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Solar Energy Materials  
& Solar Cells

Solar Energy Materials & Solar Cells 85 (2005) 545–557

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# Comparative frequency-resolved photoconductivity studies of amorphous semiconductors

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Received 10 June 2003; received in revised form 5 April 2004; accepted 28 May 2004

Available online 29 July 2004

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## Abstract

Comparative frequency-resolved photoconductivity measurements in amorphous (a-) semiconductors, such as a-Si:H p-i-n junction, a-SiGe:H and a-chalcogenides (a-Se, a-As<sub>2</sub>Se<sub>3</sub>, a-As<sub>2</sub>Te<sub>3</sub>, a-SeTe, a-As<sub>2</sub>S<sub>3</sub>, etc.) are reported. In particular, photoconductivity lifetimes as a function of light intensity and temperature were determined by using the quadrature frequency-resolved spectroscopy method. The activation energies from the temperature-dependent lifetime and photocurrent were determined and compared in different materials. The exponent  $\nu$  in the power-law relationship ( $I_{ph} \propto G^\nu$ ) between generating flux and photocurrent was also obtained at different excitation wavelengths. The results were 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.

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*Keywords:* Photoconduction; Recombination; Lifetime; Trapping

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## 1. Introduction

Photoconductivity (PC) is the change in electrical conductivity when a material is exposed to electromagnetic radiation. PC is divided into three parts: (i) generation by an external source of electron-hole pairs, (ii) transport of mobile carriers in either

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extended or localized states, and (iii) recombination of the excited electron and hole. Each part has been the subject of much research and controversy in amorphous (a-) semiconductors and only now is there perhaps some consensus about the important features of each.

The study of frequency-resolved PC as a function of temperature and light intensity in a-semiconductors is a valuable tool in achieving a good understanding of the recombination processes and distribution of localized states which control the phototransport kinetics. However, in spite of the extensive studies, the interpretation of experimental data remains difficult.

In this work, we measured the exponent  $\nu$  in the power-law relationship  $\sigma_{\text{ph}}$  or  $I_{\text{ph}} \propto G^\nu$ , the carrier lifetimes and activation energies for a variety of a-semiconductors. The temperature range covered was 20–300 K. We also compared our experimental results with the predictions of PC models proposed at high and low temperatures.

## 2. Experimental details

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

The samples of a-SiGe:H alloys were ion-bombarded thin films. They were obtained from Dundee University. Their preparation conditions and properties are described in detail elsewhere [1]. Al electrodes separated by a 0.1 mm gap were deposited onto the films by using our own vacuum-coating unit. Cu wires were then placed on the Al layers with electrically conductive silver paint.

The samples of a-chalcogenides were thin films prepared by thermal evaporation. The materials used for these samples were from BDH chemicals with a purity of 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 1  $\mu\text{m}$ . It should be indicated that measurements taken on thicker (up to 10  $\mu\text{m}$ ) and thinner (down to 0.5  $\mu\text{m}$ ) 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.

The samples were excited by the 1.96 eV line of a HeNe laser, which was replaced by an Ar<sup>+</sup> dye laser for high excitation intensities and different lines. 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 (SR 530 Stanford Research System). 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<sup>-6</sup> Torr. The intensity of the excitation light was reduced by neutral density filters. During the high-intensity (up to 30 mW) measurements, the heating effect of the Ar<sup>+</sup> laser was checked and it was found that it did not have any significant heating effect on the samples.

### 3. Results and discussion

The quadrature frequency resolved photocurrent (FRPC) response of the samples in the frequency interval between 10 Hz and 100 kHz was measured as a function of the intensity of the excitation light and temperature. Since the energy of the excitation light is much higher than the optical band gap of these materials, we assume that the carriers are photoexcited between extended states and then a trap-limited recombination occurs.

