Kinetic model for desorption of hydrogen from amorphous hydrogenated silicon

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We have previously shown experimentally that the addition of dopants causes large changes in the hydrogen desorption from a-Si:H. A new kinetic many-body semiphenomenological model for this desorption process is proposed. It takes into account the atomic and electronic properties of the material. The model is based on the kinetic many-body theory of thermally activated rate processes in solids. The model considers atomic and electronic phenomena occurring in the submicronic vicinity of a H_2 molecule desorbed from hydrogenated amorphous silicon (a-Si:H). The phenomena are synchronized with the desorption event of duration $\tau_i = 10^{-13}$–10^{-12} s. The following main results are obtained. (i) The Arrhenius-like equation for the rate coefficient K of hydrogen desorption is derived from the kinetic consideration of the desorption event without invoking the equilibrium rate theory. (ii) The Arrhenius activation energy ΔE and prefactor K_0 are expressed in terms of local parameters that characterize atomic and electronic processes induced by short-lived large energy fluctuations of surface atoms. These processes occur in the vicinity of a desorbed H_2 molecule during the desorption event. (iii) The "abnormally" large range of observed variations in the prefactor K_0 (about 14 orders of magnitude) and in the activation energy ΔE (a factor of 7), caused by dopant variations, are explained for the first time. (iv) A linear dependence between variations $\ln K_0$ and ΔE found in hydrogen desorption from a-Si:H is explained. The dependence is associated with the kinetic compensation effect (CEF). (v) Coefficients in the CEF equation and other kinetic parameters are calculated and expressed in terms of material characteristics, in good agreement with experimental data.

I. INTRODUCTION

The influence of hydrogen on the properties of hydrogenated amorphous silicon (a-Si:H) has been widely studied due to the technological importance of this material.[1–15] Such useful properties of a-Si:H as the high photoconductivity-to-dark-conductivity ratio and the rather wide controllability of electronic parameters by doping are related to the hydrogen content. These qualities of a-Si:H distinguish it from unhydrogenated pure amorphous-silicon films which have rather poor electronic properties because of a high concentration of unsaturated dangling bonds.[15] In this connection, understanding the mechanisms which govern the release of hydrogen from a-Si:H at elevated temperatures is highly desirable, since they can limit the stability of electronic devices made of a-Si:H.

Among other methods, the hydrogen concentration and stability in a-Si:H can be determined from the spectra of the hydrogen evolution rate as a function of temperature in doped and undoped a-Si:H.[1–11] The connection between the hydrogen evolution in a-Si:H and the behavior of the Fermi-level position have been established, and the influence of impurities has been studied.[5–7,9] However, kinetic mechanisms for electronic and atomic rearrangements on the surface associated

with desorption events have not yet been proposed and some experimental results (e.g., "abnormally" small observed Arrhenius preexponential factors and activation energies for desorption of H_2) have not been explained.

We propose a new kinetic many-body model of hydrogen desorption from a-Si:H. In this model, the elementary desorption event causing the release of a single H_2 molecule is treated as a transient many-body phenomenon. Many atoms and electrons located in a submicronic vicinity of the desorbed H_2 are considered to be involved.

The desorption process is controlled by a rate coefficient K:

$$K = K_0 \exp(-\Delta E / kT) , \qquad (1.1)$$

where K_0 is the Arrhenius preexponential and ΔE is the activation energy.

The model explains the observed values of $\Delta E^{(\text{obs})}$ and $K_0^{(\text{obs})}$ and their correlation. It also explains variations in these two parameters associated with doping. The explanation is presented in terms of local material parameters which characterize short-term atomic and electronic rearrangements which occur in the submicronic vicinity of the desorbed particle during the desorption event.

Evolution spectra are mainly influenced by the follow-

TABLE I. Experimental kinetic parameters for hydrogen desorption from phosphorus-doped glow-discharge a-Si:H. Substrate temperature $T_s = 313$ K.

Doping conditions (ppm)	Peak temperature T_M (K)	Activation energy $\Delta E^{(obs)}$ (eV)	Activation entropy ΔS^* (meV K^{-1})	$\log_{10}(K_0^{(obs)}$ [s^{-1}]	Activation free energy ΔG^a (eV)
$^a10^4$[PH$_3$]	639	0.92	-1.6	5.09	1.94
10^4[PH$_3$]	601	1.32	-0.78	9.17	1.79
10^4[PH$_3$]	605	1.32	-0.79	9.10	1.8
10^3[PH$_3$]	647	1.62	-0.49	10.64	1.94
3×10^3[PH$_3$]	638	1.69	-0.33	11.46	1.9
100[PH$_3$]	628	1.72	-0.24	11.9	1.87
10^3[PH$_3$]	652	1.80	-0.2	12.07	1.94
100[PH$_3$]	650	1.82	-0.15	12.35	1.92

^{a}This film was thinner than the rest.

