PHYSICAL REVIEW B VOLUME 60, NUMBER 11 15 SEPTEMBER 1999-I

Hydrogen diffusion and mobile hydrogen in amorphous silicon

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(Received 28 May 1999)

Diffusion phenomena in hydrogenated amorphous silicon (a-Si:H) are modeled assuming that mobile H excited from Si-H bonds normally annihilates at dangling-bond defects, as in the ''H collision'' model of light-induced metastability. This diffusion model explains the long-standing puzzle of the doping dependence of the hydrogen diffusion coefficient D_H. It also yields the magnitudes of the D_H Arrhenius prefactors in doped and undoped a-Si:H. Mobile H diffuses over an energy barrier of about 0.3 eV; at room temperature, its diffusion rate is slightly greater than that of H in crystalline Si. [S0163-1829(99)02536-9]

Hydrogenated amorphous silicon (a-Si:H) semiconductor thin films require 2–15 at. % of H to passivate coordination defects and reduce strain. However, long-range motion of this H is implicated in light- and carrier-induced metastable degradation of a-Si:H electronic properties. H diffusion is also a crucial step in film formation by chemical vapor deposition. Improved understanding of H in a-Si:H is therefore central to solving the scientific and technological problems presented by a-Si:H.

Recent publications[1–3] demonstrate that the ''hydrogen collision'' model can explain qualitatively and quantitatively the main experimental observations of carrier-induced degradation (the Staebler-Wronski effect[4]) in a-Si:H. For example, the model explains the creation kinetics for the production of metastable threefold-coordinated Si dangling-bond defects (DB's) by continuous illumination,[1,2] pulsed lasers,[2] and electron beams.[3]

In light-induced metastability, excitation of mobile H from deep Si-H bonds is likely the first step of defect formation.[2,5] Thermal or carrier-induced mobile H diffuses extremely rapidly by hopping between sites which are analogous to the Si-Si bond-center site in c-Si. The H collision kinetic models[1–3] require that mobile H normally annihilates at DB's to reform Si-H bonds. In this paper previously unexplained diffusion phenomena in a-Si:H are understood as consequences of this picture of H dynamics. I first describe the model of H diffusion implicit in the H collision model of metastability, then estimate the mobile H diffusion coefficient and density. I also derive an expression for the H diffusion coefficient, solve the long-standing puzzle of the doping dependence of the hydrogen diffusion coefficient (D_H), and compute the magnitude of the D_H prefactor in undoped and doped a-Si:H.

The first step of the light-induced or thermal diffusion of H is the emission of mobile H (H_m) from Si-H bonds, leaving behind an isolated DB,

$$\text{Si-H} \rightarrow \text{DB} + \mathrm{H}_m . \tag{1}$$

This mobile H diffuses rapidly through a-Si:H once it is formed.[6] Normally, H_m retraps to a DB by the reverse of reaction (1), though not necessarily to the same DB from which the H_m was excited. Isolated DB's created by reaction (1) become metastable only when

$$\mathrm{H}_m + \mathrm{H}_m \rightarrow M(\text{Si-H})_2 , \tag{2}$$

a rare side reaction in which two mobile H collide and associate to form $M(\text{Si-H})_2$, a metastable two-H complex.[2]

The H_m thermal emission rate ($\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$) for reaction (1) is given by

$$R_\mathrm{th} = N_\mathrm{H} \nu_\mathrm{th}^0 e^{-E_\mathrm{H}/kT}, \tag{3}$$

where N_H is the immobile Si-H density, ν_th^0 is a thermal emission prefactor, and E_H is the energy of mobile H emission from a Si-H bond. N_H is constant because the mobile H and $M(\text{Si-H})_2$ densities are negligible at all times compared to the density of Si-H bonds. This simplified model neglects the observed difference between clustered and isolated H environments. The trapping rate of mobile H to DB's by the reverse of reaction (1) is

$$R_\mathrm{db} = k_\mathrm{db} N_m N_\mathrm{db} . \tag{4}$$

Here N_db is the dangling-bond density, N_m is the mobile H density, and k_db is a rate constant (in $\mathrm{cm}^3\,\mathrm{s}^{-1}$).

