

RECOMBINATION-ENHANCED PROCESSES IN SOLAR CELL DEGRADATION*

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Summary

In this paper we briefly survey processes enhanced by high carrier densities and cases relevant to solar cell systems. The criteria for distinguishing between the main types of mechanism (local excitation, local heating and the Bourgoin-Corbett mechanism) are discussed. Whether or not the reaction coordinate is a normal mode proves to be of considerable importance.

1. Characteristics of recombination-enhanced processes

For the purposes of this paper we shall consider any process enhanced by raising carrier densities as recombination enhanced, even where the carrier densities are raised by ionizing radiation, injection or some indirect mechanism. These processes have two special features.

(1) Either the processes are athermal or they show only a weak temperature dependence. As a result, processes may occur at low temperatures which cannot be predicted by simple extrapolation from high temperatures.

(2) The processes occur during device operation and hardly ever "on the shelf". The rate depends on the excitation rate as well as on the total dose.

In a solar cell system, any part may be affected. The ancillary parts such as protective windows and antireflection coatings are also liable to damage. Recombination enhancement is obviously particularly important when high optical densities occur (as with solar concentrators) or other special operating conditions.

This paper is an extension of an earlier discussion [1] and in it we consider some general aspects of enhanced processes. The consequences of enhanced processes can be varied: point defect production, dislocation climb,

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transient defects, increased diffusion rates, dislocation loop and colloid production, and even phase transitions. The possible effects in solar cells are indicated later. For the present the analysis involves several mechanisms of recombination enhancement and the criteria for distinguishing between them.

2. Mechanisms of recombination enhancement

There is no general agreement on nomenclature, and some of the picturesque choices ("phonon kick", "energy release" etc.) do not define their range accurately. We shall follow the distinctions made in ref. 1. Thus there are three broad classes: (1) local excitation; (2) local heating; (3) the Bourgoin-Corbett mechanism.

In local excitation the defect changes its electronic state to another state in which diffusion is easier. The second state might be a different charge state, although generally it is only an excited state of the same charge state of the defect. Recombination energy is transferred to the electronic degrees of freedom.

In local heating the recombination energy is transferred to the vibrational degrees of freedom. The greater amplitudes of vibration lead to higher diffusion rates.

Between these two extremes of transfer to electronic and lattice degrees of freedom is the Bourgoin-Corbett [2] model, in which the defect occupies different lattice sites in different charge states and moves by successive captures of electrons and holes.

All three processes have been seen, notably in ionic crystals where the experimental evidence is clearer. Discussions of the mechanisms, not always in accord, are given in refs. 3 - 7.

3. How can we distinguish between the mechanisms?

A paper of major importance in this field is ref. 5, in which Troxell *et al.* consider a well-characterized system, interstitial aluminium in silicon, and make an impressive attempt to decide which processes are involved. They conclude that local heating is the important effect. Later in this paper we argue that local heating can be effective only in rather restrictive circumstances, though we do not discuss Si:Al_i in any detail.

Troxell *et al.* [5] use arguments which can be put into two broad categories. One class requires *consistency*. If these arguments are violated, we can be sure that a particular mechanism is unacceptable. Does the mechanism leave the system stable when there is no enhancement? Do the energies balance up correctly, and is the gap wide enough and the recombination energy sufficient? Is there saturation at levels consistent with known capture cross sections? The second class involves the arguments that are *reasonable*. It is debatable whether an argument in this class is conclusive. The main

questions here are these. Are the pre-exponential factors ω_0 reasonable? These are defined by the enhanced jump rate $\tau^{-1} = \omega_0 \exp(-E_{A,\text{eff}}/kT)$. Are the efficiencies η reasonable? Troxell *et al.* suggest that an efficiency η approximately equal to 0.1 is reasonable (*i.e.* one jump for every ten electron-hole recombination events). Clearly any case where $\eta > 1$ is questionable, although this is not impossible.

4. The “reasonable” arguments in recombination-enhanced diffusion

We now consider the questions of pre-exponential factor and of efficiency in the context of Section 3.

4.1. Pre-exponential factors

It is widely and reasonably held that pre-exponential factors are of the order of a phonon frequency, *i.e.* $10^{10} - 10^{14} \text{ s}^{-1}$. This view follows on fairly general arguments from a classical basis and (although with a less obvious lower bound) from quantum matrix-element estimates. However, if we are considering a rate process in an excited state, another factor must be included which depends on the lifetime in the excited state.

Let us suppose that excitation occurs on average every τ_x and that the lifetime of the excited state is τ^* . If the rates in the ground and excited states are R_0 and R^* respectively, then the rate overall is given by

$$\frac{1}{\tau} = \frac{R_0 \tau_x}{\tau_x + \tau^*} + \frac{R^* \tau^*}{\tau_x + \tau^*}$$

The effective pre-exponential factor is $\omega^* \tau^*/(\tau_x + \tau^*)$ and may be very much less than the value of $10^{10} - 10^{14} \text{ s}^{-1}$ suggested by simple arguments. Furthermore, if there are several excited states, these can also influence the rate achieved.

