Journal of Non-Crystalline Solids 114 (1989) 1–6
North-Holland

Section 1: The Mott lecture

LOW TEMPERATURE ELECTRONIC TRANSPORT IN NON-CRYSTALLINE SEMICONDUCTORS

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The general features of the steady state photoconductivity of several non-crystalline semiconductors at low temperatures are discussed in terms of energy loss hopping among localized tail states. New measurements of the effective mobility of photocarriers in hydrogenated amorphous silicon by means of the traveling wave method are presented and compared with time-of-flight mobilities.

1. INTRODUCTION

About two years ago, C. Cloude, W. Spear et al.[1,2] found that the predominant transport path and mechanism undergo a fundamental change near 100K for electrons and near 200K for holes in hydrogenated amorphous silicon (a–Si:H). They measured the time-of-flight (TOF) drift mobility and found a sudden rise of the drift mobilities below these temperatures. At higher temperatures one finds the familiar rise of μ with increasing T which in the multiple trapping model is attributed to the increasing fraction of time spent by charge carriers in extended states near the mobility edge. The drift mobility μ in the new low temperature transport regime increases with the intensity of the transit pulse as well as of a uniformly absorbed pre-excitation illumination. Transport in this regime is described by hopping of carriers among the localized bandtail states.[1,2]

Earlier experiments by Hoheisel et al.[3] had also shown a change in the nature of the photoconductivity σ_P. When normalized by the charge and bulk generation rate G of photocarriers, this quantity σ_P/eG is constant below 50K and has nearly the same value $0.5\text{–}2\times10^{-11}\text{cm}^2/V$ for all a–Si:H samples. In this low T range, σ_P is very nearly proportional to G, i.e., $\gamma\approx1$ in $\sigma_P\propto G^\gamma$, and the decay time of σ_P is faster than 10^{-5}s. At higher T, the decay is slow, the exponent γ decreases to 0.6 or lower, and $\sigma_P(T)$ depends on sample characteristics. These authors[3] suggest that the low temperature photoconductivity is due to photocarriers passing through the extended states before they become trapped.

In this paper I shall discuss new results which might shed some light on the nature of these low temperature transport phenomena. I begin with the steady state photoconductivity and compare the σ_P/eG values of different amorphous semiconductors with a recent theory of Shklovskii et al.[4] I then report results[5] obtained with the traveling wave technique[6,7] which confirm the presence of a new low temperature transport mechanism in a–Si:H.

2. STEADY STATE PHOTOCONDUCTIVITY

Fig. 1 shows the T-dependence of the normalized coplanar photoconductivity σ_P/eG of a–Si:H as well as of chalcogenide glasses.[8] All curves show the same general features. The quantity σ_P/eG is constant at low temperatures. This value as well as the temperature of the rapid rise of σ_P/eG depends on the material. Low quality evaporated Ge and chemical vapor deposited (CVD) Si films have σ_P/eG values surprisingly similar to high quality a–Si:H. The exponent γ of all samples is $0.96\leq\gamma\leq1$ where σ_P = constant, and it decreases to about $\gamma\sim0.5$ when σ_P begins to rise with T.

3. THEORY OF PHOTOCONDUCTIVITY

The nearly universal behavior of the low T photoconductivity suggests that the conduction process is related to very general features of amorphous semiconductors. The model of Hoheisel et al.[3] fulfills this condition, because the capture time of free carriers $\tau\approx10^{-13}$s and the extended state mobility $\mu\sim1\text{–}10\text{cm}^2/\text{Vs}$ should be

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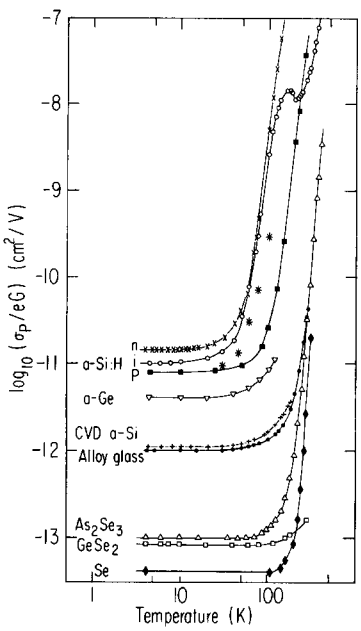

Figure 1
Temperature dependence of normalized photoconductivity. Asterisk represent theoretical values for a-Si:H. The allloy composition is $As_{34}\,Te_{28}\,S_{21}\,Ge_{16}\,Se_1$.

quite universal quantities, yielding $\sigma_P/eG = 10^{-13}$–$10^{-12}cm^2/V$. This model yields also γ–1.0 and very fast decay times. It may, however, be difficult for this model to explain the observation of Vanecek et al.[9] that σ_P/eG decreases only slowly with $h\nu$ below the gap energy and is independent of $h\nu$ above it.