Because $\tau_m = R_\mathrm{db}/N_m$ is the decay time of the mobile H population, Eq. (4) implies $k_\mathrm{db} = (\tau_m N_\mathrm{db})^{-1}$. For the diffusion-limited capture processes applicable to mobile H,[2,7] $k_\mathrm{db} = 4\pi a D_m$, where $a = 2.3\times10^{-8}$ cm is the jump distance between transport sites. Equating these expressions for k_db,

$$D_m = (4\pi a \tau_m N_\mathrm{db})^{-1}. \tag{5}$$

Recent measurements at room temperature show that τ_m is roughly 4 ms for $N_\mathrm{db} \approx 10^{16}\ \mathrm{cm}^{-3}$. Heck and Branz[8,9] obtained this estimate from metastable degradation of a-Si:H by pulsed illumination with varying dark time between pulses. Substitution of τ_m into Eq. (5) yields $D_m(25\,^\circ\mathrm{C}) \approx 10^{-7}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$, as indicated in Table I. This estimate is two orders of magnitude greater than the H diffusion coefficient

TABLE I. Estimates of the H diffusion coefficient, the mobile H diffusion coefficient, and the mobile H density at two temperatures.

	D_H ($\mathrm{cm}^2\,\mathrm{s}^{-1}$)	D_m ($\mathrm{cm}^2\,\mathrm{s}^{-1}$)	N_m (cm^{-3})
25 °C	$10^{-28\pm1}$	10^{-7}	$0.5\times10^{1\pm1}$
210 °C	2×10^{-18}	6×10^{-6}	10^{10}

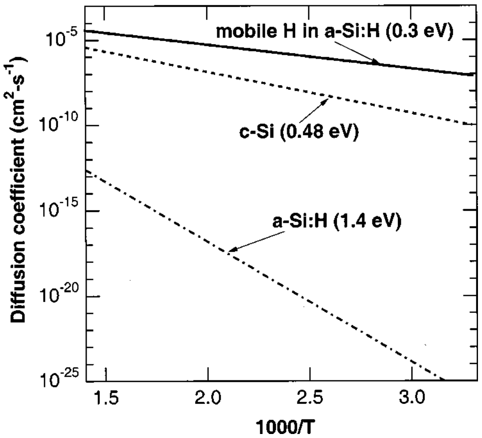

FIG. 1. Arrhenius plot of H diffusion coefficients in Si. Mobile H is estimated as described in text, c-Si is taken from Refs. 10 and 11, and a-Si:H is taken from Ref. 6. Activation energies are indicated.

(D_{H}) measured by Seager and Anderson[10] for crystalline Si (c-Si). Either H diffusion in c-Si is slowed by H trapping or mobile H in a-Si:H diffuses rapidly along disorder-induced, low-barrier percolation paths.

Mobile H diffusion can be assumed to follow the Arrhenius form

$$D_m(T)=D_0 e^{-E_m/kT}, \tag{6a}$$

with

$$D_0=2\nu_0 a^2/3. \tag{6b}$$

Here E_m is a characteristic energy barrier to the mobile H diffusion between near-equivalent sites in Si-Si bonds, ν_0 is the jump-attempt frequency, and $\frac{2}{3}$ is a factor applicable to the four-coordinated Si lattice.[11] Substituting $\nu_0 \approx 10^{13}\,\mathrm{s}^{-1}$ and a into Eq. (6b), $D_0 \approx 5\times10^{-3}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$, roughly equal to the diffusion prefactor for H diffusion in c-Si.[12,13] With the estimate of $D_m(25\,°\mathrm{C})$ (Table I), Eq. (6a) yields $E_m \approx 0.3\,\mathrm{eV}$ and $D_m(210\,°\mathrm{C}) \approx 5\times10^{-6}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$. E_m is less than the measured H diffusion activation energy of 0.48 eV in crystalline Si,[12] but is comparable to theoretical estimates.[14–16]

Figure 1 compares the T dependence of three diffusion coefficients for H in silicon: the mobile H diffusion coefficient in a-Si:H, D_{H} in undoped a-Si:H,[6,17] and the highest measured c-Si H diffusion coefficients.[10,12] The extremely low diffusion coefficient in a-Si:H is caused by trap-controlled diffusion;[6] H spends only a tiny fraction of its time in mobile configurations. Once emitted from the Si-H trap, however, H is extremely mobile until it is retrapped by annihilation with a DB. The activation energy of D_{H} and a measurement[6] of the H emission time in D tracer diffusion give an estimate of $E_{\mathrm{H}} \approx 1.4\,\mathrm{eV}$.

