, and with a moving boundary between the solid and the liquid phases which can change their composition due to the diffusion effects and possibly also between liquid and vapour; thus, kinetic phase diagrams would be necessary to solve this problem. Since the segregation coefficients generally tend to 1 rapidly with the velocity of the phase change process, we can simplify the problem and assume that there is no concentration jump at the phase interfaces. Consequently, it is sufficient to formulate the balances of internal energy across the interfaces only.

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2 Mathematical model

We suppose that the experimental setup of the physico-chemical problem described in the previous section allows us to treat it in one space dimension (see [6] for explanation). We denote by B the overall thickness of the sample and by A, $A << B$, the thickness of the Ni film. The diffusion equations for Ni and Si for $x \in [0, B]$ read

$$\frac{\partial C_{\text{Ni}}}{\partial t} = \frac{\partial}{\partial x}\left(D_{\text{Ni}}\frac{\partial C_{\text{Ni}}}{\partial x}\right) - q_{\text{Ni}}C_{\text{Ni}}, \tag{1}$$

$$\frac{\partial C_{\text{Si}}}{\partial t} = \frac{\partial}{\partial x}\left(D_{\text{Si}}\frac{\partial C_{\text{Si}}}{\partial x}\right) - q_{\text{Si}}C_{\text{Si}}. \tag{2}$$

Here, C is the concentration in mol/m^3, $D_{\text{Ni}}, D_{\text{Si}}$ are the diffusion coefficients of Ni in Si and Si in Ni, resp., $D_{\text{Ni}} = D_1 \exp(-Q_1/k_{\text{B}}T)$, $D_{\text{Si}} = D_2 \exp(-Q_2/k_{\text{B}}T)$, where k_{B} is the Boltzmann constant, and Q_1, Q_2 are the activation energies for the diffusion of Ni in Si, Si in Ni, resp., and $q_{\text{Ni}}, q_{\text{Si}}$ are determined by the amount of the minority atoms available at the particular point x.

The time development of the concentration of a silicide can be then schematically described by

$$\frac{\partial C_{\text{Ni}_x\text{Si}_y}}{\partial t} = \frac{q_w}{z}C_w, \tag{3}$$

where w denotes the minority element at a given place, $w =$ Ni or Si, C_w is the concentration of the minority atoms, q_w is also related to the minority atoms, and z is either x or y, i.e., the number of Ni or Si atoms in the silicide molecule, whichever of these is the minority element.

As we mentioned earlier, the diffusion equations (1) and (2) have to be solved together with the heat conduction equation. For a simplified case of a laser irradiated system with chemical reactions the heat conduction equation reads

$$\rho c\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(K\frac{\partial T}{\partial x}\right) + S(x,t) + \sum \Delta H_{\text{Ni}_x\text{Si}_y}\frac{\partial C_{\text{Ni}_x\text{Si}_y}}{\partial t}, \tag{4}$$

where ρ is the density, c the specific heat, K the thermal conductivity, S the heat-source term originating from the absorption of the laser energy (see [6], for example), ΔH is the reaction heat (in J/mol and negative for the formation of silicides) and the sum has from one to three terms according to the number of chemical reactions involved in the production of a particular silicide (or to the value of temperature at the particular point x). Note that all the material parameters in (4) are considered to be parameters of a mixture consisting of Ni, Si and all Ni silicides.

The initial conditions for the initial-boundary problem to be solved are

$$C_{\text{Ni}}(x,0) = C_{0,\text{Ni}}, \quad x \in [0, A], \tag{5}$$

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$$C_{\mathrm{Ni}}(x,0) = 0, \quad x \in [A,B], \tag{6}$$

$$C_{\mathrm{Si}}(x,0) = 0, \quad x \in [0,A], \tag{7}$$

$$C_{\mathrm{Si}}(x,0) = C_{0,\mathrm{Si}}, \quad x \in [A,B], \tag{8}$$

$$T(x,0) = T_0, \quad x \in [0,B]. \tag{9}$$

The concentrations of the silicides are zero at $t = 0$, of course. The boundary conditions are

$$\frac{\partial C_w}{\partial x} = 0, \quad w = \mathrm{Ni},\mathrm{Si}, \quad x = 0, x = B, \quad t \geq 0, \tag{10}$$

$$\frac{\partial T}{\partial x} = 0, \quad x = 0, \tag{11}$$

$$T(B,t) = T_0, \quad t \geq 0. \tag{12}$$

Naturally, the model allows for other standard boundary conditions as well. The temperature and the concentration fields are supposed to be continuous for $t > 0$.

