Frequency-resolved photocurrent studies of a-Se

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Abstract Optically modulated photocurrent response of amorphous selenium (a-Se) thin films was measured between 20 K and 295 K, by using the in-quadrature frequency-resolved spectroscopy method. The results show that the modulated photocurrent depends on external parameters such as excitation light intensity and temperature, giving information about recombination kinetics.

Because of its high photoconductivity [1, 2] a-Se has become a material of considerable commercial importance. It has in the past drawn great attention due to its potential use in various solid state devices and it is still widely used in xerography, TV image pick-up tubes, optical switches, detectors, etc [3, 4]. Therefore it is important to determine the band structure of a-Se in order to understand the nature of the localized states which are quite likely to exist in this material and affect its photoconductivity properties. In general it has been suggested that the shallow and deep levels are closely related to the mobility and the lifetime of carriers respectively. Hence determination of the lifetime as a function of excitation light intensity and temperature gives information about recombination kinetics in amorphous materials.

Response time or lifetime analysis can be carried out by making measurements in the time domain (time-resolved spectroscopy) or in the frequency domain (frequency-resolved spectroscopy). In principle, they are equivalent and contain the same information (related by a Fourier transform) granted they are done under the same excitation conditions. Time-resolved spectroscopy uses a δ-function (in time) excitation pulse and follows the response in time; while the frequency-resolved spectroscopy uses a sinusoidal excitation (δ-function in frequency) and follows the (complex) response in frequency. For frequency-resolved spectroscopy (FRS) the modulation is most conveniently produced with an acousto-optic modulator and the signal recovered with a phase sensitive detector such as lock-in amplifier. It turns out that the

quadrature response alone closely resembles a broadened lifetime distribution: the Fourier transform of a single well defined lifetime which yields a single exponential in time domain, produces a Lorentzian just under a decade wide in the quadrature frequency domain. The quadrature method is therefore not well suited to materials exhibiting only one or two decay times but loses little information where lifetime distributions are continuous and slowly varying. Both methods have a role and have been used in amorphous materials. While fast processes are easily studied in the time domain, the quadrature technique has a number of advantages for the slower parts of lifetime distribution [5, 6, 7].

The density of localized gap states and the related electronic transitions which control excess carrier processes thus determine the photocurrent response in a-Se. Mott et al [8] describe these states as D^+ (empty), D^- (doubly occupied) and D° (neutral) states that act traps for electrons and holes created by light excitation. The complicated nature of these states is still open to investigations. In this work, we used FRS on a-Se thin films, at different light intensities and in a temperature range of 20 K and 295 K. The exponent v in the power law relationship $I_{PC} \propto G^v$ between the photocurrent and the generation rate was also determined over the same temperature range.

1 Experimental details

The samples are thin films of a-Se prepared with thermal evaporation. The material used for these samples is from BDH chemicals, and its purity is 99.9992%. During the thermal evaporation of the films the work chamber pressure was less than 10^{-5} Torr. The substrate (Corning 7059 glass) was held at room temperature. The thickness of most of the samples were of the order of 1 μm. Gold 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 layers with electrically conductive silver paint. I-V measurements taken in dark proved that the contacts were perfectly

ohmic. The dark conductivities of the samples at room temperature were around $10^{-12}\,\Omega^{-1}\,\mathrm{cm}^{-1}$.

