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Dynamics of hydrogen in hydrogenated amorphous silicon

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Abstract. The problem of hydrogen diffusion in hydrogenated amorphous silicon (a-Si:H) is studied semiclassically. It is found that the local hydrogen concentration fluctuations-induced extra potential wells, if intense enough, lead to the localized electronic states in a-Si:H. These localized states are metastable. The trapping of electrons and holes in these states leads to the electrical degradation of the material. These states also act as recombination centers for photo-generated carriers (electrons and holes) which in turn may excite a hydrogen atom from a nearby Si–H bond and breaks the weak (strained) Si–Si bond thereby apparently enhancing the hydrogen diffusion and increasing the light-induced dangling bonds.

Keywords. Hydrogenated amorphous silicon; metastable electronic states; hydrogen diffusion.

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1. Introduction

Hydrogen passivation of dangling bonds leads to a significant improvement in the electronic properties of amorphous Si (a-Si). The behaviour of hydrogen in the amorphous materials, however, is quite complex and not fully understood. Hydrogen diffusion through the materials is known to be affected by the doping level [1] and by the presence of free carriers [2]. In addition, hydrogen motion has been shown to be correlated with the formation of both the metastable and equilibrium defects [3]. Metastable defects are created by illumination (Staebler–Wronski effect (SW) [4]) or electric fields and currents. Identification of physical mechanism underlying the metastability is one of the fundamental problems in these materials. A central process in these phenomena is the breaking of a silicon–hydrogen bond, in which hydrogen is promoted from a stable configuration (in which it is strongly bonded to a Si atom) to a higher-energy interstitial position (in which it is mobile and can easily move through the material). Hydrogen diffuses relatively rapidly through the amorphous network at low temperatures [5] and the modifications of hydrogen bonding configuration due to hydrogen migration have been proposed as a mechanism of defect generation in a-Si:H [6,7]. Thus hydrogen plays a dual role in a-Si:H: (1) acting as a

dangling bond terminator in the as-deposited a-Si:H and (2) it also appears to be involved in the microscopic processes that promote photo-induced structural changes and defect generation. The determination of the relationship of light-enhanced hydrogen motion to the photo-induced structural changes in a-Si:H is important as it will determine what role the hydrogen atom or ion motion plays in photo-induced metastability and photo-induced structural changes and thereby will provide insights into photo- and thermal annealing processes as well.

The motion of hydrogen in a-Si:H involves the much quantum-mechanical complexity including tunnelling. However, it can be described by a diffusion coefficient,

$$D_{\mathrm{H}} = D_0 \exp\left(-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right), \tag{1}$$

where E_{a} is the activation energy of hydrogen diffusion, k_{B} the Boltzmann's constant and T the absolute temperature. In doped samples, the activation energy, E_{a} is 1.2–1.3 eV while in the undoped samples it is 1.4–1.5 eV [1]. The enhancement of hydrogen motion in a-Si:H, therefore obviously, indicate the decrease in the activation energy E_{a}. It has been reported that there occurs an enhanced hydrogen motion in a-Si:H under illumination [2]. A mechanism for hydrogen diffusion in a-Si, as revealed by the tight binding molecular dynamics (TBMD) [8] calculations is that hydrogen diffuses through the amorphous network by successively bonding with nearby silicons and breaking their Si–Si bonds. The diffusing hydrogen carries with it a newly created dangling bond. These intermediate transporting states are densely populated in the network and have lower energies than H at the center of the stretched Si–Si bonds, and can play a crucial role in hydrogen diffusion.

Light-induced degradation of a-Si:H (SW effect) is the major limitation of this otherwise important material. There have been great many theory papers on the origin of light-induced degradation of a-Si:H but the true origin of SW degradation is still unknown, except for the fact that it is related to the dynamics of hydrogen in a-Si:H. Potential fluctuations in a-Si:H have been proposed and shown to play an important role in the formation of light-induced metastable defects in the material [9–11]. In this paper we reported the results of a semiclassical approach applied to the dynamics of hydrogen in hydrogenated amorphous silicon (a-Si:H). The results show a relationship between the light-enhanced hydrogen diffusion and light-induced structural changes in a-Si:H.

