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A STUDY OF TRANSITION PROPERTIES IN AMORPHOUS SEMICONDUCTORS WITH LEVEL OF INJECTION

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Abstract: In amorphous semiconductors there are three important recombination processes, namely, recombination through correlated dangling bonds, recombination of free electrons by holes in the valence band tail and recombination of holes by localized electrons in the conduction band tail. It is necessary to understand the relative importance of these processes in determining lifetime of the carriers. Therefore, a study of recombination processes in steady state has been taken up in which, a transition from dangling bond dominated region to tail states dominated region is obtained in terms of level of excitation. For low level of excitation, the distribution of electrons and holes in the conduction band and valence band and in respective tails is determined by density of dangling bonds, whereas at high level of excitation the semiconductor becomes free from the influence of dangling bonds in determining the carrier densities. We find that interpretation in terms of quasi-Fermi levels provide a new insight into the physics underlying the recombination mechanism in amorphous semiconductors.

Key Words*:* Amorphous semiconductor, Charge densities, Dangling bonds, Recombination process, Fermi levels.

1. Introduction

A study of transient response of amorphous devices [1-2] requires a basic understanding of various recombination processes involved in semiconductor. Most of the existing theoretical models in this area have used a constant lifetime for recombination of electrons, their main emphasis being on thermalization process [3-6]. Some authors have considered recombination through dangling bonds explicitly but they have neglected recombination through tail states, all together [7-8].

With this model, variation of photoconductivity and lifetime with intensity of light in amorphous semiconductors in general and amorphous silicon in particular has been extensively studied experimentally as well as theoretically [9-14]. Most of these studies show that dangling bonds are the main recombination centers [9-10, 15-16].

A model which emerges out of these studies is that recombination takes place at dangling bonds and the localized tail states are trapping centers in which electrons and holes are captured and released to their respective bands as shown in Figure 1. Transitions corresponding to recombination through tail states have been shown by dotted lines in figure. This has been attributed mainly to the role of recombination at the dangling bonds which is highly intensity dependent and is dependent on the Fermi level positions. Occupation in tail states can be varied by changing position of the Fermi levels and therefore tail states act as sensitization centers for amorphous materials [9].

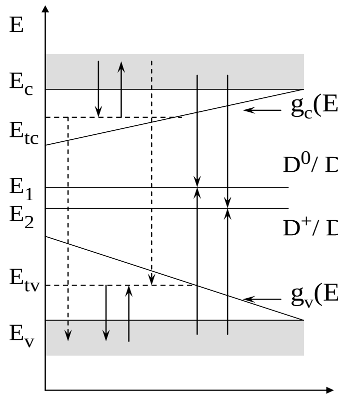

Figure 1: Schematic representations of energy states g_c (E) and g_v (E) and electronic transitions between these states.

In the present work we aim to account for all the process in a single theoretical model. The procedure is simple in which the recombination rate at dangling bonds is calculated as a function of carrier concentrations while maintaining the charge neutrality condition. Thus for a given value of free electrons the density of trapped electrons, free and trapped holes and charge density of dangling bonds is calculated for a neutral semiconductor and recombination rate for correlated dangling bond states is calculated accordingly. Since in a steady-state condition recombination rate is equal to the generation rate the dependence of photoconductivity on light intensity can easily be explained [17].

In this paper, we therefore adopt quasi Fermi level approach in which the level of excitation is given by separation of quasi Fermi level of free electrons (E_{fn}) and of free holes (E_{fp}). It is based on certain assumptions, namely, the semiconductor is assumed to exponential band tails and the density of tail states is large enough so that the multiple trapping and thermalization play an important role.

Initially we assume an ideal situation in which band tail electrons and holes are in thermal equilibrium with the free carriers [18-20] and common quasi Fermi level could be defined for free electrons and electrons in the tail states. Similarly a common quasi Fermi level is assumed for free holes and holes in the tail states. The effect of recombination via tail states will be discussed separately in a later section.

Our aim in this paper is to revisit this theoretical model with a view to provide a better insight into the underlying physical phenomenon. We investigate the phenomena with respect to an excitation level define in terms of difference in quasi-Fermi levels. We find that interpretation in terms of quasi-Fermi levels provide a new insight into the physics underlying the recombination mechanism in amorphous semiconductors. This study can help us in understanding clearly the variation in lifetime with level of excitation and its effect on photoconductivity [17]. We have developed the theory for hydrogenated amorphous silicon which has a low density of dangling bonds. This has been done due to its importance in photovoltaic devices [21, 22]. However the findings are general ones and may be applied to the other amorphous semiconductors.

