

## Diffusion of impurities in amorphous silicon

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A new model for the diffusion of impurities in amorphous silicon that takes into account the structural and electronic properties of the material is proposed. This model is based on the kinetic many-body theory of thermally activated rate processes in solids. The observed small activation energy and pre-exponential factors for the diffusion of impurities in *a*-Si are explained as well as their dependence on impurity concentration.

### I. INTRODUCTION

The diffusion behavior of impurities in amorphous silicon (*a*-Si) appears to be one of key factors controlling the recrystallization processes, the stability or the degradation, and some electrical, optical, and other properties of *a*-Si devices. In spite of its considerable fundamental and technological importance the diffusion mechanism in *a*-Si is not well understood and the number of related experimental studies are limited so far.<sup>1-6</sup>

The experimental temperature dependence of the diffusion coefficient  $D$  is usually described by an Arrhenius equation

$$D = D_0 \exp(-\Delta E/k_B T), \quad (1)$$

where  $D_0$  is the pre-exponential factor and  $\Delta E$  is the activation energy. In order to compare the diffusion parameters in *a*-Si and crystalline Si (*c*-Si), it is necessary to extrapolate the experimental results from the high-temperature range at which  $D$  is measured in *c*-Si to the much lower temperatures which are below the recrystallization point of *a*-Si. At low impurity concentrations ( $< 1$  at. %) and at low temperatures ( $< 600^\circ\text{C}$ ) the impurity diffusion in *a*-Si is similar to that of *c*-Si and is rather slow.<sup>3</sup> However, at higher impurity concentrations ( $> 1$  at. %) a rapid diffusion of impurities in *a*-Si is observed. The published experimental data clearly show that  $D$  is higher by many orders of magnitude in *a*-Si than in *c*-Si and also that  $\Delta E$  and  $D_0$  are significantly lower (see Table

I).<sup>7</sup> The mechanism for impurity diffusion in *a*-Si and its concentration dependence is not yet fully understood, and the observed diffusion parameters are still unexplained.

The aim of this paper is to propose a semiphenomenological model which should contribute to the understanding of the impurity diffusion mechanism in *a*-Si. This model will explain the experimental data using very limited information about amorphous materials available at present. Our knowledge on the physical properties of *a*-Si is much poorer than that of *c*-Si. But even in *c*-Si, after many years of investigation, a theory of diffusion is far from being completed and "atomic-diffusion processes are poorly understood."<sup>8</sup>

Various mechanisms of diffusion including electron-assisted transport have been proposed for *c*-Si.<sup>8-10</sup> The atomic diffusion which is mediated by neutral and charged defects is widely accepted but at the same time, the diffusion without defects through the concerted exchange mechanism is also considered.<sup>11</sup> The microscopic nature of the migration saddle point is not clearly understood and the inherent inaccuracy of migration energies is rather large ( $\sim 1$  eV).<sup>9</sup>

As a result, the development of a detailed microscopic theory of diffusion in *c*-Si appears to be so complicated that "nobody understands what is going on."<sup>9</sup> The situation is even worse in *a*-Si. Hence at present, one can hardly expect to develop a comprehensive detailed theory of diffusion in *a*-Si which would include the trajectories of hopping atoms, the description of the saddle point, etc.

TABLE I. Experimental diffusion coefficients  $D$ , activation energies  $\Delta E$ , and pre-exponential factors  $D_0$  in crystalline (*c*-Si) and amorphous (*a*-Si) silicon. The diffusion coefficient  $D$  values are calculated at 673 K by extrapolation from the experimental temperature range.