ing three processes: rupture of Si—H bonds, diffusion of hydrogen to the film surface, and desorption of hydrogen (mainly in the form of molecular hydrogen H$_2$). In this paper we consider mainly the kinetics of desorption of hydrogen from the surface of a-Si:H. The experimental data were obtained from hydrogen effusion experiments on a-Si:H prepared at low substrate temperatures. Observed Arrhenius preexponential factors $K_0^{(obs)}$ and activation energies $\Delta E^{(obs)}$ for hydrogen desorption were derived from a fit of the low-temperature effusion peak.[2,5,7] These parameters vary in a broad range due to doping conditions (Tables I and II):

$$K_0^{(obs)} \simeq 10 \text{ to } 10^{15} \text{ s}^{-1}$$

and   (1.2)

$$\Delta E^{obs} = 0.3 \text{ to } 2.1 \text{ eV} .$$

Thus, the experimental prefactors in the Arrhenius equation for the rate coefficient of desorption are much smaller (or larger) than the "normal" prefactor $K_{0\,norm} = 10^{13} - 10^{12}$ s^{-1} of desorption.[16] Likewise the experimental activation energies $\Delta E^{(obs)}$ are substantially lower than the lowest energy $\Delta E_{norm} \approx 2$ eV necessary for breaking of Si—H bonds when this phenomenon is accompanied by the formation of a H$_2$ molecule.[14] The experimental data show that the small (or large) preexponential factors are associated with the lower (or higher) activation energies. Similar correlation between $K_0^{(obs)}$ and $\Delta E^{(obs)}$, which has been known for many decades in surface physics and chemistry and other fields,[16-31] can be expressed in the form of the following empirical equation:

$$\ln K_0^{(obs)} = C + a \, \Delta E^{(obs)} .$$ (1.3)

TABLE II. Experimental kinetic parameters for hydrogen desorption from boron-doped glow-discharge a-Si:H. Substrate temperature $T_s = 313$ K.

Doping conditions (ppm)	Peak temperature T_M (K)	Activation energy $\Delta E^{(obs)}$ (eV)	Activation entropy ΔS^* (meV K^{-1})	$\log_{10}[K_0^{(obs)}$ $(R^{-1})]$	Activation free energy ΔG^* (eV)
10^4[B$_2$H$_6$]	490	0.3	-2.42	0.77	1.48
10^4[B$_2$H$_6$]	503	0.33	-2.37	1.03	1.43
3×10^3[B$_2$H$_6$]	563	0.57	-1.97	3.13	1.66
10^3[B$_2$H$_6$]	611	0.99	-1.33	6.35	1.81
10^3[B$_2$H$_6$]	628	1.14	-1.16	7.14	1.87
2×10^2[B$_2$H$_6$]	643	1.41	-0.77	9.25	1.9
3×10^2[B$_2$H$_6$]	634	1.45	-0.67	9.74	1.87
10^2[B$_2$H$_6$]	635	1.52	-0.58	10.2	1.89
50[B$_2$H$_6$]	645	1.98	$+0.09$	13.59	1.92
40[B$_2$H$_6$]	646	2.03	$+0.19$	14.07	1.91
50[B$_2$H$_6$]	642	2.14	$+0.35$	14.91	1.91
Compensated and undoped a-Si:H					
0.610^3[B$_2$H$_6$] -10^4[PH$_3$]	642	0.94	-1.55	5.28	1.94
Undoped	644	1.66	-0.4	11.09	1.92

This linear dependence between $\ln K_0^{(obs)}$ and $\Delta E^{(obs)}$ is known as the compensation effect (CEF). Here C and a are empirical fitting parameters which are assumed to be independent of T. In particular, experimental prefactors and activation energies found in desorption from metal surfaces vary by 15 orders of magnitude and activation energies change by a factor of 5.[16-31] The origin of the observed "abnormally" small and large prefactors and activation energies as well as that of the CEF is not quite clear yet. A summary of related experimental results and attempts for their theoretical explanations until the 1960s are presented in Refs. 25–27. More recent data concerning the observed $K_0^{(obs)}$ and $\Delta E^{(obs)}$ are summarized in Refs. 22 and 32. The conventional equilibrium rate theory has not been able to explain these experimental facts even for metals. Hence, at present, one can hardly expect to develop a comprehensive detailed microscopic theory of hydrogen desorption from a-Si:H which would include such details as the trajectories of particles overcoming energy barriers, etc.

All the aforementioned information has motivated us to suggest a new kinetic semiphenomenological approach to desorption of hydrogen from a-Si:H. The approach is similar to that which has recently been applied successfully to the interpretation of "abnormally" small and large prefactors and activation energies in different rate processes in metals and crystalline and amorphous semiconductors.[22,32-34]

The suggested approach is based on the kinetic many-body theory of short-lived large energy fluctuations (SLEF's) of atomic particles in solids of lifetime $10^{-13}-10^{-12}$ s (Fig. 1). The SLEF's supply the fluctuating particle (FP) with the energy $\varepsilon_{op} \gg kT$ sufficient to overcome the energy barrier to initiate the desorption of a single H_2 molecule from the surface.

The proposed model has a statistical semiphenomenological character. It does not consider in detail the microscopic mechanical behavior of the particles (their trajectories, potential surfaces, saddle points, etc.) about which our knowledge is very poor. Instead, the model describes the kinetics of the correlated short-term behavior of FP's overcoming an energy barrier and many surrounding particles located in the small submicronic FP vicinity, during the desorption event of duration $\tau_1 \approx 10^{-13}-10^{-12}$ s.[35] In this way we lose information about the detailed behavior of the particles involved in a single desorption event leading to desorption of a H_2 molecule. Instead, we take into account some new transient many-body atomic and electronic processes occurring in the submicronic vicinity of the desorbed particles and synchronized with the desorption event.

