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Theoretical models of fast crystallization of a-Si thin films[1]

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Abstract

In this paper, we report the models of fast recrystallization processes in a-Si thin films. An important feature of the modeling of nucleation in a-Si films is the capability of allowing description of non-equilibrium solidification including the distribution of small crystalline clusters which can be responsible for visible photoluminescence. We integrate the results of the description of nucleation and growth on the phase interface of c-Si from a-Si or l-Si. The transient time, nucleation rate and growth rate were determined as a function of temperature and the position of local extremes of these functions were stated. The solidification velocity was calculated from the nucleation rate and growth rate with respect to the temperature distribution in a system. The suitability of the particular approximations and models is discussed.

Keywords: Fast crystallization; Model; Nucleation; Silicon thin films; Solidification velocity

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1. Introduction

Irradiation of semiconductors by a short (nanosecond) laser pulse with energy density above a certain threshold produces fast melting of a thin surface layer followed by its rapid resolidification. Heating and cooling rates are orders of magnitude faster than those achieved by any other treatment; solidification at a fast-moving liquid-solid interface takes place under conditions far from thermal equilibrium. In many cases the interface motion is so fast, that strong overheating and/or undercooling must be taken into account. Such extremely non-equilibrium processing can result in the significant modification of surface properties and formation of metastable phases which can not be prepared under near-equilibrium conditions [1–3]. The formation of monocrystalline clusters in thin Si films results in the emission of visible blue light during laser illumination, which was explained by the quantum size effect (see e.g. Ref. [4]). Such material has potential for many technical applications.

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[1] Dedicated to Professor Hiroshi Suga.

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To describe the formation of a solid phase under such conditions, we have to study both the transformation of the amorphous phase (a-Si) of silicon to a highly undercooled liquid phase (l-Si) (or directly to crystalline Si, c-Si) and the subsequent ultrarapid solidification. The melting temperature of a-Si (T_m) is apparently some 150–300 K below the melting temperature of c-Si ($T_c = 1683$ K), thus molten l-Si is undercooled by hunderds of Kelvin and bulk nucleation occurs in the undercooled melts [5, 6].

Despite extensive research in the laser processing of semiconductors during the last ten years, knowledge of the solidification processes (nucleation, growth on interface) is still fairly incomplete. In this work, we discuss the mechanism of homogeneous nucleation of c-Si in both a-Si and l-Si phases and the growth rate on the phase interface. Recently, these processes were studied theoretically and experimentlly using different methods and thus the results are scattered, see e.g. Ref. [7–14]. The aim of this work is to integrate the results of the description of recrystallization processes in a-Si and to present an analysis of this process from the temperature history in the Si thin films.

In the first part, theories of homogeneous nucleation of c-Si from a-Si or l-Si phases and of growth of c-Si on an existing phase interface are summarized. We present values of the basic parameters (activation energy, surface energy, diffusion coefficient, etc.), which were taken from recent publications and modified to obtain good agreement of the theory with published experimental data, e.g. the temperature dependence of the growth rate, the rate of stationary nucleation, etc.

In the second part, we determine the relation for the time evolution of the relative volume of c-Si phase in a-Si or l-Si. Within the framework of this model, processes of nucleation and of growth at the phase interface are included and rapid changes of temperature in the system are assumed. We discuss the suitability of appropriate approximations with respect to relations between the characteristic times of particular processes (temperature changes, nucleation, growth on phase interface) which are necessary for modelling the recrystallization of a-Si thin films.

2. Nucleation of crystalline silicon from the melt

In this section, we summarize the theoretical models of nucleation from a melt that are suitable for our purposes and determine basic material constants.

2.1. The change in Gibbs free energy

In the description of nucleation processes, we start from the change in Gibbs free energy ΔG of the given volume of our system during the phase transformation l-Si → c-Si, i.e. formation of one nucleus of solid phase

$$\Delta G(g) = -g\Delta G_{\mathrm{cl}} + A(g) \tag{1}$$

where g is the number of atoms in a given volume, ΔG_{cl} is the change in Gibbs free energy per atom (chemical potential) during the transition l-Si → c-Si, and $A(g)$ is the

surface energy of the cluster of g atoms. There are several models to describe the changes in chemical potential at temperature T [1, 2, 14]. We introduce two of them:
(a) A very simple model

$$\Delta G_{\mathrm{cl}}(T) = -L_{\mathrm{c}}\frac{\Delta T}{T_{\mathrm{c}}} \tag{2}$$

where T_{c} is the equilibrium temperature of crystallization of l-Si, $\Delta T = T - T_{\mathrm{c}}$ represents the undercooling of the system, and L_{c} is the latent heat of phase transformation per atom.
(b) A More general model

$$\Delta G_{\mathrm{cl}}(T) = \Delta h(T) - T\Delta S \tag{3}$$

where the change in inner energy is given by the relation

$$\Delta h(T) = \Delta h(T_{\mathrm{c}}) + \int_{T}^{T_{\mathrm{c}}} \Delta c_p(T)\mathrm{d}T \tag{4}$$

where $\Delta h(T_{\mathrm{c}})$ is the change in enthalpy at T_{c} per atom, and $\Delta c_p(T)$ is the change in specific heat per atom. For simplicity, we assume the approximation

$$\int_{T}^{T_{\mathrm{c}}} \Delta c_p(T)\mathrm{d}T = (T_{\mathrm{c}} - T)(c_{\mathrm{l}} - c_{\mathrm{s}}) \tag{5}$$

where $c_{\mathrm{l}}, c_{\mathrm{s}}$ are the specific heat per atom at T_{c} of liquid (l) and solid(s) phase, respectively, and the change of entropy is expressed by

$$\Delta S(T) = \int_{0}^{T}\left(\frac{\Delta c_p(T)}{T}\right)\mathrm{d}T \tag{6}$$

Turning our attention to the surface energy $A(g)$, we use the relation

$$A(g) = \sigma_{\mathrm{lc}}A_{\mathrm{c}}(g) \tag{7}$$

where σ_{lc} is the density of energy per unit area on the melt–crystal interface, and $A_{\mathrm{c}}(g)$ is the total surface of crystalline phase with g atoms. Usually it is accepted that

$$A_{\mathrm{c}}(g) = \gamma g^{2/3} \tag{8}$$

where γ is the geometrical factor [1, 14].