Sample	Diffusing element	$E$ (eV)	$D_0$ (cm <sup>2</sup> /s)	$D$ (cm <sup>2</sup> /s)	Temperature region (K)	References
<i>c</i> -Si	B	3.7	10	$2 \times 10^{-27}$	1220–1470	7
<i>a</i> -Si	B	1.5	$5 \times (10^{-2} - 10^{-3})$	$3 \times (10^{-13} - 10^{-14})$	470–770	4
<i>c</i> -Si	P	3.7	10	$2 \times 10^{-27}$	1370–1620	7
<i>a</i> -Si	P	0.49	$1.3 \times 10^{-12}$	$2.8 \times 10^{-16}$	580–620	6
<i>c</i> -Si	Sb	3.9	5.6	$3 \times 10^{-29}$	1370–1620	7
<i>a</i> -Si	Sb	1.5	$4.6 \times 10^{-4}$	$2.7 \times 10^{-15}$	470–770	4

All the aforesaid has motivated us to suggest a semi-phenomenological approach, which avoids as far as possible the detailed description of the behavior of particles involved in the diffusion jumps.

We shall describe statistically the short term correlated behavior of the strongly fluctuating hopping atom and many surrounding particles in its small "mesoscopic" vicinity, associated with the diffusion jump.<sup>12-14</sup> In this way we lose information about the detailed behavior of particles involved in the diffusion jumps. However, instead, we take into account some new transient many-body atomic and electronic processes occurring in the mesoscopic vicinity of the hopping atoms which experience short-lived large energy fluctuations (SLEF's). These SLEF's enable the fluctuating atoms to overcome the diffusion barrier. This consideration leads us to simple equations which link the diffusion parameters to atomic and electronic properties and to the stability of *a*-Si. The electronic process involved in the considered diffusion mechanism differs substantially from the electron-assisted diffusion discussed in the literature.<sup>9,10</sup> Recently, this theory has been successfully used to explain anomalous self-diffusion in some monatomic metals and crystalline semiconductors;<sup>12,13</sup> the diffusion in solids under pressure<sup>12,15</sup> as well as the role of impurities in the recrystallization process of *a*-Si.<sup>14</sup> The problem under consideration is too complex to be solved exactly. This is why we shall confine ourselves to qualitative and semi-quantitative calculations which lead to experimentally verifiable results.

## II. MODEL OUTLINES

The proposed model is based on the following main principles.<sup>12-14</sup> The diffusion consists of a large number of SLEF-assisted jumps of impurity atoms over energy barriers of height  $E \gg k_B T$ . We do not specify the nature of these barriers. The barrier energy  $E$  is considered to be a phenomenological material parameter, since there is no reliable information about  $E$  in *a*-Si. We also do not specify the presence or absence of specific kinds of defects and the details of the migration path of the hopping particle in *a*-Si. The fluctuating atom hopping from one position to another, can overcome the energy barrier, because it receives the necessary thermal energy  $\epsilon_{op} \geq E$  from the  $\Delta N_1 \approx 30-100$  surrounding atoms located in volume  $\Omega_1$  of radius  $R_1 \approx 10^{-7}$  cm during a very short time  $\tau_1$  which is of the order of the lifetime  $\Delta\tau$  of a single SLEF.  $\Delta\tau = \tau_1 + \tau_2 \approx (10^{-13} - 10^{-12})$  s is composed of two parts: the SLEF formation time  $\tau_1$  when the fluctuating atom receives the energy  $\epsilon_{op}$  from its vicinity  $\Omega_1$  and SLEF relaxation time  $\tau_2$ —when the atom gives the "borrowed" energy back. The radius  $R_1$  and volume  $\Omega_1 \approx 4R_1^3/3 \approx 4(c_0\tau_1)^3$  are limited by the finiteness of the thermal energy transfer velocity  $c_0$  [which is of the order of the sound velocity  $(1-5) \times 10^5$  cm/s] and by the shortness of  $\tau_1$ . The 30–100 atoms contained in  $\Omega_1$  serve as a transient energy reservoir for the jumping impurity atom during the fluctuation lifetime  $\Delta\tau$ .