The paper is organized as follows. The proposed model is described in Sec. II. Calculations of rate coefficients of hydrogen desorption from a-Si:H are given in Sec. III. The kinetic compensation effect is considered in Sec. IV. The comparison of the theory with experimental data is presented in Sec. V. The conclusion is given in Sec. VI.

II. MODEL OUTLINE

The experimental rate of desorption of hydrogen from a-Si:H is described by[2,4,5,16]

$$\frac{dC_H}{dt} = K C_H^n .$$ (2.1)

Here the rate coefficient K is presented in the following form as given by the *equilibrium* rate theory[36]

$$K = \frac{1}{\tau_0} \exp\left[\frac{\Delta S^*}{k}\right] \exp\left[-\frac{\Delta H}{kT}\right]$$ (2.2)

or

$$K \simeq \frac{1}{\tau_0} \exp\left[-\frac{\Delta G^*}{kT}\right] ,$$ (2.2a)

where

$$\Delta G^* = \Delta H - T \Delta S^*$$ (2.2b)

is the activation free energy. Here, ΔH and ΔS^* are the activation enthalpy and entropy, respectively, $C_H = 1 - C/C_0$, C_0, and C are the initial and current hydrogen concentrations; n is the order of the reaction; $\tau_0 \approx 10^{-13}$ s or $\tau_0 \approx h/kT$, h and k are the Planck and Boltzmann constants, respectively. The preexponential factor in Eq. (2.2) is

$$K_0 = \frac{1}{\tau_0} \exp\left[\frac{\Delta S^*}{k}\right] .$$ (2.3)

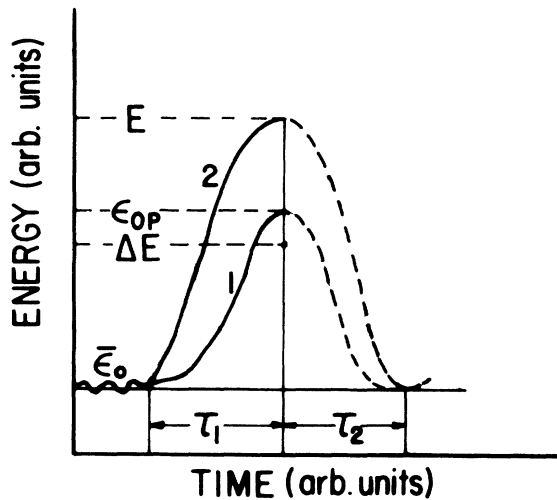The conventional rate theory[36] based on equilibrium sta-

FIG. 1. Time and energy scales of short-lived large energy fluctuations (SLEF's) of surface atoms able to initiate the desorption events. $\tau_1 \approx 10^{-13}-10^{-12}$ s and $\tau_2 \approx \tau_1$ are the SLEF formation and SLEF relaxation time intervals. ε_{op} is the maximum thermal energy per particle. E is the SLEF threshold energy the fluctuating particle (FP) needs to initiate the desorption event without the "assistance" of the electron transitions (curve 2). $\Delta E = E - |\delta E^{down}| \gg kT$ is the SLEF threshold energy sufficient to initiate the desorption event with the "assistance" of downward electron transitions (curve 1). The dashed lines show the SLEF relaxation which occurs when the desorption event does not take place and the SLEF energy ΔE (or E) is not consumed during desorption.

tistical thermodynamics has serious conceptual and technical difficulties in calculation and in the interpretation of the values ΔH, ΔS^*, and ΔG^* characterizing the transient many-body elementary event of desorption and other thermally activated rate processes in solids and on their surfaces.[22,30,37,38] Here we consider the *kinetic* model of elementary events of hydrogen desorption from a-Si:H, which is based on the kinetic many-body theory of SLEF's and SLEF-induced and electron-affected rate processes.[22,32−35]

This model, which proposes new mechanisms to explain the observed values of ΔH, ΔS^*, and ΔG^*, is based on the following idea:[22,30,32−35] Desorption consists of a large number of SLEF-induced desorption events. In each of these events a single H_2 molecule is desorbed. The desorption event with the duration of $\tau_1 = 10^{-13}-10^{-12}$ s includes the following three kinds of phenomena which occur simultaneously during τ_1: (a) the rupture of two Si—H bonds, (b) the formation and desorption of a H_2 molecule, and (c) a possible local surface reconstruction. The desorption event is associated with the necessity to overcome an energy barrier of effective height $\Delta E \gg kT$ which plays the role of the effective activation energy for hydrogen desorption. Atoms with an average thermal energy of the order of $kT \ll \Delta E$ are unable to overcome the energy barrier to cause desorption of a H_2 molecule. The desorption event is initiated by a SLEF of one (or $N_0 \gtrsim 1$) surface atom (e.g., a Si atom bound to a H atom) which acquires a large thermal energy $\varepsilon_{op} > \Delta E$ sufficient to generate the desorption event (Fig. 1). The fluctuating particles (FP's) receive the energy ε_{op} during a short time interval τ_1 (Fig. 1) from the small surrounding volume $\Omega_1 \approx 2R_1^3$ of radius $R_1 \approx \tau_1 c_s \approx 10^{-7}$ cm (Fig. 2).[22,30,32−34] This radius is determined by the short time τ_1 of SLEF formation and by the energy transfer velocity c_s (of the order of the sound velocity $\approx 3 \times 10^5$ cm/s). More remote material atoms located out of the volume Ω_1 cannot contribute directly to the SLEF formation due to the shortness of τ_1 and the finiteness of c_s (the causality condition).

