

The quasineutrality condition in amorphous semiconductors: Reformulation of the 'lifetime/relaxation' criterion

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Abstract

The concepts of lifetime and relaxation semiconductors introduced by van Roosbroeck and Casey are reconsidered for *amorphous* semiconductors and the effect of localized states on the lifetime/relaxation criterion specified: The quantity to be considered is τ_p/T_d , where T_d is (as before) the dielectric relaxation time, but τ_p is now the lifetime of the *total* charge including charge stored in localized states. τ_p is equal to the free carrier lifetime times a correction factor that is much larger than unity for amorphous semiconductors. Bandtail states and dangling bonds act differently on the criterion. The correction factor is frequency-dependent and decreases at higher frequencies. Two illustrative experimental examples (low substrate temperature a-Si:H, a-SiC:H alloys) are given, showing borderline cases.

1. Introduction

In classical semiconductor device theory, as developed e.g. for crystalline silicon, 'quasi-neutrality' is a key concept. Quasineutrality simplifies the mathematical treatment of the drift-diffusion equations in the 'bulk' regions of p-n diodes; it is used to define the concept of an 'ambipolar diffusion length L_{amb} ' for intrinsic (i) material.

In 1972 van Roosbroeck and Casey [1] pointed out that typically in large-gap and/or amorphous semiconductors, quasineutrality may no longer be guaranteed in the same situations as before; they distinguished between 'lifetime' and 'relaxation' semiconductors: The first category behaves in the same way as e.g. crystalline silicon and quasi-linear-

ity is easily achieved, the second category behaves in an altogether different fashion. The criterion introduced by them to distinguish between lifetime and relaxation semiconductors is the ratio τ/T_d , where τ is the carrier lifetime and $T_d = \epsilon/\sigma$ the dielectric relaxation time (ϵ : dielectric constant; σ : electrical conductivity).

Because dangling bonds present in amorphous hydrogenated silicon (a-Si:H) act as recombination centers, Ritter et al. [2], who successfully introduced the grating method to measure L_{amb} for a-Si:H, were worried about the lifetime status here. Indeed, if a-Si:H does not behave like a lifetime semiconductor, then SSPG (solid state photoconductive grating) would not yield the value of the ambipolar diffusion length at all. Theoretically, Hubin et al. [3] came to the conclusion that a-Si:H would typically *not* be a lifetime semiconductor. In their analysis, Hubin et al. neglected, like all previous authors, the space charge contributed by charged dangling bonds and took as

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the carrier lifetime τ to be inserted into the Roosbroeck–Casey criterion the free carrier lifetime.

Since then a considerable amount of work has been published on the measurement of L_{amb} in a-Si:H. Surprisingly, no indication at all was found to the effect that a-Si:H behaves other than as a lifetime semiconductor, and this even for degraded samples.

There are, in fact, two ‘experimental tests’ to determine whether the SSPG measurement is actually conducted under quasineutral conditions and therefore yields the correct value of L_{amb} : The first test is phenomenological: one plots the quantity obtained and suspected to be L_{amb}^2 versus bias light intensity; if this quantity varies only slightly, e.g. according to a power law with an exponent γ whose magnitude is about 0.3 or less, than one has in all likelihood really obtained L_{amb}^2 (A low value of γ can be theoretically predicted for L_{amb}^2 [4], whereas the square of the corresponding characteristic length for the relaxation regime would have a power-law exponent near to 1.) The second test has a more theoretical basis: one plots the quantity $1/\Lambda^2$ versus $\sqrt{2/(1-\beta)}$ (where Λ is the geometrical grating period and β is the ratio between photocurrent with and without grating). This plot was introduced by Balberg et al. [5]. As shown by Sauvain, without taking into account the dangling bond charge [6], or considering all localized state charges [7], the linearity of this so-called ‘Balberg plot’ is a test for the prevalence of the lifetime regime; this plot yields a straight line if and only if both the lifetime regime and the ambipolarity condition hold.

