Measurement and modelling of transport in amorphous semiconductors

C Main and S Reynolds
University of Dundee, School of Engineering, Physics and Mathematics, Small’s Wynd, Dundee DD1 4HN, UK.

E-mail: c.main@dundee.ac.uk

Abstract. Experimental transient photoconductivity in a-Si:H and μc-Si:H is analysed by a Fourier Transform technique to reveal a relative density of states. It is often found that a deep-lying structure probably associated with defects, at around 0.5 – 0.6 eV depth exhibits an apparent shift against the background of band-tail states as the temperature is varied. We investigate by numerical modelling whether this shift arises from differential attempt-to-escape frequencies in a multi-trapping context, or from a temperature-dependent hopping transport energy.

1. Introduction

Joe Marshall was a mentor, colleague and personal friend for over 40 years. In his scientific work he was scrupulously honest, valuing truth and possessing a healthy disrespect for authority. His philosophy could be encapsulated in the motto of the Royal Society - “Nullius in Verba” which translates as ‘on the word of no one’. He was also keen to promote the interests and development of younger scientists, in his teaching and in support of their attendance at schools and conferences. All who knew Joe as a friend or colleague, will miss him.

The transient photocurrent response (TPC) following excitation by a short laser pulse is determined by a combination of carrier transport processes. The non-equilibrium distribution of excess carriers created by such a pulse will diffuse and drift while relaxing in energy toward thermal equilibrium. If the immediate ‘post-pulse’ excess carriers initially exist in extended states, their relaxation and transport will involve the participation of localised states either by ‘multi-trapping’ (MT) processes in which transitions occur only between localised and extended states, or by direct inter-site tunnelling or ‘hopping’. In the former case, any measured current arises from trap-limited band transport, whilst in the latter case the current arises from hopping transport.

It is possible to model numerically the TPC in a distribution of localized states (DOS) mediated by either of the above processes. Marshall [1,2] has studied, by computer modelling applicable to an arbitrary DOS, the case of transient photocurrents in the case of hopping transport, employing Monte-Carlo techniques. The present authors have further developed a finite difference numerical model based on Marshall’s work which includes transport by either of the above processes, or even a simultaneous combination of both MT and hopping [3,4].

To complement such work, Fourier Transform (FT) techniques have been developed by the present authors to reveal, in a spectroscopic fashion, information on the energy distribution of localised states (DOS) from measurements of the transient photocurrent decay [5,6], assuming in the first instance that
MT processes dominate transport. It its basic form, as described below, this method can only give a relative DOS scale and a relative energy scale as determined by a fixed value of attempt-to-escape frequency \( \nu \), although there are ways to alleviate this difficulty.

The motivation for this work arises from studies over a range of temperatures, of TPC in undoped a-Si:H and \( \mu \)c-Si:H, the DOS being obtained by MT-FT analysis. These studies, while revealing such features as band-tails and deep defect structure, often show an apparent systematic shift of the defects to deeper relative energy, against the tail state ‘background’ as temperature is increased in the range 100K – 300K. A typical set of results is shown in figure 1 illustrating the TPC in an a-Si:H sample over the temperature range 150K – 330K, and figure 2 showing the FT derived DOS for these data, using an attempt-to-escape frequency \( \nu = 10^{12} \) Hz. There is an apparent shift of the defects of about 0.05 eV over this temperature range. One possible explanation for this is simply that the defect states have a much smaller attempt-to-escape frequency than the tail states. It turns out that a value of \( 10^{10} \) Hz would ‘fix’ the defects relative to the tail states. However, there is also an indication that this shifting ceases above room temperature, which would be difficult to explain in this way, since the ‘shift phenomenon’ would continue to apply at elevated temperatures.

An alternative explanation might invoke hopping transport, where it has been shown [7,8] that in an exponential band-tail, there is an energy within the band tail, at which hopping transport is maximum – the so-called ‘transport energy’. This energy is temperature dependent, approaching the conduction band edge as temperature is increased. In such a situation, any deeper lying levels which have a significant influence on the effective drift of excess carriers would appear to lie at successively deeper energies below the transport energy as the temperature rises.

The purpose of the present work is therefore to evaluate whether the energy shift arises as a numerical artefact of the FT analysis or as a physical consequence of changes in the dominant energy location of hopping transport with temperature.

