

Kinetic many-body model of recrystallization of pure and doped amorphous silicon

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A new kinetic many-body model for the regrowth mechanism of pure and highly doped amorphous silicon is reported. This model, which is applicable to the study of other regrowth processes, is based on the kinetic many-body theory of thermally activated rate processes in solids. It explains (a) the enhanced recrystallization rate when B, P, and As atoms are introduced into amorphous Si, (b) the reduced recrystallization rate when amorphous Si contains O and C atoms, and (c) the impurity-concentration dependence of the regrowth rate.

The regrowth of pure and doped materials from amorphous to crystalline structures is a thermally activated process, with a rate coefficient described by the Arrhenius equation

$$K = K_0 \exp\left(-\frac{\Delta E}{kT}\right), \quad (1)$$

where k is Boltzmann's constant and the measured activation energy for the regrowth of pure amorphous Si (a -Si) is $\Delta E = 2.3$ eV.¹⁻⁴ This regrowth rate is enhanced by a factor of 20 to 40 when the a -Si contains high concentrations of dopant impurities ($a_{\text{im}} \approx 0.5$ –1 at. % of B, P, or As).^{5,6} The ratio between the regrowth rate coefficients of pure and doped Si is

$$\frac{K_I'}{K_P} = \frac{K_{0I}'}{K_{0P}} \exp\left(-\frac{\delta E'}{kT}\right) \approx 20 \text{ to } 40, \quad (2)$$

where P and I stand for pure and impurity-doped a -Si, respectively, and $\delta E' = \Delta E_I' - \Delta E_P < 0$ is the negative difference between the activation energies in doped and pure a -Si. On the other hand, the regrowth rate is reduced when O, C, N, and noble gases are introduced into a -Si.⁴ Then $K_I'' < K_P$, $\delta E'' = \Delta E_I'' - \Delta E_P > 0$.

It has been suggested that the recrystallization of pure a -Si occurs through nucleation followed by epitaxial growth.⁷ The regrowth is governed and limited by a self-diffusion mechanism.⁸ When a -Si contains dopant impurities, it has been assumed that the impurities modify the position of the Fermi level,^{9,10} which helps the recrystallization process. However, a mechanism for the atomic rearrangement and for its modification by impurities, which changes the regrowth rate, has not yet been proposed.

In this paper we propose a new kinetic many-body model which explains the recrystallization of pure a -Si and of a -Si containing high impurity concentrations. The recrystallization is considered to be a thermally activated rate process, and a new kinetic many-body theory of rate processes^{11,12} is used to calculate the rate coefficients K_P and K_I . The problem under consideration is too complex to be solved exactly; we will therefore confine ourselves to qualitative and semi-quantitative arguments which lead to experimentally verifiable effects which are in excellent agreement with observa-

tions. This model can be extended to the study of the recrystallization of other materials, surface segregation, particle migration, adsorption, crystal growth of mixed crystals, etc. The basic concepts of this theory and its application to diffusion and melting have been summarized in Ref. 11. This theory has been applied to various processes, such as exoelectronic emission,¹³ transient local defects^{11,14} and their interaction with electrons,^{11,15} electron tunneling,^{11,15} field-emission flicker noise,¹⁶ and the surface thermally activated rate processes.^{11,17,18}

The recrystallization process in amorphous Si consists of a large number of fluctuation-assisted jumps of Si atoms from disordered positions to more ordered ones, over the energy barrier of height $E \gg kT$. Only those atoms whose maximum thermal energy $\epsilon_{0p} \geq E$ can overcome this barrier and contribute to "ordering" jumps. These jumps of distances of the order of the interatomic spacing d occur with the help of short-lived large energy fluctuations (SLEF's) of hopping atoms and take place when $\epsilon_{0p} \geq E \gg kT$, as seen in Fig. 1.

The single SLEF lifetime $\Delta\tau = \tau_1 + \tau_2 \approx 10^{-13}$ – 10^{-12} s is composed of two parts: the SLEF formation τ_1 and relaxation τ_2 times (Fig. 1). During the time τ_1 , the fluctuating Si atom receives thermal energy $\delta\epsilon_{01} \approx \epsilon_{0p} \gg kT$ from its immediate vicinity limited by a sphere of radius $R = c_0\tau_1 \approx (10$ – $20) \times 10^{-8}$ cm and volume $\Omega_1 \sim R^3$ due to the shortness of τ_1 and the finiteness of the thermal-energy transfer velocity $c_0 \approx 3 \times 10^5$ m/s. The sphere serves as a transient energy reservoir for the jumping Si atom; it contains $\Delta N_1 \approx 50$ – 100 particles, where ΔN_1 and $\Omega_1 \approx \Delta N_1 d^3$ depend on ϵ_{0p} and on the material parameters.