The purpose of the present paper is twofold: First, to show how exactly the van Roosbroeck–Casey criterion has to be interpreted when one deals with amorphous semiconductors; second, to give some results on ‘borderline’ cases, where the lifetime condition is barely fulfilled or even not fulfilled.

2. Theoretical development

Consider an uniform layer in which only free carriers contribute to the electronic steady-state transport, by diffusion and under the effect of a local electric field; this means that only diffusion currents and dielectric relaxation currents contribute to trans-

port (case of negligible external applied field). Use a small-signal approach, considering a small perturbation of an otherwise spatially uniform situation. The uniform situation can result from thermal equilibrium or from a large-signal ‘working point’ due to a large bias illumination (as in SSPG). Local neutrality is assumed to be maintained under the non-perturbed situation. For the special case where there is no external excitation one has:

$$0 = -\Delta R + \frac{1}{e} \operatorname{div}(\Delta j_{n,p}^{\text{relax}} + \Delta j_{n,p}^{\text{diff}}). \quad (1)$$

Here, the symbol Δ indicates small-signal quantities, $\Delta j_{n,p}$ are the current densities of free electrons and holes, respectively, $\Delta j_{n,p}^{\text{diff}}$ the diffusion current densities, ΔR is the recombination rate, and $\Delta j_{n,p}^{\text{relax}}$ the dielectric relaxation current densities, given by $(\sigma_{n,p} \Delta E)$ with $\sigma_{n,p}$ as the electron and hole contributions to conductivity. ΔE is the internal electric field and is due only to a small-signal space charge $\Delta \rho = \Delta \rho^+ - \Delta \rho^-$, so that $\operatorname{div}(\Delta E) = \Delta \rho / \epsilon$. $\Delta \rho$ includes free as well as localised carrier densities. Thus, one obtains:

$$\operatorname{div} \Delta j_{n,p}^{\text{relax}} = \Delta \rho / T_{dn,dp}. \quad (2)$$

Note that for the case of bias illumination (as in SSPG), $\sigma_{n,p}$ will have to be substituted by $\sigma_{phn,p}$, i.e. by the contribution of electrons and holes, resp., to the photoconductivity at bias illumination.

By combining Eqs. (1) and (2), one obtains:

$$0 = -\Delta R + \frac{1}{e} \frac{\Delta \rho}{T_{dn,dp}} + \frac{1}{e} \operatorname{div} \Delta j_{n,p}^{\text{diff}}. \quad (3)$$

The lifetime condition expresses that in Eq. (3), the second term (the dielectric relaxation current) is much larger than the first term ΔR . The lifetime criterion for amorphous semiconductors therefore reads:

$$\tau_{\rho}^{-,+} = \frac{1}{e} \frac{\Delta \rho^{-,+}}{\Delta R} \gg T_{dn,dp}. \quad (4)$$

That is to say: one has to introduce the lifetime of total charge (free carriers + localized carriers) $\tau_{\rho}^{-,+} = \Delta \rho^{-,+} / (e \Delta R)$ instead of the lifetime of free carriers alone, and it is this new quantity that has to be compared with $T_{dn,dp}$. (In relaxation semiconductors one has on the contrary $\tau_{\rho}^{-,+} \ll T_{dn,dp}$.)

Let η represent either the free electron density n_f or the free hole density p_f . $\tau_{\rho}^{-,+}$ can then be expressed as the product of the free carrier lifetime $\tau_{\eta f} = \Delta\eta/\Delta R$ times a corresponding correction factor:

$$\tau_{\rho}^{-,+} = \frac{1}{e} \frac{\Delta\rho^{-,+}}{\Delta R} = \frac{1}{e} \frac{\Delta\rho^{-,+}}{\Delta\eta} \tau_{\eta f}, \quad \eta = n_f, p_f. \quad (5)$$

In a-Si:H, the total charge is essentially constituted by localized carriers (free carrier contribution being negligible). Thus, the correction factor in Eq. (5) is much larger than unity and $\tau_{\rho}^{-,+} \gg \tau_{\eta f}$.