2. Basic Equations

The basic feature in which an amorphous semiconductor deviates from the crystalline one is presence of band tail states. These states arise due to disorder in the lattice resulting in potential fluctuations and hence localization [23, 24]. In the simplest model [24] the electrons are free above energy, E_c, called the conduction band edge and are localized in energy states distributed exponentially in the band tail. We represent free electron density by n and the trapped electron density in the conduction band tail by n_t.

2.1 Charge Densities in Dangling Bonds

The main defect centers in amorphous semiconductors are dangling bonds. Transitions at dangling bonds are characterized by two energy levels; E_1 and E_2. The statistics of occupancies of dangling bonds is decided by correlation between them and has been studied in the literature quite extensively [25, 26]. These studies are mostly in terms of free electron and hole concentrations. For given values of n and p occupation probabilities for the three charge states f^+, f^- and f^0 are calculated by Dhariwal and Rajvanshi [8], then the recombination rate through dangling bonds is given as,

$$R_{db} = N_{db}\left[nc_{n1}\left(\frac{pc_{p1}+n_1c_{n1}}{nc_{n1}+p_1c_{p1}}\right)+nc_{n2}-n_1c_{n1}-n_2c_{n2}\left(\frac{nc_{n2}+p_2c_{p2}}{pc_{p2}+n_2c_{n2}}\right)\right]\times \left[1+\left(\frac{pc_{p1}+n_1c_{n1}}{nc_{n1}+p_1c_{p1}}\right)+\left(\frac{nc_{n2}+p_2c_{p2}}{pc_{p2}+n_2c_{n2}}\right)\right]^{-1} \quad (1)$$

here N_{db} is the dangling bond density and c_{n1}, c_{p1} and c_{n2}, c_{p2} are the capture rates for energy levels E_1 and E_2 for electrons and holes respectively, whereas n_1 and n_2 are the densities of electrons in the conduction band when Fermi level coincides with the energy levels E_1 and E_2 respectively. Similarly p_1 and p_2 are the densities of holes in the valence band when Fermi level coincides with the respective levels. We further introduce C_1 and C_2 as the ratio of charge to neutral capture rates by the dangling bonds at levels E_1 and E_2 respectively, so that $C_1 = c_{n1}/c_{p1}$ and $C_2 = c_{p2}/c_{n2}$.

In our discussion in the absence of availability of exact experimental data we shall assume the same value for this ratio as $C = C_1 = C_2$. However this is only assumed for convenience and C_1 and C_2 can be varied separately, if required.

2.2 Charge densities and Recombination at the tail states

Let us consider first a situation in which recombination proceeds mainly via dangling bonds. If we idealize such a situation we can neglect capture of holes by charged electrons tail states and that of electrons by charged holes tail states. Under this approximation, electrons and holes form independent thermodynamic systems; the electrons in the conduction band and in the tail states being in equilibrium with each other and the free and tail states holes being separately in equilibrium with themselves [19-20, 26]. Under these quasi equilibrium conditions one can write $E_{fnt}=E_{fn}$ and $E_{fpt}=E_{fp}$. For such a situation, for a reasonably excited semiconductor simple expressions for band tail electron and hole densities can be obtain in terms of their corresponding free states values. In thermodynamic equilibrium we have,

$$E_{fn} = E_{fp} = E_{f0} \tag{2}$$

When recombination proceeds through tail states, density of electrons and holes in these states get modified. If we assume tail states to behave like Shockley-Read traps, the recombination rate through valence band tail [27] is given by,

$$R_{tp} = c_{nvt}\, p_{tt} n \tag{3}$$

and that through conduction band tail is,

$$R_{tn} = c_{pct} n_{tt} p \tag{4}$$

where p_{tt} and n_{tt} are the density of holes in the valence band tails and density of electron in the conduction band tails respectively. The value c_{nvt} corresponds to capture rate for electrons trapped at energy level E_t in the valence band tail and c_{pct} is the capture rate for holes trapped at energy level E_t in the conduction band tail.

Since tail states are formed by large local potential energy fluctuations [24], a neutral conduction band tail state is also attractive to electrons, the same way as the charged trap state will be attractive to holes. Also, capture in charged tail states may be through a ladder of excited states and may follow statistics applicable to cascade capture [28, 29] allowing a large rate of re-emission. Thus the ratio of charge to neutral capture rates for band tail states may not be the same as that for dangling bonds. In the absence of much available data on the subject and less theoretical development in this area, we assume three typical values of ratio of charged and neutral capture rates for conduction and valance band tail states i.e. $C_{ct} = C_{vt} = C_t$ as 100, 1 and 0.01.