2. Numerical methods

2.1. Modelling hopping and multi-trapping transport

Following Marshall [1], we represent the continuous distribution \( g(E) \) of localised states by a ‘ladder’
of state grouped into slices of energy with $\Delta E$. Thus, the level ‘$i$’ of this discretised distribution has an approximate density $g(E_i)\Delta E$ cm$^{-3}$. Firstly, we write the probability of hops to iso-energetic or deeper sites at energy $E_j$ from a site at energy $E_i$ as

$$p_{i,j} = v_0 \left( g(E_j) \Delta E / N_{i,\text{deep}} \right) \exp \left( -r_{i,\text{deep}} / 2R_0 \right),$$

(1)

where $v_0$ is an attempt-to-hop frequency, $N_{i,\text{deep}} = \int_{E_i}^{E_j} g(E) dE \approx \sum_k g(E_k) \Delta E$ ($k \geq i$) is the total number of iso-energetic and deeper sites, with corresponding mean separation $r_{i,\text{deep}} = \left( N_{i,\text{deep}} \right)^{1/3}$, and $R_0$ is a localisation parameter for the sites. In this paper, we restrict $R_0$ to a typical value of around $7 \times 10^{-8}$ cm. The ratio $g(E_j)\Delta E / N_{i,\text{deep}}$ represents the fraction of all such sites in slice ‘$j$’, since the probability of hopping to a given slice is proportional to the fractional concentration of sites it contains. For hops upward in energy, from a site in a deeper slice at energy $E_j$ up to $E_i$, detailed balance gives the inverse hop probability

$$p_{j,i} = p_{i,j} \left( g(E_i) / g(E_j) \right) \exp \left( -(E_i - E_j) / kT \right),$$

(2)

where $kT$ is the thermal energy.

Similarly, multi-trapping transition probabilities may be written, for trapping of a carrier in the conduction band by a trap in slice ‘$i$’,

$$p_{c,j} = (v/N_C)g(E_i)\Delta E,$$

(3)

while for the inverse process, thermal re-emission, the expression is

$$p_{i,c} = v \exp \left( -(E_C - E_i) / kT \right),$$

(4)

where $v$ is an attempt-to escape frequency, $N_C$ is the effective density of states in the conduction band, and $E_C$ is the mobility-edge energy. We assume that the occupancy of states is always low, so that the system may be assumed linear.

The various probabilities above may be incorporated into a set of rate equations describing the time dependence of the densities of electrons in both localised and extended states. With appropriate initial conditions, such as the introduction of excess free or localised carriers, these will describe the progress of carrier relaxation in for example, a transient photocurrent experiment. The rate equations are as follows:

$$\frac{dn}{dt} = -n \sum_i p_{i,j} + \sum_i n_i p_{i,c}$$

(5)

$$\frac{dn_i}{dt} = np_{c,j} - n_i p_{i,c} + \sum_j n_j p_{j,i} - n_i \sum_j p_{i,j},$$

(6)

where $n$ is the instantaneous density of free electrons, and $n_i$ is the density of electrons on sites in slice ‘$i$’. In the following, we will assume that there are ‘$M$’ levels, including the conduction band.

To perform a discrete ‘time-stepping’ numerical solution, we can use these equations to compute updated values of each of the variables $n$, $n_i$, ... as time is incremented by a step $\Delta t$, using previous values of the variables. Re-casting the above equations in matrix-vector form, we obtain
\[ \mathbf{n}(t + \Delta t) = \mathbf{A} \mathbf{n}(t), \quad (7) \]

where \( \mathbf{n}(t) \) is the vector of the instantaneous free and localised carrier densities, and \( \mathbf{A} \) is an \( M \times M \) ‘stochastic’ transition matrix with elements

\[
A_{i,i} = 1 - \sum_{j=2}^{M} p_{e,i} \Delta t, \quad A_{i,i} = p_{e,i} \Delta t, \quad A_{i,i} = p_{i,i} \Delta t, \quad (8a,b,c)
\]

\[
A_{i,i} = 1 - \left( p_{e,i} + \sum_{j=2}^{M} p_{e,j} - p_{i,i} \right) \Delta t, \quad A_{i,i} = p_{j,i} \Delta t \quad (j \neq i). \quad (8d,e)
\]

The system of equations (5) and (6) is ‘stiff’. In practice this means that time step \( \Delta t \) cannot exceed the shortest time-constant of the system, in this case, the overall trapping time of free carriers into the ensemble of traps \( \tau_{\text{trap}} = \left( \sum_{i} p_{e,i} \right)^{-1} \). It is possible to deal with such systems using stable ‘implicit’ numerical methods, and the authors have done so in previous work on MT simulation [9]. However, in the present case, there is a simple artifice, which allows the explicit formulation described above, to be used to follow the time evolution of the system over very long time-spans. Using a suitably small value for \( \Delta t \) of \( 10^{-14} \) s, we can, by continued squaring of the matrix \( \mathbf{A} \), generate very long effective time steps, viz-

\[ \mathbf{n}(t + 2^n \Delta t) = \mathbf{A}^{2^n} \mathbf{n}(t). \quad (9) \]

In this way, we may extend the simulation time-scale from \( 10^{-14} \) s to \( 10^6 \) s, in only 72 steps, although extended-precision arithmetic is required to minimise truncation errors. Initial conditions for the simulation of TPC, with MT-only transport or MT+hopping, are determined by setting the leading element of vector \( \mathbf{n}(0) \) to a normalised value of e.g., 1.0, and all other elements to zero.