When a fluctuating atom jumps a distance $\approx d$, a transient point defect is formed because d is much larger than the amplitude of oscillation of the surrounding particles.^{11,14,15} The fluctuating atom stretches and cuts off some covalent bonds and creates new bonds in its new position. During the same time $\Delta\tau$ other bonds are strongly shrunken.

The SLEF-induced transient local defect breaks down the local structural symmetry and stability, which results in the breakdown of the Born-Oppenheimer adiabatic approximation and of the band-theory model during $\Delta\tau$. This creates severe local electronic perturbations and rearrangements of

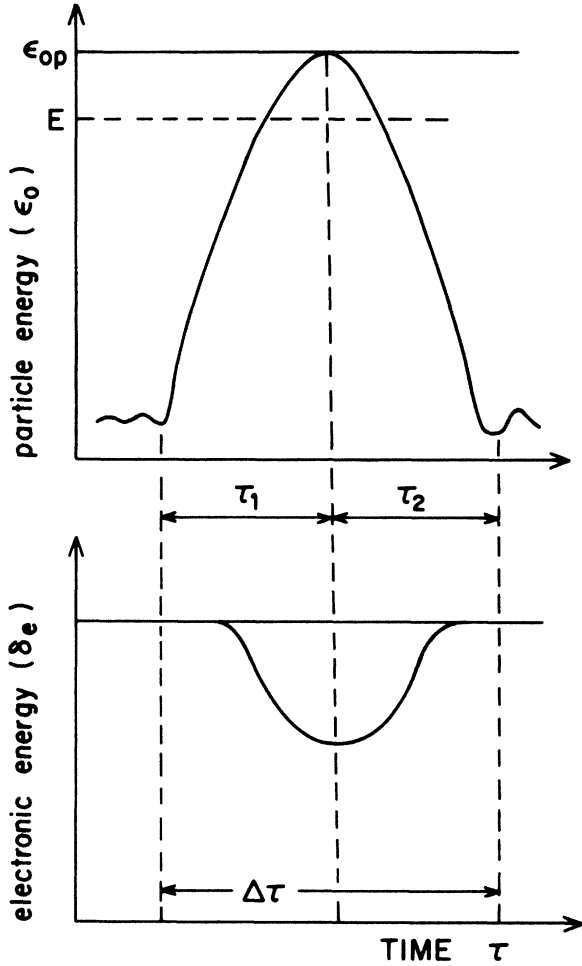


FIG. 1. Thermal energy ϵ_0 of the fluctuating hopping Si atom and the SLEF-induced local transient electron level $\delta e(\tau)$ as functions of time. $\bar{\epsilon}_0$ is the mean atom thermal energy. ϵ_{0p} is the maximum thermal energy of the fluctuating atom at the instant $\tau_p = 0$ of the SLEF peak. τ_1 and τ_2 are the SLEF formation and relaxation times, respectively.

the local electronic states¹¹⁻¹⁵ leading to the formation of a transient local time-dependent potential well for mobile electrons of depth $\Delta U(\tau)$, radius $\Delta\rho(\tau)$, and lifetime $\Delta\tau_w \approx \Delta\tau$.^{11,15} $\Delta U(\tau)$ and $\Delta\rho(\tau)$ increase during the SLEF formation time $\tau_1 \approx \Delta\tau/2$ up to the maximum values $\Delta U_m = \Delta U(\tau_p = 0)$ and $\Delta\rho_m = \Delta\rho(\tau_p = 0)$ at the instant $\tau_p = 0$ of the SLEF peak (see Fig. 1); then $\Delta U(\tau)$ and $\Delta\rho(\tau)$ decrease to zero during the SLEF relaxation time $\tau_2 \approx \Delta\tau/2$. The SLEF-induced potential well creates a transient local electronic time-dependent level $\delta e(\tau)$ in the forbidden gap (see Fig. 1), when $\Delta U \Delta\rho^2 \geq \hbar^2/2m^*$, where m^* is the electron effective mass. These transient electron levels are in some degree analogous to fluctuational electron levels in liquid semiconductors.¹⁹

Thus the SLEF-induced potential wells can trap electrons during $\Delta\tau_w$ and create transient localization of mobile electrons near the jumping atoms simultaneously with the ordering jump of these atoms. This transient localization of weakly bonded electrons results in the release of an energy δE_1 in the vicinity of the hopping atom. The energy release can contribute to the energy needed by the hopping atom to

overcome the energy barrier. As a result, the effective activation energy $E - |\delta E_1| < E$ decreases and the probability for ordering jumps and, therefore, the regrowth rate, increases by a factor of $\exp(\delta E_1/kT)$.

