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Hydrogen motion and stretched-exponential relaxation in a-Si:H

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Abstract. Relaxation phenomena involving the motion of hydrogen in hydrogenated amorphous silicon, that have traditionally been described with a distribution of relaxation times and a stretched-exponential functional, were recently analysed by Van de Walle (Van de Walle C G 1996 *Phys. Rev.* B **53** 11 292) in terms of retrapping in a three-level energy diagram. We show that the expression derived by Van de Walle can also be obtained on the basis of hydrogen transport via interstitial positions which are in thermal equilibrium with a set of hydrogen traps located about 1 eV below the hydrogen chemical potential. However, the models based on hydrogen retrapping only give a good account of the relaxations for temperatures above room temperature. Dispersive behaviour is assumed to be responsible for the discrepancy at lower temperatures.

1. Introduction

Relaxation processes for which the time dependence of the relaxing quantity X can be described by the relation

$$X = X_0 \exp[-(t/\tau_K)^\beta] \qquad \beta < 1 \tag{1}$$

(the so-called stretched or Kohlrausch exponential, where τ_K and β are constants, and X_0 is the initial value of X) have been observed for many physical properties of disordered materials. For hydrogenated amorphous silicon (a-Si:H), the recovery of the photocreated defect density [1–4], the relaxation of either defects or a dark current induced by thermal quenching [5–8], and the variation of the band-tail carrier density caused by bias annealing [9] have been found to fit the stretched-exponential pattern. Since it was further shown [5, 10] that the time dependence of hydrogen diffusion in the material fits in well with the stretched-exponential parameters deduced from the other experiments, and given the fact that a link between the relaxational behaviour and hydrogen motion had been assumed all along, the stretched-exponential law has become widely accepted for describing relaxations in a-Si:H.

A particular form of equation (1) can be derived from $\mathrm{d}X/X\ \mathrm{d}t$, the rate equation for the observed quantity, when either one of the following two possibilities is realized.

(i) Instead of a single rate constant, there is a distribution of relaxation times [11–13]. In other words, the observed departure from equilibrium, $X(t)$, is the sum of many components, each of which has its single specific rate constant. Experimental data can then be explained by making a suitable choice of the rate-constant distribution for a concrete

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relaxation [2, 3]. In this way, each observed process may have its own rate distribution, with no fundamental link between the distributions for different observed quantities. This approach has, therefore, been called microscopically arbitrary.

(ii) The rate constant has a power-law time dependence $t^{-(1-\beta)}$ (a formalism already used by Kohlrausch) [10]. It is the observation [5] of such a power law for the time-dependent diffusion coefficient for hydrogen in a-Si:H that has linked hydrogen to the a-Si:H relaxations as mentioned above. In addition, the activation energy for H diffusion (1.2–1.5 eV) [14–16] is of the order of the activation energies (generally in the range of 0.9–1.0 eV) that are found for the relaxation times τ which correspond to the various relaxation processes [1, 5, 8, 9].

While there clearly is sufficient evidence to support the notion that a direct link exists between hydrogen motion and defect relaxation [14, 17–21], the mechanism of that coupling remains unresolved. The combination of a power-law time dependence for the H diffusion and an exponential distribution of weak Si–Si bonds that can act as H sites [5, 10] might invite a comparison with electronic dispersive transport models, but the activation energies near 1 eV for the relaxation times τ are much too large to be accounted for by such descriptions. Consequently, there is still room for new approaches to the problem. Li and Biswas [22] recently developed a model in which a distribution for the formation energy of the metastable defects that are assumed to be created by exciting bonded hydrogen into interstitial states arises from a bond-length disorder in the weak Si–Si bonds of the material. However, the calculational results deviate from the experimental data much more than is the case with a stretched-exponential description, especially at long relaxation times. Another model for explaining the stretched-exponential character of the relaxations, and one that does not invoke a distribution of energies, was recently proposed by Van de Walle [23]. It contains a natural explanation for the experimentally observed activation energy of the relaxations. According to this model, a departure from equilibrium caused by external factors, for instance thermal quenching and light soaking, results in the excitation of H from reservoir states to trapping states. The relaxation of the departure from equilibrium occurs when H escapes from the traps, migrates some distance via interstitial states, and then falls back into the reservoir states. The relaxation is described by the expression [23]

$$t = -\tau \ln \frac{X}{X_0} + \gamma \left(\frac{X}{X_0} - 1 \right) \tag{2}$$

where τ and γ are constants which depend on the system parameters. Despite the functional difference between equation (2) and the stretched-exponential form of equation (1), it was found [23] that the fit of equation (2) to some of the experimentally observed relaxations is virtually indistinguishable from the one provided by equation (1). The model was hence seen as a demonstration of the fact that a distribution of H trapping energies is not necessary to account for relaxations which are of the stretched-exponential type. The only requirement is that there be deeper-lying hydrogen levels that can act as a reservoir.