2.3 Semiconductor with small level of doping

In the calculations presented so far we have confined ourselves to a theoretical pure semiconductor in which dangling bonds are the only mid gap states besides the localized band tail states. Such a situation is not always possible in practice and in actual semiconductors thermodynamic equilibrium Fermi level, E_{f0}, differs from its ideal position. This is mainly due to presence of additional ionized impurities in the semiconductor and will remain fixed at a value of ($N_d^+ - N_a^-$), where N_d^+ and N_a^- are the concentrations of ionized impurities which are assumed to be shallow and hence ionized to the same extent throughout the calculations. The presence of these impurities moves the thermal equilibrium Fermi level up and down. We consider here a case in which such impurities make the semiconductor slightly n type.

2.5 The charge neutrality condition

Thus, charge neutrality condition for an amorphous semiconductor with considerations discussed above, becomes

$$\rho/q = p + p_{tt} - n - n_{tt} + N_{db}\left(f^{+} - f^{-}\right) + \left(N_d^{+} - N_a^{-}\right) = 0 \tag{5}$$

For a given value of n, one can determine the p, n_{tt}, p_{tt}, f^+, f^- and f^0 by a iterative methods to obtain a charge neutrality condition. Recombination rates can then be calculated by using Eq. (1), (3) and (4).

3. Calculations of Quasi-Fermi Levels

Our aim here is to understand the effect of various recombination mechanisms on the positions of quasi-Fermi levels.

3.1 An idealized case

We are starting with a highly idealized condition. Therefore, fully aware about the fact, we first consider a semiconductor in which there is very low density of recombination centers so that they do not contribute towards space charge neutrality i.e., we consider a semiconductor in which charge neutrality is maintained between localized and free electrons and holes.

Charges n, n_t, p and p_t are intrinsic to an amorphous semiconductor and even if low defect states exist, these charges will neutralize each other allowing one to determine Fermi level in thermal equilibrium and quasi-Fermi levels when excited. First let us consider an ideal situation in which all other charges have negligible densities, as compare to these four intrinsic charges. Thus an ideal intrinsic semiconductor is one, for which

$$\rho/q = p + p_t - n - n_t = 0 \tag{6}$$

As a further simplification we can assume at room temperature $n \ll n_t$ and $p \ll p_t$. This gives $n_t \approx p_t$ and therefore the position of the Fermi level in thermal equilibrium is given by,

$$E_{f0}^{i} \approx \frac{\alpha_1 E_c + \alpha_2 E_v}{\alpha_1 + \alpha_2} \tag{7}$$

Here α_1 and α_2 are the dispersion parameter for conduction and valance band tails respectively [27]. Now we apply, an excitation to the semiconductor, so that the excited carriers separate the quasi-Fermi level of electrons and holes by,

$$\Delta E = E_{fn} - E_{fp} \tag{8}$$

and therefore,

$$n \cdot p = \left[N_c N_v \exp \left(-E_g/kT \right) \right] \exp\left(\Delta E/kT \right) \tag{9}$$

where E_g is band gap of the semiconductor.

In terms of this excitation the individual quasi-Fermi levels, for an ideal semiconductor ($N_{db} \rightarrow 0$), become

$$E^i_{fn} = \frac{\alpha_1 E_c + \alpha_2 E_v}{\alpha_1 + \alpha_2} + \frac{\alpha_2 \Delta E}{\alpha_1 + \alpha_2} \tag{10a}$$

$$E^i_{fp} = \frac{\alpha_1 E_c + \alpha_2 E_v}{\alpha_1 + \alpha_2} - \frac{\alpha_1 \Delta E}{\alpha_1 + \alpha_2} \tag{10b}$$

The variations of E^i_{fn} and E^i_{fp} with respect to ΔE are plotted in Figure 2(a). For these calculations we have assumed parameters for amorphous silicon (a-Si :H) given in Table 1. These set of parameters have been assumed for illustration. However the findings are general are not restricted to this material. We shall like to emphasize that, this is an ideal condition which will exist in absence of all defects including dangling bonds. We term these levels as intrinsic quasi-Fermi levels. For a-Si:H, our calculations show that the intrinsic quasi-Fermi level of electrons is nearer to the conduction band as compare to that of holes. This is because of smaller depth of band tail states of conduction band, compared to the valence band tail states. Because of this property and due to the fact the mobility of electrons is large compare to that of holes; the conductivity of the semiconductor is determined mainly by electrons. As the excitation is applied, E^i_{fn} varies slowly compare to E^i_{fp} as shown in the Figure 2(a).