Computation of the transient current for free carriers, uses the instantaneous extended state conductivity \( \sigma_{\text{ext}} = nq\mu_{\text{ext}} \), where \( q \) is the electronic charge and \( \mu_{\text{ext}} \) is the free carrier mobility. For hopping carriers, and for low fields, we compute the effective diffusivity of carriers in each slice, as determined by the hop rate from sites in a given slice, and some ‘average’ hop distance, here – the distance from slice ‘i’ to slice ‘j’ taken as the mean separation of sites in slice ‘j’, viz.,

\[
\bar{r}_{ij} = \left( g(E_i) \Delta E \right)^{1/3}.
\]

The contribution \( \sigma_{i} \) of each level to the hopping conductivity, and the total hopping conductivity \( \sigma_{\text{hop}} \) may then be found, after application of the Einstein relation giving,

\[
\sigma_i = n_i q^2 \sum_j p_{i,j} \bar{r}_{ij}^2 / 6kT, \quad (10)
\]

\[
\sigma_{\text{hop}} = \sum_i n_i q^2 \sum_j p_{i,j} \bar{r}_{ij}^2 / 6kT. \quad (11)
\]

It is useful to note here the analytical approximate result obtained by Monroe [7], which for an exponential tail produces a ‘transport energy’ \( E_i \) at which the hopping transport peaks, viz-
\[ E_* = 3E_0 \ln \left( \frac{2kT}{3E_0R_0(A\pi N_0/3)^{1/3}} \right), \quad (12) \]

where \( E_0 \) is the characteristic tailing energy and \( N_0 \) is the integrated DOS of the tail. The temperature dependence of this energy appears in the logarithmic factor.

2.2. Computing the DOS (MT only)

Applying a Fourier transform to equations (5) and (6), omitting the hopping terms, gives in the frequency domain,

\[ \tilde{n}(\omega) = \int_0^\infty n(t)[\cos(\omega t) - j \sin(\omega t)]dt = \frac{N_0}{(A_\omega + j B_\omega)}, \quad (13) \]

where, treating the density of states (DOS) as continuous in energy,

\[ A_\omega = \omega_k + \int_0^{E_c} \nu \sigma g(E) \left( 1 + \exp \left( -\frac{2(E_\omega - E)}{kT} \right) \right)^{-1} dE \]

and

\[ B_\omega = \frac{i(0) \sin(\phi(\omega))}{\tilde{I}(\omega)} = \omega + \int_0^{E_c} \frac{\nu \sigma}{2} g(E) \text{sech} \left( \frac{E_\omega - E}{kT} \right) dE. \quad (15) \]

In the above, \( \tilde{I}(\omega) \) represents the frequency domain photocurrent associated with \( \tilde{n}(\omega) \), \( i(0) \) is the initial value of the transient photocurrent – i.e. when all \( N_0 \) excess carriers are free, and \( E_f \) is the Fermi energy. The term \( k \) is Boltzmann’s constant, and \( T \) is the absolute temperature.

Equation (15) is a Fredholm integral equation of the first kind, and is ‘ill-conditioned’. A simple approximate solution [6] replaces the peaked sech function with a delta function, to give

\[ g(E_\omega) \approx \frac{N_e^2}{\nu \pi kT} \frac{i(0) \sin(\phi(\omega))}{\tilde{I}(\omega)} - \omega. \quad (16) \]

with energy scale

\[ E_\omega = kT \ln \left( \frac{\nu}{\omega} \right). \quad (17) \]

We note that if the value of the attempt-to escape frequency \( \nu \) is known then a given feature in the DOS will produce a feature in the computed \( g(E_\omega) \) at a specific frequency \( \omega = \nu \exp \left( -\frac{E_\omega}{kT} \right) \) which varies with temperature so that the computed \( E_\omega \) remains fixed at all temperatures. Otherwise, an incorrect value of \( \nu \) will result in a ‘shifting’ feature.