4.2. Efficiencies in local heating

Local heating is a much more complicated problem and is closely related to issues in non-radiative transition theory. There are three important questions concerning this problem.

(1) How long does the local excitation persist? A diffusive jump involves motion along a *reaction coordinate*, which is not usually a *normal mode* of the defect lattice. The question is whether the lattice can maintain a systematic motion in the reaction coordinate long enough to be effective. The mechanisms and rates of damping are crucial.

(2) Is the phonon kick in the right direction? Can the desired motion be excited with a non-negligible efficiency? This obviously depends on the route by which the excited state (vibrational or electronic) is reached.

(3) How rapidly is thermalization achieved? This is important both theoretically (since the most convenient formulae have only a simple form

for a thermal equilibrium distribution) and for the practical issues of persistence of excitation. Formulae valid only for equilibrium include Kac's [8] formula for the number of times that the reaction coordinate exceeds a critical value when increasing, Bloch's [9] theorem on the gaussian distributions of the reaction coordinate and its conjugate momentum, and results on the temperature dependences of mean square displacements and momenta [10].

If the normal modes involve displacements x_n given by

$$x_n = u_n e_n \exp(i\omega_n t)$$

where u_n is the amplitude and e_n the eigenvector, then the reaction coordinate can be defined by $R \equiv \sum_n A_n e_n$ with amplitudes A_n . Two extremes can be distinguished [3, 6, 11]. If the reaction coordinate is a normal mode or a very sharp resonance, the excitation can be produced efficiently, it will persist and it will thermalize only slowly. This limit will be common in small molecules. If the reaction coordinate is built from many modes over a wide range ΔE of energy, the excitation will not persist long, thermalization can be rapid and efficient excitation will be difficult. This second extreme probably includes all cases where the effective vibration frequency in the reaction coordinate lies near a peak in the phonon density of states of the host [6].

The efficiency of excitation involves issues paralleling those discussed in ref. 11. A more complete account will be given elsewhere. For present purposes we give two examples of methods for obtaining a particular excited vibronic state. One method, typically used with optical absorption or emission, involves a Franck-Condon transition. In the other method a higher vibronic state is excited with a distinct electronic state; the system then passes into the desired state via a cross-over of two configuration coordinate curves.

When the desired state arises from a cross-over, the efficiency depends both on the branching ratio at the cross-over (*i.e.* the probability that the system does make the desired switch in electronic state) and on whether the generalized force $\nabla_Q E(Q)$ is in the right direction. This can be seen equally clearly for the Franck-Condon excitations where the behaviour is determined by the mode Huang-Rhys factors S_n (see, for example, ref. 12, Chap. 10). If the difference in defect forces between initial and final states is F_n , then the mode Huang-Rhys factors are $S_n \equiv \frac{1}{2} F_n^+ (1/\hbar\omega_n^3) F_n$ and the kick is along $T \equiv \sum_n F_n (1/\frac{1}{2} m\omega_n^2) e_n$. The energy transfer is proportional to $(R \cdot T)^2$ and it is apparent that the probability that much energy gets into the reaction coordinate will be small unless R and T are both normal modes. There is one other feature of interest. If $R \cdot T$ is large, this means that the forces F_n tend to move the diffusing particle in the desired direction: in the excited state the new equilibrium will be displaced in the same direction as the diffusive motion. There is thus a distinct resemblance to the Bourgoin-Corbett mechanism, which can be considered a limiting instance.

5. Possible recombination-enhanced processes in solar cells

It is useful to turn from the technical issues of Sections 2 - 4 to some of the cases where recombination enhancement (in the broad sense of Section 1) is possible in solar cells.

In silicon cells, three cases are apparent, involving both impurities and defects generated by radiation damage. First, there are transient defects. Thus a recombination centre involving silver and a lattice defect has been identified [13] which is usually inactive but which can be activated. Secondly, there are processes broadly of the local excitation type. These include the charge-state-dependent motion of vacancies and vacancy complexes [14] and the ionization enhancement of interstitial motion [15]. If the interstitial motion is like that in diamond, it is probably not by the Bourgoin-Corbett mechanism [6]. Thirdly, there are various cases such as Si:Al_i where local heating may be effective [5]. In the III-V systems a range of phenomena (dislocation climb, colloid formation and defect reactions) has also been attributed to local heating (see refs. 1, 5, 6 and 16 for further discussion). Another interesting possibility occurs in CdS/Cu₂S cells where the Cu₂S may occur in the desirable chalcocite form or in the more stable but undesirable djurleite form. Some of the conditions for the phase transition are well understood. Can it be enhanced by high carrier densities also?

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