3.2 Effect of charges at dangling bonds

The actual semiconductor differs from the ideal one mainly due to the presence of dangling bonds. Because of which, the Fermi levels in thermal equilibrium and quasi-Fermi levels under excitation get modified to give neutrality condition (Eq. 5). For these calculations, we are neglecting the tails recombination; the value for C_t has been taken equal to zero. Figure 2(b), (c) and (d) show the variation of quasi-Fermi levels for three values of dangling bond density N_{db} equal to $10^{15}cm^{-3}$, $10^{16}cm^{-3}$ and $10^{17}cm^{-3}$ respectively. An important feature of these results is that the presence of dangling bonds pushes the thermal equilibrium Fermi level to the middle of dangling bond states E_1 and E_2 from where, E_{fn} moves up and E_{fp} moves down till they meet the intrinsic levels E^i_{fn} and E^i_{fp}.

The role of dangling bonds in amorphous semiconductor is therefore, not only in determining the recombination but also in modifying the quasi-Fermi levels of electrons and holes. As the level of excitation is increased the semiconductor tends to get itself free from the influence of dangling bonds. Thus in terms of excitation the semiconductor can be divided in two parts; for low levels of excitation E_{fn}, E_{fp} and carrier densities are determined by dangling bonds, whereas at higher excitations the semiconductor behaves like an intrinsic semiconductor as far as charge distribution is concerned. These results show that the shifting of thermal equilibrium Fermi level due to dangling bonds is almost independent of density of dangling bonds.

However, the level of excitation at which the transition occurs from defect dominated to intrinsic region varies with dangling bond density. It is important to note that the excitation level ΔE represents the separation between the quasi-Fermi levels of electrons and holes and for devices like solar cell made of such materials corresponds to an excitation voltage V which is equal to the terminal voltage under the open circuit condition and the flat band approximation [21-22]. Thus the calculation of quasi-Fermi levels and their transition can also be understood in terms of circuit conditions.