2.2. *Critical nucleus*

It has been shown [2, 14] that at a given temperature $T < T_{\mathrm{c}}$ the function $\Delta G(g)$ has a maximum at some critical value g^*. The nuclei $g < g^*$ are spontaneously dissolved, the nuclei with $g > g^*$ grow (ΔG decreases during growth). In case (a) we obtain

$$g^*(T) = \frac{32\pi}{3}\frac{a^6 T_{\mathrm{c}}^3 \sigma_{\mathrm{lc}}^3}{L_{\mathrm{c}}^3(T_{\mathrm{c}} - T)^3} \tag{9}$$

In case (b) we have

$$g^*(T) = \frac{32\pi}{3} \frac{a^6 \sigma_{\mathrm{lc}}^3}{(\Delta h(T) - T\Delta S)^3} \tag{10}$$

where a is the effective radius of an Si atom in the crystalline phase. In this way, we described the nucleation in liquid silicon. These models were used for the description of recrystallization in a-Si.

2.3. The nucleation rate

This section describes the kinetics of the nucleation process. From the point of view of the course of nucleation, we can distinguish three different conditions.

Stationary regime

The following assumptions are usually accepted, which enable us to determine the nucleation rate in a useful shape [1, 2, 14]: the temperature is constant; only monomers (single atoms) can contribute to the growth (we neglect the integration of larger clusters); f_0 is constant (see later); and the nucleation rate is the rate of formation of critical nuclei.

The steady-state nucleation rate j_{ss} at constant temperature T is given by the relation (see [1, 2, 8, 9])

$$j_{\mathrm{ss}}(T) = Z\beta(g^*) f_{\mathrm{eq}}(g^*) \tag{11}$$

where β is the rate of monomer addition, $f_{\mathrm{eq}}(g)$ the equilibrium distribution function of clusters with g atoms, Z is the Zeldovitsch factor [15]

$$Z = \left[-\frac{(\partial^2 \Delta G / \partial g^2)_{g=g^*}}{2\pi k_{\mathrm{B}} T} \right]^{1/2} = \left(\frac{W^*}{k_{\mathrm{B}} T 3\pi (g^*)^2} \right)^{1/2} \tag{12}$$

where k_{B} is Boltzmann's constant, W^* is the work needed for the creation of a critical nucleus

$$W^* = \Delta G(g^*) \tag{13}$$

and β is frequently approximated by the relation

$$\beta(g^*) = \Gamma \rho_{\mathrm{s}} A_{\mathrm{c}}(g^*) \tag{14}$$

where Γ is the frequency of transition of one atom from liquid to solid phase (per unit time), and ρ_{s} is the number of atoms on the surface of a nucleus per unit area. For our calculations, we use the approximation (see [1, 2])

$$\Gamma = \frac{6}{l^2} D_0 \exp\left(-\frac{Q}{k_{\mathrm{B}} T} \right) \tag{15}$$

where l is the jump length of an atom during a change of position in the liquid, D_0 is a kinetic factor, and Q the activation energy of self-diffusion. In Eq. (12) we sybstitute (see[1,2])

$$f_{\mathrm{eq}}(g^*) = f_0 \exp\left(-\frac{\Delta G(g^*)}{k_{\mathrm{B}}T}\right) \tag{16}$$

where f_0 is the density of centers of nucleation in the liquid phase. This value f_0 can depend on temperature or on the history of the temperature treatment of the system. In the ideal case f_0 is equal to the number of atoms per unit volume (homogeneous nucleation), thus in this case

$$f_0 = V_{\mathrm{m}}^{-1} \tag{17}$$

where V_{m} is the effective volume of one atom.

Non-stationary nucleation; constant temperature

Under non-stationary nucleation at constant temperature, there is an increase in nucleation rate from zero to its stationary value at a given temperature. We recommend use of the known Kashchiev relation for the nucleation rate $j(t)$ as a function of time t beacuse of its easy practical use and satisfactory precision in comparison with other models and experimental data (see Ref. [1,2,8,14,16])

$$j(t) = j_{\mathrm{ss}}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp\left(-n^2\frac{t}{\tau_{\mathrm{k}}}\right)\right] \tag{18}$$

where τ_{k} is the "time lag", a characteristic period for transition into the steady state nucleation

$$\tau_{\mathrm{k}} = \frac{4}{\pi^2 Z^2 \beta(g^*)} \tag{19}$$

More exact relation for $j(t)$ and τ_{k} are presented in Ref [14, 16].

Non-stationary nucleation; time-dependent temperature

If the temperature in the system changes slowly in comparison to the nucleation process, the relations of the stationary nucleation theory can be used for the description of the evolution of the system, but now the temperature is a function of time. In the case of rapid changes in temperature, the description of the evolution of the phase transformation is much more complex (see Ref. [16-18] where some numerical calculations of non-stationary nucleation rates are demonstrated), and we shall not deal with this case.