As a result, the fluctuation probability is determined by the transient correlated behavior of the jumping atom

and of the  $\Delta N_1$  surrounding particles and by their total change of energy and entropy during  $\tau_1$ .<sup>12-14,16</sup> These atomic jumps can be accompanied by either downward or upward transient electron transitions in the small vicinity of the fluctuating atom and by the corresponding local additional energy release  $\delta E_1 < 0$  or consumption  $\delta E_1 > 0$ . The electron transitions cause, respectively, negative  $\delta S_1 < 0$  or positive  $\delta S_1 > 0$  changes in the local configurational entropy of the  $N_1 = 1 + \Delta N_1$  atoms.

The downward electron transitions with  $\delta E_1 < 0$  and  $\delta S_1 < 0$  cause a decrease in the activation energy

$$\Delta E = E - |\delta E_1| < E \quad (2)$$

and in the pre-exponential factor

$$D_0 \sim \exp \left[ -\frac{|\delta S_1|}{k_B} \right] \ll 1. \quad (3)$$

As a result, the diffusion coefficient increases by the factor  $\exp(|\delta E_1| - T|\delta S_1|)/k_B T \gg 1$  since  $|\delta E_1| - T|\delta S_1| > 0$ . In the case of upward electron transitions, the local energy and entropy increase resulting in a decrease of  $D$ .

The electron transitions which occur simultaneously with the diffusion jump modify the probability per second of the SLEF-assisted jump<sup>12-14,16</sup>

$$K = \frac{1}{\Delta\tau} \exp \left[ \mp \frac{|\delta S_1|}{k_B} \right] \exp \left[ -\frac{E \mp |\delta E_1|}{k_B T} \right], \quad (4)$$

where the minus and plus signs are associated with the downward and upward electron transitions, respectively. Thus in the presence of downward electron transitions the diffusion coefficient can be written as<sup>12,13</sup>

$$D = \frac{\Delta\rho^2}{6\Gamma} K = D_{00} \exp \left[ -\frac{|\delta S_1|}{k_B} \right] \exp \left[ -\frac{E - |\delta E_1|}{k_B T} \right], \quad (5)$$

where  $\Delta\rho \approx d$  is the length of the diffusion jump,  $d$  is the interatomic distance,  $\Gamma$  is a geometrical factor which depends on the local material structure, and  $D_{00} = \Delta\rho^2/6\Gamma\Delta\tau$  is of the order  $(10^{-3} - 10^{-4})$  cm<sup>2</sup>/s.<sup>12,13</sup>

Hence one can see that the pre-exponential factor

$$D_0 = D_{00} \exp \left[ -\frac{|\delta S_1|}{k_B} \right] \quad (6)$$

can be much smaller than  $D_{00}$  in the case of downward transitions when  $|\delta S_1| > k_B$ . The activation energy  $\Delta E$  can be significantly lower than  $E$  when  $|\delta E_1|$  is comparable with  $E$ .

## III. MECHANISM ACCELERATING IMPURITY DIFFUSION IN *a*-Si

In order to explain the observed small values of  $\Delta E$  and  $D_0$  which results in a large diffusivity  $D$  of impurities in *a*-Si, the following questions have to be answered.

(1) Why do the downward transitions occur in *a*-Si at relatively low temperatures, and what are the mecha-

nisms which enhance the diffusion?

(2) How does the change in the impurity concentration influence these mechanisms, which in turn affect  $D_0$ ,  $\Delta E$ , and  $D$ ?

(3) What causes the reduction of  $\Delta E$  and  $D_0$  in  $a$ -Si with respect to  $c$ -Si?