Thus, for amorphous semiconductors, the free carrier lifetimes can be of the same order of magnitude or smaller than the dielectric relaxation times, even while the 'total charge lifetime' $\tau_{\rho}^{-,+}$ is still large enough so that the lifetime regime holds.

Let us distinguish now between traps (typically bandtail states) and recombination centers (typically dangling bond states): (a) Traps are in interaction mainly with a single type of free carriers and will, thus, directly contribute to $\tau_{\rho}^{-,+}$ without affecting $\tau_{\eta f}$. They will therefore reinforce the lifetime status. (b) Recombination centers interact with both types of free carriers, their charge state typically depending on the ratio (n_f/p_f). If everything was symmetrical w.r.t. holes and electrons, their charge state would not change with $\Delta\eta_f$. a-Si:H has an asymmetrical density of states (difference in bandtails) and therefore they contribute here to $\Delta\rho^{-,+}$. On the other hand, they also decrease $\tau_{\eta f}$, so that they have, in a-Si:H, little net effect on the lifetime status.

In contrast to the lifetime condition, the *ambipolarity condition* has to do with the particular excitation function present (in the case of SSPG, the 'small-signal' excitation function, e.g. the grating itself).

For quasineutrality to be present (and, thus, for the SSPG experiment to be correctly executed) both lifetime and ambipolarity conditions will in general have to be fulfilled. This is evident if one studies a mathematical development [8], in terms of the eigenvectors of the corresponding linearized system of differential equations, linearized around the 'working point' as defined by the bias light.

The *dynamic grating experiment* [9] has recently provoked interest. To obtain a manageable formalism

for this experiment one should be able to judge, a priori, whether one is working in a lifetime or in a relaxation situation. As the process of exchange between charge stored in localized states and free carriers is subject to time delays which can be much larger than those involved in free carrier movement, it is quite possible to envisage an amorphous semiconductor that has a lifetime character for steady-state but becomes a relaxation semiconductor for dynamic situations at higher frequencies. In other words, the correction factor $1/e \cdot \Delta\rho^{-,+}/\Delta R$ is frequency-dependent and basically decreases with frequency. One needs to study this problem in future far more carefully, in order to obtain any useful information from dynamic grating experiments.

3. Illustrative experimental examples

The authors have studied two 'limit' cases: (A) 'Bad quality' a-Si:H produced at low substrate temperatures and (B) a-Si,C:H alloys. Fig. 1 shows typical results for the first case (layer deposited at 100°C): There is here no doubt at all w.r.t. the lifetime condition. Both tests are o.k.: The deduced value of L_{amb}^2 follows a power law with an exponent (-0.2) and the 'Balberg plot' is clearly linear. Fig. 2 shows a typical result for an a-Si,C:H alloy (possessing a Tauc gap of 1.85 eV): The Balberg plot appear to be nonlinear, so that no value of L_{amb} can be