For trap-limited diffusion,[11]

$$N_m D_m = N_H D_H, \tag{7}$$

because the tiny minority of H that is mobile makes the only contribution to D_{H}. Equation (7) is analogous to treating trap-controlled transport by equating total current to free-carrier current.[18] Table I lists the measured value of $D_{\mathrm{H}}(210\,°\mathrm{C})$ and an extrapolated estimate of $D_{\mathrm{H}}(25\,°\mathrm{C})$, both taken from tracer diffusion data.[6,17] By substituting the values of D_{H} and D_m and $N_{\mathrm{H}}=5\times10^{21}\,\mathrm{cm}^{-3}$ into Eq. (7), we obtain the thermal mobile H densities (Table I). Even at 210 °C, N_m is only about $10^{10}\,\mathrm{cm}^{-3}$, far below spectroscopic limits.

I next derive a useful expression for D_{H}. At steady state, $R_{\mathrm{th}}=R_{\mathrm{db}}$, because capture to DB's dominates over capture by H collisions. From Eqs. (3) and (4),

$$N_m=(N_{\mathrm{H}}\nu_{\mathrm{th}}^0/k_{\mathrm{db}}N_{\mathrm{db}})e^{-E_{\mathrm{H}}/kT}. \tag{8}$$

Substituting N_m from Eq. (8) and $k_{\mathrm{db}}=4\pi a D_m$ into Eq. (7),

$$D_{\mathrm{H}}=(\nu_{\mathrm{th}}^0/4\pi a N_{\mathrm{db}})e^{-E_{\mathrm{H}}/kT}. \tag{9}$$

Equation (9) can also be obtained directly from the well-known kinetic formula for diffusion,[11]

$$D_{\mathrm{H}}=\nu_{\mathrm{H}}\lambda_t^2=R_{\mathrm{th}}\lambda_t^2/N_{\mathrm{H}}. \tag{10}$$

Here, $\nu_{\mathrm{H}}=R_{\mathrm{th}}/N_{\mathrm{H}}$ is the emission rate per Si-H of mobile H, and λ_t is the mean distance that H_m travels before retrapping. Because a mobile H annihilates only when it meets a DB, it takes roughly $N_{\mathrm{Si}}/N_{\mathrm{db}}$ random steps before retrapping.[19] For the random walk in three dimensions, it can be shown[11] that

$$\lambda_t \approx (6aN_{\mathrm{db}})^{-1/2}. \tag{11}$$

Substituting λ_t [Eq. (11)] and R_{th} [Eq. (3)] into Eq. (10) yields $D_{\mathrm{H}}=(\nu_{\mathrm{H}}^0/6aN_{\mathrm{db}})\exp(-E_{\mathrm{H}}/kT)$, identical to Eq. (9) apart from a factor of roughly 2.

Street *et al.*[20] observed that $D_{\mathrm{H}}(240\,°\mathrm{C})$ *increases* roughly linearly with N_{db} as the dopant density is varied in n- and p-type a-Si:H. This observation appeared to exclude $D_{\mathrm{H}} \propto 1/N_{\mathrm{db}}$ [Eq. (9)] and remained unexplained for a decade. However, their result is obtained by combining the present model of H diffusion with the observed thermal equilibrium DB densities.

The formation energy (F) of charged DB's in a-Si:H depends on the electronic Fermi energy (E_f) because of charge exchange with the Fermi sea.[21] Pierz, Fuhs, and Mell[22] observed that

$$N_{\mathrm{db}} \propto e^{|E_0-E_f|/kT_e} \tag{12}$$

in both n- and p-type material, showing that the defect density does, in fact, equilibrate with the electronic Fermi energy. Here, T_e is an effective equilibration temperature of about 350 °C in n-type and 200 °C in p-type samples,[23] and E_0 is a near-midgap reference energy. Equation (12) suggests that $F(E_f)$ has the expected forms[21] F_n-E_f (n type) and F_p+E_f (p type), where F_n and F_p are reference energies. Earlier publications[20,24] showed that the reduction of the H diffusion activation energy in doped a-Si:H emerges from assuming H emission [reaction (1)] is a step in H diffusion and noting the E_f dependence of F.