Now let us consider the following two kinds of phenomena which promote the downward electron transitions and cause considerable reduction of  $\Delta E$  and  $D_0$ . The first mechanism is similar to that described in Ref. 14 which explains the recrystallization of  $a$ -Si. Hopping atoms stretch and cut off bonds with neighbors in their initial position and create new bonds in their new positions. As a result, transient point defects are created, which break down the local material stability and symmetry, and perturb the local electronic states. This results in the formation of transient time-dependent potential wells for electrons or holes of depth  $\Delta u(\tau)$ , of radius  $\Delta \rho(\tau)$ , and of lifetime  $\Delta \tau_w \approx \Delta \tau$ . The SLEF-induced transient local defects and electronic states created by the hopping atoms can trap mobile electrons for a short while and cause the energy release  $\delta E'_1$  in the vicinity of the fluctuating atom. Every well can trap during time  $\Delta \tau_w$  a certain number  $\delta n_e \approx n_e v_e \Gamma_e \Delta \tau_w$  of weakly bounded electrons which propagate with the velocity  $v_e$  in the vicinity of the well. Here  $\Gamma_e$  is the trapping cross section and  $n_e$  is the concentration of electrons available. Hence we can easily see that a considerable increase in  $n_e$  (e.g., due to a large concentration  $a_{im} > 1\%$  of dopant impurities) causes the corresponding enhancement in  $\delta n_e$ . Every trapped electron releases the average energy  $\langle \delta e \rangle > k_B T$  and decreases the local electronic configurational entropy by a factor of the order of  $k_B$ . As a result, the trapping of  $\delta n_e$  electrons per one hopping atom is accompanied by an energy release  $\delta E'_1$  and by the related negative change in entropy  $\delta S'_1$ :<sup>14</sup>

$$\delta E'_1 \approx -\delta n_e \langle \delta e \rangle \quad \text{and} \quad \delta S'_1 \approx -k_B \delta n_e. \quad (7)$$

These equations show that  $\delta E'_1 \sim n_e \sim a_{im}$  and  $\delta S'_1 \sim n_e \sim a_{im}$  depend on the impurity concentration  $a_{im}$ .

Consider now the second and more important mechanism for downward electron transitions which can explain the observed small values of  $\Delta E$  and  $D_0$  for the diffusion of impurities in  $a$ -Si. It is well known<sup>17-19</sup> that whatever model is used to describe  $a$ -Si, electron states are always found in the gap. These states are separated one from another and from the edge of mobile or bound electrons by relatively small energies  $\Delta e_{jk} = (0.05 \div 0.2)$  eV. It is also known that  $a$ -Si is a metastable state and starts to recrystallize at relatively low temperatures  $T_i = 800-850$  K (Refs. 19-22) where  $c$ -Si does not experience any phase or polymorphic transformations. Impurities of concentration  $a_{im} \gtrsim 1\%$  decrease the temperature of recrystallization by about 100 K and at the same time enhance considerably the concentration of weakly bound electrons. The recrystallization of  $a$ -Si is associated with considerable atomic and electronic rearrangements. High impurity concentration can reconstruct significantly the electron energy spectrum and distribution  $\varphi_e(e_j, T, a_{im})$ . These properties of doped  $a$ -Si are

strongly linked together through the fundamental concept<sup>23</sup> which connects the material stability with the rigidity of the electron energy distribution. According to this concept the existence of a transformation from doped  $a$ -Si into  $c$ -Si at relatively low temperatures is associated with a higher instability and higher sensitivity of the electron energy distribution  $\varphi_e(e_j, T, a_{im})$  in  $a$ -Si to small changes  $\Delta T$  of temperature. This means that a relatively small decrease (or increase)  $\Delta T$  of the temperature  $T$  can cause downward (or upward) electron transitions and the corresponding shifts in the electron energy distribution<sup>12</sup>

$$\begin{aligned} \Delta \varphi_e(e_j, \Delta T, T, a_{im}) &= \varphi_e(e_j, T \pm |\Delta T|, a_{im}) \\ &\quad - \varphi_e(e_j, T, a_{im}) \\ &\approx (d\varphi_e/dT) \Delta T. \end{aligned}$$

These shifts are negative for cooling ( $\Delta T < 0$ ) and positive for heating ( $\Delta T > 0$ ).