When phase changes arise in the system, the equations (1), (2) and (4) are then formulated in the particular phases separately and additional conditions at the phase interfaces have to be formulated. With the increase of the temperature of the liquid phase surface, also evaporation may become important. Thus, we have a three-phase system with two moving boundaries which can be converted to a two-phase system with two moving boundaries after some simplifications (see [7] for details).

The balances of internal energy at the phase interfaces read

$$\rho^l L_{\mathrm{v}} \dot{Z}_1 = K^l \left(\frac{\partial T^l}{\partial x}\right)_{x=Z_1(t)+} - \epsilon\sigma_{SB}(T_{Z_1}^4 - T_{\mathrm{e}}^4), \tag{13}$$

$$\rho^s L_{\mathrm{m}} \dot{Z}_2 = K^s \left(\frac{\partial T^s}{\partial x}\right)_{x=Z_2(t)+} - K^l \left(\frac{\partial T^l}{\partial x}\right)_{x=Z_2(t)-}, \tag{14}$$

where Z_1 is the position of the liquid/vapour interface (the surface of the sample), Z_2 the position of the solid/liquid interface, T_{Z_1} is the temperature of the interface Z_1, T_{e} the temperature of the surroundings, $\dot{Z}_1 = \mathrm{d}Z_1/\mathrm{d}t$, $\dot{Z}_2 = \mathrm{d}Z_2/\mathrm{d}t$, L_{v} the latent heat of evaporation, L_{m} the latent heat of melting, σ_{SB} the Stefan-Boltzmann constant, ϵ the emissivity, and the indices l, s denote the liquid and the solid phase, respectively. In the Eq. (13), we assume only radiation heat transfer between the sample and the surroundings since the most experimental work on the laser irradiation of metal-Si systems is performed under vacuum conditions.

The positions of the liquid/vapor and solid/liquid interfaces, Z_1, Z_2, are functions of time, as well as the domains occupied by the respective phases. Therefore, Eqs. (13) and (14) are to be supplemented by further conditions.

We suppose the phase changes to have a nonequilibrium character and formulate the following conditions describing the kinetics of the liquid/vapour and the solid/liquid interfaces (see [7]):

$$\dot{Z}_1 = \frac{C_2}{\rho}\sqrt{\frac{M}{2\pi R_g}}\, T_{Z_1}^{C_0} \cdot 10^{(-A/T_{Z_1})+B}, \tag{15}$$

$$\dot{Z}_2 = -C_1 \exp\left(\frac{-Q}{k_B T_{Z_2}}\right)\left\{1 - \exp\left[-\frac{L_p}{k_B}\left(\frac{1}{T_{Z_2}} - \frac{1}{T_{eq}}\right)\right]\right\}, \tag{16}$$

where M is the molar mass, R_g the universal gas constant, C_0, C_1, C_2, A, B are other material constants, L_p the latent heat of fusion per particle, Q the activation energy for self-diffusion in the liquid, k_B the Boltzmann constant, T_{eq} the equilibrium melting temperature, and T_{Z_2} is the temperature of the interface Z_2.

The system of equations (1), (2), (4), (13)–(16) is then solved for the unknowns $C_{Si}, C_{Ni}, T, Z_1, Z_2, T_{Z_1}, T_{Z_2}$.

3 Numerical solution

First, we use the Landau transformations in order to convert both the liquid and solid regions into fixed space intervals $\xi = [0, 1]$. We write

$$\xi = \frac{x - Z_1(t)}{Z_2(t) - Z_1(t)}, \quad x \in [Z_1(t), Z_2(t)] \tag{17}$$

in the liquid and

$$\xi = \frac{x - Z_2(t)}{D - Z_2(t)}, \quad x \in [Z_2(t), D] \tag{18}$$

in the solid.

Then, we apply a standard Galerkin finite element discretization in space and in time resulting in a system of equations which can be formally written as

$$[A_1]\{C_{Ni}\}_{t+\Delta t} = [B_1]\{C_{Ni}\}_t + \{Y_1\}, \tag{19}$$

$$[A_2]\{C_{Si}\}_{t+\Delta t} = [B_2]\{C_{Si}\}_t + \{Y_2\}, \tag{20}$$

$$[A_T]\{T\}_{t+\Delta t} = [B_T]\{T\}_t + \{Y_T\} \tag{21}$$

Equation (13) is used as a Newton boundary condition for (4), equation (14) is used to couple the matrices of the solid and liquid phases originated from the discretization of (4).

