Modulation Frequency-Dependence of Photocurrent in Amorphous Si:H p-i-n and Chalcogenides

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Received 12.07.1999

Abstract

The effects of modulation frequencies (up to 35 kHz) on the intensity- and temperature-dependence of photocurrent of amorphous (a-) Si:H p-i-n and chalcogenide glasses (a-Se and a-As$_2$Se$_3$) were investigated in detail. The variation of exponent $\nu$, and in the power-law relationship $\sigma_{ph} \propto G^{\nu}$ between the photoconductivity (or photocurrent) and the generation flux, with modulation frequency in chalcogenide glasses is found to be much stronger than that of a-Si:H p-i-n. The activation energies, calculated from the temperature-dependent photocurrent, were determined at different modulation frequencies. We conclude that the activation energy increases with increasing modulation frequencies at low excitation intensities. The results are also compared with the predictions of multiple-trapping (MT) and distant-pair (DP) models developed for photoconductivity of a-semiconductors at high and low temperatures, respectively.

PACS no.: 72.80.Ng; 73.50.Gr; 73.60.Cs

1. Introduction

The band structure of a real amorphous semiconductor shows energy levels associated with defect states in the gap, and this directly indicates the complexity of the analysis of the experimental photocurrent (PC) data. Therefore it is important to understand the nature of the gap states of a-semiconductors and the effect of these states on the recombination of photogenerated carriers. Many techniques have been applied to investigate the gap states of a-semiconductors. PC measurements, particularly as a function of temperature and illumination intensity are quite common in the characterization of a-semiconductors, and yield considerable information about recombination kinetics. Although these measurements are relatively easy to carry out, the interpretation of data is still difficult.

In this paper, we present some frequency dependent PC results for a-Si:H p-i-n and chalcogenide glasses. Both in-phase ($\phi = 0^\circ$) and in-quadrature ($\phi = 90^\circ$) outputs were used. The in-quadrature output is the most useful form, the in-phase version can also give important additional information on the existence of fast processes beyond the time domain of the in-quadrature measurements. It is worth remembering that, if one knows the quadrature response from angular frequency $\omega = 0 \rightarrow \infty$, a Kramers-Kronig transform [1] will give the in-phase response. That is, all the information is in either response, if complete in $\omega$. In the literature there are many reports of PC studies on the materials examined here, however in almost all these, the data were taken under steady state (d.c or f=0) conditions. Our results, in contrast, are taken at modulation frequencies up to 10 kHz.

2. Experimental Details

The samples of a-Si:H p-i-n junction solar cells used in this work were obtained from the company Casio, which uses them in commercially available pocket calculators. Their intrinsic layer thicknesses were about 0.8 – 1 $\mu$m. For electrical measurements, one of the many individual cells (each of 1 cm$^2$ area) was chosen,
and by removing the aluminium insulating paint on its back, suitable copper wire contacts were made with electrically conductive silver paint.

The samples of a-calcogenides (a-Se and a-As₂Se₃) used were thin films prepared by thermal evaporation. The materials used for these samples are from BDH chemicals, and their purities were 99.9992%. During the thermal evaporation of the films, the work chamber pressure was less than 10⁻⁶ Torr. The substrate (Corning 7059 glass) was held at room temperature (295 K). The thicknesses of most of the samples were of the order of 1μm. It should be indicated that measurements taken on thicker (up to 10μm) and thinner (down to 0.5μm) samples showed that the results were independent of the thickness in this range. Gold or aluminium contacts were then evaporated on the film in a coplanar configuration. The planar distance between the contacts was 0.1 mm. Copper wires were placed on the gold or aluminium layers with electrically conductive silver paint. The current-voltage (I-V) measurements taken in dark proved that the contacts were perfectly ohmic. As noted previously [2], gold contacts perform better in injecting hole carriers and thus give larger photocurrents than aluminium contacts for these a-chalcogenide samples.

Fact sample was excited by the 1.96 eV (632.8 nm) line of a HeNe laser. An acousto optic modulator (IntraAction Corp., Model AOM-125) was used to modulate the light sinusoidally in the frequency range of 10 Hz to 100 kHz. The modulation amplitude amounted to 46% of the bias light intensity. The modulated photocurrent signal excited in this way was measured and analysed by a lock-in amplifier (Stanford Research Systems SR 530). The advantage of this frequency locked a.c. measurement is that it rejects stray light, dark current and other unmodulated signals. During the measurements the sample was kept in a helium exchange-gas cryostat in which the temperature could be varied between room temperature and 20 K. The vacuum pressure of the cryostat was about 10⁻⁶ Torr. The intensity of the excitation light was reduced by neutral density filters (1 mW corresponds to about 1 × 10¹⁹ photons cm⁻² s⁻¹ in our results).