These electronic properties of  $a$ -Si suggest the following mechanism for transient local downward electronic transitions in the vicinity of the hopping impurity atoms, initiated by local fluctuational cooling of small volumes  $V_1$  simultaneously with the diffusion jump. The  $N_1 \approx 30-100$  particles involved in the SLEF-assisted diffusion jumps are subject to fluctuational coolings or heatings  $\Delta T_1 = T_1 - T$  during short-time intervals  $\Delta t_{01}$  which occur with the frequency<sup>12,13</sup>

$$t_1^{-1} = \Delta t_{01}^{-1} \exp \left[ -\frac{3}{2} N_1 Z(T) \left( \frac{\Delta T_1}{T} \right)^2 \right], \quad (8)$$

where  $\Delta t_{01} \approx (10^{-12} - 10^{-11})$  s is the lifetime of the temperature (energy) fluctuation and  $k_B Z(T)$  is the heat capacity per degree of freedom. Hence one can see that rather large fluctuational cooling or heating  $\Delta T_1 \approx \mp T/N_1^{1/2} \approx (0.1-0.2)T$  can occur with high frequencies  $(10^{-1} - 10^{-2}) \Delta t_{01}^{-1} \approx (10^9 - 10^{11})$  s<sup>-1</sup>. These fluctuations  $\Delta T$  cause transient local downward (or upward) electron transitions and corresponding downward (or upward) shifts  $\Delta \varphi_e$  of electron energy distribution in the volume  $V_1$ . Such electron transitions are associated with the corresponding release  $\delta E''_1 < 0$  (or consumption  $\delta E''_1 > 0$ ) of energy and negative  $\delta S''_1 < 0$  (or positive  $\delta S''_1 > 0$ ) changes in the local configurational entropy. When these phenomena occur simultaneously with the SLEF-assisted diffusion jump of an atom, the activation energy  $\Delta E$  and the pre-exponential factor  $D_0$  become small (or large) according to Eqs. (2) and (5).

It is known<sup>20-22</sup> that high concentrations of doping ( $a_{im} > 1\%$ ) of  $a$ -Si by such impurities as P, B, As, etc. change considerably electronic and other properties of the material. In particular this doping increases the rate coefficient of recrystallization and therefore reduces correspondingly the stability of the material and of its electronic distribution  $\varphi_e(e_j, T, a_{im})$ . On the other hand the high concentration of impurities reduces the "threshold" recrystallization temperature to  $T_i = 700-750$  K. These temperatures are rather close to experimental temperature range used for the measurements of the diffusion coefficient  $D$  in  $a$ -Si (see Table I). In this temperature

range the stability of doped *a*-Si is considerably lower than that of pure *a*-Si. Hence one can conclude that at such temperatures the electron energy distribution  $\varphi_e(e_j, T, a_{im})$  of the doped material is more sensitive to changes of temperature than that in pure *a*-Si. This means that the energy distribution of  $4\Delta N_1 \approx 100-400$  electrons located in the SLEF-related volume  $V_1$  is rather sensitive to fluctuational collings  $\Delta T < 0$  (heatings  $\Delta T > 0$ ) of the  $N_1$  particles. Therefore the transient coolings  $\Delta T_1 < 0$  of the volume  $V_1$  can cause downward transitions of  $\Delta n_e < 4\Delta N_1$  electrons during the SLEF lifetime  $\Delta\tau$ . The number  $\Delta n_e$  is proportional to  $n_e$  and depends on the ratio  $\Delta\tau/t_{jk}^d$  for the fluctuational coolings (or  $\Delta\tau/t_{jk}^{up}$  for heatings), where  $t_{jk}^d$  or  $t_{jk}^{up}$  are the characteristic relaxation time intervals for downward or upward electron transitions between the levels  $e_j$  and  $e_k$ . The shorter  $t_{jk}^d$  or  $t_{jk}^{up}$  the larger the number of electrons performing downward  $\Delta n_e^d$  or upward  $\Delta n_e^{up}$  transitions, respectively. As a result of downward transitions a certain amount of energy  $\delta E_1''$  is released in the volume  $V_1$ :

$$\delta E_1'' = -\Delta n_e^d \langle \Delta e \rangle \sim -n_e \frac{\Delta\tau}{\langle t_{jk}^d \rangle} \langle \Delta e \rangle. \quad (9)$$

