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A model for steady-state photoconductivity in amorphous selenium

D. Carles, G. Lefrançois and J. P. Larmagnac

L.E.C.A.P., Faculté des Sciences de Rouen, B.P. 67, 76130 Mont Saint Aignan, France

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Résumé. — La photoconduction dans le sélénium amorphe dépend linéairement de l'intensité lumineuse. Ce résultat ne peut être interprété par le mécanisme classique de génération de paires électron-trou suivie de recombinaison. Nous supposons que les photons incidents génèrent des défauts photo-induits de structure semblable aux paires proches à valence alternée. L'excitation optique ou thermique de ces défauts provoque la photoconductivité. Ce modèle explique la proportionnalité observée entre le photocourant et l'intensité lumineuse.

Abstract. — The photoconductivity of amorphous selenium varies linearly with light intensity. This result cannot be interpreted by the classical mechanism of electron-hole pair generation followed by recombination through gap states. We assume that the incident photons create photoinduced defects whose structure is IVAP-like. The optical or thermal excitation of those defects yields the photoconductivity. In this model, the theoretical photocurrent is proportional to light intensity as observed.

1. Introduction.

Steady-state photoconductivity is the equilibrium state reached after an infinite time when a semiconductor is illuminated by incident light of suitable wavelength. The photocurrent results from two competing processes : photogeneration and recombination of charge carriers. In amorphous semiconductors, this phenomenon exhibits almost the same features as those observed in the crystalline phase : a plot of the photocurrent *versus* light intensity F has two different regimes : when the photocurrent is less than the dark current I_{ϕ} , the recombination is monomolecular and I_{ph} is proportional to F whereas, for larger values of the light intensity, which yield a photocurrent larger than I_{ϕ} , the recombination becomes bimolecular and I_{ph} is then proportional to the square root of the light intensity [1].

Previous results [2] obtained on amorphous selenium films do not follow this theoretical model. The experimental data show a sublinear variation of I_{ph} given by

$$I_{ph} \sim F^x$$

where x is equal to 0.75. Under pulsed illumination [3], the same behaviour is observed. Follow-

ing Rose [4], these results were interpreted in terms of an exponential distribution of hole traps N_t , lying in the band-gap above the valence band-edge E_v ,

$$N_t = A \exp \left[- (E - E_v)/kT_c \right].$$

A and T_c are the characteristic constants of the distribution. Owen and Spear [5] proposed that this exponential tail of defects is the background density of localized states extending right across the mobility gap.

However, the interpretation of the results given in reference [2] has two major disadvantages : (i) the exponential tail of traps is not in agreement with the models of charged defects [6, 7]. These models are now well established and describe correctly the experimental data on amorphous chalcogenides, (ii) the experimental results were obtained on 0.5 μm thick samples. For such a thickness, the illumination is not uniform because of the large value of the absorption coefficient [8] in the spectral range where significant photoconductivity takes place.

This paper deals with new experimental results of steady state photoconductivity obtained on amorphous selenium films whose thickness is small enough to ensure a nearly uniform illumination.

2. Experimental results.

The selenium films were obtained by thermal deposition (evaporation rate $\sim 10 \text{ \AA/s}$) under ultra high vacuum conditions (2×10^{-9} torr). They were provided with gold electrodes for bias contacts. The sample had a planar structure and the light incident flux was at right angles to the sample plane. The film thickness was 60 nm and the interelectrode distance 200 μm . With an applied voltage equal to 100 V, the electric field is small enough to prevent space charge effects and the dark current is ohmic at room temperature. The incident flux depends upon the spectral response of both the light source and the grating system but is nearly equal to 0.1 W/m^2 . Neutral filters enable us to vary light intensity over three orders of magnitude.

Figures 1 and 2 show the experimental results typically observed. Whatever the wavelength — in the spectral range 350 nm ; 800 nm — and the temperature — between 143 K and 305 K —, the logarithmic plot of the photocurrent *versus* light intensity is a straight line with a slope equal to one.

The influence of the electric field was also studied. For bias voltages in the range 1 V ; 1 000 V, the photocurrent stayed ohmic and no field effect was observed.

3. Discussion and conclusion.

Amorphous selenium has a low dark conductivity and the measured dark current I_d is equal to 3×10^{-15} A at room temperature. Here, we are concerned with photocurrents larger than I_d . Thus, a log-log plot of I_{ph} vs. F should exhibit the square root regime as already mentioned. As this is not the case, we have to find a model which explains this discrepancy.

The first model of photoconductivity for amorphous chalcogenides was proposed by Street and Mott [9] and is based upon the model of charged defects : a bond is transferred from one chalcogen atom to another resulting in two defects : one negatively charged, one-fold coordinated and one positively charged, three-fold coordinated, labelled respectively D^- and D^+ . The requirement of neutrality leads to an equal density of D^+ and D^- which are associated in pairs called [7] valence alternation pairs (VAP). Some of them can be close enough to be localized on neighbouring atoms. In such a case, they are called intimate valence alternation pairs (IVAP). When free carriers are photogenerated, they are rapidly trapped by the charged defects which become neutral (D^0). The neutral defects can release free carriers in their respective bands and

the steady state photocurrent is established when thermal equilibrium is reached. Recombination of the carriers occurs by tunnelling of an electron between two D^0 's, the VAP being restored by the relationship.