The volume Ω_1 contains $\Delta N_1 \approx 30-100$ atoms which serve as a transient FP energy reservoir during the SLEF formation. This volume also contains $\approx 4 \Delta N_1$

FLUCTUATING ATOM

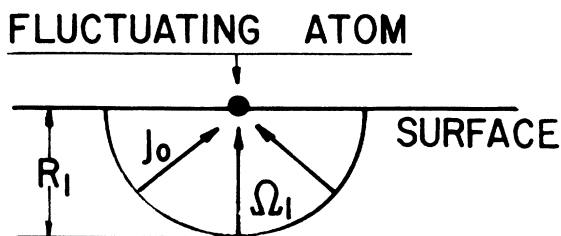

FIG. 2. Characteristic space scales of surface SLEF's. The volume $\Omega_1 \approx 2R_1^3$ of radius $R_1 \approx \tau_1 c_s$ containing $\Delta N_1 \approx 30-100$ atoms which serve as a transient energy reservoir for the fluctuating atom during SLEF formation. $c_s \approx (1-5) \times 10^5$ cm/s is the sound velocity. j_0 are transient energy fluxes transferring the fluctuation energy from the ΔN_1 particles to the fluctuating atom during the SLEF formation time τ_1.

$\approx 100-400$ valence electrons with the energy distribution $\phi(e_j; T; a_H; a_d)$ which depends on temperature T, relative concentrations of hydrogen a_H and dopants a_d (e.g., boron), and electron energy levels e_j, e_k, etc. that exist in the gap in a-Si:H; $j,k = 1,2, \ldots$. The electron distribution ϕ is changed by an increase in temperature or by changes in the hydrogen a_H and impurity a_d concentrations.

These changes in ϕ influence the SLEF probability W and rate coefficient $K \sim W$.[22,32,33] Besides, mobile electrons or holes (intrinsic or caused by the presence of impurities) with velocities $v_{e,h} \approx 10^7$ cm/s $\gg c_s$ can come into the volume Ω_1 from larger distances $r_{e,h} \approx v_{e,h}\tau_1 \approx 10^{-6}-10^{-5}$ cm during the SLEF time τ_1. These carriers can also influence markedly W and K.

We consider the following semiphenomenological model by the SLEF-induced desorption event. The desorption event is initiated by the SLEF of one surface Si atom bound to a H atom and having as a neighbor another surface Si atom also bound to a H atom (Fig. 3). The SLEF initiates large deviations $\delta q_0 = |q_0 - \bar{q}_0|$ in coordinates q_0 of the fluctuating Si atom from the mean values $\bar{q}_0$. Values of δq_0 can be of the order of the mean distance $d \approx 2.4$ Å between Si atoms. The fluctuating Si atom carrying the H atom bound to it approaches the neighboring Si atom at a distance d_t considerably smaller than d. Therefore the SLEF induces strong shrinking of some bonds and considerable stretching of some other bonds with neighbors during the SLEF lifetime $\approx 10^{-13}-10^{-12}$ s. As a result, the SLEF generates a strong local transient atomic distortion or a transient point defect of lifetime τ_1.[22,32,33] During this time the fluctuating Si atom comes close to the neighboring Si atom; and therefore the two Si atoms and two H atoms bound to the Si atoms form a transient atomic "cluster" within which interatomic distances d_t are considerably smaller than d. This SLEF-induced transient dynamic point defect creates severe local electron perturbations and rearrangements in its vicinity.[22,32−34] In the case of hydrogen desorption, the transient electron rearrangements are associated with the rupture of the Si—H bonds, the formation and desorption of a H_2 molecule, and a possible local reconstruction of Si—Si bonds on the surface. These local processes involve not only atoms, but many surrounding valence electrons in the volume $V_1 = \Omega_1 + V_0 \simeq \Omega_1$ and the related surface area $\approx V_1^{2/3} \approx (10-20)d^2$, where $V_0 \ll \Omega_1$ is the volume occupied by the fluctuating parti-
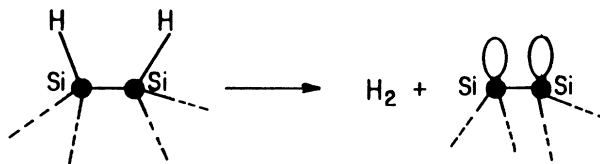

FIG. 3. A scheme for hydrogen desorption requiring minimum energy, in which Si—H bond breaking is accompanied by the formation of a H_2 molecule.

cle, $d = 2-3$ Å. The electrons strongly perturbed in the course of the desorption event can experience downward and/or upward transitions. The number Δn^{down} or Δn^{up} of valence electrons which can experience downward and/or upward transitions during the desorption event will be estimated in the following sections.