Here  $\langle \Delta e \rangle > k_B T$  is the average energy released per one electron and  $\langle t_{jk}^d \rangle$  is the time  $t_{jk}^d$  averaged over all energy levels involved. At the same time with the energy release  $\delta E_1''$  the local configurational entropy decreases by a factor

$$\delta S_1'' \approx -k_B \Delta n_e \quad \text{or} \quad \delta S_1'' \approx -k_B \frac{|\delta E_1''|}{\langle \Delta e \rangle}. \quad (10)$$

As a result of energy release and entropy change, the measured activation energy  $\Delta E$  and pre-exponential factor  $D_0$  can become rather small when

$$\Delta n_e \gg 1, \quad E - |\delta E_1''| \ll E, \quad \text{and} \quad |\delta S_1''| \gg k_B \quad (11)$$

and the diffusion coefficient can increase by many orders of magnitude, according to Eq. (5).

The following questions arise in this context. (i) Why are the downward electron transitions prevalent at low temperatures? (ii) When do upward transitions start to play an important role? To answer these questions one should take into account that at low temperatures the probability for downward electronic transitions can be much larger than that for upward ones; this situation changes at higher temperatures. The terms "low temperature  $T^{(L)}$ " or "high temperature  $T^{(H)}$ " are determined by the magnitude of the ratio  $\eta_{jk} = \Delta e_{jk}/k_B T$ , where  $\Delta e_{jk} = e_j - e_k$  is the distance between electronic levels in the material. This criterion can be obtained for *a*-Si in the way similar to that used earlier for other materials.<sup>12</sup> Low temperatures  $T^{(L)}$  satisfy the condition  $\eta_{jk}^{(L)} = \Delta e_{jk}/k_B T^{(L)} \gg 1$ . In this case the electron distributions are relatively stable with respect to upward transitions, but not with respect to the downward ones. At high temperatures ( $\eta_{jk}^{(H)} = \Delta e_{jk}/k_B T \approx 1$ ) the electron distributions  $\varphi_e$  are sensitive to the temperature increase and to the local temperature fluctuations  $\Delta T_1 > 0$ . The

expectation time for downward  $t_{jk}^d$  and upward  $t_{jk}^{up}$  transitions between the  $j$ th and  $k$ th electronic levels are linked by a Boltzmann factor  $t_{jk}^{up} = t_{jk}^d \exp(\Delta e_{jk}/k_B T)$ . Hence one can see that the ratio between the number of electrons performing downward  $\Delta n_{jk}^d$  and upward  $\Delta n_{jk}^{up}$  electron transitions is determined by

$$\Delta n_{jk}^d / \Delta n_{jk}^{up} \approx t_{jk}^{up} / t_{jk}^d \approx \exp(\Delta e_{jk}/k_B T). \quad (12)$$

At low temperatures, when  $\Delta e_{jk} = e_j - e_k > k_B T^{(L)}$ , this ratio is very large. Therefore  $\Delta n_{jk}^{up} \ll \Delta n_{jk}^d$  and upward transitions cannot occur. On the other hand, the downward transitions can take place during the fluctuational cooling  $\Delta T_1 < 0$  with much higher probability since  $t_{jk}^d \ll t_{jk}^{up}$  and  $\Delta\tau/t_{jk}^d \gg \Delta\tau/t_{jk}^{up}$ . Upward transitions become more important at higher temperatures when  $\Delta e_{jk}/k_B T$  becomes smaller and  $\Delta\tau/t_{jk}^{up}$  larger. Therefore the transition from the low-temperature  $T^{(L)}$  to the high-temperature  $T^{(H)}$  regimes occurs at temperatures  $T_d \approx \langle \Delta e \rangle / k_B$  which can be taken as a measure of  $\langle \Delta e \rangle$ . This provides an empirical way to estimate  $\langle \Delta e \rangle$  from experimental data.