Mobile H is either an analog of bond-centered H in c-Si or a complex of a Si-H bond and an accompanying DB.[1,25] Emission of a mobile H into transport [Eq. (1)] therefore requires the formation of two midgap levels, one at the original Si-H site and one that moves with H_m (either a bond-centered H or a DB level). These defect levels are charged in doped a-Si:H. The formation energy of H_m is roughly the formation energy of two charged defects, each of which depends upon E_f.

Assuming that the H emission is controlled by the formation energy, rather than by any energy barrier, the emission rate is

$$\nu_H \propto e^{2|E_0-E_f|/kT}. \tag{13}$$

The factor of 2 arises because two charged midgap defects are formed. Combining Eqs. (12) and (13),

$$\nu_H \propto N_{db}^2 \tag{14}$$

for $T \approx T_e$, as during H diffusion measurements in a-Si:H. Substituting Eqs. (11) and (14) into Eq. (10),

$$D_H \propto N_{db}. \tag{15}$$

Equation (15) describes the results of Street *et al.*[20] for films with varying E_f. However, if the DB density changes at constant E_f, Eq. (9) ($D_H \propto 1/N_d$) may apply.

Equation (9) supplies an expression for the diffusion prefactor, $D_H^0 = \nu_{th}^0/4\pi a N_{db}$. D tracer emission rates measured[6] by early-time diffusion between 180 °C and 300 °C give $\nu_{th}^0 = 10^{8\pm1}\ \mathrm{s}^{-1}$. H-for-D exchange emission of D is about 100 times more likely than direct thermal emission of D;[26] therefore, $\nu_{th}^0 = 10^{6\pm1}\ \mathrm{s}^{-1}$ is a better estimate. Given the equilibrium value of $N_{db} \approx 10^{16}\ \mathrm{cm}^{-3}$ at these temperatures,[27] Eq. (9) yields $D_H^0 \approx 3\times10^{-4\pm1}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$. This crude estimate is consistent with measured values of D_0 in undoped a-Si:H, which range from about $2\times10^{-3}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$ to $10^{-2}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$.[6,17,28]

Equation (9) suggests that the prefactor of D_H varies inversely with N_{db}. There are about 100 times more DB's in doped than in undoped a-Si:H.[22] The experimental estimates of D_0 in doped a-Si:H vary widely, but D_0 is clearly much smaller than in undoped a-Si:H. In many n-type samples,[20] $D_0 = 10^{-5\pm1}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$, and in some p-type samples,[28] $D_0 = 3\times10^{-4}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$, from 1 to 3 orders of magnitude below undoped samples.[6,17,28] Thus, the decrease of D_0 in doped samples is qualitatively consistent with Eq. (9).

Mobile H annihilation at DB defects is a key element of the ''H collision'' model of metastability. This assumption leads to an expression for D_H and ties together previously unexplained H diffusion phenomena. The linear dependence of D_H on N_{db} is understood by considering the effects of E_f and N_{db} on ν_H and λ_t. The magnitude of the Arrhenius prefactor of D_H depends inversely on N_{db} and is therefore several orders of magnitude smaller in doped than in undoped a-Si:H. Remarkably, the mobile H diffusion coefficient in a-Si:H is comparable to the H diffusion coefficient in c-Si. However, D_H in a-Si:H is reduced by 10–20 orders of magnitude, because nearly all H in a-Si:H is bound deeply as Si-H. Even at 210 °C, there are only about $10^{10}\ \mathrm{cm}^{-3}$ mobile H in a-Si:H, well below spectroscopic detection limits. This paper, together with papers on light-induced[1,2] and electron-beam-induced[3] defect creation, creates a consistent framework for understanding both H diffusion and metastability phenomena in a-Si:H.

I thank Panos Tzanetakis for helpful discussions and for providing an excellent scientific environment at the University of Crete. Eric Schiff and Richard Crandall provided useful readings of the manuscript. The research was largely supported by the U.S. DOE under Contract No. DE-AC36-83CH10093. The Fulbright Foundation and the Foundation of Research and Technology Hellas (FORTH) in Greece supplied additional financial support.

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