The question which arises is as follows: What is the probability for electrons to be located in the SLEF-induced transient electronic states created by the transient potential well? As we will see below, this probability is small for pure *a*-Si containing small concentrations of weakly bonded and mobile electrons, but it is greatly enhanced when dopant impurities (B, P, or As) are introduced and reduced when *a*-Si contains electron-trapping impurities (O, N). In other words, the probability of releasing $\delta E_1 < 0$ is enhanced when dopant impurities are introduced and decreased when electron-trapping impurities are present.

In pure amorphous materials the native concentration of defects Π_d is high.^{9,19} As a result, the rate coefficient given by Eq. (1) can be written with a preexponential factor

$$K'_{0l} = \frac{1}{\Delta\tau} g \chi \Pi_d \exp\left(\frac{\delta S'_l}{k}\right) \quad (3)$$

and an activation energy $\Delta E'_l = E - |\delta E'_l|$. χ is the number of the nearest neighbors around the hopping atom, $\chi \Pi_d$ is the mean number of nearest-neighbor defects, g characterizes the material and is unimportant in this study, and $\delta S'_l$ is the change in the local entropy associated with the electron localization.

Let us consider the ratio between the regrowth rate coefficients of *a*-Si containing dopant impurities, K'_l , and pure *a*-Si, K_p , where $\Delta E_p \approx E$:

$$\frac{K'_l}{K_p} = \exp\left(\frac{\delta S'_l}{k}\right) \exp\left(\frac{|\delta E'_l|}{kT}\right), \quad (4)$$

with

$$\delta E'_l = \delta E_1 = -|\delta E_1| \quad (5)$$

and

$$\delta S'_l = \delta S'_{l1} - \delta S_{1p}. \quad (6)$$

As we will see below, the influence of $\delta S'_l \approx -k$ on the ratio is much weaker than that of $|\delta E'_l| > kT$.

To calculate δE_l , δS_l , and the number of trapped electrons, one should take into account that the hopping Si atom with the peak energy $\epsilon_{0p} \geq E \gg kT$, which stretches and cuts off some covalent bonds and establishes other bonds with the neighboring atoms, creates a transient local time-dependent electron energy level (see Fig. 1)^{11,15}

$$\delta e(\tau) \approx \frac{\hbar^2}{2m^*} [\Delta\rho(\tau)]^{-2}. \quad (7)$$

For $\Delta\rho_m \approx 2.5 \times 10^{-8}$ cm and $m^* \approx m$, one finds $\delta e_m \approx 0.6$ eV. Thus $\delta e(\tau)$ increases to its maximum value $\delta e_m \approx 0.6$ eV during the SLEF formation time τ_1 and then decreases to zero during the SLEF relaxation time τ_2 (see Fig. 1).

The number of electrons δn_e which are trapped by the well during the electron level lifetime $\Delta\tau_e \leq \Delta\tau$ is

$$\delta n_e \approx j_e \sigma_e \Delta\tau \approx n_e v_e \sigma_e \Delta\tau_e, \quad (8)$$

where j_e is the current density, n_e is the concentration of mobile electrons of the mean velocity $v_e \approx 10^7$ cm/s, and σ_e is the well electron-trapping cross section. We can easily see that an increase in n_e (by several orders of magnitude),

when dopant impurities are introduced ($a_{im} \approx 1\%$), causes the corresponding increase in $\delta n_e \sim n_e \sim a_{im}$.²⁰

When *a*-Si contains dopant impurities such as *P*, there is an additional impurity level $\Delta e_{im} \approx 0.2$ eV in the band of localized levels of amorphous Si below the mobility edge.^{21,22} For crystalline material, the *P* level is $\Delta e_c = 0.045$ eV below the conduction band. During most of the SLEF-assisted jumps of Si atoms from disordered to more ordered positions, Si remains amorphous and $\Delta e_{im} > \Delta e_c$, but at a later stage of recrystallization Δe_{im} can become closer to Δe_c .

The degree of ionization of *P* impurities at the recrystallization temperature $T = 770$ K is

$$b_{im} = \exp\left(-\frac{\Delta e_{im}}{2kT}\right) \approx 0.25 \quad (9)$$

The cross section σ of the trapped impurities in the potential well is $\sigma = \pi r_{im}^2$, r_{im} is the orbit radius of the trapped impurity electrons, $r_{im} = Ad$ with $A \approx 3$.²³ Then, from Eq. (8)

$$\delta n_e^t = \pi A^2 b_{im} a_{im} d^2 N v_e \Delta \tau_e \quad (10)$$

with $N \approx d^{-3}$, $a_{im} = 10^{-2}$, $\Delta \tau_e \approx 10^{-13}$ s, one finds $\delta n_e^t \approx 3$. This means that during any SLEF-assisted "ordering jump" of a Si atom in heavily doped material, some mobile electrons are trapped, and they release an average energy $-\langle \delta e \rangle = \delta E'$ in the immediate vicinity of the fluctuating atom. Here $\langle \delta e \rangle$ is the released energy averaged over many similar events.