2.4. *Numerical results*

In this section, we summarize the numerical results of c-Si nucleation from melt in dependence on the undercooling of the melt and on the choice of material constants. The values of the respective parameters are summarized in Table 1. The basic values of

Table 1
The values of material constants describing recrystallization in l-Si

Parameter	Value	Unit	Ref.
T_c	1687	K	[10]
L_c	8.4×10^{-20}	J/atom	[10]
c_l	0.452×10^{-22}	JK^{-1}/atom	[10]
c_s	0.481×10^{-22}	JK^{-1}/atom	[10]
S_r	2.756×10^{-24}	JK^{-1}/atom	[8]
σ_{lc}	0.31	Jm^{-2}	[8]
γ	$4.836a^2$	m^2	
a	1.35×10^{-10}	m	[8]
k_B	1.308×10^{-23}	$J\,deg^{-1}$	
l	2.72×10^{-10}	m	
D_0 (for l-Si)	1.5×10^{-6}	m^2s^{-1}	[14]
Q (for l-Si)	0.5	eV	[14]
ρ_s	1.35×10^{19}	m^{-2}	
f_0	3×10^{18}	m^{-3}	
V_m	2.01585×10^{-29}	m^3	[8]
ρ_c	2.32	$g\,cm^{-3}$	[10]
ρ_l	2.52	$g\,cm^{-3}$	[10]

Table 2
The value of parameters for nucleation in a-Si

Parameter	Value	Unit	Ref.
T_a	960	K	[8]
T_m	1250	K	[8]
$\Delta H(T_a)$	1.98435×10^{-20}	J/atom	[8]
Δc_p^a	$-3.71961 \times 10^{-25} + 7.9706 \times 10^{-24}T/T_c$	JK^{-1}/atom	[8]
S_a	2.7565×10^{-24}	JK^{-1}/atom	[8]
c_{11}	$1.6564 \times 10^{11}[1 - 9.4 \times 10^{-5}(T - 298)]$	K	[8]
c_{12}	$0.6393 \times 10^{11}[1 - 9.8 \times 10^{-5}(T - 298)]$	K	[8]
$\Delta V/V_0$	0.08733		
σ_{ac}	0.31	Jm^{-2}	[8]
D_0 (for a-Si)	1.68×10^{-5}	m^2s^{-1}	[8,9]
Q (for a-Si)	2.95	eV	[8,9]

the material constants were taken from the literature [8–14] (see Tables 1–3) and then modified to obtain good agreement of our theory with published experimental data for nucleation, and later for the growth rate, which depends on the same parameters. For this procedure we used the results of Refs. [19, 20] where the estimations of the maximum value of the time lag τ_k and the minimum of j_{ss} were published. In particular, the value of f_0 was determined with respect to experimentally determined j_{ss}.

For the numerical conclusions, we use the (a) model of the change in Gibbs free energy, Eqs. (1) and (2). The dependences of $g^*(T)$, $\tau_k(T)$ and $j_{ss}(T)$ on temperature T are

Table 3
The values of the parameters describing recrystallization in a-Si thin layers

Parameter	Value	Unit	Ref.
D_p	3.5×10^{-7}	$m^2 s^{-1}$	[14]
ΔU	0.56	eV	[14]
$\Delta S/k_B$	2.2		[14]
fd/Λ^2	1.5×10^{11}	m^{-1}	[14]
A_1	2.362×10^{-27}	Jdeg^{-2}/atom	
A_2	-3.71961×10^{-25}	Jdeg^{-1}/atom	
A_3	-1.82×10^{-21}	J/atom	
B_1	-3.71961×10^{-25}	Jdeg^{-}1/atom	
B_2	4.7247×10^{-27}	J deg^{-2}/atom	
C_1	-2.3627×10^{-27}	Jdeg^{-2}/atom	
C_2	-3.128×10^{-24}	Jdeg^{-1}/atom	
C_3	3.71961×10^{-25}	Jdeg^{-1}/atom	
C_4	1.8023×10^{-20}	J/atom	

presented in Figs. 1–3. It follows from these results, that the time lag has a minimum near the temperature $T = 1150$ K. The value $\tau_k(1150)$ is determined mostly by the kinetic parameter $\beta(T)$ and for our values of parameters it is about 10^{-12}s. This value could be sufficient for the evolution of nucleation even during rapid recrystallization of