Fig. 1 shows a comparative plot of the FRPC response in different kinds of samples as a function of inverse temperature. The light intensity (632 nm from HeNe laser) and modulation frequency were kept constant at 2.3 mW (about  $2.3 \times 10^{19}$  photons cm<sup>-2</sup> s<sup>-1</sup>) and 1 kHz, respectively, for each sample. However the applied electric field is different for some samples because of the different geometries (co-planar and sandwich). We should note that the applied electric field has no important effect on the curves shown in Fig. 1, except for FRPC magnitude [3]. The temperature dependence of the FRPC response (from Fig. 1) indicates three regimes: (i) At low temperatures ( $\leq 60$  K for a-Si:H p-i-n,  $\leq 100$  K for chalcogenides) the FRPC tends to be constant. (ii) At intermediate temperatures, the FRPC starts to rise with temperature by several orders of magnitude. (iii) At high temperatures ( $\geq 100$  K), the FRPC increases rapidly with increasing temperatures. In this region, the FRPC behaviour is approximately linear. It means that the FRPC response is an activated process, i.e.,

$$I_{\text{ph}} = I_0 \exp(-E_a/kT), \quad (1)$$

where  $I_0$  is an initial constant. The activation energies ( $E_a$ ) calculated from the slopes of  $\ln I_{\text{ph}}$  vs.  $1000/T$  curves are  $42 \pm 10$ ,  $147 \pm 35$ ,  $80 \pm 18$ , 52,  $77.5 \pm 2.5$  and  $114 \pm 19$  meV for the samples of a-Si:H p-i-n, a-Se, a-As<sub>2</sub>Se<sub>3</sub>, a-SeTe, a-SiGe:H, and a-As<sub>2</sub>Te<sub>3</sub> respectively. Later these results will be compared with those of activation energy from temperature-dependent lifetime measurements. However, at low temperatures the intensity of FRPC response does not show an activated

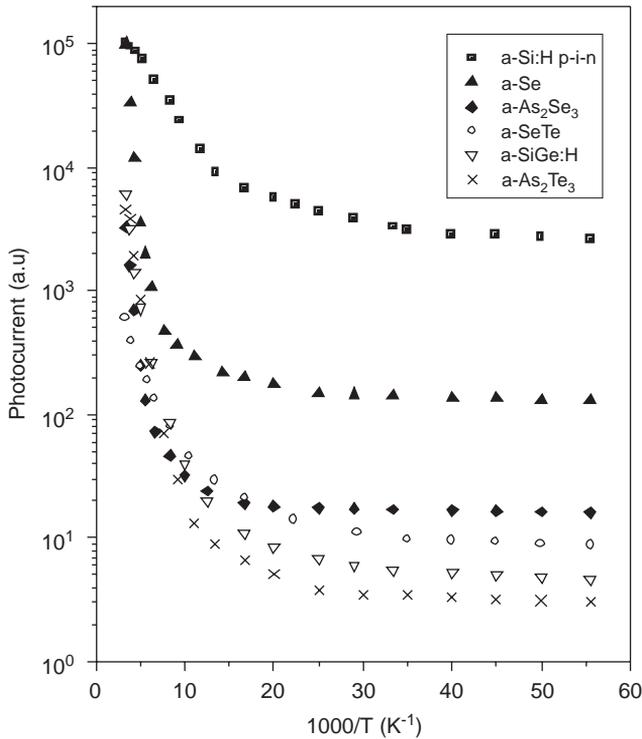


Fig. 1. Temperature dependence of FRPC for different types of amorphous samples. The applied electric field is different for each sample. Excitation: 2.3 mW (632 nm) (a.u. arbitrary units).

behaviour. It means that the recombination processes do not depend on temperature in this temperature region.

Another main interest is the dependence of photocurrent  $I_{ph}$  on the photogeneration rate  $G$ ,

$$I_{ph} \propto G^{\nu}. \quad (2)$$

It is differentially defined by

$$\nu = d[\ln(I_{ph})]/d[\ln(G)]. \quad (3)$$

It is now well-known that the value of the exponent  $\nu$  differs in various materials. In most cases, a sublinear dependence is found and the exponent  $\nu$  in this power-law relation has quite complicated variations with temperature, photon energy and light intensity [4].