#### IV. CALCULATION OF THE DIFFUSION PARAMETERS

The next important question is to estimate the electron concentration  $n_e$  and to link it with the dopant concentration  $a_{im}$  in order to calculate the concentration dependence of the diffusion parameters. Equations (9) and (10) show that the amount of energy release  $\delta E_1'' \sim n_e$  and entropy change  $\delta S_1'' \sim n_e$  can increase considerably when dopant impurities are introduced. This increase in  $n_e$  can be estimated by<sup>14</sup>

$$n_e = a_{im} N \exp(-\Delta e_{im}/2k_B T), \quad (13)$$

where  $a_{im}$  is the relative impurity concentration,  $N$  is the total number of particles per  $\text{cm}^3$ , and  $\Delta e_{im}$  is the additional impurity level in the band of localized levels of *a*-Si below the mobility edge. For phosphorus as an impurity in *a*-Si,  $\Delta e_{im} = 0.2$  eV and one finds  $\Delta e_{im}/2k_B T^{(L)} = 1.9$  and  $n_e = 0.15 a_{im} N$  at  $T^{(L)} \approx 600^\circ\text{K}$ . Therefore impurities can increase  $n_e$  substantially and reduce considerably the activation energy

$$\Delta E = E - |\delta E_1'| - |\delta E_1''| = E - \delta n_e \langle \delta e \rangle - \Delta n_e \langle \Delta e \rangle \quad (14)$$

and the pre-exponential factor

$$D_0 = D_{00} \exp(-\delta n_e - \Delta n_e), \quad (15)$$

where

$$\delta n_e + \Delta n_e = \frac{\Delta S_1}{k_B} = \frac{\delta E_1'}{\langle \delta e \rangle} + \frac{\delta E_1''}{\langle \Delta e \rangle}. \quad (16)$$

At present there are no data for direct calculations of  $\Delta n_e$  and  $\langle \Delta e \rangle$ ; therefore we shall use available experimental results to estimate these parameters. For example, as we mentioned earlier  $\langle \Delta e \rangle$  can be estimated from the characteristic temperature  $T_d$ , which separates low-

and high-temperature Arrhenius "branches" of the experimental plots  $\ln D$  versus  $1/T$ :<sup>12</sup>

$$\langle \Delta e_{jk} \rangle \approx k_B T_d \quad \text{and} \quad |\delta E'_1| \approx -\Delta n_e k_B T_d. \quad (17)$$

The number  $\Delta n_e + \delta n_e$  of electrons which undergo downward transitions can be estimated from the experimental values of  $D_0$  through the following equation:<sup>12</sup>

$$\Delta n_e + \delta n_e \approx |\ln(D_0/D_{00})| \approx |\delta S_1| / k_B. \quad (18)$$

This result can be used to calculate the activation energy. From Eqs. (15) and (16) one finds

$$\begin{aligned} \delta E_1 = -|\delta E'_1| - |\delta E''_1| = -k_B T_d [\ln(D_0/D_{00}) - \delta n_e] \\ - \langle \Delta e \rangle \delta n_e. \end{aligned} \quad (19)$$