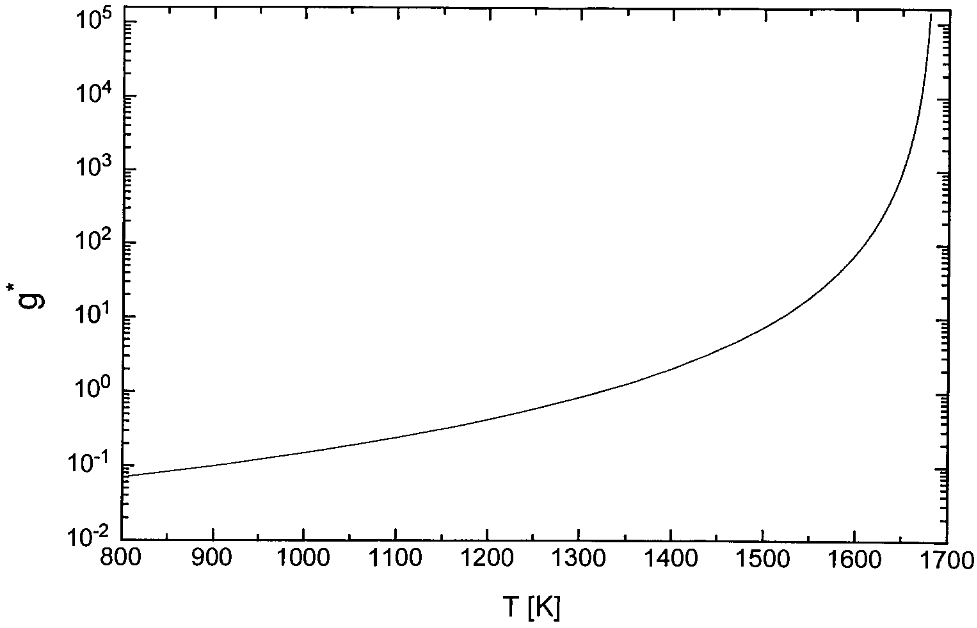

Fig. 1. The temperature dependence of the number of atoms g^* in a critical nucleus during the l-Si → c-Si phase transformation.

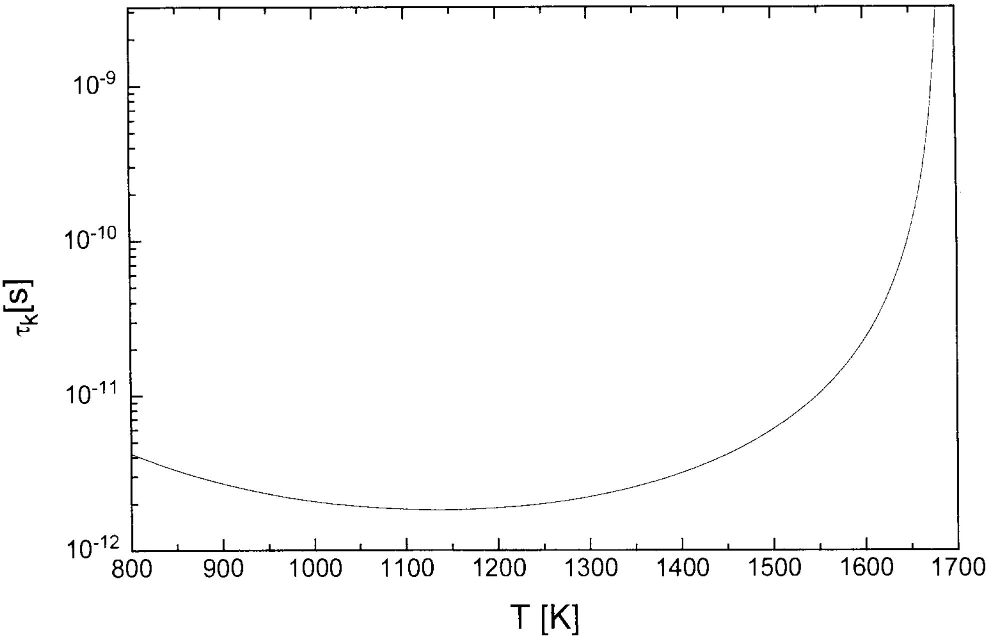

Fig. 2. The temperature dependence of the time lag τ_k for the l-Si → c-Si phase transition.

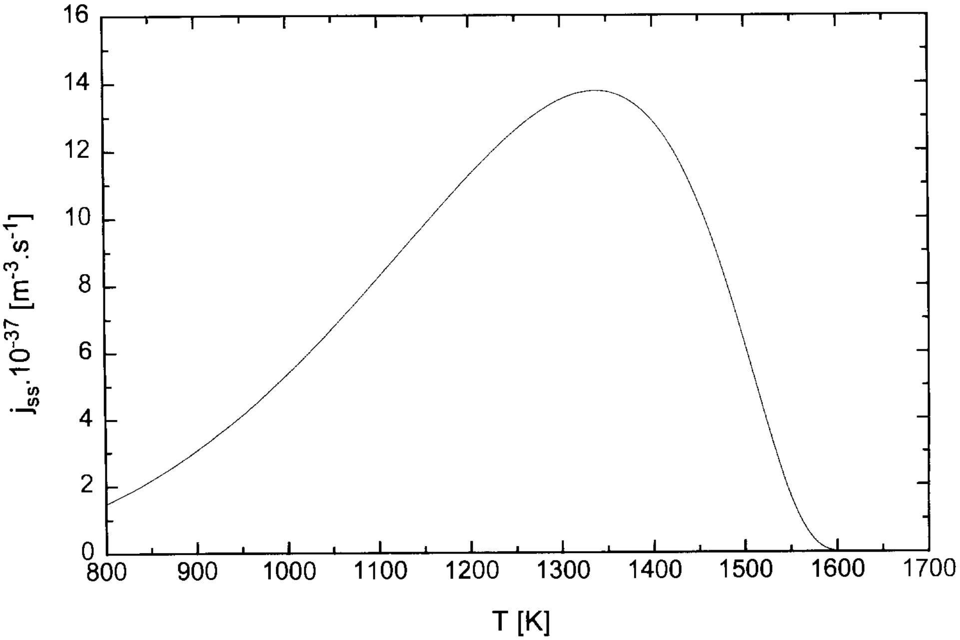

Fig. 3. The temperature dependence of the stationary nucleation rate j_{ss} for the l-Si → c-Si phase transition.

Si thin layers. It could be demonstrated that the position of the τ_k minimum depends only on the value of the parameter Q within the framework of the (a) model.