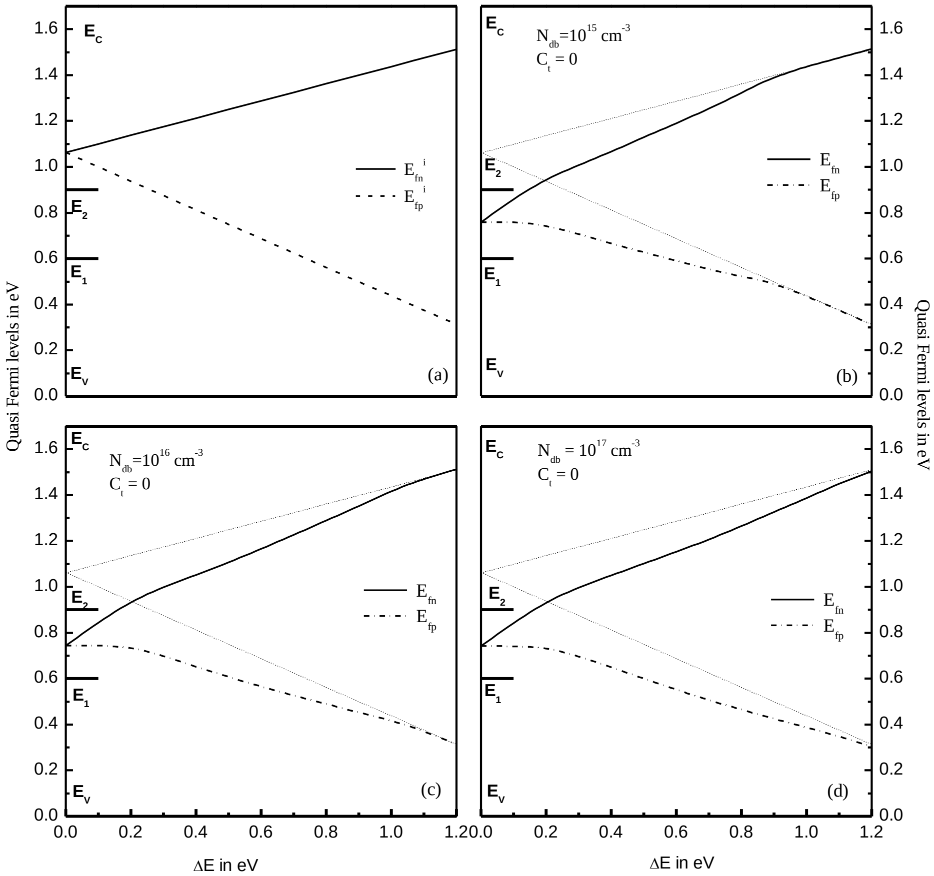

Figure 2: Plot of quasi-Fermi levels E_{fn} and E_{fp} against $\Delta E = (E_{fn} - E_{fp})$. Figure (a) shows E_{fn}^{i} and E_{fp}^{i} when semiconductor is intrinsic. Dotted lines show the quasi-Fermi levels for intrinsic case. Figure (b), (c) and (d) are for dangling bond density N_{db} equal to 10^{15} cm^{-3}, $10^{16} cm^{-3}$ and 10^{17} cm^{-3} respectively

Table 1: Semiconductor parameters used for numerical calculations

Parameters	Values
E_g	1.7 eV
E_1- E_v	0.6 eV
E_2- E_v	0.9 eV
C	100
c_{n2}, c_{p1}	10^{-9} cm^3 sec^{-1}
c_{n1}, c_{p2}	10^{-7} cm^3 sec^{-1}
c_{nct}, c_{pvt}	10^{-9} cm^3 sec^{-1} (when C_t = 100)
c_{nvt}, c_{pct}	10^{-7} cm^3 sec^{-1}(when C_t = 100)
c_{nct}, c_{pct}, c_{nvt}, c_{pvt}	10^{-8} cm^3 sec^{-1} (when C_t = 1)
c_{nct}, c_{pvt}	10^{-7} cm^3 sec^{-1} (when C_t = 0.01)
c_{nvt}, c_{pct}	10^{-9} cm^3 sec^{-1}(when C_t = 0.01)
μ_n	20 cm^2/V-sec
μ_p	2 cm^2/V-sec
α_1	0.95(at 300 K, E_{tc} = 0.0272)
α_2	0.57(at 300 K, E_{tv} = 0.0454)

3.3 Effect of small doping

Let us now consider the effect of change in thermal equilibrium Fermi level, E_{f0}, due to doping on the neutrality condition (Eq.5). The quasi-Fermi levels, when the semiconductor is excited and the charge neutrality is maintained, are calculated for different values of thermal equilibrium Fermi level, E_{f0}. Figure 3(a) shows the plot for E_{fn} and E_{fp} without any impurity level so that E_{f0} is equal to 0.75eV, whereas in Figure 3(b), (c) and (d), the thermal equilibrium Fermi levels are assumed at 0.85eV, 0.95eV and 1.05eV respectively.