The downward (or upward) electron transitions cause local energy release $\delta E^{down} < 0$ (or consumption $\delta E^{up} > 0$) and negative $\delta S^{down} < 0$ (or positive $\delta S^{up} > 0$) change in the local configurational entropy. Then, the total energy and entropy changes of the particles involved in the desorption event are

$$\delta E = \delta E^{up} - |\delta E^{down}| \quad \text{and} \quad \delta S = \delta S^{up} - |\delta S^{down}| . \quad (2.4)$$

The effective activation energy is

$$\Delta E = \begin{cases} \Delta E^{down} = E - |\delta E^{down}| + \delta E^{up} < E \\ \text{for } |\delta E^{down}| > \delta E^{up}, & (2.5) \\ \Delta E^0 = E \quad \text{for } |\delta E^{down}| = \delta E^{up}, & (2.6) \\ \Delta E^{up} = E - |\delta E^{down}| + \delta E^{up} > E \\ \text{for } |\delta E^{down}| < |\delta E^{up}|, & (2.7) \end{cases}$$

likewise,[22,32] the preexponential factor $K_0 = (1/\tau_1)\exp(-\delta S/k)$ becomes

$$K_0 = \begin{cases} K_0^{down} = (1/\tau_1)\exp\left[\dfrac{\delta S^{up} - |\delta S^{down}|}{k}\right] < \dfrac{1}{\tau_1} \\ \text{for } \delta S^{up} < |\delta S^{down}|, & (2.8) \\ K_0^0 = 1/\tau_1 \quad \text{for } \delta S^{up} = |\delta S^{down}|, & (2.9) \\ K_0^{up} = (1/\tau_1)\exp\left[\dfrac{\delta S^{up} - |\delta S^{down}|}{k}\right] > \dfrac{1}{\tau_1} \\ \text{for } \delta S^{up} > |\delta S^{down}|, & (2.10) \end{cases}$$

where $\tau_1 \approx 10^{-13}-10^{-12}$ s. Here, E is the energy parameter that presents the SLEF threshold energy necessary to induce the desorption event without the influence of local electron transitions accompanying the desorption event. Thus, E is equal to the activation energy of hydrogen desorption when neither downward nor upward electron transitions dominate during the desorption event, i.e.,

$$E = \Delta E^0 \quad \text{when} \quad \delta E = 0, \quad \delta S = 0, \quad \text{and} \quad K_0 \approx \frac{1}{\tau_1} . \quad (2.10a)$$

Numerical values of E will be found in the following sections.

The calculated rate coefficient obtained from the kinetic theory is[22,34,35]

$$K = \frac{1}{\tau_1}\exp\left[\frac{\delta S}{k}\right]\exp\left[-\frac{\Delta E}{kT}\right] \quad (2.11)$$

or, in terms of Eqs. (2.4)–(2.7),

$$K = \frac{1}{\tau_1}\exp\left[-\frac{\Delta G}{kT}\right] , \quad (2.12)$$

where

$$\Delta G = E + \delta E - T\,\delta S \quad \text{or} \quad \Delta G = E + \delta G \quad (2.13)$$

is the effective activation free energy obtained from the kinetic theory[22,34,35] and $\delta G = \delta E - T\,\delta S$.

Equations (2.11)–(2.13) obtained from the kinetic rate theory are formally similar to Eqs. (2.2) and (2.2a) obtained from the equilibrium rate theory and generally used for the treatment of experimental data. Therefore, one can compare directly the kinetic rate theory and the experimental results through the obvious equations

$$\Delta E = \Delta H, \quad \delta S = \Delta S^*, \quad \text{and} \quad \Delta G = \Delta G^* . \quad (2.14)$$

In Tables I and II, the experimental ΔG^* and ΔS^* were evaluated using Eqs. (2.3) and (2.2b) with

$$\Delta H = \Delta E^{(obs)} \quad \text{and} \quad K_0 = K_0^{(obs)} . \quad (2.14a)$$

It is seen from Eqs. (2.4)–(2.14) that (i) the prefactor K_0 can be much smaller or larger than $K_{0\,norm} \approx 10^{13}$ s^{-1}, (ii) likewise, the effective activation energy ΔE can be appreciably smaller or larger than E, and (iii) the effective activation energy ΔE is equal to the energy parameter E and $K_0 = K_{0\,norm}$ in the "neutral" case for $\delta E = 0$ and $\delta S = 0$.

All the cases mentioned above are found in real experimental situations for hydrogen desorption from a-Si:H. The results obtained enable us to draw the following conclusion, important for applications, which is presented in the form of an empirical "rule of thumb."

When the experimental preexponential factor $K_0^{(obs)}$ is much smaller (larger) than 10^{13} s^{-1}, one can expect that downward (upward) electron transitions dominate in the FP vicinity during the desorption event. In this case $\Delta E < E$ (or $\Delta E > E$). When $K_0^{(obs)} \approx 10^{13}$ s^{-1}, one can expect that neither downward nor upward transitions dominate in the FP vicinity during the desorption event and $\Delta E = E$.

Applying this empirical rule to the experimental data presented in Tables I and II, one can conclude that (a) in the majority of experimental conditions considered, the observed $K_0^{(obs)} < 10^{13}$ s^{-1} and therefore downward electron transitions dominate during the desorption events in these cases; (b) in some other cases (Table II) the prefactor $K_0^{(obs)} > 10^{13}$ s^{-1}, and therefore upward electron transitions dominate during these desorption events.

The empirical rule and experimental data presented in Tables I and II enable one to estimate the energy parameter E:

$$1.82 \text{ eV} < E < 1.98 \text{ eV} . \quad (2.15)$$

The lower limit in (2.15) is given by experimental $\Delta E^{(obs)} = 1.82$ eV associated with the *maximum* value $K_0^{(obs)} = 10^{12.35}$ s^{-1} among prefactors *lower* than 10^{13} s^{-1} (the last line in Table I). The upper limit in (2.15) is given

by $\Delta E^{(\text{obs})} = 1.98$ eV associated with the *minimum* factor $K_0^{(\text{obs})} = 10^{13.59}$ s^{-1} among experimental prefactors larger than 10^{13} s^{-1} (Table II, for 50 ppm of B_2H_6). The estimate (2.15) is in agreement with values of E estimated by another approach, as we shall see in Sec. V, Eq. (5.4). It is also consistent with the net energy balance associated with hydrogen desorption (Fig. 3), as found in Refs. 9 and 14.