The behaviour of the stationary rate of nucleation j_{ss} is also important; $j_{ss}(T)$ as a function of temperature has a sharp maximum near $T_j = 1350$ K. The position of this maximum depends on the values of latent heat (L_c) and surface energy (σ_{lc}). The value T_j decreases with increase in σ_{lc}, and increases with L_c. Also the values of τ_k in its minimum (τ_m) depend on σ_{lc} and L_c: τ_m increases with σ_{lc} and τ_m decreases with increase in L_c. It follows from our analysis that the position of the maximum of $j_{ss} - T_j$ also depends on a and on the energy barrier $Q - T_j$, increasing with increase in Q and decreasing with increase in a. We can use these qualitative dependences to consider the nucleation processes in l-Si and to estimate the basic parameter values. The position of the τ_k minimum shows the undercooling at which nucleation is most probable, the mutual position of the maxima of j_{ss} and of the growth rate of the crystalline phase show the possibility of a-Si formation. The model (b) gives similar results.

3. Nucleation of crystalline Si in amorphous phase

It has been observed (e.g. [7,21]) that at a temperature above 900 K nucleation of c-Si can proceed directly from a-Si, since the amorphous phase is a metastable phase and the system tends to transform into the stable crystalline phase.

3.1. Models of nucleation

In the description of nucleation in a-Si, we start from the change in Gibbs free energy ΔG of a given volume of a-Si during the phase transformation a-Si → c-Si. In contrast to the previous case, in a description of the nucleation of c-Si in an amorphous phase we must also take the strain energy (which arises during the structure changes in a solid phase) into account. So

$$\Delta G(g) = -g\Delta G_v + A(g) \tag{20}$$

where g is the number of atoms in one nucleus, ΔG_v is the change of Gibbs free energy per atom during the phase transformation a-Si → c-Si, and $A(g)$ is the surface energy of a cluster with g atoms. ΔG_v is divided into two parts

$$\Delta G_v = \Delta G_{ac} + \Delta G_s \tag{21}$$

where ΔG_{ac} represents the change in chemical potential between a-Si and c-Si, and ΔG_s represents the strain energy per atom. For ΔG_{ac}, we use the model (b) from the previous section

$$\Delta G_{ac}(T) = \Delta H(T) - T\Delta S(T) \tag{22}$$

where

$$\Delta H(T) = \Delta H(T_a) + \int_{T_a}^{T} \Delta c_p^a(T)\,dT \tag{23}$$

where T_a is the kinetic temperature of crystallization, i.e. the temperature at which critical nuclei occur during thermal anneling, Δc_p^a is the difference between the specific heats of the amorphous and crystalline phases, and $\Delta H(T)$ is the enthalpy difference between the amorphous and crystalline phases at T

$$\Delta S(T) = S_a + \int_0^T \left(\frac{\Delta c_p^a(T)}{T} \right) \mathrm{d}T \tag{24}$$

where S_a is the residual entropy of the amorphous phase; it is the entropy of the amorphous phase at $T = 0$. For the strain energy we use the relation published in Ref. [8]

$$\Delta G_s = \frac{V_m B}{2} \left(\frac{\Delta V}{V_0} \right)^2 \tag{25}$$

where

$$B = \frac{c_{11} + 2c_{12}}{3} \tag{26}$$

V_m is the volume of one atom, V_0 is the volume of a-Si which transforms into c-Si, ΔV is the change of the volume of this part of a-Si which transforms into c-Si, and c_{ij} are the elastic constants of the c-Si phase. As above, we accept that

$$A(g) = \sigma_{ac} A_{ac}(g) \tag{27}$$

where σ_{ac} is the density of surface energy between a–Si and c–Si phase, and

$$A_{ac}(g) = \gamma g^{2/3} \tag{28}$$

where γ is the geometrical factor (see Table 1). Under these conditions we can proceed to the study of nucleation of crystalline phase in a–Si.

Within the framework of our model, the number of atoms in a critical nucleus is given by the relation

$$g^*(T) = \frac{32\pi}{3} \frac{a^6 \sigma_{ac}^3}{[\Delta H(T) - T\Delta S(T) + \Delta G_s]^3} \tag{29}$$

The stationary nucleation rate and nonstationary nucleation rate are given by the same relations as in Section 2.3, but now we must use Eq. (29) for the value of the number of atoms in the critical volume and also the corresponding values of appropriate constants summarized in Table 2.

3.2. Numerical results

In this chapter we summarize the numerical results of nucleation of c-Si in a-Si in dependence on temperature and material parameters. The values of appropriate parameters are listed in Tables 1 and 2. The basic values of the material constants were collected from publications [8–14] and later they were defined with more precision to obtain better agreement of our theory with published experimental data. We compared the temperature dependences (in the range 830–930 K) of τ_k and j_{ss} published in Ref. [7,21].