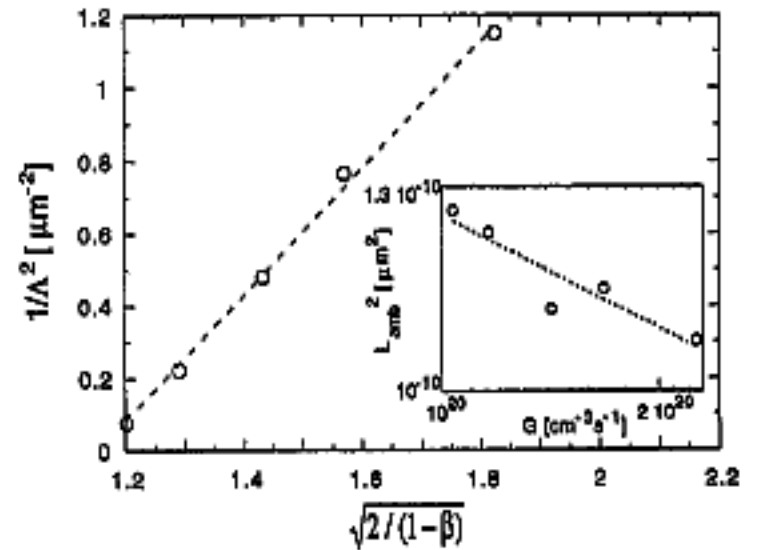


Fig. 1. SSPG plot for a-Si:H deposited at low substrate temperature (100°C); $1/A^2$ versus $\sqrt{2/(1-\beta)}$ is here a straight line (see text), indicating lifetime conditions. Inset: L_{amb}^2 versus generation rate exhibit a power law exponent of -0.2.

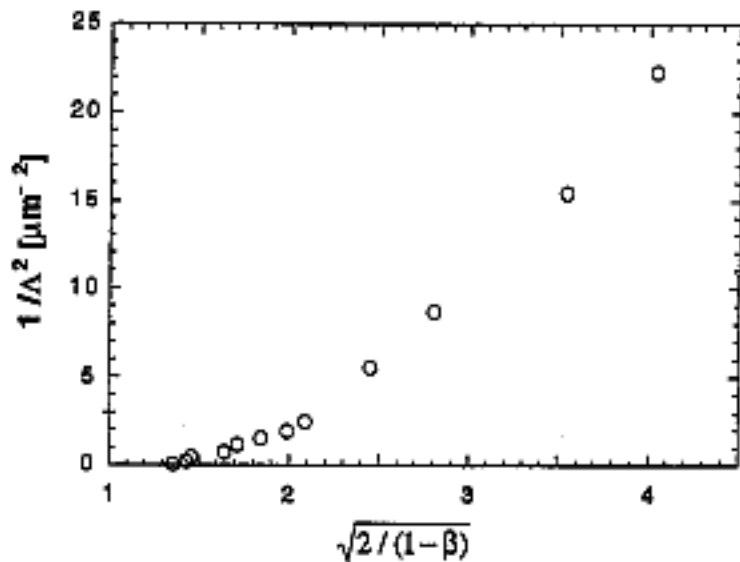


Fig. 2. SSPG plot as in Fig. 1, but for an a-Si,C:H sample ($E_{\text{opt}} = 1.85$ eV). No straight line is obtained and lifetime conditions are not assured.

reasonably deduced. Thus, the first test for the prevalence of lifetime conditions, i.e. a 'weak' dependence of L_{amb}^2 on bias light intensity (e.g. power law exponents with a magnitude well below 0.5) was not performed. The authors have found, for most a-Si,C:H layers investigated, Balberg plots which are nonlinear. A doubt persists because the non-linearity may be due a strong (and rapid) light-induced degradation effect that could possibly have taken place *during* the SSPG measurement itself or due to a change in the reflexion coefficient for the laser beams at small grating lengths. Thus further experimental work is needed here.

4. Conclusions

Ever since the introduction of the concept of 'relaxation semiconductor' [1], there has been a strong suspicion that certain amorphous semiconductors should fall into this category. It was shown here that the van Roosbroeck-Casey criterion [1] for distinguishing between relaxation and lifetime semiconductors needs to be modified, by adding a correction

factor that increases the 'effective' lifetime, taking thereby into account charge stored within localized states. This explains why illuminated a-Si:H, even if degraded and/or of poor quality is, in general, a lifetime semiconductor. The latter statement has been substantiated here by the use of two experimental tests, as shown in illustrative experimental examples. It would be intellectually satisfying if a clear example of a relaxation semiconductor could be identified. As of now, a-Si,C:H seems to be a borderline case, but a clear diagnosis cannot be given as yet. Of practical significance for the immediate future is an adaptation of the above considerations to the dynamic case. This task is a priority, if one wants to make sense of dynamic grating experiments.

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