III. RATE COEFFICIENTS OF HYDROGEN DESORPTION FROM a-Si:H

We shall express values δE, ΔE, δS, K_0, and ΔG in terms of atomic and electronic parameters of the a-Si:H surface, that is, of the Si and H atoms and the H_2 molecules involved in the SLEF-induced elementary event of desorption. Since microscopic theoretical or experimental data on the parameters involved are not known at present, we shall use a semiphenomenological approach similar to that used earlier for the consideration of other rate processes in solids.[22,32-34]

Consider Δn^{down} downward electron transitions between energy levels separated by the average separation $\langle \Delta e^{\text{down}} \rangle < 0$, and Δn^{up} upward transitions between levels of average energy distance $\langle \Delta e^{\text{up}} \rangle > 0$, which occur in the volume $V_1 = \Omega_1 + V_0 \approx \Omega_1$ during the desorption event. The energy release $\delta E^{\text{down}} < 0$ or consumption $\delta E^{\text{up}} > 0$ caused by these transitions is given by

$$\delta E^{\text{down}} = -\langle \Delta e^{\text{down}} \rangle \Delta n^{\text{down}} < 0$$

and (3.1)

$$\delta E^{\text{up}} = \langle \Delta e^{\text{up}} \rangle \Delta n^{\text{up}} > 0 .$$

The local change in the configurational entropy associated with the local electron transitions accompanying the desorption event is[22,32-34]

$$\delta S = A^{\text{down}} k \, \Delta n^{\text{down}} + A^{\text{up}} k \, \Delta n^{\text{up}} = \delta S^{\text{down}} + \delta S^{\text{up}} , \quad (3.2)$$

where $A^{\text{down}} < 0$ and $A^{\text{up}} > 0$ are the logarithms of the ratio of the electron statistical weight for one transition, and

$$\delta S^{\text{down}} = A^{\text{down}} k \, \Delta n^{\text{down}} < 0 \quad \text{and} \quad \delta S^{\text{up}} = A^{\text{up}} k \, \Delta n^{\text{up}} > 0$$

(3.3)

are partial changes in the local configurational entropy associated with the downward and upward electron transitions, respectively. In many cases $A^{\text{up}} \approx 1$ and $|A^{\text{down}}| \approx 1$.[22,32]

Using Eqs. (3.1)–(3.3), the parameters ΔE and K_0 can be expressed in terms of the SLEF parameters $\langle \Delta e^{\text{down}} \rangle$, $\langle \Delta e^{\text{up}} \rangle$, Δn^{down}, and Δn^{up}, by substitution in Eqs. (2.5)–(2.10).

Similarly, one can rewrite the effective activation free energy [Eq. (2.13)] in the following form:

$$\Delta G = E - \Delta n^{\text{down}}(|\langle \Delta e^{\text{down}} \rangle| - |A^{\text{down}}| kT)$$
$$+ \Delta n^{\text{up}}(|\langle \Delta e^{\text{up}} \rangle| - |A^{\text{up}}| kT) . \quad (3.4)$$

This equation shows that variations in Δn^{down},

$\langle \Delta e^{\text{down}} \rangle$, Δn^{up}, and $\langle \Delta e^{\text{up}} \rangle$ that can be caused by variations in concentrations of hydrogen and dopants can cause changes in ΔG. The rate coefficient of hydrogen desorption is determined by Eqs. (2.12) and (3.4).

IV. KINETIC COMPENSATION EFFECT

From Eqs. (2.4), (3.1), and (3.2) one can see that both δE and δS are linear functions of Δn^{down} and Δn^{up}. Hence it follows that variations in Δn^{down} and Δn^{up} cause a linear dependence between δS and δE, and therefore between δS and ΔE. This leads directly to the CEF Eq. (1.3), as we shall see below. The results obtained in the previous sections enable us to express coefficients C and a in Eq. (1.3) in terms of the SLEF parameters if we assume that $|A^{\text{down}} \approx A^{\text{up}} \approx 1$ because we allow individual electron transitions only one step up or down. We find

$$\delta S = -k(\Delta n^{\text{down}} - \Delta n^{\text{up}}) , \quad (4.1)$$

$$K_0 = \frac{1}{\tau_1} \exp[-(\Delta n^{\text{down}} - \Delta n^{\text{up}})] , \quad (4.2)$$

and

$$\delta E = -(\Delta n^{\text{down}} - \Delta n^{\text{up}})|\langle \delta e \rangle| . \quad (4.3)$$

Here, $|\langle \delta e \rangle|$ is the averaged energy difference between the energy levels involved in the dominating downward (or upward) electron transitions during the desorption event. From Eqs. (4.1)–(4.3) one finds

$$\frac{\delta S}{k} = \frac{\delta E}{|\langle \delta e \rangle|} = \Delta n^{\text{down}} - \Delta n^{\text{up}} \quad (4.4)$$

or

$$\delta S = \frac{\Delta E - E}{|\langle \delta e \rangle|} k . \quad (4.5)$$

Thus δS is a *linear* function of ΔE. That, combined with Eq. (4.2), leads directly to the following relation:

$$\ln K_0 = \ln \left[\frac{1}{\tau_1} \right] - \frac{E}{|\langle \delta e \rangle|} + \frac{\Delta E}{|\langle \delta e \rangle|} . \quad (4.6)$$