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. FRPC measurements were made with a lock-in amplifier (SR 530 Stanford Research System). The advantage of this frequency-locked a.c. measurement is that it rejects any stray light, dark current and any other unmodulated signal or signals modulated at other frequencies. The photocurrent was excited by a HeNe laser beam (1.96 eV) which was modulated by an acousto-optic modulator (IntraAction Corp., Model AOM-125). The beam width was wider than the planar distance of 0.1 mm between the contacts and with a thickness of about 1 μm. We can assume that the sample was uniformly excited. The modulation amplitude amounted to 46% of the bias light intensity. The HeNe laser was replaced by an Ar^+ laser for high excitation intensities. The samples were placed 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. By using neutral density filters, the intensity of the HeNe excitation light was varied between 2.3 mW–1 μW and the Ar^+ excitation light intensity was varied between 3 mW–100 μW (1 mW corresponds to $\sim 1 \times 10^{19}$ photons·s^{-1}·cm^{-2}). During measurements the heating effect of lasers was controlled and it was determined that it did not have any significant heating effect on the samples.
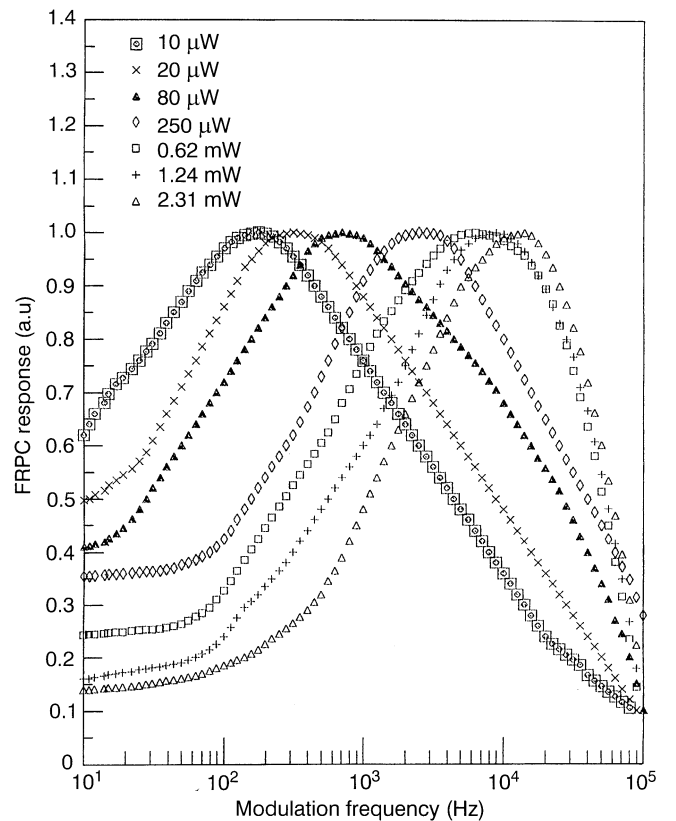
2 Results and discussion

The results presented here are derived from measurements performed on 15 samples. All the samples were produced under same conditions and the measurements were taken right after they were produced. The samples did not show any changes in the measured quantities with aging.

The energy of the excitation light is bigger than the optical band gap of these materials. We therefore assume that the carriers are photoexcited between extended states and then a trap limited recombination occurs.

Figure 1 shows the FRPC response of one of the samples for different excitation intensities (632.8 nm from HeNe laser) at room temperature (290 K). The data were taken under an electric field of 5×10^4 Vcm^{-1}. All curves are normalised to the respective signal heights at the maximum of the distribution. Obviously the well-defined single peak found in the spectrum shifts towards the higher frequency region as the intensity of excitation light increases. Similar results were also found in a–As_2Se_3 [9].

The in-phase and quadrature photoluminescence response in amorphous materials have been treated in detail by Depinna and Dunstan [10], Risten [11], Stachowitz, Schubert and Fuhs [7], and Oheda [12]. They show 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 ∞. This treatment has been applied to frequency-resolved photocurrent response in amorphous materials [7, 13, 14, 15, 16, 17, 18, 19]. According to this

Fig. 1. FRPC response of a-Se at 290 K for the indicated excitation intensities. Each curve is normalized with respect to its maximum value

theory, for a system with a single characteristic time τ the quadrature frequency-resolved spectrum is a symmetric line of half-width 0.7 decades peaked at the frequency

$$\tau = \frac{1}{2\pi f_{\mathrm{peak}}} \tag{1}$$

Figure 2 shows the peak frequency as a function of the excitation intensity for the samples given in Fig. 1, at room temperature (290 K). The intensity of the excitation light is proportional to the generation rate, G, and the dependence of f_{peak} on G can be expressed as [20, 21],

$$f_{\mathrm{peak}} \propto G^{v'}. \tag{2}$$

Hence the slope of $\ln f_{\mathrm{peak}}$ vs $\ln G$ will give the value for the exponent v'. For the sample given in Fig. 2, this value was determined to be 0.83. For all the samples measured $v' = 0.78 \pm 0.15$.