Table 1 shows the  $\nu$  values for a large number of different type samples at three wavelengths and room temperature (290K). The values of  $\nu$  were averaged from the data taken at the modulation frequencies between 10Hz and 1kHz. The dependence of  $\nu$  on temperature (20–295K) for some of the samples given in Table 1 were presented in detail elsewhere [3]. Rose [4] suggests that  $\nu = 1$  corresponds to

Table 1

The average values of exponent  $\nu$  in the power-law relationship  $\sigma_{\text{ph}} \propto I_{\text{ph}} \propto G^{\nu}$ , for different samples and wavelengths at RT (290 K). Data taken at the modulation frequencies between 10 Hz and 1 kHz

Material	Average $\nu$ values		
	Red (632 nm)	Green (528 nm)	Blue (476.5 nm)
a-As	$0.72 \pm 0.03$	$0.72 \pm 0.07$	$0.85 \pm 0.09$
a-AsTe	$0.70 \pm 0.04$	—	—
a-As <sub>2</sub> S <sub>3</sub>	—	$0.74 \pm 0.01$	$0.69 \pm 0.07$
a-As <sub>2</sub> Te <sub>3</sub>	$0.84 \pm 0.11$	$0.57 \pm 0.03$	$0.62 \pm 0.04$
a-As <sub>2</sub> Se <sub>3</sub> Te	$0.49 \pm 0.06$	$0.54 \pm 0.05$	$0.45 \pm 0.02$
a-AsSe	$0.60 \pm 0.07$	0.54	0.54
a-As <sub>2</sub> Se <sub>3</sub>	$0.55 \pm 0.02$	$0.58 \pm 0.06$	$0.54 \pm 0.06$
a-As <sub>2</sub> Se <sub>4</sub>	$0.58 \pm 0.03$	—	—
a-As <sub>2</sub> Se <sub>6</sub>	$0.58 \pm 0.03$	—	—
a-As <sub>2</sub> Se <sub>8</sub>	$0.59 \pm 0.03$	—	—
a-AsS	—	$0.66 \pm 0.01$	$0.68 \pm 0.01$
a-As <sub>2</sub> S <sub>3</sub> Se	—	$0.69 \pm 0.02$	$0.97 \pm 0.01$
a-Ge	$0.70 \pm 0.07$	$0.74 \pm 0.03$	$0.59 \pm 0.04$
a-Se	$0.55 \pm 0.07$	$0.74 \pm 0.15$	$0.76 \pm 0.04$
a-SeTe	—	—	$0.54 \pm 0.05$
a-Si:H p-i-n (Casio)	$0.89 \pm 0.02$	$0.90 \pm 0.05$	0.96
a-Si:H p-i-n (Sanyo)	—	—	0.95
a-Si:H p-i-n (Chronar)	—	—	1.01
a-SiGe:H (10)	$0.75 \pm 0.05$	$0.76 \pm 0.02$	$0.73 \pm 0.08$
a-SiGe:H (16)	$0.64 \pm 0.08$	—	—
a-SiGe:H (51)	$0.90 \pm 0.02$	—	—
a-SiGe:H (61)	$0.69 \pm 0.07$	—	—

monomolecular recombination and  $\nu = 0.5$  to bimolecular recombination. However, in the case of continuous distribution of traps the value of  $\nu$  may be anywhere between 0.5 and 1.0 depending on the intensity and the temperature range. As can be seen from Table 1, the values of exponent  $\nu$  lie between about 0.5 and 1.0 for the samples used in this work, indicating the presence of a continuous distribution of localized states in the energy gap.

Lifetime can be measured in terms of the frequency-resolved spectroscopy (FRS) method [5]. This method has been widely applied to the study of lifetime and recombination processes [6–9]. According to FRS method, the in-phase and quadrature photoluminescence response in amorphous materials have been treated in detail and showed that the quadrature response function gives the lifetime distribution of the system whereas the in-phase response is the integral of the lifetime distribution between the limits  $\tau \propto 2\pi f^{-1}$  and  $\infty$ . This treatment has been applied to frequency-resolved photocurrent (FRPC) response in amorphous materials [10–13].