However, a more extensive examination of available experimental data indicates that agreement with the model is not always as good as was originally thought. In this paper we, therefore, propose a modified approach, still based on the concept of H retrapping, for obtaining the relaxation expression of equation (2). The analysis provides a simple physical meaning for the parameter τ, and leaves room for adjustments to suit changing experimental conditions. We will also discuss the difference between the forms of equation (1) and equation (2) in some detail.

2. The simplified retrapping model

In our analysis, we do not introduce the concept of 'reservoir states' explicitly. In fact, the difference between traps and 'reservoir states' as used by Van de Walle [23] lies basically in their position on the energy scale, but is not specified further. We propose to let a set of traps take the role of both the 'T' and 'R' states of the Van de Walle model. An initial external disturbance can redistribute the hydrogen amongst those states, but near equilibrium, or when relaxing towards equilibrium, diffusive hydrogen motion will be dominated by traps at the top of the distribution due to the exponentially decreasing probability of emission from the deeper ones [24]. Thermalization of the interstitial levels with respect to the top of the trap distribution is assumed. In our model we will hence assume that hydrogen which participates in the hydrogen diffusion will be found in one of only two states, either in an interstitial state from where H can migrate, or in a trap where H is immobile until released into an interstitial position.

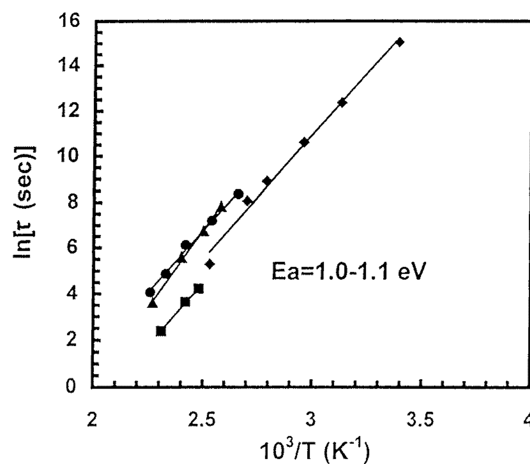

Figure 1. The parameter τ of equation (2) as a function of temperature. The diamonds, squares, triangles, and circles represent the values of τ obtained by fitting the relaxation data in, respectively, figure 1 of reference [5], figure 1 of reference [1], figure 7 of reference [8], and figure 8 of reference [8].

Support for such a simple model can be derived from the results shown in figure 1. Shown there are the values of τ obtained by fitting equation (2) to the experimental data for (a) the recovery of photocreated defects in undoped a-Si:H (figure 1 of reference [1]), (b) the decay of the excess carrier density induced by rapid thermal quenching of doped a-Si:H (figure 1 of reference [5]), and (c) the variation in the dark conductivity caused by a small disturbance in the thermodynamic equilibrium (figures 7 and 8 of reference [8]). It is seen that the parameter τ exhibits an Arrhenius behaviour, with a common activation energy of ~1.0–1.1 eV. Consequently, it should be possible to collectively model these phenomena in a simple way. Specifically, and whatever the actual underlying processes, it may be helpful to think of the dominant microscopic processes in the relaxation as being the capture of H into a trap, e.g. corresponding to the H bonding to a Si and passivation of a silicon dangling bond (Si–), and the release of H from a Si–H bond to the interstitial state, representing the formation of a silicon dangling bond and a bond-centre site (Si–H–Si) known to be the lowest-energy interstitial site [10, 25, 26]. The formation and annihilation

of the metastable defects can then symbolically be described by the relation

$$\text{Si–H} + \text{Si–Si} \rightleftharpoons \text{Si–} + \text{Si–H–Si}. \tag{3}$$