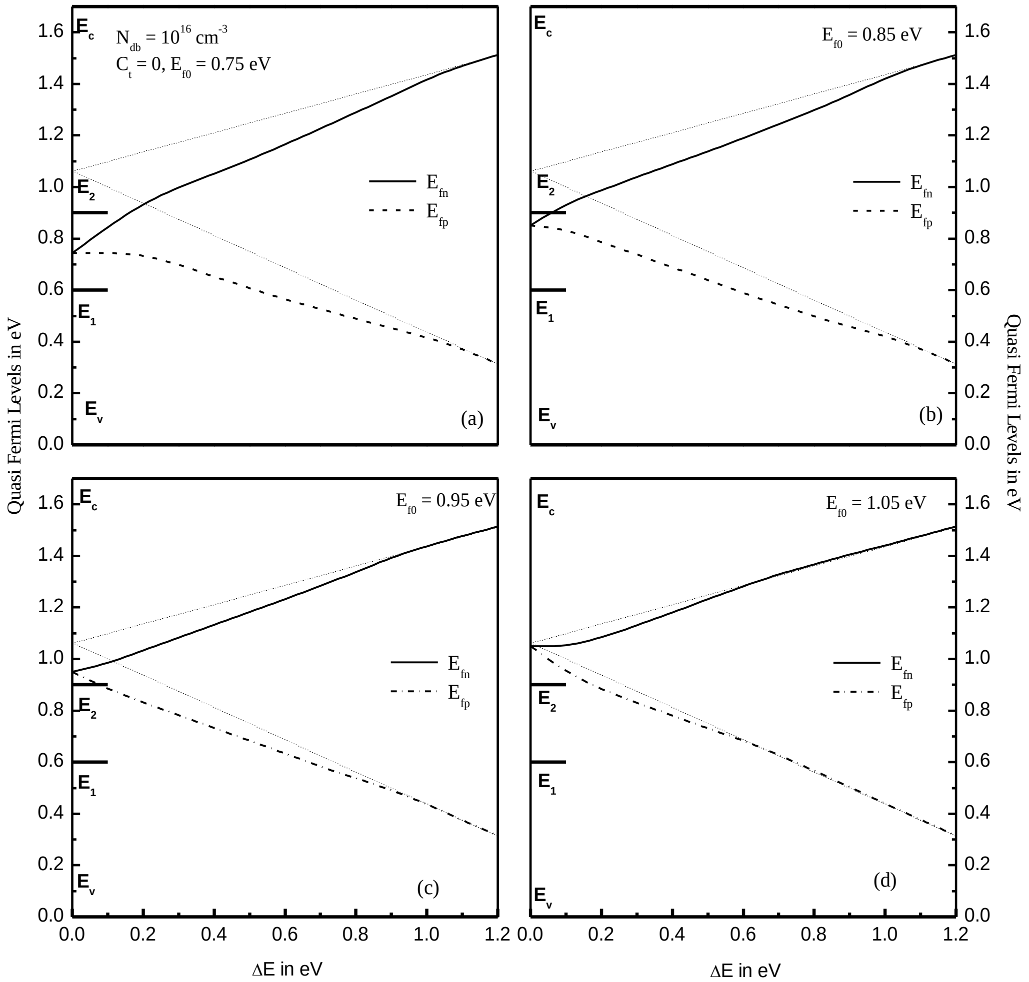

Figure 3: Quasi-Fermi levels E_{fn} and E_{fp} plotted against ΔE when small doping exists in semiconductor. For the calculations $N_{db}=10^{16}$ cm^{-3}and $C_t = 0$ has been assumed. Figure (a) shows the curve for $E_{f0} \approx 0.75$ eV (without impurities) and in figures (b), (c) and (d), thermal equilibrium Fermi level E_{f0} is taken at 0.85ev, 0.95ev and 1.05ev respectively.

As is clear from this figure, the upward movement of E_{f0} moves the transition from higher excitation level to lower excitation level. Thus the role of impurities other than the dangling bonds is to move the level of excitation for the transition backward or forward depending on the nature and density of impurities.

We find that shift is mainly due to a change in the density of neutral dangling bonds in thermal equilibrium. When E_{f0} moves up the density of D^0 states reduces and quasi-Fermi levels are shifted as shown in the figure. This result is in agreement with the theoretical calculations of Bube et al [5], Zeldov and Weiser [30] who have observed a similar shift in photoconductivity in terms of generation rate as the Fermi level position is changed. We obtained the result in terms of the excitation level and transition of quasi-Fermi levels. Thus our calculations provide a physical interpretation to prediction made by Bube et al [30].

3.4 Effect of recombination through tail states

Now let us calculate the variation in quasi-Fermi levels of electrons and holes due to the recombination through tail states. The variation in quasi-Fermi levels, by changing the values of E_{f0} for C_t = 100 is shown in Figure 4. Transitions similar to those shown in Figure 3 arise here also, though the sharpness of transition is somewhat reduced and we find that transition shifts to lower energy value for a higher value of E_{f0}. In Figure 5(a) a comparison.

has been made of quasi-Fermi levels for C_t = 100 and by taking different values of E_{f0} whereas in Figure 5(b) calculations have been done by varying the C_t. We have done these calculations for a single dangling bond density ($N_{db} = 10^{16}$ cm^{-3}). We find that, the value of ΔE at which transition occurs does not depend much of the value of C_t.