2. Calculations

It is assumed that the diffusion of hydrogen in a-Si:H causes fluctuations in the hydrogen concentration at the local points which may create the extra local potential wells. In this paper a simple case considered here is that the created extra local potential well has the spherical symmetry and is of the form

$$\Delta V = G(c - c_0), \tag{2}$$

where G is assumed to be positive so that an attractive local potential well results whenever $c \ll c_0$, c being the instantaneous concentration at a local point and c_0, the average concentration of hydrogen in the hydrogenated amorphous silicon. If the system is both incompressible and isotropic, the change in Helmholtz free energy due to fluctuations in the local concentration of hydrogen is given as

$$W = \int_\tau [f(c) - f(c_0) + g(\bigtriangledown c)^2] \mathrm{d}\tau, \tag{3}$$

where $f(c)$ is the Helmholtz free energy per unit volume per atom of a homogeneous system of concentration c and $g(\bigtriangledown c)^2$ is a gradient energy that hinders spontaneous concentration fluctuations. Since the fluctuations must conserve about average concentration, i.e.

$$\int_\tau (c - c_0) \mathrm{d}\tau = 0. \tag{4}$$

Using eq. (4), eq. (3) can be rewritten as

$$W = \int_\tau \left[f(c) - f(c_0) - \left(\frac{\mathrm{d}f(c)}{\mathrm{d}c} \right)_{c=c_0} (c - c_0) + g(\bigtriangledown c)^2 \right] \mathrm{d}\tau. \tag{5}$$

If it is assumed that W is unique due to the entropy change of the system so that the gradient term is negligible, and using the thermodynamic relation given below

$$f(c) = \frac{k_\mathrm{B} T}{\Omega} \sigma(c),$$

we get

$$W = \frac{k_\mathrm{B} T}{\Omega} \int_\tau \left[\sigma(c) - \sigma(c_0) - \left(\frac{\mathrm{d}\sigma(c)}{\mathrm{d}c} \right)_{c=c_0} c - c_0 \right] \mathrm{d}\tau, \tag{6}$$

where Ω is the atomic volume of hydrogen, $\mathrm{d}\tau$ the volume element and $\sigma(c)$ the entropy of the system at concentration c given by

$$\sigma(c) = c \ln c + (1 - c) \ln(1 - c). \tag{7}$$

If the electron localizes itself in the potential well created by the fluctuation, the total energy change is given as

$$\Delta F = \frac{\hbar^2}{2m} \int_\tau |\nabla \psi|^2 \mathrm{d}\tau + \int_\tau \Delta V \psi^2 \mathrm{d}\tau + W. \tag{8}$$

The first two terms represent the kinetic energy and the attractive potential energy of the localization of the electron with the wave function ψ corresponding to the bottom of the conduction band (taken as reference zero of energy). The third term is the thermodynamic energy which creates fluctuation. If one proceeds with a trial wave function given as

$$\psi(r) = (2\pi R_0)^{-1/2} \left(\frac{\sin(\frac{\pi r}{R_0})}{r} \right), \tag{9}$$

where R_0 represents the localization radius such that

$$\begin{aligned} \psi(r) &= (2\pi R_0)^{-1/2} \left(\frac{\sin(\frac{\pi r}{R_0})}{r} \right), \quad & r \le R_0 \\ &= 0, & r > R_0 \end{aligned} \tag{10}$$

and the concentration

$$c(r) = c, \quad r \le R_0$$
$$= c_0, \quad r > R_0. \tag{11}$$

Equation (10) gives us $|\psi|^2 = 1/(\frac{4}{3}\pi R_0^3)$ over the sphere of radius R_0 and allows to express ΔF as a function of localization radius R_0. Using eqs (10) and (11), the volume integration of different terms of eq. (8) gives

$$\frac{\hbar^2}{2m}\int_\tau |\nabla\psi|^2 \mathrm{d}\tau = \frac{\hbar^2}{2m}(2\pi R_0)^{-1}\int_\tau \left|\frac{\partial}{\partial r}\left(\frac{\sin(\frac{\pi r}{R_0})}{r}\right)\right|^2 \mathrm{d}\tau$$
$$= \frac{\hbar^2}{2m}\left(\frac{4\pi}{2\pi R_0}\right)\int_0^{R_0}\left|\frac{\pi}{R_0}\left(\frac{\cos(\frac{\pi r}{R_0})}{r}\right) - \left(\frac{\sin(\frac{\pi r}{R_0})}{r^2}\right)\right|^2 \mathrm{d}r.$$