The density N_i of H at a trap level i is consequently determined by the competition between the release and the trapping of H:

$$\frac{\mathrm{d}N_i}{\mathrm{d}t} = -\nu_i N_i + \sigma N_I (N_{Ti} - N_i) \tag{4}$$

where N_I is the H concentration in the interstitial states, N_{Ti} the concentration of possible trapping sites for H at the level i, ν_i the release coefficient of H, and σ the capture parameter for H. While release depends exponentially on the energy of the trap since $\nu_i = \nu_0 \exp(-E_i/kT)$, with ν_0 the attempt frequency, E_i the energy of the trap, k the Boltzmann constant, and T the temperature, this is not the case for capture, and hence the parameter σ may be taken as constant. The relationship between the equilibrium hydrogen concentrations $\overline{N_I}$ in the interstitial states and $\overline{N_i}$ in the trap level i, at a given temperature, is given by equation (4) and the condition $\mathrm{d}\overline{N_i}/\mathrm{d}t = 0$ as

$$\nu_i \overline{N_i} = \sigma \overline{N_I} (N_{Ti} - \overline{N_i}). \tag{5}$$

Since the total amount of H in the system remains constant, we also have

$$\sum N_i + N_I = \sum \overline{N_i} + \overline{N_I} = C^{st}. \tag{6}$$

By summing all of the rate equations with respect to the level index i, and using equation (6) to replace $\sum N_i$, we obtain a rate equation for the concentration of H in interstitial states:

$$-\frac{\mathrm{d}N_I}{\mathrm{d}t} = -\sum \nu_i N_i + \sigma N_I \left[\sum (N_{Ti} - \overline{N_i}) - \overline{N_I}\right] + \sigma N_I^2 \tag{7}$$

and with the use of equation (5) to eliminate $N_{Ti} - \overline{N_i}$:

$$\frac{\mathrm{d}N_I}{\mathrm{d}t} = \sum \nu_i N_i + \left(\sigma \overline{N_I} - \left(\sum \nu_i \overline{N_i}\right) \Big/ \overline{N_I}\right) N_I - \sigma N_I^2. \tag{8}$$

When the departure from equilibrium conditions remains modest, the approximation $\sum \nu_i N_i = \sum \nu_i \overline{N_i}$ will be valid, and equation (8) can be readily integrated to yield

$$\left(\sigma \overline{N_I} + \left(\sum \nu_i \overline{N_i}\right) \Big/ \overline{N_I}\right) t = -\ln\left\{\left(\frac{N_I - \overline{N_I}}{N_{I0} - \overline{N_I}}\right)\left(\left[N_{I0} + \left(\sum \nu_i \overline{N_i}\right) \Big/ (\sigma \overline{N_I})\right] \times \left[N_I + \left(\sum \nu_i \overline{N_i}\right) \Big/ (\sigma \overline{N_I})\right]^{-1}\right)\right\} \tag{9}$$

where N_{I0} is the value of N_I at $t = 0$. By defining the departure from equilibrium of the interstitial hydrogen concentration $N_I - \overline{N_I}$ as the relaxing quantity X, we can proceed with equation (9) to obtain an expression in the form of equation (2). That same expression can also be obtained when the $\sum \nu_i N_i = \sum \nu_i \overline{N_i}$ approximation cannot be made, but then a more complex definition needs to be used for X.

In either case, the interpretation of equation (9) becomes more straightforward, and the meaning of the coefficients more transparent, when we substitute $\overline{N_I}$ for the expression $(\sum \nu_i \overline{N_i})/(\sigma \overline{N_I})$. It may be seen from equation (5) that this amounts to putting $\overline{N_I} = \sum (N_{Ti} - \overline{N_i})$. In the context of the simple model of equation (3), the difference between the density of possible H traps, N_{Ti}, and the equilibrium density of occupied traps represents the (much lower) dangling-bond density, and coupled with it the density of interstitial hydrogen. Equation (9) can thus be reformulated as

$$2\sigma \overline{N_I} t = -\ln \frac{X}{X_0} + \ln \frac{X + 2\overline{N_I}}{X_0 + 2\overline{N_I}} \tag{10}$$

or, since the argument of the second logarithmic term will be close enough to 1 to allow restriction of a series expansion to the leading term,

$$t = -\tau' \ln \frac{X}{X_0} + \gamma' \left(\frac{X}{X_0} - 1 \right) \tag{11}$$