FRPC measurements done under different excitation wavelengths of 488.0 nm and 514.5 nm produced similar dependence as of Fig. 1 on the modulation frequency at different intensities and hence similar results for v'.

The frequency dependence of the FRPC response at 3 mW (488.0 nm) for different temperatures under an electric field of 5×10^4 V cm^{-1} is shown in Fig. 3 where the logarithmic scale shows the correct relation between the absolute intensity values. In contrast to room temperature results, the spectra show two peaks below room temperature. One of them, which we shall call the main peak, is
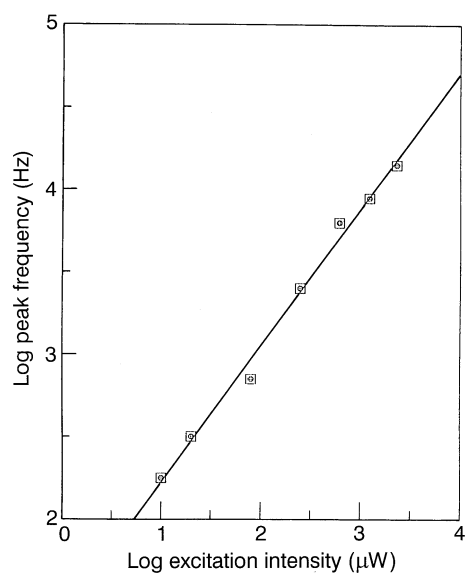
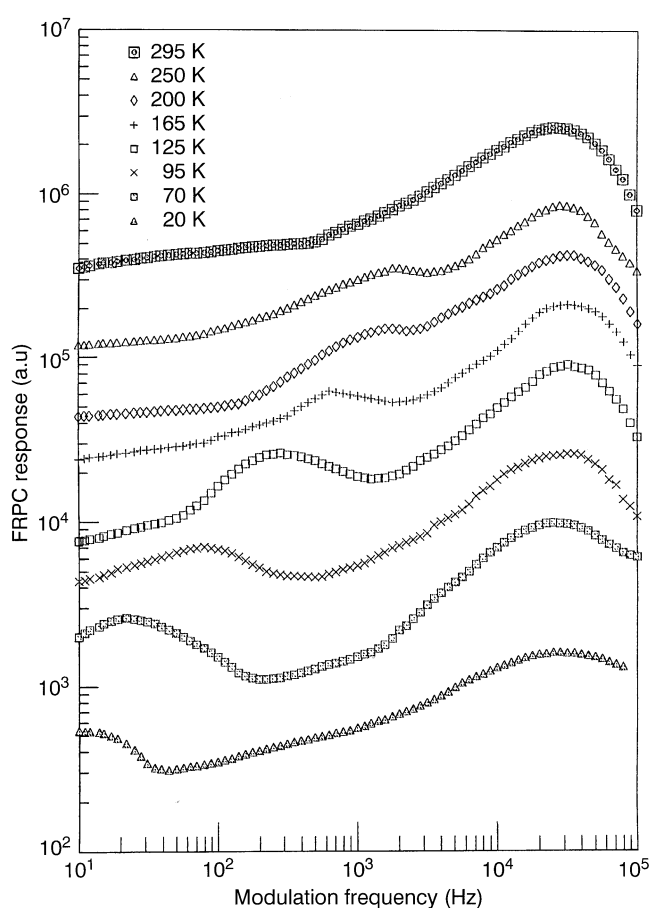**Fig. 2.** Peak frequency vs excitation intensity in a-Se. T = 290 K

Fig. 3. FRPC response of a-Se at the indicated temperatures for an excitation intensity of 3 mW