The derived equations enable us to estimate the parameters for the diffusion of impurities in *a*-Si. For example, when phosphorus diffuses into *a*-Si, we have  $\Delta \tau \approx 3 \times 10^{-13}$  s,  $\Gamma \approx 1$ ,  $\Delta \rho \approx 2.5 \times 10^{-8}$  cm and we estimate  $T_d \approx 750$  K which is of the order of the recrystallization temperature  $T_i \approx 700$ – $750$  K in doped *a*-Si. Assuming  $D_0 = 10^{-3}$  cm<sup>2</sup>/s, we find from Eqs. (13) and (16)  $\delta n_e + \Delta n_e = 20$ , where  $\delta n_e \approx 1$  is estimated in Ref. 14. As a result, from Eqs. (7) and (15) and assuming  $\langle \delta e \rangle \approx 0.3$  eV (Ref. 14) one finds  $|\delta E'_1| \approx 1.2$  eV and  $\delta E_1 \approx -1.5$  eV. From Eq. (2) we obtain the barrier energy  $E = \Delta E + |\delta E_1| \approx 2$  eV which can be considered as the "renormalized" activation energy not "masked" by accompanying electronic phenomena. The energy  $E$  is about four times larger than the experimental activation energy  $\Delta E$  and probably it is associated with the binding energies of impurities in *a*-Si. This result seems to be fairly general for low-temperature diffusion, when downward electronic transitions play an essential role, reducing  $\Delta E$  and  $D_0$ . The opposite effect (not considered herein) takes place at higher temperatures when  $\Delta E$  and  $D_0$  can be much larger due to upward electronic transitions when  $\delta E_1 > 0$  and  $\delta S_1 > 0$ .<sup>12</sup>

## V. ESTIMATES OF THE CRITICAL IMPURITY CONCENTRATION FOR DIFFUSION

Let us estimate now the critical concentration of impurities  $a_{im}^c$  which causes a considerable increase of the

diffusion coefficient. It can be estimated in a way similar to that used in calculations of impurity-concentration dependence of recrystallization in doped *a*-Si:<sup>14</sup>

$$\delta n_e = n_e \Gamma_e v_e \Delta \tau_w \approx 1, \quad (20)$$

or

$$a_{im}^c = (N \Gamma_e v_e \Delta \tau_w)^{-1} \exp \left[ \frac{\Delta e_{im}}{2k_B T^{(L)}} \right]. \quad (21)$$

For  $N \approx d^{-3}$ ,  $\Gamma_e = \pi r_{im}^2$  and  $r_{im} = 3d$ ,  $v_e = 10^7$  cm<sup>2</sup>/s,  $T^{(L)} = 600$  K,  $d \approx 3 \times 10^{-8}$  cm, and  $\Delta \tau_w \approx \tau_1 \approx 10^{-13}$  one obtains  $a_{im}^c \approx 1\%$ . Therefore the impurity diffusion coefficient in *a*-Si becomes rather large at  $a_{im} > 1\%$  which is in good agreement with experimental observations.

For low impurity concentrations  $a_{im} \ll a_{im}^c$  the electron concentration  $n_e$  given by Eq. (13) is low,  $\delta n_e \ll 1$  and there are not enough electrons available for downward transitions. As a result, the material becomes more stable and diffusion jumps are performed mainly without the "assistance" of downward electron transitions. This results in a considerable decrease in  $|\delta E_1|$  and increase in  $\Delta E = E - |\delta E_1|$  and therefore in the corresponding large reduction of the diffusion coefficient according to Eq. (5).

In conclusion, we have shown that the proposed semiphenomenological many-body kinetic theory of diffusion can explain the main features of the impurity diffusion mechanism in *a*-Si. It also provides explanations for the observed concentration dependence of  $\Delta E$ ,  $D_0$  and  $D$ . It appears that the problem of impurity diffusion is closely linked with the stability of *a*-Si and its electronic energy distribution. The semiphenomenological character of the presented theory enables one to consider diffusion in *a*-Si with minimum available information about material properties. We think that the proposed model can be applied to explain the impurity diffusion in other amorphous materials.

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