From this model, the photoconductivity must be proportional to $(\eta F)^{1/2}$ for large photocurrents ($I_{ph} > I_d$) and to ηF for small photocurrents ($I_{ph} < I_d$). η is the quantum efficiency of photogeneration. Experimental results are in disagreement with this model : (i) the predicted I_{ph} vs. F curves (Figs. 1 and 2) are not observed ; (ii) figure 3 show that the spectral dependence of the photoconductivity (curve a) does not follow the variation of the quantum efficiency (curve b) as observed by Knights and Davis [10]. According to them, the quantum efficiency is electric field dependent whereas no field effects were observed in our results. The difference in the behaviour of the photoconductivity and the quantum efficiency suggests that the photogeneration of free carriers is not the main process giving rise to a photoconductive effect.

Fig. 1. — Log(photocurrent) as a function of log(light intensity) for different values of incident wavelength at room temperature.

Frye and Adler [11] had proposed a model which takes into account the relaxation effects occurring for neutral defects. However they find the same variation of I_{ph} with F and η as the Street-Mott model.

Following Street [12], we assume that the photogenerated electron-hole pairs geminate giving rise to a photoinduced defect. This defect is a (D^+, D^-) pair but the atoms concerned are close together so that the structure is IVAP-like. This defect can exist because of the strong electron-phonon coupling in chalcogenides. The transition from the ground state to a closed (D^+, D^-) pair can occur either by self trapping of an exciton (path I followed by a local relaxation — Fig. 4 — Ref. [12]) or by direct excitation (path II — Fig. 4 — Ref. [13]). No free carriers are

Fig. 2. — Log(photocurrent) as a function of log(light intensity) for different temperatures. Incident photon energy = 2.92 eV.

generated by this process and the photocurrent is obtained in the following way : the photo-induced defects are converted into (D^0, D^0) pairs [14]. The excitation can be either thermal or optical. As in the Street-Mott model [9], the carriers trapped in the D^0 's centres are thermally excited in the bands, giving rise to photoconductivity. When a defect — in the (D^0, D^0) configuration — releases a carrier, a charged pair is created.

If we denote by C the chalcogen atom in its normal bonding configuration, we can summarize all the phenomena by the following reactions

Thus, the photoinduced defects can be in one of the following configuration : (D^+, D^-) , (D^0, D^+) , (D^0, D^-) , (D^0, D^0) . Two of them are neutral and the other two are oppositely charged with respect to the thermally excited carriers. Thus, a free hole will be most probably captured by a (D^0, D^-) pair because of the Coulombic interaction, which is not the case for the other three configurations. The same argument holds for electrons and (D^0, D^+) 's. In other words, a (D^0, D^0) pair gives rise both to a free carrier and a trapping centre. The recombination occurs by restoring the (D^+, D^-) pair which can self annihilate [15] and return to the ground state.

Now we are able to deduce the expression of the photocurrent. The density of photoinduced defects — (D^+, D^-) pairs — is proportional to the incident light intensity. Thus, the density of (D^0, D^0) pairs consists of two parts : the first one, resulting from optical excitation, is pro-

Fig. 3. — Spectral dependence of photoresponse (curve a) and quantum efficiency (curve b — from Ref. [10]). The saturated high energy values of both curves has been normalized to unity.

Fig. 4. — Configurational coordinate diagram for a self-trapped exciton in chalcogenides. The self-trapped exciton is a close (D⁺, D⁻) pair (see Ref. [12]).

portional to both the incident flux and the density of (D⁺, D⁻) pairs, the second part, due to thermal transitions, being only proportional to the density of (D⁺, D⁻) pairs. Thus, taking N_0 for the density of (D⁰, D⁰) pairs, we can write

$$N_0 \sim AF^2 + BF$$

where A and B are constants. Neglecting the electron contribution to the photocurrent, the hole generation rate is proportional to N_0 whereas the density of free holes Δp is equal to the density of hole trapping centres — (D^0 , D^-) pairs. Under steady state conditions, we can write

$$N_0 \sim (\Delta p)^2.$$

Thus

$$(\Delta p)^2 \sim AF^2 + BF.$$

For high light intensity, $\Delta p \sim F$ and the photocurrent varies linearly with light intensity.

Finally, we can analyse the spectral dependence of the photocurrent. For the higher values of the photon energy — part I, Fig. 3 — the photocurrent saturates as the quantum efficiency does. It can be assumed that the photon energy is larger than the optical transitions of the figure 4. Electron-hole pairs are created as predicted by the Knights-Davis model [10]. For values of $\hbar\omega$ lying in the range 2.1-3.5 eV (part II), direct excitation of (D^+ , D^-) pairs occurs and free carriers are created by means of the intermediate (D^0 , D^0) state or by direct excitation of a hole — and a correlated (D^- , D^0) pair — or an electron — and a (D^+ , D^0) pair — as suggested by Biegelsen and Street [16]. The tail of the curve (part III) is close to that of the quantum efficiency [10] and can be attributed to the formation of excitons near VAP's which exist in amorphous chalcogenides. This assumption is confirmed by the observed excitation spectrum of photoluminescence [17] which exhibits a maximum at 2.1 eV.

In summary, we propose a model which explains the observed photoconductivity in amorphous selenium. It should be used for solids where photoinduced defects can be created with a density higher than that the native ones whereas the Street-Mott model can be applied to solids where native defects play the most important part in the recombination processes of the photogenerated carriers.

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