Fig. 4. FRPC response of a-Se at 120 K for the indicated excitation intensities

centered around 20 kHz and is independent of temperature while the second one, called the second peak here, seems to be temperature dependent, shifting to lower frequencies with decre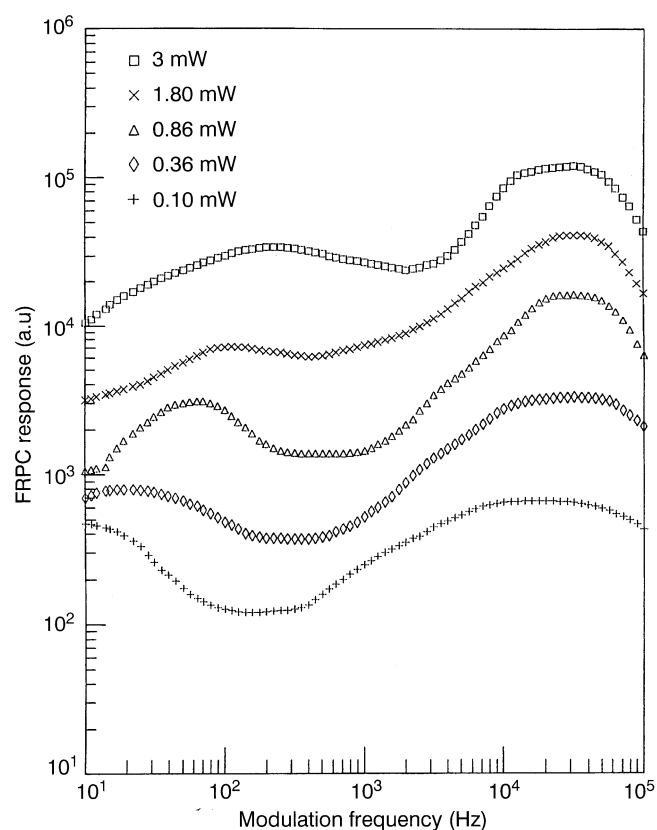asing temperatures. Figure 4 shows the intensity dependence of FRPC at 120 K under the same applied electric field. Clearly the position of the second peak is intensity dependent and shifts to lower frequencies with decreasing light intensities. A plot of these second peak frequencies vs the excitation intensity is shown in Fig. 5 at 120 K. It can be approximated by a straight line with a slope of 1.1 ± 0.02. The main peak, however, is independent of intensity at this temperature. It has been suggested that these results can also provide a way of distinguishing between capture and recombination rates: if the carriers move in extended states, and detrapping is not important, then only one peak is expected in the quadrature frequency-resolved photocurrent, corresponding to the total capture rate into localised levels. At higher temperatures carriers may be thermally ionised from recombination or trapping states. Simple models indicate that a second lifetime proportional to the detrapping rate will be seen even if only one recombination path is present. However, because the release rate is thermally activated both the second lifetime and the strength of its contribution will be strongly temperature dependent [14, 22].

The distribution of lifetimes ($\tau \propto f^{-1}_{peak}$) with respect to generation rate have been used to determine what kind of recombination occurs between the photoexcited carriers [23, 20]. It has been 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. 5 shows that the peak frequencies and consequently the lifetimes, are dependent on the generation rate and therefore can be interpreted as supporting the DP model.

In both the temperature- and intensity-dependent FRPC measurements mentioned above the peak position, i.e., f_{peak} was independent of the applied electric field.

Figure 6 shows the temperature dependence of photocurrent for three excitation intensities (633 nm) determined at an electric field of 5×10^4 Vcm^{-1} and 100 Hz.