Firstly, we determined the integrals in Eqs. (23) and (24) for the function Δc_p^a presented in Table 2

$$\int_{T_a}^{T} \Delta c_p^a(T)\,\mathrm{d}T = A_1 T^2 + A_2 T + A_3 \tag{30}$$

and

$$\int_{0}^{T} \frac{\Delta c_p^a}{T}\,\mathrm{d}T = B_1 \ln T + B_2 T \tag{31}$$

So we obtain the change ΔG_{ac} in the form

$$\Delta G_{ac} = \Delta H(T_a) - TS_a + C_1 T^2 + C_2 T + C_3 T \ln T + C_4 \tag{32}$$

where constants the A_1–A_3, B_1, B_2 and C_1–C_4 are given in Table 3. The numerical calculations result in the following conclusions:

1. The temperature T_a does not play a role in the temperature of phase transformation, since ΔG_v is positive even for $T > T_a$.
2. For temperatures $T > 1000$ K, $g^* < 1$ and the existence of a critical nucleus is questionable. Very fast recrystallization takes place.
3. In agreement with Ref. [3] where the annealing of a–Si was studied was studied experimentally for temperatures below 1000 K, it is shown that the nucleation rates are enormously slow ($j_{ss} \sim 10^{22}$).
4. τ_k and j_{ss} are monotonous functions of temperature; j_{ss} increases and τ_k decreases with increasing temperature.
5. For $\frac{\mathrm{d}\tau_k}{\mathrm{d}t} = 0$, we obtain a considerably complex relation which results in the dependence of the position of the minimum τ_k not only on Q, but also on $\Delta H(T_a)$, T_a, Δc_p^a and ΔS.

4. The growth of stable clusters from Si melt and a-Si

In this section, we focus on the determination of the growth of supercritical (stable) clusters. The calculations of growth velocities are divided into two regions:

(1) Growth of clusters with small radius r.

(2) Growth of large clusters in which velocity can be approximated by the model of growth on a flat interface ($r \to \infty$).

(1) According to Ref. [8], the velocity of the change in number of the atoms in a cluster of size g is given by the relation

$$v_g(g) = \frac{\mathrm{d}g}{\mathrm{d}t} = \beta(g)\left[1 - \exp\left(\frac{1}{k_B T}\frac{\partial \Delta G(g)}{\partial g}\right)\right] \tag{33}$$

For the velocity of radius changes, we obtain

$$v_r(r) = \frac{dr}{dt} = v_g\left[g(r)\right]\frac{dr(g)}{dg}\bigg|_{g=g(r)} \tag{34}$$

The function $\beta(g)$ is given by relations (14) and (15). The function $\Delta G(g)$ is described by relations (1), (3) or (20) and respective relations. It remains to determine (dr/dt). In the case of a sphere, it is

$$\frac{dr}{dg} = \left(\frac{a^3}{36\pi}\right)^{1/3} g^{-2/3} \simeq 0.2068\, a\, g^{-2/3} \tag{35}$$

(2) In the case of growth on a flat interface, we use the relation published in Ref. [14], (p. 601), which is suitable for crystallization in l-Si

$$v_p = \frac{D_1}{\Lambda^2} f d \exp\left(-\frac{\Delta S}{k_B}\right)\left[1 - \exp\left(-\frac{\Delta\mu}{k_B T}\right)\right] \tag{36}$$

where v_p is the velocity of the interface shift, Λ is the mean free path of atoms in the liquid phase, D_1/Λ^2 is the atomic jump frequency, f the active site fraction on the interface, d the thickness of the layer of liquid atoms that are sufficiently close to the crystal and which can reach crystal lattice sites with a single jump, ΔS the entropy of phase transformation, and $\Delta\mu$ the difference in chemical potential of atoms in the two phases (given by relations (2) and (3) for growth from liquid phase, and (21) for growth from amorphous phase). Also the temperature dependence of the diffusion coefficient is taken as

$$D_1 = D_p \exp\left(-\frac{\Delta U}{k_B T}\right) \tag{37}$$

where parameters D_p and ΔU characterize the mobility of atoms in the mother phase. The results in Ref. [14] show that there are small differences in growth rates on surfaces (100) and (111). This phenomenon is not included in our theory.

For numerical calculations of growth rates, we use the parameters given in Table 3, which correspond to the published values in Ref. [14]. The temperature dependence of v_p for growth from l-Si was published in Ref. [14,22], and for growth from a-Si in Ref. [4,21,23]. Our calculations of the growth rate $v_p(T)$ from liquid Si are shown in Fig. 4. It can be shown that the shape-dependent growth rate v_r approximately approaches the value v_p at the limit $r \to \infty$ for our choice of parameters. This is an additional independent check of the suitability of our model.

5. Kinetics of the growth of the crystalline Si from the melt and amorphous phase

Up to now we have studied the processes of nucleation and growth of supercritical nuclei separately. Now we combine both descriptions of phase transformations in one theory and develop the equations which describe the time evolution of the crystalline phase from the liquid phase and the amorphous phase of silicon.