To proceed with the solution from time t to time $t + \Delta t$ we then have to solve the system of equations (19)–(21), (15), (16). We use the following iteration algorithm in each time step:

1. Put $Z_1^{(1)}(t+\Delta t) = Z_1(t)$, $\dot{Z}_1^{(1)}(t+\Delta t) = \dot{Z}_1(t)$, $Z_2^{(1)}(t+\Delta t) = Z_2(t)$, $\dot{Z}_2^{(1)}(t+\Delta t) = \dot{Z}_2(t)$.
2. Compute $\{C_{Ni}\}_{t+\Delta t}^{(1)}$, $\{C_{Si}\}_{t+\Delta t}^{(1)}$, and $\{T\}_{t+\Delta t}^{(1)}$, from (19)–(21) using

$Z_1^{(1)}(t+\Delta t)$, $\dot{Z}_1^{(1)}(t+\Delta t)$, $Z_2^{(1)}(t+\Delta t)$, $\dot{Z}_2^{(1)}(t+\Delta t)$.

3. Compute $\dot{Z}_1^{(2)}(t+\Delta t)$ from (15) and $\dot{Z}_2^{(2)}(t+\Delta t)$ from (16) using $\{T\}_{t+\Delta t}^{(1)}$.

4. If

$$\left|\frac{\dot{Z}_1^{(2)}(t+\Delta t)-\dot{Z}_1^{(1)}(t+\Delta t)}{\dot{Z}_1^{(1)}(t+\Delta t)}\right| > \delta \quad \text{or} \quad \left|\frac{\dot{Z}_2^{(2)}(t+\Delta t)-\dot{Z}_2^{(1)}(t+\Delta t)}{\dot{Z}_2^{(1)}(t+\Delta t)}\right| > \delta,$$

where δ is a user tolerance, then choose $q \in (0,1]$, put

$$\begin{aligned}
\dot{Z}_1^{(1)}(t+\Delta t) &= q\dot{Z}_1^{(2)}(t+\Delta t)+(1-q)\dot{Z}_1^{(1)}(t+\Delta t),\\
\dot{Z}_2^{(1)}(t+\Delta t) &= q\dot{Z}_2^{(2)}(t+\Delta t)+(1-q)\dot{Z}_2^{(1)}(t+\Delta t),\\
Z_1^{(1)}(t+\Delta t) &= Z_1(t)+\Delta t\dot{Z}_1^{(1)}(t+\Delta t),\\
Z_2^{(1)}(t+\Delta t) &= Z_2(t)+\Delta t\dot{Z}_2^{(1)}(t+\Delta t),
\end{aligned}$$

and go back to Step 2.

Otherwise, put

$\{C_{\mathrm{Ni}}\}_{t+\Delta t}=\{C_{\mathrm{Ni}}\}_{t+\Delta t}^{(1)}$, $\{C_{\mathrm{Si}}\}_{t+\Delta t}=\{C_{\mathrm{Si}}\}_{t+\Delta t}^{(1)}$, $\{T\}_{t+\Delta t}=\{T\}_{t+\Delta t}^{(1)}$,

$\dot{Z}_1(t+\Delta t)=\dot{Z}_1^{(2)}(t+\Delta t)$, $\dot{Z}_2(t+\Delta t)=\dot{Z}_2^{(2)}(t+\Delta t)$,

$Z_1(t+\Delta t)=Z_1(t)+\frac{1}{2}\Delta t[\dot{Z}_1^{(2)}(t+\Delta t)+\dot{Z}_1(t)]$,

$Z_2(t+\Delta t)=Z_2(t)+\frac{1}{2}\Delta t[\dot{Z}_2^{(2)}(t+\Delta t)+\dot{Z}_2(t)]$

and go to the next time step.

4 Numerical experiments

We simulated the chemical reactions in a Ni-Si system with $A \in$ [200nm, 5μm], $B = 8$ μm, $E \in$ [0.8 Jcm^{-2}, 1.5 Jcm^{-2}], induced by XeCl excimer laser with the wavelength of 308 nm and the pulse length of 28 ns FWHM (full width at half maximum).

First, we tested the numerical accuracy and stability of our algorithm. We varied the length of finite elements L_i in the particular phases and materials and the maximum allowable time step $\Delta t_{\max}$, we also tested the influence of the numerical parameters of the iteration procedure, namely the relaxation factor q and the tolerance δ. We adopted the following criterion in the optimizing of the numerical parameters: The characteristic values of temperature, concentration, solid/liquid interface position and velocity had to agree to 0.1% accuracy when going up with L_i, $\Delta t_{\max}$ and δ, compared to the chosen maximum-accuracy case. We found the following optimum values of the numerical parameters: $\Delta t_{\max} = 5 \times 10^{-3}$ns, $\mathrm{L}_{\mathrm{l-Ni}} = 0.2$nm, $\mathrm{L}_{\mathrm{s-Ni}} = 1$nm, $\mathrm{L}_{\mathrm{l-Si}} = 1$nm, $\mathrm{L}_{\mathrm{s-Si}} = 8$nm, $\delta = 10^{-3}$, where for instance the index l-Ni represents the liquid part of the region initially occupied by Ni. The influence of the relaxation factor $q \in (0,1]$ was found to be critical for the convergence of the iteration procedure described in Sec. 3. The choice of $q = 0.5$ gave satisfactory results in all the experiments performed.