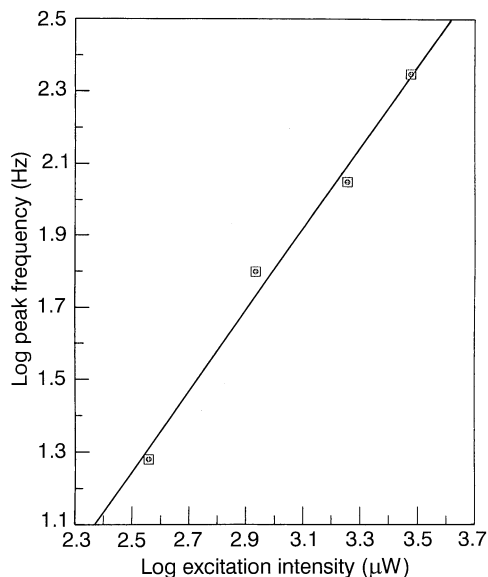The general behaviour of this result did not change for frequencies up to 10 kHZ. In all three curves, above 150 K, the behaviour is approximately linear. For the 2.3 mW curve the activation energy of this linear region is about (172 ± 10)meV. This result is in agreement with the d.c. photocurrent results of other researchers: Marshall et al [24] give 260 meV for a wider temperature range; Viger et al [25] report 120 meV for $T < 190$ K; and recently from the transient photocurrent (for holes) measurements, Moses [26] has determined an activation energy of 160 meV for 225 K $< T <$ 300 K.

As the intensity decreases, the activation energy increases, indicating that the position of the Fermi level is moving down to deeper energy levels. At low temperatures (below about 60 K), the intensity of photocurrent does not show an activated behaviour.

An important characteristic of photoconductivity is the dependence of photocurrent on the incident light intensity. It is now known that the nature of this dependence differs in various semiconductors. It may be described that the intensity of the photocurrent is proportional to the generation rate: $I_{PC} \propto G^v$, where the exponent v is determined to be temperature dependent. This dependence can be seen in Fig. 7 where the exponent calculated from $[d(\ln I_{PC})/d(\ln G)]$ is plotted against temperature. Rose [27] suggests that $v = 1$ correspond to monomolecular recombination and $v = 0.5$ to bimolecular recombination. However in the case of continuous distribution of traps the value of v may be anywhere between 0.5 and 1.0 depending upon the intensity and the temperature range. As can be seen from Fig. 7 the value of the exponent lies between about 0.55 and 1.00 (obtained at the frequency range 10 Hz–1 kHz) for the a-Se samples studied in this work, indicating the presence of a continuous distribution of localized states in the energy gap. The curve has a maximum (about 1.00) at about 110 K, and

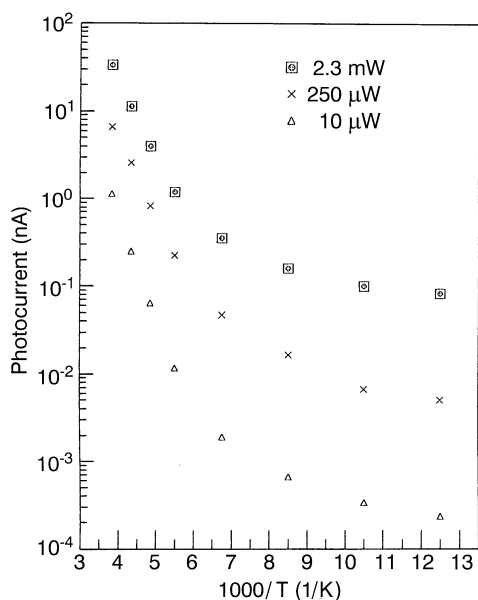**Fig. 5.** Peak frequency vs excitation intensity for the second peak of a-Se (see text). T = 120 K