Fig. 2 shows a comparative quadrature FRPC response of some different a-semiconductors for one particular intensity (2.3 mW, 633 nm) and temperature (295 K). It should be noted that the applied electric field has no important effects on the peak positions given in Fig. 2. The curves are normalized to the respective signal

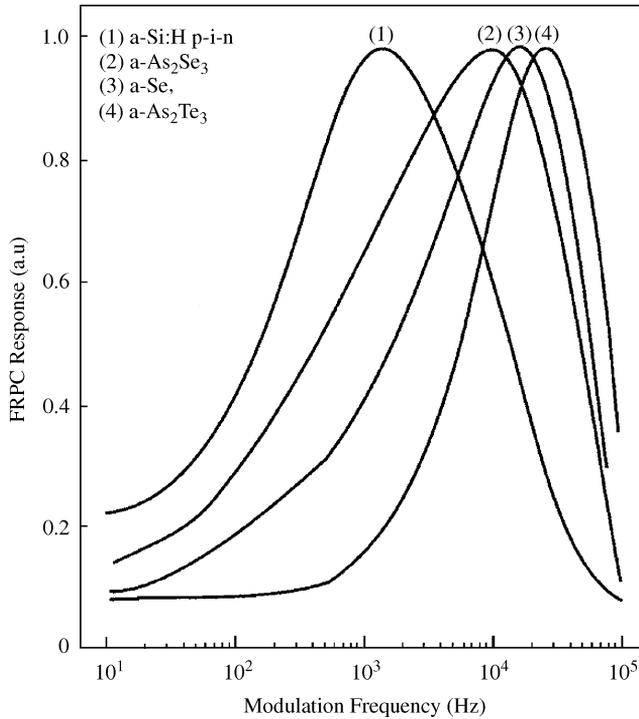


Fig. 2. A comparative plotting of FRPC spectra in different samples. Each curve is normalized with respect to its maximum value. Excitation: 2.3 mW (632 nm).  $T = 295$  K. (a.u., arbitrary units).

heights at the maximum of the distribution. In the framework of the FRS method, Wagner et al. [10] suggest that for a system with a single characteristic time  $\tau$ , the quadrature frequency-resolved spectrum is a symmetric line of half-width 0.7 decades peaked at the frequency

$$\tau = 1/2\pi f_{\text{peak}}. \quad (4)$$

Using this relation, from Fig. 2 the lifetimes of about 118, 17, 8.5 and 5.6  $\mu\text{s}$  were calculated for the samples of a-Si:H p-i-n, a-As<sub>2</sub>Se<sub>3</sub>, a-Se and a-As<sub>2</sub>Te<sub>3</sub>, respectively. Obviously, the lifetime distributions of a-chalcogenides occur at higher frequencies (or shorter lifetimes) than that of the a-Si:H p-i-n junction under the same excitation and temperature. Further, a-chalcogenides have a larger lifetime distribution width than that of a-Si:H p-i-n junctions at low frequencies (10 kHz). Similar behaviour was also observed at different temperatures.

Fig. 3 shows the temperature dependence of lifetime for a-Si:H p-i-n junction solar cell (Chronar-type). Clearly, three ranges of different behaviour can be defined: (a) the high-temperature range ( $295 \text{ K} < T < 100 \text{ K}$ ), (b) the intermediate temperature range ( $100 \text{ K} < T < 50 \text{ K}$ ), and (c) the low-temperature range ( $50 \text{ K} < T < 20 \text{ K}$ ). A quantitative interpretation of these results requires in principle a set of rate equations

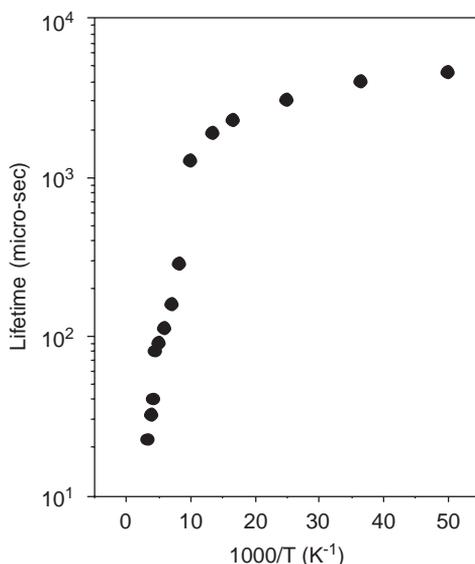


Fig. 3. Lifetime vs.  $1/T$  in Chronar-type a-Si:H p-i-n junction solar cell. Excitation: 30 mW (488 nm).