where $\tau' = 1/(2\sigma \overline{N_I})$ and $\gamma' = \tau' X_0/(X_0 + 2\overline{N_I})$. This expression duplicates the form of equation (2), but with different definitions of the coefficients to those used in [23]. The coefficient τ' represents the average lifetime of H in the interstitial states at a given temperature, while γ' reflects the degree of departure of the observed relaxation from the conventional exponential pattern. Without the $(\sum \nu_i \overline{N_i})/(\sigma \overline{N_I}) = \overline{N_I}$ substitution, the coefficients τ' and γ' will be more complex and contain the quantity $\sum \nu_i \overline{N_i}$, but equation (11) remains valid. A further difference from [23] lies in the definition of the relaxing quantity X. Van de Walle [23] uses the hydrogen concentration in the traps 'T' of his model as the relaxing quantity, while we use the departure from equilibrium of the occupation at the interstitial positions. But since these two quantities are assumed to be in dynamic equilibrium—both here and with respect to the other (reservoir) states in [23]—the two definitions are equivalent: variations in occupation of one will be mirrored in variations in occupation of the other one.

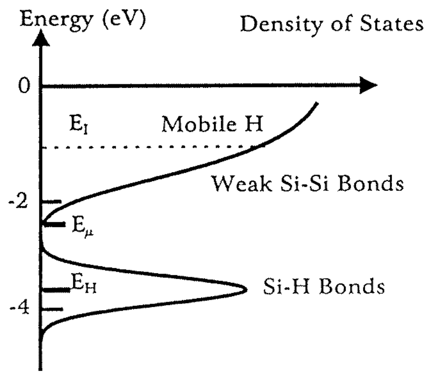

Figure 2. The hydrogen density of states in a-Si:H. Zero energy corresponds to the energy of a free hydrogen in vacuum. E_I stands for the energy of the interstitial Si–H–Si states via which transport takes place. The Si–H bond states (hydrogen traps at E_i) and weak Si–Si bond states are below and above the hydrogen chemical potential E_μ, respectively. The contribution of weak Si–Si bonds to the relaxation processes is neglected in the present analysis.

3. Discussion

The activation energy of $\sim$1.0 eV which is found in figure 1 for the τ of equation (2) equally applies of course to the $\tau' = 1/(2\sigma \overline{N_I})$ of equation (11). If we assume the capture coefficient σ to be independent of temperature to a first approximation, then this activated behaviour can also be assigned to the $\overline{N_I}$ of our model, which is in thermal equilibrium with the active traps. As was pointed out above, the density $\overline{N_I}$ will change along with the density of silicon dangling bonds. Since the equilibrium hydrogen distribution (and hence dangling-bond density) is determined by the energy difference between the hydrogen chemical potential E_μ and the trap levels E_i, we can write

$$\overline{N_I} \propto \sum N_i \exp[-(E_\mu - E_i)/kT]. \tag{12}$$

Given the narrow range of activation energies that follows from figure 1, we may conclude that the combined contribution of the hydrogen trapping states to the relaxation phenomena can be represented by a single effective level E_H, located $\sim$1.0–1.1 eV below E_μ. Figure 2 illustrates the energy levels in an a-Si:H hydrogen density-of-states diagram [10] that are compatible with the above argument. Taking the energy of neutral hydrogen atoms in vacuum as a zero reference, the energy level E_I for the interstitial Si–H–Si site is located at ~ -1 eV [10, 25]. Taking into account the activation energy $E_I - E_\mu \simeq 1.4$ eV for hydrogen diffusion [10, 19] in a-Si:H, one arrives at $E_\mu \simeq -2.4$ eV. A value of $E_H \simeq -3.6$ eV has been estimated by Van de Walle and Street [25] for the energy of a Si–H bond in a (crystalline) silicon environment. Consequently, a natural corollary of this energy scheme is a value $E_\mu - E_H \simeq 1.2$ eV, which is in reasonable agreement with the activation energies $\sim$1.0–1.1 eV deduced from figure 1. However, this activation energy is somewhat larger than the values of 0.6 to 0.8 eV deduced for the formation energy of silicon dangling bonds from either experiment [6] or theoretical considerations [27, 28].