3. Theory: Phase Shift Analysis

The photocurrent (PC) and its dependence on the intensity of illumination and temperature were used to characterize the recombination and the carrier lifetimes. In crystalline semiconductors, steady state PC has been extremely successful in determining the recombination centre parameters, in particular, the location of the level in the forbidden gap. If one type of dominant recombination centre is present, the nonequilibrium lifetime is governed by the processes of electron capture and subsequent hole capture by the local levels of the dominant centre, and for this simple case the rate analysis is straightforward. In steady state, the generation rate of carriers is equal to the recombination rate. However, when different defect centres act as trapping and (or) recombination levels, the analysis becomes much more complicated since one has to consider a whole set of possible electron and hole transitions and write down corresponding equations describing the rate of change of occupation of the levels.

Phase shift analysis of modulated photocurrent has been reviewed in a number of articles [3, 4, 5, 6, 7]. The method is based on the analysis of the phase shift between a sinusoidally modulated excitation light and its inducting photocurrent as shown in Figure 1(a). It is suggested that this method is useful for a-semiconductors in which the localized states are distributed quasi-continuously in the band gap. The model derived by Oheda [3] for modulated photocurrent assumes unipolar extended-state conduction by electrons, with trapping in states distributed below the mobility edge. Following Oheda, we present some derivations here. Figure 1(b) illustrates a semiconductor with four transition processes considered. The band-to-band generation rate of mobile carriers can be expressed as the sum of a dc term \( f_o \) and an alternating term of amplitude \( f_1 \) and angular frequency \( \omega \). Interaction of electrons with the distribution \( N(E) \) of localized states occurs by trapping of mobile electrons \( n \), and release of the distributed trapped electrons \( n_t(E) \). Recombination of mobile electrons is represented by a transition with characteristic small-signal time constant \( \tau \). Then the rate equations for the mobile and trapped electron densities can be described as

\[
\frac{dn}{dt} = f_o + f_1 \exp(i\omega t) - \int_{E_{fc}}^{E_c} \frac{dn(E) dE}{dt} - \frac{n - n_d}{\tau}
\]  

(1)
Figure 1. (a) Existence of phase shift between sinusoidally modulated excitation light and the induced current; (b) Energy level diagram for the analysis of the modulated photocurrent, showing the energy states and processes taken into account.

\[
\frac{dn_t(E)}{dt} = n \vartheta \sigma \left[ N_t(E) - n_t(E) \right] - N_e \vartheta \sigma n_t(E) \exp\left(-\frac{E_c - E_{F_n}}{kT}\right) \tag{2}
\]

where \(n_d\) is the value of \(n\) in the dark, \(E_{F_n}\) is the electron quasi-Fermi level, \(\vartheta\) is the thermal velocity, \(\sigma\) the electron capture cross-section and \(N_e\) the effective density of states in the conduction band. The solution of the rate equations are expected to have the form

\[
n = n_o + n_1 \exp(\imath \omega t) \tag{3}
\]

with alternating term

\[
n_1 = \frac{f_1}{(A^2 + B^2)^2} \exp(\imath \phi), \tag{4}
\]

where the “in-phase” term \(A\) is given by

\[
A = \frac{1}{\tau} + \int_{E_{F_n}}^{E_c} G_2(E) \vartheta \sigma N_t(E) dE, \tag{5}
\]
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the “in-quadrature” term $B$ is given by

$$B = \omega + \int_{E_f}^{E_c} G_1(E) \partial \sigma (E) dE,$$

and the phase shift $\phi$ between the excitation and the modulated current is given by

$$\tan \phi = \frac{B}{A}.$$  

(7)

The weighting functions $G_1(E)$ and $G_2(E)$ reflect the relative contributions of traps in the distribution to the in-phase and in-quadrature components, respectively, of the modulated photocurrent at frequency $\omega$. Furthermore, Oheda [3] also made use of the special form of the integrands in Eqs. (5) and (6) to approximate the weighting functions by replacing $G_1(E)$ in $B$ by a $\delta$ -function, and replacing $G_2(E)$ in $A$ by a step function. These approximations emphasize the clear relation between the phase-shift and the density of states (DOS). The $\delta$ -function effectively “selects” states at $E_C$, with mean re-emission time $1/\tau$, which should have the largest effect on the quadrature component of the photocurrent and the numerator of Eq. (7). Here $E_C$ is defined by

$$E_C - E_\omega = kT \ln(N_c \partial \sigma / \omega),$$

and the release time at $E_\omega$ is equal to $1/\omega$. The step-function selects states below $E_\omega$, which produce the largest contribution to the in-phase response and the denominator of Eq. (7).