[14–19] based on assumptions about the density of states—in particular trapping and recombination centres—to be fitted to the experimental data. However, there is not yet such a complete model which would be able to explain the observed behaviour. Therefore we would restrict our interpretation at present to some qualitative remarks. The temperature dependence of the peak frequency reflects changes that occur in the recombination mechanism. In particular, the general behaviour can be described by competition between tunnelling transitions between band tail states and dangling bonds, and direct capture of free carriers by dangling bonds. At high temperatures, the lifetime is excitation intensity-dependent and falls rapidly and almost linearly with decreasing temperature. Therefore the de-trapping from states around  $E_w$ , which is a frequency-dependent activation energy defined below, determines the lifetime. The modulation frequency  $f_m$  is converted to the energy  $E_w$  through the relationship [14],

$$w(= 2\pi f_m) = w_0 \exp[-E_w/kT], \quad (5)$$

where  $w(= 2\pi f_m)$  is related to the lifetime  $\tau$  as  $w = \tau^{-1}$ ,  $w_0$  is the pre-exponential constant,  $k$  is the Boltzmann factor and  $T$  is the measured temperature. From the high-temperature range (see Fig. 3), an activation energy value of about 42 meV was obtained for  $E_w$ .

The recombination rate in undoped a-Si:H film is limited by the diffusion of trapped band tail holes towards the dangling bonds [20]. In the temperature range where the diffusion becomes thermally enhanced, or when the trapped holes are

excited to the conduction states, the recombination rate increases, resulting in a pronounced increase of lifetime.

At intermediate temperatures, the capture of free carriers into dangling bonds occurs in addition to tunnelling. The lifetime is complicated in this case, but there is an obvious increase with increasing temperature. The rounded shoulder of the plot of lifetime vs.  $1000/T$  (see Fig. 3) shows that the single activation energy mechanism of Eq. (5) will not work in detail, since it would lead to a sharp shoulder.

At low temperatures, the lifetime seems to be nearly constant. The recombination takes place by tunnelling transitions from localized conduction band tail states to neutral dangling bonds. Since the tunnelling processes are only slightly temperature-dependent, the lifetime will therefore be nearly constant.

A comparison of activation energies obtained from both temperature-dependent lifetime ( $E_w$ ) and photocurrent ( $E_a$ ) measurements is given in Table 2 for some of the samples studied here.

Fig. 4 shows the lifetime vs excitation intensity (632 nm) for one of the chalcogenide glasses, a-As<sub>2</sub>Se<sub>3</sub>, at room temperature (295 K). Searle [21] proposed a distant-pair (DP) model which allows analytical relations to be obtained for the correlation between excitation intensity, carrier density, and the corresponding lifetime. According to this model, the excitation rate  $G$  which produces an equilibrium carrier density  $n$  with a lifetime  $\tau$ , is given by

$$G = n/\tau = nw_0 \exp(-n^{-1/3}/R_0) \quad (6)$$

where  $R_0$  is the electron Bohr radius (if the holes are strongly localized), and  $w_0$  is a constant. In this model the geminate recombination is ignored and the average distance between (non-geminate) pairs is supposed to be given by  $R \simeq (1/2)n^{-1/3}$ . This equation enables us to calculate  $n$  immediately and from it,  $\tau$ . Alternatively, by substituting  $\tau^{-1} = w_0 \exp(-n^{-1/3}/R_0)$  into  $G = n/\tau$ , the resulting equation

$$GR_0^3\tau[\ln(w_0\tau)]^3 = 1 \quad (7)$$

can be solved to find  $\tau$ . Furthermore, writing Eq.(7) in the form

$$\tau = AG^g, \quad (8)$$

Table 2

A comparison of activation energies obtained from lifetime ( $E_w$ ) and photocurrent ( $E_a$ ) measurement

Material	Activation energies	
	$E_w$ (meV)	$E_a$ (meV)
a-Si:H p-i-n (Casio)	40 ± 10	45
a-Si:H p-i-n (Chronar)	42	56
a-Si:H p-i-n (Sanyo)	94	—
a-Se	40 (second peak)	172 ± 10
a-As <sub>2</sub> Se <sub>3</sub>	160	220
a-SeTe	35	35
a-As <sub>2</sub> Te <sub>3</sub>	—	93.12 ± 1.27
a-SiGe:H	—	70.9 ± 2.3