Using standard integrations, it is found that

$$\frac{\hbar^2}{2m}\int_\tau |\nabla\psi|^2 \mathrm{d}\tau = \frac{\hbar^2}{2m}\frac{\pi^2}{R_0^2}. \tag{12}$$

The second term

$$\int_\tau \Delta V \psi^2 \mathrm{d}\tau = G(c - c_0)\int_\tau \psi^2 \mathrm{d}\tau$$

since

$$\int_\tau \psi^2 \mathrm{d}\tau = 1.$$

Therefore

$$\int_\tau \Delta V \psi^2 \mathrm{d}\tau = G(c - c_0). \tag{13}$$

The third term

$$W = \frac{k_\mathrm{B}T}{\Omega}\left[c\ln c + (1-c)\ln(1-c) - c_0\ln c_0 - (1-c_0)\ln(1-c_0)\right.$$
$$\left. - (\ln c_0 - \ln(1-c_0))(c-c_0)\right]\int_\tau \mathrm{d}\tau,$$

since

$$\int_\tau \mathrm{d}\tau = \frac{4}{3}\pi R_0^3 = \frac{1}{|\psi|^2}.$$

Therefore

$$W = \frac{k_\mathrm{B}T}{\Omega}\frac{1}{|\psi|^2}\left[c\ln\left(\frac{c(1-c_0)}{(1-c)c_0}\right) + \ln\left(\frac{1-c}{1-c_0}\right)\right]. \tag{14}$$

Thus using eqs (12), (13) and (14), eq. (8) becomes

$$\Delta F = \frac{\hbar^2\pi^2}{2mR_0^2} + G(c-c_0) + \frac{k_\mathrm{B}T}{\Omega}\frac{1}{|\psi|^2}\left[c\ln\left(\frac{c(1-c_0)}{(1-c)c_0}\right) + \ln\left(\frac{1-c}{1-c_0}\right)\right]. \tag{15}$$

Now ΔF is minimized with respect to the hydrogen concentration (c) to obtain the ground state energy of electronic states. Minimizing ΔF with respect to c, i.e., $\mathrm{d}\Delta F/\mathrm{d}c = 0$ gives

$$\frac{c}{1-c} = \frac{c_0}{1-c_0}\exp\left(\frac{-G\Omega|\psi|^2}{k_\mathrm{B}T}\right). \tag{16}$$

Using eq. (16) in (15) one gets

$$\Delta F = \frac{\hbar^2\pi^2}{2mR_0^2} - Gc_0 - \frac{k_\mathrm{B}T}{\Omega}\left(\frac{4}{3}\pi R_0^3\right)\ln\left[(1-c_0) + c_0\exp\left(\frac{-G|\psi|^2\Omega}{k_\mathrm{B}T}\right)\right]. \tag{17}$$

In terms of dimensionless variables for energy and length

$$E(y) = \frac{\Delta F}{E_\mathrm{H}}; \quad l = \frac{R_0}{a_\mathrm{B}}, \tag{18}$$

where

$$E_\mathrm{H} = \frac{E_\mathrm{H}^0}{\varepsilon^2}; \quad E_\mathrm{H}^0 = \frac{me^4}{\hbar^2} = 27.2\ \mathrm{eV}, \tag{19}$$

$$a_\mathrm{B} = a_\mathrm{B}^0\varepsilon; \quad a_\mathrm{B}^0 = \frac{\hbar^2}{me^2} = 0.53\ \text{Å}, \tag{20}$$

where ε is the static dielectric constant of silicon, taken as equal to 12. Equation (17) becomes

$$E(y) = \frac{\pi^2}{2\eta^{2/3}y^2} - \frac{Gc_0}{E_\mathrm{H}} - \frac{Gy^3}{E_\mathrm{H}}\ln\left[(1-c_0) + c_0\exp\left(\frac{-1}{y^3}\right)\right], \tag{21}$$

where

$$\eta = \frac{G\Omega}{k_\mathrm{B}T}\frac{1}{\frac{4}{3}\pi a_\mathrm{B}^3} \tag{22}$$