3. Simulation results and discussion

The simulation method described in section 2 gives a typical result for hopping transport as shown in figure 3. Here the progress of the peak of the charge density and the mean hopping energy are shown. The results agree with the Monroe model. Parameters used for this and subsequent computations are \( E_\omega = 30 \text{meV}, R_0 = 7.3 \times 10^5 \text{cm}, g(E_\omega) = 4 \times 10^7 \text{cm}^3\text{eV}^{-1}, \) and \( \nu = 10^{15} \text{Hz}. \) We find that the temperature
Figure 3. Numerical simulation of hopping transport at 100K in an exponential tail of characteristic energy 0.03eV. The progress of the peak of the charge density and the mean hopping energy are shown. The results agree with the Monroe model.

dependence of the transport energy also agrees with the Monroe model, equation (12). Note however, that we justify use of the numerical simulation on grounds that it may be applied to situations with an arbitrary DOS.

Figure 4. Numerical simulation of the Temperature dependence of the apparent energy shift for a deep feature in the computed DOS for MT transport, using $\nu=10^{12}$ Hz when the correct value was $10^{10}$ Hz, and for hopping transport which gives a shift of the transport energy. Exponential tail of characteristic energy 0.03eV.

We wish to test whether this upward movement of the transport energy with temperature effectively results in an increase in the apparent depth of the underlying defects comparable with that observed. Figure 4 shows the result of this computation with the hopping parameters given above. It does indeed seem possible that this is a reasonable explanation, even to the extent that the shifting ceases at elevated temperatures, as observed.

On the same figure we illustrate the alternative explanation – that the chosen value of $\nu$ may be correct for bandtail states, but incorrect for the defect states. Here we find that the required 0.05 eV
shift between 200K and 300K may be obtained by assuming that the correct $v$ for the defect states is much lower, viz. $\sim 10^{10}$ Hz. While this does give the required shift, it can be seen that this continues as the temperature rises above 300K, in disagreement with the observation.

However, it may be pointed out that the FT-DOS method applies only when we ignore the possibility of hopping and that the above argument, though plausible, may thus be invalid. To partly answer such an objection, we computed the TPC for a DOS containing an exponential bandtail and a Gaussian defect feature, allowing the possibility of simultaneous MT and hopping processes, using the same parameters as before. The defect feature is centred at 0.5 eV below Ec, has characteristic energy 0.06 eV, and peak density $10^{17}$ cm$^{-3}$ eV$^{-1}$.

Figure 5 shows the computed relative TPC currents (using a free carrier mobility of 10 cm$^2$ V$^{-1}$ s$^{-1}$) for the hopping and extended state transport components, at 200K. At this temperature, with the chosen parameters, the hopping component is slightly higher than the free carrier component over most of the time range. Figure 6 shows the same computation, now at 300K. Here the free carrier current is larger than the hopping current by a factor of about 4. Perhaps surprisingly, using quite reasonable values for hopping parameters, even at room temperature the hopping current is not insignificant.

In figure 7 we show the FT-computed DOS for the simulated free + hopping TPC transients. Although the existence of hopping current may again invalidate the analysis, the result is directly comparable to that obtained experimentally. The shift of peak defect energy matches the experimental result, and the cessation of shifting above 300K is also evident. The figure also demonstrates that the inclusion of hopping into the simulation has a significant effect even at 300K. One of the DOS curves for $T = 300K$ (filled square symbol) was obtained from a simulation including simultaneous MT and hopping processes; the other (open circle symbol) from an ‘MT-only’ simulation.

4. Conclusions

We have compared alternative explanations of the apparent shifting in energy, of features in the FT-derived DOS in a-Si:H as obtained from TPC measurement. The alternatives are firstly – that the shift...
Figure 6. Numerical simulation of TPC for simultaneous MT and hopping transport at 300K for the same DOS as in Figure 5. The relative free carrier and hopping transport currents are shown, and the total current. At 300K, the free carrier current is larger than the hopping current by a factor of about 4.

Figure 7. Computed FT – DOS from numerical simulations of TPC for simultaneous MT and hopping transport for a DOS with tail and defect states, at several temperatures. The apparent shift of defect states is a result of the shift of the hopping transport energy.

is merely an artefact of the FT calculation, involving an incorrect value of attempt to escape frequency, and secondly – that it arises from the physical shift in the transport energy when hopping conduction predominates. A definitive answer is not yet possible, as the FT analysis assumes only transport of free carriers with multiple trapping. However the latter explanation seems to be more
plausible at the time of writing. Further development of the FT analysis, to include hopping, would be useful.

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