We can then estimate $\delta E'_1 = -\langle \delta e \rangle \approx -0.5 \delta e_m \approx -0.3$ eV assuming that the time-dependent potential electron level $\delta e(\tau)$ is a linear function of time. From (4) one finds $(K'_I/K_P) \approx 30$ at $\delta S'_1 \approx -k$, which is in good agreement with experimental results.⁶ We can neglect the energy released in pure *a*-Si as $\delta E_{1P} \ll \delta E'_1$, because the low relative concentration of mobile electrons

$$b_P \approx \exp\left(\frac{-E_g}{2kT}\right) \approx 3 \times 10^{-4} - 10^{-5} \ll b_{im}$$

and

$$\delta n_e^p \approx (10^{-1} - 3 \times 10^{-3}) \delta n_e^t$$

Similar conclusions can be drawn when *a*-Si contains As or B.

On the other hand, it is known that O and C introduced into silicon behave as deep traps for electrons. In the temperature range 700–800 K the degree of ionization of such traps is relatively small. This promotes local transient upward electron transitions and local energy consumption $\delta E'' > 0$ in the vicinity of the fluctuating particles. These upward electron transitions and $\delta E'' > 0$ are caused by fluctuational heating $\Delta T \approx (0.1-0.2)T = 70-160$ K of the $N_1 = 1 + \Delta N_1$ particles directly involved in a single

SLEF.^{11,12} This results in $K'_I < K_P$, in accordance with experimental data,⁴ since $\delta E'' \approx \delta E'_I > 0$.

Consider now the dependence of K_I on the impurity concentration. When the *P* concentration is high enough, $a_{im} \approx 0.5$ to 1%, every SLEF-assisted Si jump is accompanied by trapping of mobile electrons by the transient potential well and by the energy release $\delta E'_I$. When a_{im} is too small and $\delta n_e < 1$, only part of the wells, $a_{im}/a_{im}^c < 1$, contains trapped electrons which release the energy $\delta E'_I$, the other part, $1 - (a_{im}/a_{im}^c)$, of the jumps of Si atoms occurs without such energy release in pure Si.

The critical impurity concentration a_{im}^c is determined by

$$\delta n_e^{t,c} \approx n_e^c v_e \sigma_e \Delta \tau_e \approx 1 \quad (11)$$

or

$$a_{im}^c = d(\pi A^2 b_{im} v_e \Delta \tau_e)^{-1} \quad (11a)$$

where a_{im}^c depends on Δe_{im} and T through $b_{im}(\Delta e_{im}, T)$. The condition (11) is derived from (10) with the assumption that a_{im}^c is associated with one electron trapped, on the average, by a SLEF-induced potential well. Numerical estimates for a *P* impurity in *a*-Si give $a_{im}^c \approx 3 \times 10^{-3} \leq a_{im}$, where $a_{im} \approx 0.5-1\%$ are the experimental impurity concentrations.^{5,6} The total regrowth rate coefficient is

$$K = \left(1 - \frac{a_{im}}{a_{im}^c}\right) K_P + \left(\frac{a_{im}}{a_{im}^c}\right) K_I \quad (12)$$

Here the second term is associated with ordering jumps of Si atoms assisted by the electron trapping and energy release $\delta E_I < 0$, as in doped *a*-Si. The first term is associated with Si-atom jumps occurring without such assistance. The first term becomes important when

$$\left(1 - \frac{a_{im}}{a_{im}^c}\right) K_P \approx \left(\frac{a_{im}}{a_{im}^c}\right) K_I \quad (13)$$

or

$$a_{im} \approx \left(1 + \frac{K_I}{K_P}\right)^{-1} a_{im}^c = \tilde{a}_{im}^c \quad (14)$$

Hence a purity criterion can be found when impurities do not influence the regrowth rate, i.e., when

$$\left(\frac{a_{im}}{a_{im}^c}\right) K_I \ll \left(1 - \frac{a_{im}}{a_{im}^c}\right) K_P \quad (15)$$

or $a_{im} \ll \tilde{a}_{im}^c$. Under this condition $K \rightarrow K_P$. Since for *P* impurities $K'_I/K_P \approx 30$, one has $a_{im} \ll \tilde{a}_{im}^c \approx 0.03 a_{im}^c$. This conclusion is in agreement with the criterion for material purity found in Ref. 11.

When $a_{im} > \tilde{a}_{im}^c$, the second term on the right-hand side of Eq. (12) becomes predominant. This could be deduced from experimental results when available.

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