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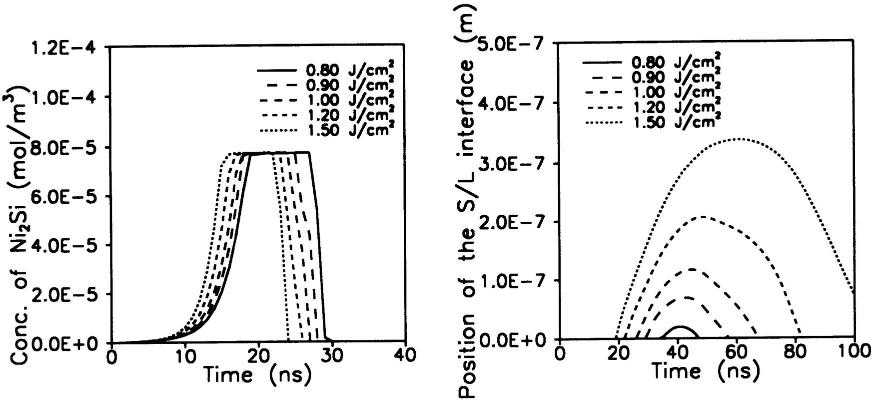

Figure 1: The history of a) Ni_2Si concentration at the initial Ni-Si interface, b) position of the solid/liquid interface for A = 500 nm, $E \in$ [0.8 Jcm^{-2}, 1.5 Jcm^{-2}]

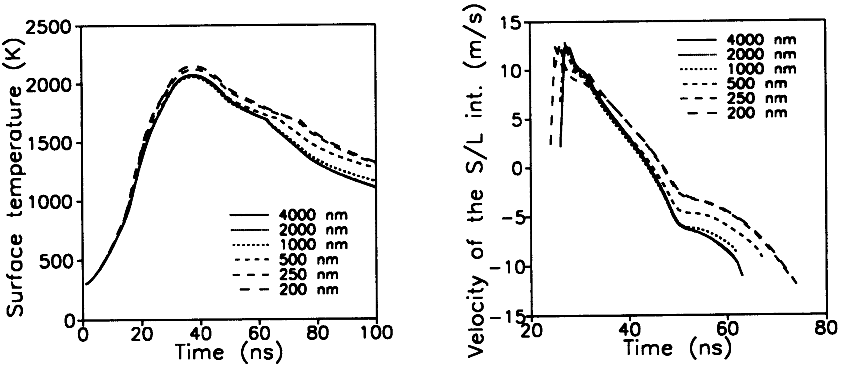

Figure 2: The history of a) surface temperature, b) solid/liquid interface velocity for E = 1.0 Jcm^{-2}, $A \in$ [200nm, 5μm]

Our numerical experiments were done on a HP 720 workstation. A typical simulation in the time interval of 100 ns with the above optimum numerical parameters took approximately 10 hours computing time in the single-user regime.

In the second part of our calculations we simulated the influence of energy density E of the laser pulse for $E \in$ [0.8 Jcm^{-2}, 1.5 Jcm^{-2}], which are the values above the melting threshold of the system. We have chosen $A = 500$ nm and $B = 8\,\mu$m as the values of the initial thicknesses of the Ni and Si layers. The results of these computational experiments are illustrated in Figs. 1a,b showing the histories of the concentration of Ni_2Si at the initial Ni-Si interface and of the position of the solid/liquid interface.

Finally, we studied the influence of the initial thickness A of the Ni layer for $A \in$ [200nm, 5μm] with E = 1.0 Jcm^{-2}. Typical results are shown in Figs. 2a,b where the histories of the surface temperature and of the

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solid/liquid interface velocity are depicted.

5 Conclusion

Laser synthesis of silicides has not been experimentally investigated frequently in the past, first papers appeared just recently [8,9]. Therefore, we did not have many opportunities to compare our results with the real experiments. However, we note that our computational results qualitatively agree quite well with the preliminary experimental results of [8]; for instance, the whole 500 nm layer of Ni has fully reacted after one laser pulse in our calculations as well as in the experiments.

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