Equation (4.6) corresponds to the CEF Eq. (1.3), where the coefficients C and a are expressed in terms of material parameters by

$$C = \ln \left[\frac{1}{\tau_1} \right] - \frac{E}{|\langle \delta e \rangle|} \quad \text{and} \quad a = \frac{1}{|\langle \delta e \rangle|} . \quad (4.7)$$

Equations (4.5)–(4.7) show that one can also expect a linear dependence between $\delta S = \Delta S^*$ and $\Delta E = \Delta H$ in hydrogen desorption from a-Si:H. The linear dependence between δS and δE, which determines the two terms with the opposite signs in Eq. (2.13) for δG and ΔG, decreases substantially variations of δG and ΔG according to

$$\delta G = \delta E - T \delta S = \left[\frac{|\langle \delta e \rangle|}{kT} - 1 \right] T \delta S , \quad (4.8)$$

and

$$\Delta G = E + \left[\frac{|\langle \delta e \rangle|}{kT} - 1 \right] T \, \delta S \ . \tag{4.9}$$

Hence one can see that deviations $\delta G = \Delta G - E$ in the activation free energy ΔG from E can be relatively small if the following condition is satisfied:

$$\left| \left[\frac{|\langle \delta e \rangle|}{kT} - 1 \right] T \, \delta S \right| \ll E \ . \tag{4.10}$$

V. COMPARISON OF THEORETICAL CALCULATIONS WITH EXPERIMENTAL DATA FOR HYDROGEN DESORPTION FROM a-Si:H

Our theory predicts that $\delta S = \Delta S^*$ and $\ln K_0$ are linear functions of the activation energy $\Delta E = \Delta H$, according to Eqs. (4.5) and (4.6). This conclusion is in good agreement with the experimental data presented in Fig. 4. This means that hydrogen desorption from a-Si:H obeys the CEF Eq. (1.3), where the coefficients C and a are given by Eq. (4.7). In order to calculate these coefficients, the values of E and $\langle \delta e \rangle$ are needed. Since the microscopic theory at present does not provide information about $\langle \delta e \rangle$ and E, we shall calculate them from Eq. (5.1), which is derived from Eqs. (4.5) and (2.14), using two experimental points taken from Tables I and II:

$$\Delta S^* = \left[\frac{\Delta E - E}{|\langle \delta e \rangle|} \right] k \ . \tag{5.1}$$
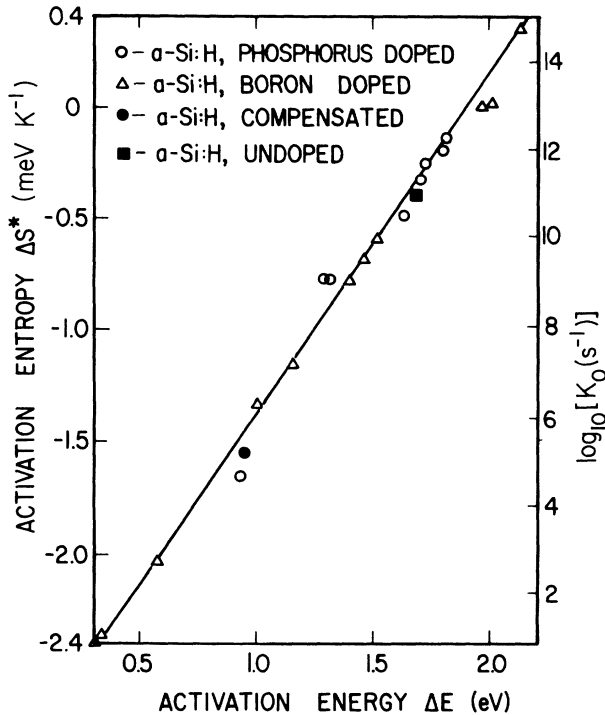

FIG. 4. The compensation effect (CEF) in hydrogen desorption from a-Si:H. Comparison of theoretical calculations (the solid line) with experimental data.

The two extreme experimental points were chosen:

$$\Delta E_1 = 0.33 \text{ eV}, \quad \Delta S_1^* = -2.37 \times 10^{-3} \text{ eV K}^{-1} \ ,$$

and

$$\log_{10}[K_{01}^{(\text{obs})} \ (\text{s}^{-1})] = 1.03 \quad \text{for} \quad T_M = 503 \text{ K} \tag{5.2}$$

and

$$\Delta E_2 = 2.14 \text{ eV}, \quad \Delta S_2^* = +0.35 \times 10^{-3} \text{ eV K}^{-1} \ ,$$

and

$$\log_{10}(K_{02}^{(\text{obs})} \ (\text{s}^{-1}) = 14.91 \quad \text{for} \quad T_M = 642 \text{ K} \ . \tag{5.3}$$

From these data and Eqs. (5.1)–(5.3) one finds

$$E \approx 1.90 \text{ eV} \quad \text{and} \quad |\langle \delta e \rangle| \approx 0.057 \text{ eV} \ . \tag{5.4}$$