4. Results and Discussion

An important characteristic of photoconductivity is the dependence of PC $I_{ph}$ on the photogeneration rate $G : I_{ph} \propto G^\nu$. It is defined differentially by $\nu = d[\ln(I_{ph})]/d[\ln(G)]$. In most cases, a sublinear dependence is found and $\nu$ has a quite a complicated variation with temperature, photon energy and light intensity. Rose [8] demonstrated that values of $\nu$ between 0.5 and 1 are obtained if the localized states in the gap are exponentially distributed, these states acting as trapping centres or recombination centres depending on the light intensity. However, although in a-Si:H states in the conduction band (valence band) tail are often supposed exponentially distributed from the mobility edge $E_C(E_V)$ [9, 10], the dangling-bond-related defects may have a Gaussian-shaped distribution [11]. Therefore the photogeneration rate (or intensity) dependence of PC cannot be described in terms of only one exponential density of states; the complete subgap distribution should be taken into account.

We emphasized in the introduction to this paper that an important difference between this and earlier work is the use here of modulated light. This permits us to examine, for the first time, the frequency dependence of $\nu$. Using the quadrature signal yields $\nu$ for those components of the current controlled by recombination rates close to $f$ (modulation frequency); the in phase signal gives an average $\nu$ from all components faster than $f$. In Figure 2 we show the results of in-phase measurements of the frequency dependence of $\nu$ for a-Si:H p-i-n at 20 K. Although they were not shown here, similar results were also observed at the other temperatures up to room temperature (300 K). All $\nu$ values determined at such temperatures were between 0.85 and 1.06 depending on the modulation frequency measured. Qualitatively the plot (Figure 2) shows that the power dependence changes from sub- to superlinearity ($\nu > 1$) as the frequency is increased. This may partly explain why our low temperature values of $\nu$ are higher (1.04) than some reported elsewhere [12] from d.c. ($f=0$) measurements. Clearly we find an upper limit to the d.c. of about 0.94 at 20K.

Figures 3 and 4 show the frequency dependence (in-phase) of $\nu$ for a-Se and a-As$_2$Se$_3$ at room temperature (300 K). In-quadrature output almost gives similar results for $\nu$. In Figure 5, we present a comparison of $\nu$ values for a-Si:H p-i-n and chalcogenide glasses. As can be seen, in both a-Si:H p-i-n junction and chalcogenide glasses the PC depends on modulation frequency; the effect in chalcogenide glasses is much stronger; $\nu$ varies from about 0.5-0.6 to 1.0 (above about 1 kHz), compared with 0.94 to 1.06 in a-Si:H p-i-n.

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Figure 2. Modulation frequency effect on the excitation intensity-dependent photocurrent of a-Si:H p-i-n at 20 K.

Figure 3. Modulation frequency effect on the excitation intensity-dependent photocurrent of a-Se at 290 K.

Figure 4. Modulation frequency effect on the excitation intensity-dependent photocurrent of a-As$_2$Se$_3$ at 290 K.

Figure 5. Comparison of exponent $\nu$ in the power-law relationship $I_{ph} \propto G^{\nu}$ as a function of modulation frequency for the three different samples. Data taken from Figures 2, 3 and 4.
 junction at low temperature. The a-Si:H p-i-n junction data, recorded in conditions where the DP model [13] might apply are hard to understand, and the increase poses problems for such models. For example Searle [13], using Shklovskii’s result [14] for PC in a material with exponential tails finds \( \nu \approx 1 - 1/\ln(w_o \tau) \), where \( w_o \) is the radiative recombination pre-exponential and \( \tau \) is the radiative lifetime. Identifying \( \tau \) with \( f^{-1} \) leads to the incorrect prediction that \( \nu \) should fall with frequency (f). Clearly further theoretical work is needed to understand these new results. This approximation also makes obvious the problems posed by the observed \( \nu > 1 \) for the DP model.

The much stronger frequency dependence seen in chalcogenide glasses (see Figure 5) is easier to understand, qualitatively at least. In the denominator of Eq. (4) occur the two terms \( A \) and \( B \) which contain overall three frequency dependent terms which are independent of excitation density, plus \( \tau \) which is G dependent. Thus if \( B \) or the integral in \( A \), \( A' \) say, is much greater than \( \tau^{-1} \), the carrier density will just depend linearly on G (\( f_1 \propto G \) in Eq. (4)) and so \( \nu = 1 \). If, however the term \( \tau^{-1} \) is the largest in the denominator, non-linearities will appear; the carrier density is now determined conventionally by \( G \tau \). Since \( A' \) and \( B \) both increase with frequency, as shown by the requirement that both the in-phase and quadrature components go to zero at high frequency, the non-linearities will be strongest at low frequencies where \( \nu \) will have the MT value \( T_o/(T + T_o) \) [8] and decrease as the frequency is raised and \( \nu \to 1 \). This qualitatively describes the data of Figure 5, with \( \nu \) rising from about 0.5 or 0.6 to 1 with increasing frequency.