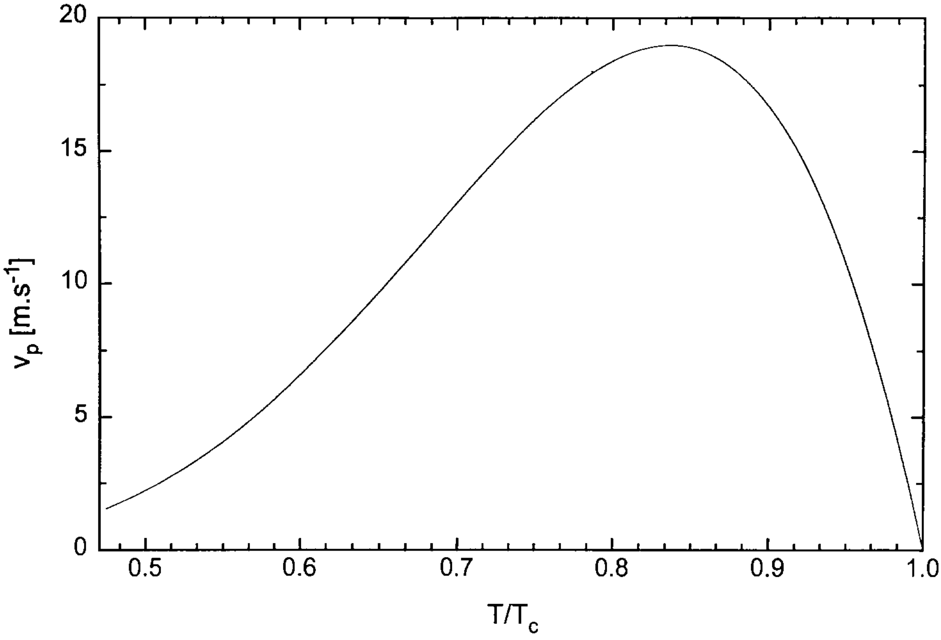

Fig. 4. The temperature dependence of the growth rate on the flat phase interface v_p for the l-Si → c-Si phase transition.

5.1. Crystallization from liquid Si

The isothermal process

The kinetics of the isothermal phase transformation from a melt is described by the JMAK (Johnson–Mehl–Avrami–Kolmogorov) equation [1,2,24–29]

$$\ln(1 - X(t))^{-1} = \gamma j_{ss} v_p^n t^{n+1}/(n + 1) \tag{38}$$

where $X(t)$ is volume fraction of crystalline phase ($X(t) \in (0, 1)$) in a given volume, γ is the geometrical factor, j_{ss} the stationary nucleation rate, v_p the growth rate on the flat interface, and n the dimension of the process. Eq. (38) has a limited vadility and can only be used if the following assumptions are valid: j_{ss} is time independent; v_p is independent of the shape and size of the nuclei; nucleation is a random process; the growth process is controlled by the surface kinetics (not by diffusion). However, the coalescence of nuclei is considered. For our purpose we use relations (11 and 36) for the functions occurring in Eq. (38) and $n = 3$ (see Ref. [24], p.155). The meaning of the parameters and functions is explained above .

Nonisothermal crystallization

In general the equation

$$X(t) = \gamma \int_0^t \left[\int_\tau^t v_V(t)\,\mathrm{d}t \right] j(\tau)\,\mathrm{d}\tau \tag{39}$$

is solved where $v_V(t)$ is the volume growth rate, which is proportional to the product $\sim v_{\mathrm{p}}^3 t^3 (4\pi/3)$. We must substitute in relation (39) the non-steady-state nucleation rate $j(t)$ and the dependence of the growth rate on the size and temperature, relation (34). Integration of Eq. (39) is very difficult, but we can simplify it under the additional assumption that the temperature in the system changes with constant velocity and does so sufficiently slowly in comparison with the time lag of nucleation. In this case we obtain [24,29]

$$X(t) = \frac{4\pi}{3(\dot{T})^4} \int_{T_1}^{T_2} j_{\mathrm{ss}}(T')\,\mathrm{d}T' \left[\int_{T_1}^{T_2} v_{\mathrm{p}}(T'')\,\mathrm{d}T'' \right]^3 \tag{40}$$

where $v_{\mathrm{p}}(T)$ is the temperature-dependent growth rate, independent of the shape and size of the nucleus, T_1, T_2 determine the temperature interval during which we observe the phase transformation, and $\dot{T}$ is the constant rate of cooling or heating.

5.2. *Crystallization from amorphous phase of Si*

In this case we can use the same relations, (38) and (40), but the nucleation rate and growth rate must be replaced by the appropriate relations for the growth and nucleation from the amorphous phase of Si.

5.3. *Recoalescence*

During the phase transformation (as from l-Si and a-Si), latent heat is released. This energy heats up the surroundings of the growing nuclei which can lead to cessation of growth or even to remelting of the crystalline phase. The value of the heat released during the phase transformation of volume $V(\Delta t)$ (a part of the reference volume V_0) in the time interval Δt must be determined. We shall not deal with the distribution of this energy into the whole volume. The amount of heat $R_{\mathrm{L}}(\Delta t)$ during this process per Δt is

$$R_{\mathrm{L}}(\Delta t) = L_V V(\Delta t) \tag{41}$$

where L_V is the latent heat of crystallization per unit volume. The change of the mean temperature ΔT in volume V_0, as a consequence of released heat, can be estimated by the relation

$$\Delta T \bar{c}_p V_0 = R_{\mathrm{L}} \tag{42}$$

where c_p is the mean value of the specific heat (averaged through the crystalline and liquid phase in volume V_0) per unit volume. So we obtain

$$\Delta T = \frac{R_{\mathrm{L}}}{c_p V_0} = \frac{L_V}{\bar{c}_p} X(\Delta t) \tag{43}$$

The time changes of temperature in volume V_0 are determined by the relation

$$\frac{\Delta T}{\Delta t} = \frac{L_V}{\bar{c}_p} \frac{X(t) - X(t - \Delta t)}{\Delta t} \tag{44}$$

and at the limit $\Delta t \to 0$

$$\dot{T} = \lim_{\Delta t \to 0} \frac{\Delta T}{\Delta t} = \frac{L_V}{c_p} \dot{X}(t) \tag{45}$$

How do these changes in temperature affect the transport of energy in the whole system? If we neglect the latent heat of phase transformation, the time evolution of temperature distribution in the system is described by the heat conductivity equation (in a one-dimensional model)

$$\frac{\partial T}{\partial t} = D \frac{\partial^2 T}{\partial x^2} \tag{46}$$

where D is thermal diffusivity. It is not simple to couple Eqs. (38) or (40) with (45) and (46), since all functions are time dependent and each process has its own relaxation time. The coupling process can be done under special assumptions.