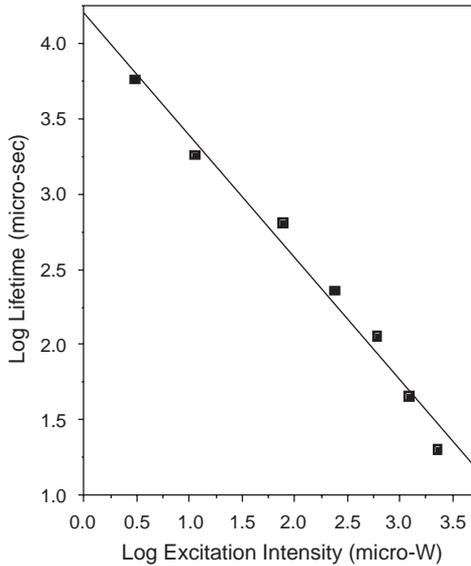


Fig. 4. Lifetime vs. excitation intensity in a-As<sub>2</sub>Se<sub>3</sub>. Excitation: 632 nm.  $T = 290$  K.

gives

$$g = -1/[1 + 3/\ln(w_0\tau)], \tag{9}$$

$$n = BG^{1+g}. \tag{10}$$

Despite the variation of  $g$  with  $G$  implied by Eq. (8),  $g$  is likely to remain nearly constant in most experiments which cover only two to four orders of magnitude in  $G$ . For the DC PC at low temperature (LT) and with the additional assumption of exponential tails, Searle has found that the PC can be expressed by

$$\sigma_{ph} = G^{1-(1+g)/3} \equiv G^v. \tag{11}$$

It is confirmed that this definition is in agreement with experimental observations.

Alternatively, in the MT model as in the distant pair (DP) model treated above, the result depends on the shape of the density of states (DOS). Bullo et al. [22] showed that for an exponential DOS, characterized by the temperature  $T_0$ , the lifetime varies as

$$\tau = G^{-v'}, \tag{12}$$

where  $v' = T_0/(T + T_0)$  as given by Rose [4]. Note that  $T_0$  may not be that of the band tails if  $E_f$  lies elsewhere. The decrease in lifetime with power in this model relates to the movement of the quasi-Fermi level towards  $E_c$ .

Considering the above expressions, the slope of  $\ln \tau$  vs.  $\ln G$  in Fig.4 gives the value for  $v'$ . Its value for room temperature was determined to be  $-0.81$ . The distribution of lifetimes with respect to generation rate has been used to determine what kind of

recombination occurs between the photoexcited carriers [21,23]. It was suggested that in the geminate type of recombination the distribution of lifetimes will be insensitive to generation rates, whereas in distant pairs model, DP, where it is assumed that recombination takes place between nearest available neighbours non-geminately, the lifetimes should decrease with increasing generation rate. The result of Fig. 1 shows that the lifetime is dependent on the generation rate with a negative slope and therefore can be interpreted as supporting the DP model. Although the DP model is assumed to be valid only at low temperatures, our measurements give similar results even at room temperature.

Table 3 shows a complete comparison of measured exponents  $\nu'$  in  $\tau \sim G^{\nu'}$  and  $\nu$  in  $\sigma_{\text{ph}} \sim I_{\text{ph}} \sim G^{\nu}$  with calculated  $\nu$  values from the multiple trapping model (MT) [22] and distant pair model (DP, where  $g = \nu'$ ) [21] for different samples measured at both room temperature (290 K) and low temperature (20 K). Here, the data taken were averaged over many samples produced under the same conditions. However, at

Table 3

A comparison of measured exponents  $\nu'$  in  $\tau \propto G^{\nu'}$  and  $\nu$  in  $\sigma_{\text{ph}} \propto I_{\text{ph}} \sim G^{\nu}$  with calculated  $\nu$  values from the multiple trapping model (MT) [22] and distant pair model (DP, where  $g = \nu'$ ) [21]