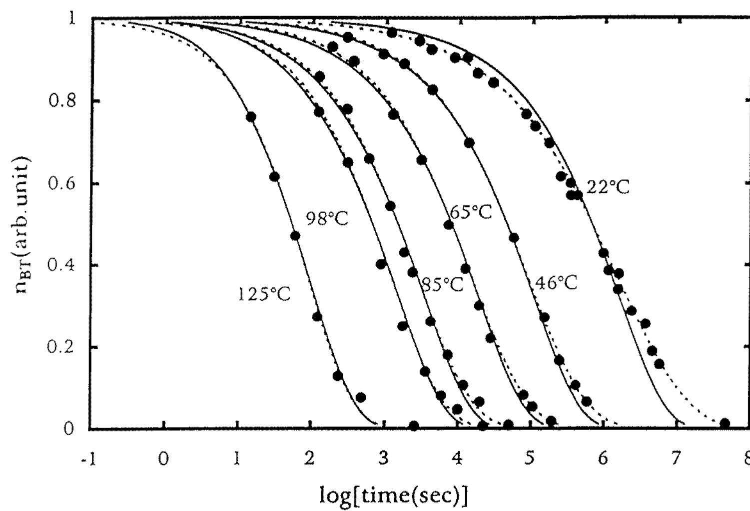

Figure 3. The time dependence of the normalized density of shallow occupied band-tail states of n-type a-Si:H at the temperatures indicated. The data points are taken from figure 1 of reference [5]; the solid lines represent a best fit with equation (11), while the dashed lines indicate the fit with equation (1).

Returning now to a comparison of the specifics of equation (1) and equation (11), we examine the slopes of the two functions in the type of semi-logarithmic plot that is generally used to present the relaxation data sets. The derivatives of X/X_0 with respect to $\log_{10} t$ are

$$\frac{\mathrm{d}(X/X_0)}{\mathrm{d}(\log_{10} t)} = \beta(X/X_0)\ln(X/X_0)\ln 10 \tag{13}$$

for equation (1), and

$$\frac{\mathrm{d}(X/X_0)}{\mathrm{d}(\log_{10} t)} = \frac{\gamma'(-1 + X/X_0) - \tau'\ln(X/X_0)}{\gamma' - \tau'(X_0/X)}\ln 10 \tag{14}$$

for equation (11). The derivative of the stretched-exponential relation is proportional to β, and hence can become very small along with β for relaxation at low temperatures [2, 4]. Even for relaxation at room temperature (RT), where $\beta = 0.45$ follows from

figure 1 of reference [5], the derivative is about -0.36 at $X/X_0 = 0.5$, which is smaller than the derivative in equation (14) can ever be. Indeed, it follows from the definition $\gamma' = \tau' X_0/(X_0 + 2\overline{N_I})$ that γ' will always be less than τ' and that the slope at $X/X_0 = 0.5$ will never be smaller than -0.44. With such difference between the RT derivatives of the two functions, one obviously cannot expect a good fit to the RT data from both expressions. In figure 3, we present the fits produced using equation (1) and equation (11) to the relaxation of shallow occupied band-tail states, obtained for temperatures between 22 and 125 °C by Kakalios, Street and Jackson (figure 1 of reference [5]). The dashed lines, corresponding to equation (1), are superimposed on the data points for all temperatures over the whole timescale, while the solid lines, produced using equation (11), fit the data well at the higher temperatures but show significant deviations from the relaxation data at RT. In other words, the simple model based on a mono-energetic set of hydrogen traps and transport through interstitial positions is too simple to account correctly for the temperature dependence of the relaxations. Given the disordered nature of the a-Si:H lattice, such a discrepancy is not surprising; hydrogen diffusion will progressively become more dispersive as the temperature is lowered, and actual distributions of traps and transport states would have to be introduced to describe that dispersion. The case of multiple-trapping *hydrogen* transport in a *hydrogen density of states* is obviously very much analogous to that of multiple-trapping *electronic* transport in the *electronic density of states* of the same a-Si:H samples. The transport becomes non-dispersive at higher temperatures, and the simple model works.

4. Conclusion

The various relaxation processes in hydrogenated amorphous silicon that have traditionally been described by a stretched-exponential expression, and that were recently modelled by Van de Walle [23] in terms of three discrete energies, can also be understood in terms of hydrogen transport at an interstitial level and trapping into a distribution of states stretching down from ~1.0–1.1 eV below the hydrogen chemical potential. However, models based on just two or three discrete energy levels are less satisfactory for describing relaxation at room temperature or below.

Acknowledgments

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