and

$$y = \frac{l}{\eta^{1/3}}. \tag{23}$$

Now if two electrons are localized in the same potential well so that $|\psi^2| = 2/(\frac{4}{3}\pi R_0^3)$ and there will be Coulomb repulsion ($\sim e^2/R_0$) between the two electrons inside the potential well (for localization of an electron–hole pair $\sim -e^2/R_0$) and hence the total energy change in this case will be

$$E_2(y) = \frac{\pi^2}{\eta^{2/3}y^2} + \frac{1}{\eta^{1/3}y} - \frac{2Gc_0}{E_\mathrm{H}} - \frac{Gy^3}{E_\mathrm{H}}\ln\left[(1-c_0) + c_0\exp\left(\frac{-2}{y^3}\right)\right], \quad (24)$$

where the second term is the Coulomb repulsion of two electrons (for electron–hole pair this term will be −ve) written in dimensionless variables. The energy of two infinitely separated electrons localized in two separate wells will be twice the right-hand side of eq. (21), viz.

$$E_2^0(y) = \frac{\pi^2}{\eta^{2/3}y^2} - \frac{2Gc_0}{E_\mathrm{H}} - \frac{2Gy^3}{E_\mathrm{H}}\ln\left[(1-c_0) + c_0\exp\left(\frac{-1}{y^3}\right)\right]. \quad (25)$$

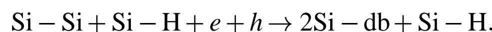
3. Results and discussion

In this paper the problem of hydrogen dynamics in a-Si:H is elucidated by applying a semiclassical approach to the dynamics of hydrogen in a-Si:H. The potential fluctuations in a-Si:H are assumed to be caused by the hydrogen concentration fluctuations at local points. A simple case of spherically symmetric potential wells has been considered. However, this may not be the actual cause of potential fluctuations and formation of metastable defects in a-Si:H but it is shown how the hydrogen concentration fluctuations can lead to the electrical degradation of the material on exposure to light. The conclusions which can be drawn from this simple approach are interesting and supports the earlier studies [12,13].

The single-electron free energy $E(y)$ given by eq. (21) and the free energy of two electrons trapped in the same potential well relative to that of two electrons separately trapped in two infinitely separated potential wells, i.e. $E_2(y) - E_2^0(y)$ are plotted as a function of y in figures 1 and 2 respectively. The free energy of electron–hole pair is plotted in figure 3. It is found that the single- and two-electron localized states are energetically favourable only beyond a critical value of G. And with the changing value of G, the localization radius shifts very little. An analysis [14] of these localized electronic states shows that they are metastable and get destroyed by the increasing temperature.

The formation of extra potential wells in hydrogenated amorphous silicon due to intense local fluctuations in the hydrogen concentration seemingly leads to a different problem. But these potential wells on interaction with the electrons certainly leads to the localized electronic states in the band gap. There is an enhanced hydrogen diffusion in the hydrogenated amorphous silicon on exposure to light which is attributed to the presence of free charge carriers [2]. The enhanced hydrogen diffusion causes intense local fluctuations in the hydrogen concentration which in turn leads to the formation of extra potential wells.

From figures 2 and 3 it is clear that the two-electron states and electron–hole states readily occur. Thus these states possibly will be the recombination centers for the photogenerated charge carriers (electrons and holes) when a-Si:H is exposed to illumination. The recombination of photo-generated charge carriers may in turn excite the hydrogen from a nearby Si–H bond and break a weak Si–Si bond thereby apparently enhancing further the hydrogen diffusion and increasing the light-induced dangling bonds in a-Si–H. This can be described by the following chemical reaction:



$$\mathrm{Si-Si} + \mathrm{Si-H} + e + h \rightarrow 2\mathrm{Si-db} + \mathrm{Si-H},$$

where 'db' stands for the dangling bond associated with the silicon atom.

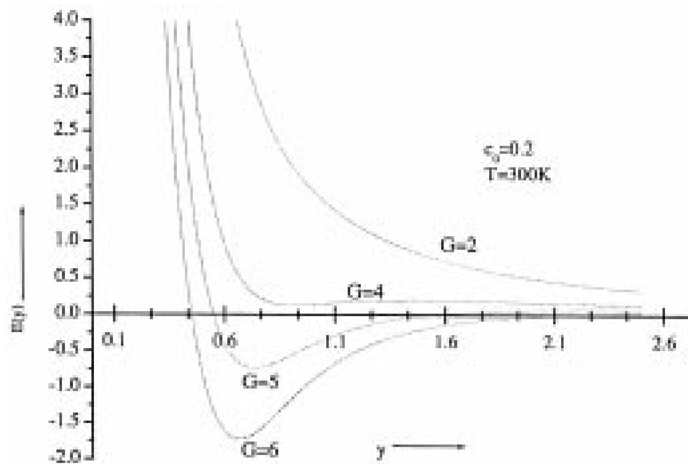


Figure 1. Single electron free energy $E(y)$ vs. y.