We should note that the \( \nu \) value determined for chalcogenide glasses closes to 0.9-1.0 at low temperatures below about 100 K for all modulation frequencies measured [15, 16]. This shows that the recombination which controls the photocurrent becomes a dominant process rather than MT at low temperatures. The temperature-dependent photocurrent data given below also supports this result.

Figure 6 shows the effect of modulation frequency on the temperature-dependent photocurrent of a-Si:H p-i-n for a low excitation intensity of 50 \( \mu \)W. As can be seen, the PC tends to be constant at low temperatures below about 60 K. The recombination takes place by tunnelling transitions from localized conduction band tail states to neutral dangling bonds [14]. Since the tunnelling processes are only slightly temperature dependent, the photocurrent will be therefore nearly constant. Below about 50 K, in Figure 6 there is also a minor increase in PC intensity at high modulation frequencies above about 5 kHz. However this effect disappears at higher excitation intensities (above about 1 mW) used. As the temperature grows excess electrons start to hop in the tail of the conduction band (CB) giving rise to PC while holes are still immobile because they are trapped in deeper states immediately after thermalization [17]. The rate of the low temperature recombination is limited by tunnelling of excess electrons towards localized holes [18]. As the temperature increases the trapped-carrier transport or multiple-trapping which is commonly used at high temperatures predominates the PC process. In this high temperature region (> 100 K), the PC behaviour is approximately linear (see Figure 6) for all modulation frequencies indicated. It means that PC response is an activated process, i.e.,

\[
I_{ph} = I_o \exp(-E_a/kT),
\]

where \( I_o \) is an initial constant. The activation energies \( E_a \) calculated from the slopes of \( \ln I_{ph} \) vs 1000/T curves are plotted in Figure 7, as a function of modulation frequency. As can be seen, the activation energy increases with increasing modulation frequency. However, this is an unexpected result in the framework of phase shift analysis in which the activation energy decreases with modulation frequency (see Eq. (8)). The data given in Figure 6 were taken under a very small excitation intensity value of 50 \( \mu \)W. However, at higher excitation intensities, the activation energy was found to be almost independent of modulation frequency. Similar results were also observed in chalcogenide glasses. For instance, the activation energy values of about 245 meV and 280 meV were obtained in a-Se and a-As\(_2\)Se\(_3\) respectively at 10-100 Hz and 10-50 \( \mu \)W. These activation energies increase with increasing modulation frequencies as in the case of a-Si:H p-i-n. However, in contrast to a-Si:H p-i-n (\( E_a \approx 40\) meV, which is independent of intensity) [19], the activation energies of such chalcogenide glasses [15, 16] increase with decreasing light intensities, indicating that the position of the Fermi level is moving down to deeper energy levels. The energy of the excitation light is larger than the optical bandgap (\( \sim 1.8 \)eV) of chalcogenide samples [20]. We therefore assume that the carriers are photoexcited between extended states and then a trap-limited recombination occurs. The small values of activation energy (245 meV for a-Se, 280 meV for a-As\(_2\)Se\(_3\)) place the quasi-fermi level close to the valence
band, at around the lower part of an exponentially increasing tail state.

![Graph showing modulation frequency effect on temperature-dependent photocurrent of a-Si:H p-i-n at a low excitation intensity of 50μW.](image1)

**Figure 6.** Modulation frequency effect on the temperature-dependent photocurrent of a-Si:H p-i-n at a low excitation intensity of 50μW.

![Graph showing activation energy vs modulation frequency in a-Si:H p-i-n.](image2)

**Figure 7.** Activation energy vs modulation frequency in a-Si:H p-i-n.

5. Conclusion

Modulation frequency effects on the intensity- and temperature-dependence of PC were reported in detail for a-Si:H p-i-n and chalcogenide glasses (a-Se and a-As₂Se₃). We observed that the PC depends on modulation frequency in both a-Si:H p-i-n and chalcogenide glasses. However, the effect in chalcogenide glasses was found to be much stronger than that of a-Si:H p-i-n. This was explained, qualitatively at least, in the framework of MT model.

The activation energy values determined from the temperature-dependent PC at high temperatures were found to be modulation frequency dependent for both types of materials (a-Si:H p-i-n and chalcogenides) under very low excitation intensities. We conclude that the activation energies of such materials increase as the modulation frequency increases. However, it is difficult to explain this result in the framework of phase shift analysis. Further, our results also act as a guide to the best experimental conditions for comparing our data to the d.c results in the literature.

Acknowledgements

We would like to thank Dr T. M. Searle for helpful discussions.

References