Fig. 6. Temperature dependence of photocurrent in a-Se for three different excitation intensities measured at 100 Hz
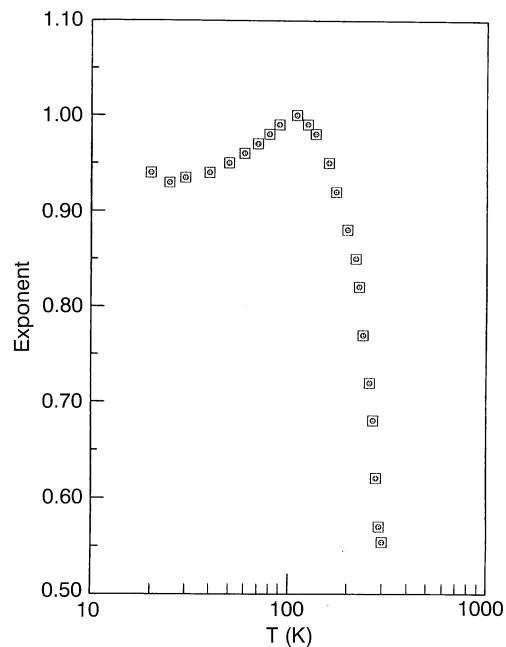

Fig. 7. Temperature dependence of the exponent v in a-Se

above this temperature it falls rapidly with increasing temperature, but below 110 K it decreases slowly with decreasing temperature until around 50 K and then reaches more or less a constant value (0.94). The observed constant value of v cannot be explained by the multiple-trapping model [27]. At low temperatures, Shklovskii et al [28] and Searle [20] have developed geminate and DP models respectively for the photoconductivity processes in amorphous semiconductors. These models are essentially the same in the absence of significant geminate pair effects and allow, in particular, analytical relations to be obtained for the correlation between the excitation light intensity, the carrier density and the corresponding lifetime. According to these models, at low temperatures, photoexcited carriers can lose energy only by tunnelling to lower energy states, such as localized tail states or by recombination. Since the tunnelling processes are only slightly temperature dependent, the exponent v will be therefore nearly constant. The predicted values of the models for v are slightly less than unity, which are in agreement with our low-temperature results.

The v values were found to be independent of the applied electric field and the frequency (10 Hz–1 kHz) in whole temperature range indicated in Fig. 7.

3 Conclusion

The quadrature frequency-resolved photocurrent response (FRPC) of a-Se thin film samples between 10 Hz and 100 kHz was measured as a function of the intensity of the excitation light and temperature. The temperature range covered was 20–295 K. It was observed that the FRPC response shows a single broad peak (main peak) at room temperature, and its peak frequency depends on the excitation intensity at room temperature. The dependence on the intensity can be approximated by a power law $f_{\text{peak}} \propto G^{0.78 \pm 0.15}$ for all the samples used.

Below about 250 K a weak peak (the second peak) was discovered in the FRPC spectra at the low frequency range, in addition to the main peak. Searle [14] and Ambros et al [22] suggest that this second peak is related to detrapping rate. It splits away markedly from the main peak as the temperature drops at an excitation intensity of 3 mW. The peak frequency of the second peak varies with the excitation intensity as $f_{\text{peak}} \propto G^{1.1 \pm 0.02}$ at 120 K. This supports the distant pair model in which the peak frequencies and thus carrier lifetimes depend on the excitation intensity at low temperatures. However the peak frequency of the main peak was found to be independent of temperature and also excitation intensity at low temperature. The intensity of the photocurrent at a fixed frequency is also found to be temperature dependent. The high temperature regions of photocurrent vs inverse temperature curves show an activated behaviour with an activation energy of (172 ± 10) meV for an excitation intensity of 2.3 mW. For lower excitation intensities the activation energies increase owing to the shift of quasi-Fermi level. Below about 60 K the intensity of the photocurrent does not show an activated behaviour.

The exponent v in the power law relationship of the intensity of the photocurrent on the generation rate is found to be strongly temperature dependent between 100 K and 295 K. It varies between 1.00 and 0.55, indicating a continuous distribution of localized states within the mobility gap. However, below 100 K its value decreases very slowly with decreasing temperature until about 60 K, and then it reaches more or less a constant value (0.94), and thus the activation energy becomes zero as expected. This result, which is in contradiction with the predictions of the multiple-trapping model, may be explained by the models developed by Shklovskii et al [28] and Searle [20] based on the theory of energy-loss hopping of photocarriers through a distribution of localized band-tail states.

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