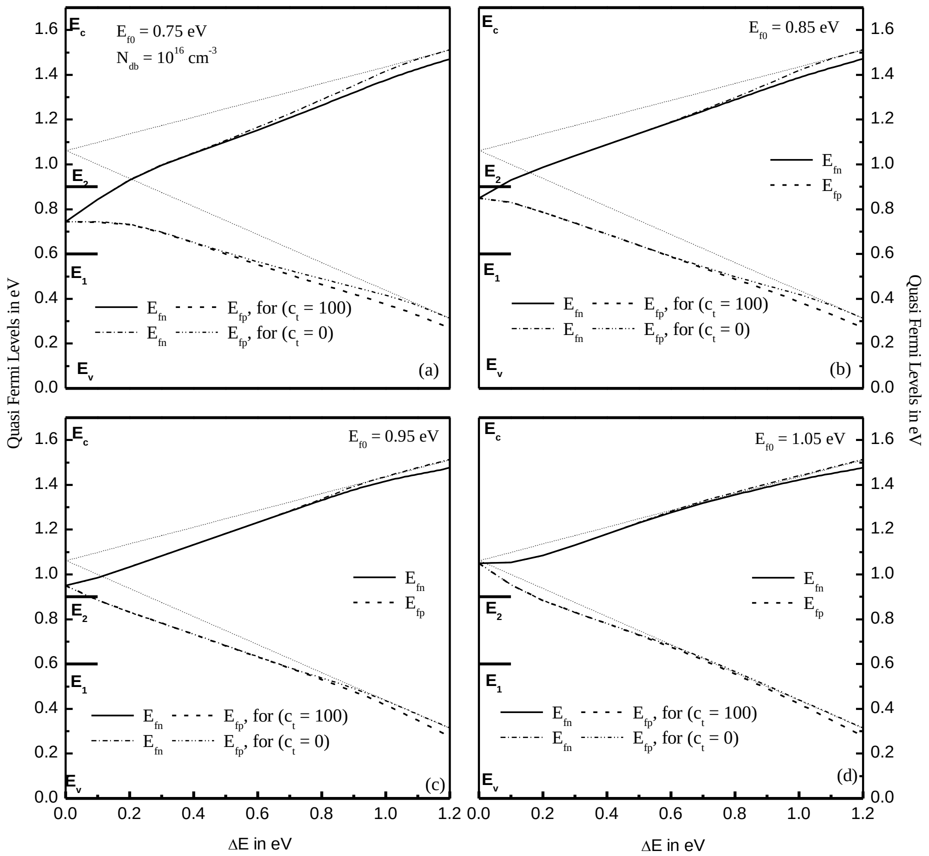

Figure 4: Plots of quasi-Fermi levels E_{fn} and E_{fp} against ΔE, by taking tails recombination also into account for $N_{db} = 10^{16}$ cm^{-3} and C_t =100. Figures (a), (b), (c) and (d) are plotted by varying the thermal equilibrium Fermi level, E_{f0} as 0.75, 0.85, 0.95 and 1.05 eV respectively.

The calculations presented so far reveal that in terms of level of excitation the semiconductor has two regions; one for low level of excitation in which defects and impurities determine E_{fn} and E_{fp} and the other at higher level of excitation for which charge distribution is determined by the intrinsic level of the semiconductor defined in terms of density of states in conduction band and valence band and their tail states. The transition is quite well defined and has important consequences in determining photoconductivity and carrier lifetime.