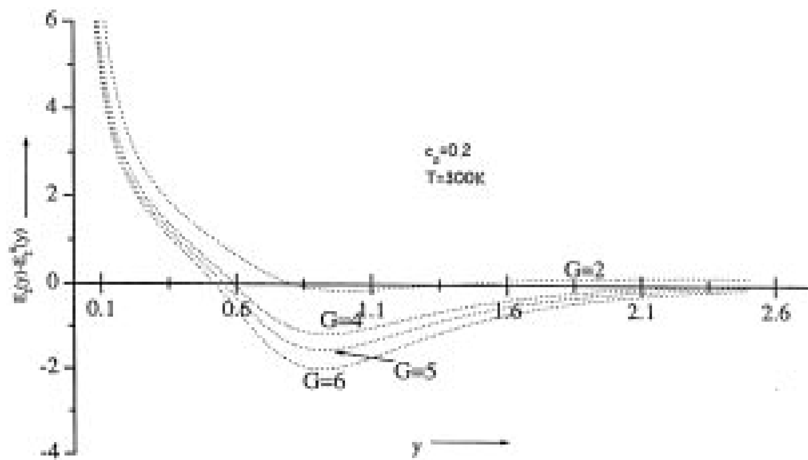


Figure 2. Two-electron state free energy with respect to that of the two separately localised electrons vs. y.

The non-radiative electron–hole recombination has also been proposed as a mechanism for the H-emission during metastable degradation of a-Si:H [12,13]. The trapping of charge carriers (electrons and holes) in these localized electronic states also lead to the degradation of electronic properties of the material. The prolonged light-exposure of hydrogenated amorphous silicon leads to the degradation by orders of magnitude making all device-applications problematic but the normal state can be recovered by a thermal anneal at 150–200°C [4]. Various other light-induced metastable defects have been observed in a-Si:H. Morgado *et al* [15] have also explained the relation between the light-induced metastable defects and the degradation of the photoconductivity in a-Si:H on the basis of a recombination model.

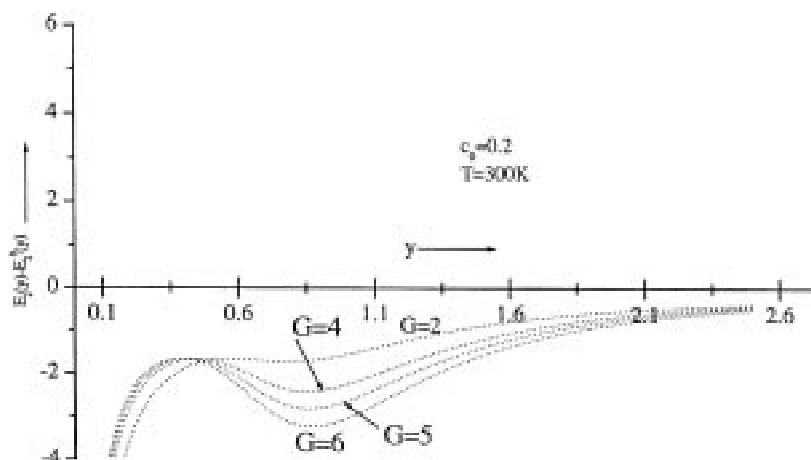


Figure 3. The electron–hole state free energy with respect to that of the two separately localized electrons vs. *y*.

4. Conclusions

The local hydrogen concentration fluctuations-induced extra potential wells, if intense enough, lead to the localized electronic states in a-Si:H. These localized states are metastable. The trapping of electrons and holes in these states leads to the electrical degradation of the material. These states also act as recombination centers for photo-generated carriers (electrons and holes) which in turn may excite a hydrogen atom from a nearby Si–H bond and breaks the weak (strained) Si–Si bond thereby apparently enhancing the hydrogen diffusion and increasing light-induced dangling bonds formation.

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