Using these values, one finds from Eq. (4.7) coefficients $C = -3.40$ and $a = 17.5 \text{ eV}^{-1}$. Thus, the CEF Eq. (1.3) for hydrogen desorption from a-Si:H is

$$\ln[K_0 \ (\text{R}^{-1})] = (17.5 \text{ eV}^{-1}) \Delta E - 3.40 \tag{5.5}$$

or

$$\log_{10}[K_0 \ (\text{s}^{-1})] = (7.60 \text{ eV}^{-1}) \Delta E - 1.48 \ , \tag{5.6}$$

and Eq. (5.1) becomes

$$\delta S^* = [(1.51 \text{ eV}^{-1}) \Delta E - 2.87](10^{-3} \text{ eV K}^{-1}) \ . \tag{5.7}$$

The comparison of the theoretical calculations and experimental results is given in Fig. 4 where the solid line represents Eqs. (5.6) and (5.7). From Fig. 4 one can see that the proposed model is in good agreement with observations for a broad range of variations in K_0 (about 14 orders of magnitude) and $\Delta E = \Delta H$ (a factor 7).

One can also see that the value of $E = 1.90$ eV is in good agreement with (a) the energy (≈ 2 eV) necessary to break two Si—H bonds when a H_2 molecule is formed simultaneously,[14] and (b) our estimate $E = 1.9$ eV from Eq. (2.15).

One can make some other calculations and compare them with experimental results. In Eqs. (5.2) and (5.3) one can see that

$$K_{01}^{(\text{obs})} \approx 10 \text{ s}^{-1} \ll 10^{13} \text{ s}^{-1}$$

and

$$K_{02}^{(\text{obs})} \approx 10^{14.9} \text{ s}^{-1} \gg 10^{13} \text{ s}^{-1} \tag{5.8}$$

for the two cases in question. This means that downward (upward) electron transitions dominate during the desorption event in the first (second) case, according to the discussion in Sec. II. Then, using Eqs. (4.1)–(4.3), $1/\tau = 10^{13} \text{ s}^{-1}$, and the experimental prefactors (5.2,5.3) one finds for each of the two cases in question:

$$\Delta n_1^{\text{down}} - \Delta n_1^{\text{up}} \approx 27.5, \quad \delta E_1 \approx -1.57 \text{ eV} \ , \tag{5.9}$$

and

$$\Delta n_2^{\text{up}} - \Delta n_2^{\text{down}} \approx 4.1, \quad \delta E_2 \approx +0.23 \text{ eV} \ . \tag{5.10}$$

With these results, one can verify that the ΔG that can be

calculated from Eq. (3.4) are consistent with the experimental values of Table II. (We recall that in our case $|A^{up}| \approx |A^{down}| \approx 1$ and $|\delta e^{up}| \approx |\delta e^{down}| \approx |\langle \delta e \rangle| \approx 0.057$ eV.) For example, for the same two points above,

$$\Delta G_1^{(calc)} = 1.52 \text{ eV} \quad \text{and} \quad \Delta G_2^{(calc)} = 1.91 \text{ eV} . \quad (5.11)$$

It has been shown[9] that a Fermi-level dependence of ΔG exists. The reduction of ΔG in doped materials was correlated with the energy supplied by carriers trapped by dangling-bond centers situated in the gap of a-Si:H. This is consistent with our model where doping makes the mobile electrons available to the SLEF volume, thus affecting δE [Eq. (4.3)]. Furthermore, our model shows why at low doping levels ΔG remains unaffected, since in this regime the condition of Eq. (4.10) applies.

VI. CONCLUSION

A new kinetic many-body model of hydrogen desorption from a-Si:H, which takes into account transient atomic and electronic processes in the submicronic vicinity $\Omega_1 \sim R_1^3$ of the desorbed particles of a radius $R_1 \approx 10^{-7}$ cm, is considered. These transient phenomena accompany the desorption events of duration $\tau_1 \approx 10^{-13} - 10^{-12}$ s which cause desorption of single H_2 molecules. The desorption events are induced by short-lived large energy fluctuations (SLEF's) of surface atoms (e.g., Si atoms bound with H atoms) of lifetime $10^{-13} - 10^{-12}$ s. During the SLEF, the fluctuating atom acquires a thermal energy

$\varepsilon_{op} \gtrsim \Delta E \gg kT$ sufficient to initiate the desorption event which includes transient local atomic and electronic phenomena occurring simultaneously in Ω_1.

The model has been used in order to calculate the rate coefficient K of hydrogen desorption, the Arrhenius preexponential factor K_0, the activation energy ΔE, the entropy δS, and the effective activation free energy ΔG. The calculated parameters are in good agreement with observations. The proposed model, for the first time, explains the large observed variations in experimental prefactors and activation energies:

$$K_0^{(obs)} = 10 - 10^{15} \text{ s}^{-1}$$

and (6.1)

$$\Delta E^{(obs)} = 0.3 - 2.14 \text{ eV} ,$$

which has been shown to be associated with changes in dopant concentrations. The model also explains the observed linear correlation between the variations in $\ln K_0^{(obs)}$ and $\Delta E^{(obs)}$ associated with the kinetic compensation effect (CEF).

It was found that the net bond rupture energy associated with H_2 desorption calculated independently from the model (1.90 eV) is consistent with that predicted with models that arrive at a value by accounting for the difference in bond strengths of two Si—H bonds an a resulting desorbed H_2 molecule. It is also consistent with the value we found for processes unassisted by surrounding electrons.

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