Material	$T(\text{K})$	Measured $\nu'$	Measured $\nu$	Calculated $\nu$	
				MT (= $-\nu$ )	DP [= $1-(1+g)/3$ ]
a-Si:H p-i-n (Casio)	290	$-1.03 \pm 0.1$ ( $> 1 \text{ mW}$ )	$0.9 \pm 0.04$	1.03	*
a-Si:H p-i-n (Chronar)	290	$-0.45 \pm 0.01$ ( $> 1 \text{ mW}$ )	$1.01 \pm 0.05$	0.45	*
a-Si:H p-i-n (Sanyo)	290	$-1.49 \pm 0.05$ ( $> 1 \text{ mW}$ )	$0.95 \pm 0.03$	1.49	*
a-Se	290	$-0.78 \pm 0.15$ (main peak)	$0.68 \pm 0.09$	0.78	*
a-As <sub>2</sub> Se <sub>3</sub>	290	$-0.82 \pm 0.05$	$0.56 \pm 0.03$	0.72	*
a-SeTe	290	$-0.87 \pm 0.01$	$0.54 \pm 0.05$	0.87	*
a-SiGe:H	290	0	$0.75 \pm 0.08$	0	*
a-Si:H p-i-n (Casio)	20	0	1.04	0	$\frac{2}{3}$
a-Si:H p-i-n (Chronar)	20	0	0.95	0	$\frac{2}{3}$
a-Si:H p-i-n (Sanyo)	20	0	1.01	0	$\frac{2}{3}$
a-Se	120	$-1.10 \pm 0.02$ (2nd peak)	$1.05 \pm 0.04$	1.10	1.03
a-As <sub>2</sub> Se <sub>3</sub>	20	+	$1.04 \pm 0.01$	+	+
a-SeTe	20	$-0.61 \pm 0.04$	$1.01 \pm 0.02$	0.61	0.87
a-As <sub>2</sub> Te <sub>3</sub>	20	+	$0.8 \pm 0.5$	+	+
a-SiGe:H	20	+	$0.84 \pm 0.02$	+	+

\* High temperature where DP model not appropriate; + not measurable/not calculable; the zeroes (0) indicate power independence.

RT, the  $\nu'$  value varies between 0.6 and 1.1 for sample to sample of a-Se and a-As<sub>2</sub>Se<sub>3</sub> [3]. At low intensities (<1 mW), the lifetime of an a-Si:H p–i–n junction does not depend on excitation intensity at RT [24], the zeroes in Table 3. The PC lifetime may therefore be dominated by capture into defects, rather the tunnelling recombination of the DP model.

At room temperature one might expect the multiple trapping (MT) model to apply to all our materials, and the exponent  $\nu$  of the intensity dependence of  $\sigma_{\text{ph}}$  or  $I_{\text{ph}}$  does indeed lie between 1 and 0.5. According to [22], the MT model for exponential tails gives  $\nu = -\nu'$ , and these values are given in the “calculated/MT” column of Table 3. Comparison of the calculated and experimental values of  $\nu$  only show reasonable agreement for the Casio type a-Si:H p–i–n junction solar cell and for the a-Se sample. True power-laws only arise in the MT model with exponential DOS, but other distributions may give close approximations. Such DOS effects are likely to complicate the relation between  $\nu$  and  $\nu'$ .

For those samples in which  $\tau$  does vary with  $G$  at low temperatures where either the DP or the MT model might apply, similar calculations might distinguish between them. For the DP model with an exponential DOS, the Searle [21]/Shklovskii [25] analysis yields  $\nu = 1 - (1 + g)/3$  (see Eq. (11)), and this is also shown in Table 3. In fact, only a-Se and a-SeTe provide such a test, and for the former the predictions are too close to distinguish. For a-SeTe the observation ( $1.01 \pm 0.02$ ) is closer to the DP value (0.87), but not particularly good.

Evidently more analysis of the effects of the form of the DOS on  $\nu$  and  $\nu'$  need to be made. As far as we know, the present work is the first to measure and compare these two exponents on the same samples, apart from the early work of Main et al. [26] who looked at the transition from monomolecular to bimolecular kinetics in chalcogenides. We suggest that at low temperature and with samples where  $\tau$  is  $G$  dependent the method provides a useful test of models and perhaps of the form of the DOS.