In a general case, we should solve the set of equations.

$$\frac{\mathrm{d}T(t)}{\mathrm{d}t} = \frac{L_V}{\bar{c}_p} \frac{\mathrm{d}X}{\mathrm{d}t} \tag{47}$$

$$X(t) = \gamma \int_0^t \left[\int_\tau^t v_V(T(t'), t')\,\mathrm{d}t' \right] j(T(\tau), \tau)\,\mathrm{d}\tau \tag{48}$$

where functions v_V and j depends not only on temperature T but also on time t since they do not represent the steady-state growth and nucleation rates.

The solutions of Eqs. (47) and (48) is complicated and can be simplified by the assumption of a "local equilibrium" (introduced later). The relation between $\dot{T}$and the rate of temperature diffusion will play a decisive role in our analysis.

Let us analyse the diffusion of heat in one-dimensional space of size L. The relaxation time τ_D characterizes the velocity of the heat transport by means of which the system tends towards equilibrium

$$\tau_D = \frac{L^2}{D} \tag{49}$$

The relationship strongly depends on the characteristic size of the system L.

If $\tau_D \gg \tau_k$, we can assume that the temperature is frozen during the time needed for the approach of a stationary nucleation rate. The nucleation can be described by $j_{ss}(T(t))$ where temperature T is now a function of time. We shall solve Eq. (46) together with Eq. (45) ($\dot{T}$ plays the role of source in Eq. (46)), where $X(t)$ is given by Eq. (38) and is a function of space coordinates and time.

In contrast, if $\tau_D \ll \tau_k$ the nucleation is the slowest processes and the heat, e.g. released during phase transformation, is instantly distributed over the whole system. In the volume L, temperature is a constant, being a function of the space coordinate, and the kinetics of phase transformation is determined by Eqs. (38) or (40) for $\dot{T} \neq 0$.

From this analysis, a critical size L_{cr} exists for which $\tau_D \simeq \tau_k$.

Using the values $D \sim 10^{-4}$ m^{2}s^{-1} and $\tau_k \sim 10^{-12}$s, we obtain $L_{cr} = \sqrt{D\tau_k} = 10^{-8}$m $= 10$ nm. Therefore for a space of characteristic size ≤ 10 nm, we can assume that $\tau_D \ll \tau_k$.

This analysis results in the following procedure for calculation of the kinetics of phase transformation:

(a) We determine L_{cr} from τ_k and D. Now we introduce some "Local equilibrium";
(b) In a sufficiently small space scale $L < L_{cr}$, we assume that the latent heat of phase transformation is instantly distributed in the volume L and that the relation (45) is valid over the whole volume L, but that the average temperature changes slowly with time;
(c) For a sufficiently large space scale $L > L_{cr}$, we solve Eq. (46) with the source term (45) where

$$\dot{X}(t) = \gamma j_{ss}(T(t))\, v_p^3(T(t)) \tag{50}$$

If $X \to 1$ we must use the equation

$$\frac{1}{1-X}\dot{X} = \gamma j_{ss}(T(t))\, v_p^3(T(t)) \tag{51}$$

to include the size effects

We will validate these assumptions. Consider both processes, i.e. crystallization and time changes of temperature, separately in the volume $L < L_{cr}$

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{L_V}{\bar{c}_p}\frac{\mathrm{d}X}{\mathrm{d}t} = a j_{ss}(T(t))\, v_p^3(T(t))\, t^3 = aq(T) \tag{52}$$

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \frac{1}{\tau_q}\frac{\mathrm{d}q(T)}{\mathrm{d}T} aq(T) \tag{53}$$

where τ_q is the relaxation time during which q approaches the stationary value ($\tau_q \sim \tau_k$). The changes of temperature are slower than τ_q if

$$\frac{\tau_q}{a}\left(\frac{\mathrm{d}q}{\mathrm{d}T}\right)^{-1} \ll 1 \tag{54}$$

From our models of j_{ss} and v_p, it is evident that this condition is fulfilled; this means that our condition of "local equilibrium" can be accepted and that on a scale larger than L_{cr}, the calculations following (c) solve the problem of recrystallization in a-Si thin films. These results are for crystallization from l-Si and a-Si.

6. Conclusions

In this paper, we have summarized the theoretical models of the description of time evolution of recrystallization processes in a-Si thin films under ultrafast temperature changes. These models and model parameters (activation energy, surface energy, diffusion coefficient, etc.) were adjusted to obtain good agreement with the various published experimental data, not only for nucleation, but also for the growth rate (see Eq. (33)). It was found that the time lag $\tau_k(T)$ of the stationary nucleation from l-Si has a minimum near the temperature 1150 K. The maximum of the nucleation rate $j_{ss}(T)$ was found at 1350 K. These courses of τ_k, j_{ss} and growth rate $v\,(T)$ are important, since the relative positions of local extremes of $j_{ss}(T)$ and growth rate $v(T)$ prevent the system from forming amorphous phases and from forming crystalline nuclei. In the case of nucleation from a-Si, $\tau_k(T)$ and $j_{ss}(T)$ are monotonous functions of temperature T.

A general model of recrystallization has been formulated which covers both nucleation and growth processes (in l-Si and a-Si) and recoalescence. In contrast to the former models, it has wider application with more precisely defined conditions and calculates for fast heating or cooling. This theoretical model describes the type of recrystallization processes in a-Si thin films irradiated by a pulsed excimer laser and is able to predict the resulting phases.

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