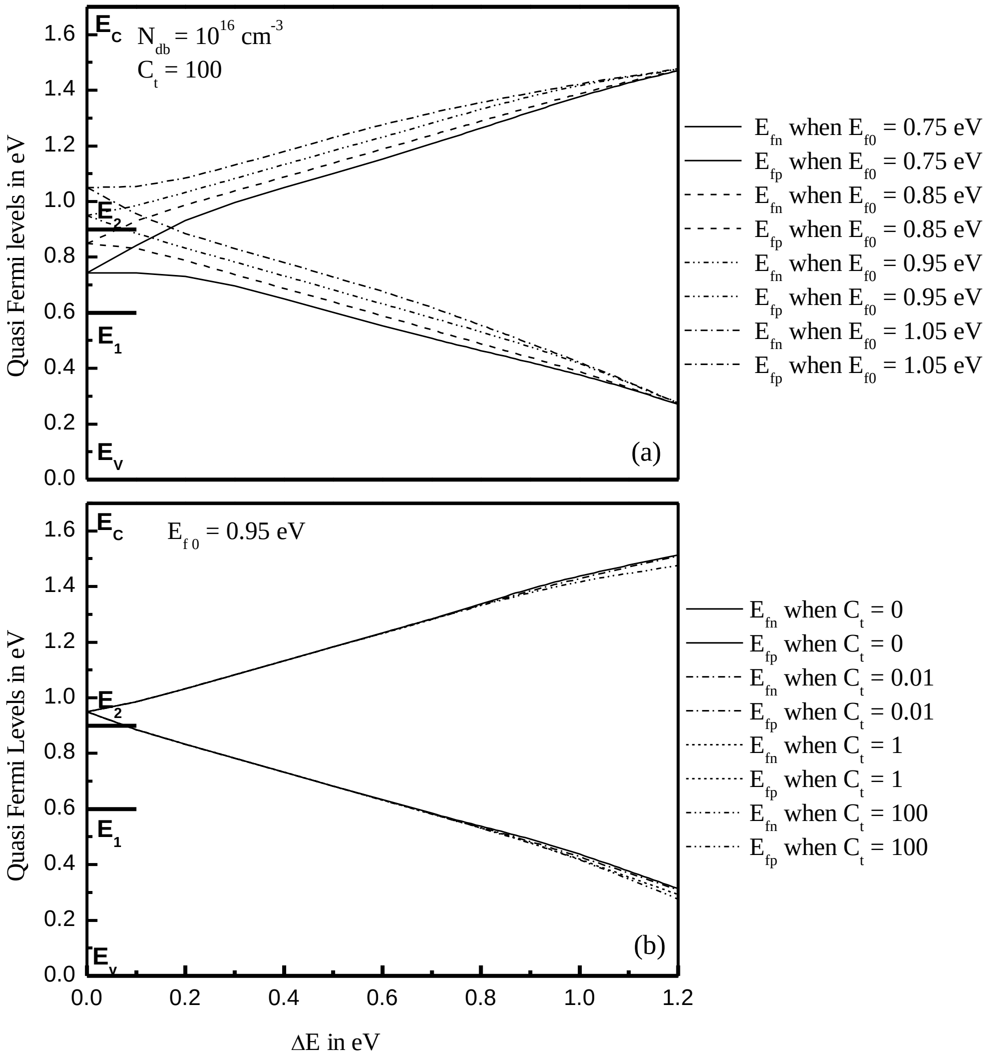

Figure 5: Plots of quasi-Fermi levels E_{fn} and E_{fp} against ΔE, by taking tails recombination also into account for $N_{db} = 10^{16}$ cm^{-3}. Figure (a) is plotted for various values of E_{f0} = 0.75, 0.85, 0.95 and 1.05 eV by taking C_t =100. Figure (b) is plotted for C_t = 100, 1 and 0.01 at E_{f0} = 0.95 eV.

4. Results and Conclusions

From the calculations presented above we find that recombination in amorphous semiconductors is a more complicated phenomenon than in crystalline semiconductors because of comparable charge densities in tail states and in the dangling bonds resulting in two distinctly separate regions; one dominated by dangling bond charges and other by tail state charges intrinsic to the semiconductor. The analysis is presented in terms of level of excitation $\Delta E = E_{fn} - E_{fp}$. Values of various parameters corresponding to amorphous silicon have been chosen for illustration. However conclusions are general ones and can be applied to other materials also. We summarize our findings below,

1. We can define an ideal semiconductor by the properties of the conduction band and valence band states (both continuous and localized). For this ideal condition two intrinsic quasi-Fermi levels E^{i}_{fn} *and* E^{i}_{fp} can be define as shown in Figure 2(a). These quasi-Fermi levels results from the consideration of basic properties of the material and are intrinsic to the semiconductor therefore we have named them as intrinsic quasi-Fermi levels.
2. Dangling bonds form an essential part of an amorphous semiconductor. In their presence we obtain the actual quasi-Fermi levels E_{fn} and E_{fp}. Under the assumption of thermalization of free and trapped charges we can assume $E_{fnt} \approx E_{fn}$ and $E_{fpt} \approx E_{fp}$.
3. Movement of thermodynamic Fermi level E_{f0} due to the presence of other impurity in the semiconductor may shift the position of the transition as shown in Figure 3.
4. Though physically the dangling bonds must be the main recombination centers if recombination should proceed through tail states also, their effect is to charges to neutral capture rates may not be same for dangling bonds and the tail states.
5. We find that in terms of level of excitation $E_{fn} - E_{fp}$, the semiconductor can be divided in two regions; the first region is dangling bond charge density dominated and the second is tail states charge dominated. For low level of excitation, the distribution of electrons and holes in the conduction band and valence bands and in respective tails is determined by the density of dangling bonds, whereas at high level of excitation the semiconductor becomes free from the influence of dangling bonds in determining the carrier densities.

An assumption common with all other workers has been that the capture cross-section ratio of all neutral localization states is equal and can be given a single value. Similarly the ratio of rates of charged to neutral captures has been assumed to be a constant for a given material. These assumptions have been taken in the absence of insufficient experimental data available in this area, which of course simplifies the calculation. However, even with these simplifications there is a much scope for study by varying the various physical parameters and by using different materials. Since we have aim ourselves to developing a model for the calculation these comparative calculation have not been done except for the movement of Fermi level which is crucial for the device operation.

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