The lifetime data on a-Si:H suggested the presence of a shunt process that limited the lifetime at low temperatures. Another effect of such a process should be to lower the PC. Typically, photocurrents are 10 nA at  $-1$  V bias under  $10 \mu\text{W}$  external illumination in our cells. Assuming an optimum thickness of  $1 \mu\text{m}$  yields a PC  $\sigma_{\text{ph}} = 1 \times 10^{-14} \text{AV}^{-1}\text{cm}^{-1}$ . Johanson et al. [27] expressed their results in terms of  $\sigma_{\text{ph}}/(Ge) = \eta\mu\tau Ge$  is the power density, roughly  $5 \mu\text{W}$  (assuming a reflectivity of 50%) in a volume equal to the absorption length times the excited area, about  $10^{-6}\text{cm}^3$  in our case. We therefore obtain  $\sigma_{\text{ph}}/(Ge) \approx 5 \times 10^{-13} \text{cm}^2\text{V}^{-1}$ , which is lower than Johanson et al.'s value of  $1 \times 10^{-11} \text{cm}^2\text{V}^{-1}$  by about a factor of 20.

In a-Se, at LT (<200 K), we observed a second peak whose lifetime is intensity ( $\tau \sim G^{-1.1}$ ) and temperature dependent in contrast to the main peak [13]. This second peak is well marked at around 120 K. Its activation energy calculated from  $d(\ln \tau)/d(1/T)$  is about 40 meV (see Table 2).

A comparison between the results on the temperature dependence of PC and those on the temperature dependence of the lifetime in a-Si:H p–i–n cells further emphasizes the role of thermal release from traps in the higher temperature region. If the measured lifetime  $\tau$  was due to recombination, the photocurrent would be

proportional to  $G\tau$ , and a decreasing lifetime would result in a decrease in PC. Our data show the reverse. The reason is of course that it is the release rate from traps which controls both the PC and the lifetime. In these cells and under our excitation conditions, these energies are about the same. This does not have to be so, as shown by the analysis of Oheda [14]. The peak of the lifetime distribution is that of the maximum of the quadrature response, whilst the in-phase behaviour also contains contributions from all traps with release rates slower than the inverse of the modulation frequency. Since the “weighting function”  $G_1(E)$  [14] which determines the effective range of states involved in the quadrature response (at, say, the maximum) falls exponentially with characteristic energy  $kT$ , the similarity of the activation energies found for PC ( $40 \pm 10$  meV) and the lifetimes (45 meV) suggests that the DOS falls fast compared with the thermal energy. In fact, the CB logarithmic slope is about 30 meV, compared with 25 meV for  $kT$  at RT, so this condition is nearly, but not quite, met.

In a-Se and a-As<sub>2</sub>Se<sub>3</sub> the energies are generally larger than the Urbach energy (the exception being  $E_w$  in a-Se, though this is the second peak) and are, again, not equal to each other. In a-Se  $E_w$  is less than  $E_a$ , for the reasons given above for a-Si:H. In a-As<sub>2</sub>Se<sub>3</sub> the lifetime is controlled by deeper states.

The higher value of the photocurrent activation energy seen in a-SiGe:H (see Table 2) could be related to increasing of the conduction band tail due to extra chemical disorder and the possibility of both Si and Ge dangling bonds.

#### 4. Conclusions

The lifetime, intensity and temperature dependence of the modulated photocurrent were measured for three types of commercial a-Si:H p–i–n junction solar cells (Casio, Chronar and Sanyo types) and evaporated chalcogenide thin films (a-Se, a-As<sub>2</sub>Se<sub>3</sub>, a-SeTe, a-As<sub>2</sub>Te<sub>3</sub>) with coplanar Au or Al electrodes at temperatures between 20 and 300 K. The measurements were also extended to ion-bombarded a-SiGe:H alloys. It was observed that the lifetimes and photocurrents show an activated behaviour at high temperatures (100–290 K), so that the activation energies obtained from both results were calculated and compared. It was found that the carrier lifetimes depend on the intensity of the excitation light which may be interpreted as supportive of the DP model. The exponent  $\nu$  in the power-law relationship  $\sigma_{ph}$  (or  $I_{ph}$ )  $\sim G^\nu$  is determined under different conditions to characterize the recombination kinetics. We have interpreted the results in terms of at least two distinct regions: At LT, the DP model explains the constant value of  $\nu$  seen in most materials, and the MT model explains the fall in  $\nu$  typically above 100 K. However, there are difficulties with the detailed predictions of  $\nu$  for both models.

#### Acknowledgements

The author is grateful to Dr. T. M. Searle for helpful discussions.

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