Alternatively one might consider the theory of Shklovskii et al.[4] At low temperatures, photoexcited carriers can only lose energy by tunneling to lower energy states, such as localized tail states or by recombination. The generality of the solution of the problem of simultaneous tunneling diffusion and radiative recombination in a spectrum of localized states stems from two factors. First, the prefactors ν_o and τ_o^{-1} of the rates for tunnel diffusion to a center at distance r and recombination with a hole at distance R

$$\nu_d(r)=\nu_o \exp(-2r/a) \tag{1}$$

$$\nu_r(R)=\tau_o^{-1}\exp(-2R/a) \tag{2}$$

are expected to be nearly the same for most materials $\nu_o \approx 10^{12}$–$10^{13}s^{-1}$ and $\tau_o \approx 10^{-8}s$. Also the localization radius should be of the order of a=1nm. Secondly, it turns out that the concentration of states of lower energy, and hence available for tunnel diffusion, decreases on the average by a factor 1/2 after each tunnel transition independent of the shape of the density of states.[4] These general features yield a probability $\eta(R)\approx R_c/R$ that a photoexcited pair does not recombine geminately and diffuses to a separation $R>R_c$ where $R_c=(a/2)\ln(\nu_o\tau_o)$ is of the order 5nm. In order to contribute to photoconduction the electron has to recombine with a hole from a different photo-created pair (non-geminate recombination) and it therefore has to survive the fate of geminate recombination by diffusive tunneling to a distance $R\sim\frac{1}{2}n^{-1/3}$, the average half distance to neighboring holes in a steady state concentration n.[10] This concentration is obtained by equating the surviving electron concentration reaching a separation $\frac{1}{2}n^{-1/3}$ per unit time with the rate of radiative recombination over that distance:

$$G\,\eta(\tfrac{1}{2}n^{-1/3})=n/\tau_o \exp(n^{-1/3}/a) \tag{3}$$

A photocurrent is obtained as a result of the special asymmetry of hopping in an electric field E. To calculate this, one needs a density of states function $g(\varepsilon)$ for which we assume an exponentially decaying tail

$$g(\varepsilon)=(N/\varepsilon_o)\exp(-\varepsilon/\varepsilon_o) \tag{4}$$

with energy ε counted positive into the gap. One then obtains the current density

$$j=G\,\eta(r)[\frac{1}{3}\frac{e^2<r^2>E}{\varepsilon_o}] \tag{5}$$

where the square bracket is the average dipole moment arising from a tunnel hop over a length r in a field E. With the survival probability $\eta(r)\sim R_c/r$ and $r=\frac{1}{2}n^{-1/3}$, where $n^{-1/3}/a\equiv L$ is determined by Eq. (3), one obtains for the low temperature photoconductivity[10]

$$\sigma_P=G\,\frac{e^2a^2}{24\varepsilon_o}\ln(\nu_o\tau_o)L \tag{6}$$

Since the steady state concentration n and hence L

depend only weakly on G through Eq. (3) one finds

$$\gamma=1-(1/L) \tag{7}$$

Using values for n-type a–Si:H, $\nu_o\tau_o=10^4$ and $G=10^{20}\text{cm}^{-3}\text{s}^{-1}$ one finds $\sigma_P/eG=3\times10^{-12}\text{cm}^2/\text{V}$ and $\gamma=0.93$ in good agreement with experiments.[3,8] The low temperature values of σ_P/eG and γ should be similar for many different materials because a^2 and ε_o are the only material dependent parameters in Eq. (6). In deriving Eq. (6) we assumed electron-hole recombination to dominate. However, when the concentration of recombination centers exceeds n as is likely in low quality amorphous semiconductors such as evaporated or CVD deposited a–Ge and a–Si, then L in Eq. (6) is to be replaced by $N_r^{-1/3}/a$ and $\gamma=1$.

At very low temperatures no upward hops are possible. The steady state photocarrier concentration n and p nearly fill up the band tails up to a filling energy ε_f

$$n=N_e^{-\varepsilon_{fe}/\varepsilon_o} \tag{8}$$

Most of the nongeminate recombination contributing to σ_P proceeds from electron energies near ε_{fe} to holes near their filling energy ε_{fh} because that is where the majority of carriers are in an exponential distribution $g(\varepsilon)$ of localized tail states. The dependence of σ_P on temperature in the hopping regime was considered elsewhere.[11] A temperature dependence of σ_P can be expected to begin when the Adler-Monroe transport energy[12,13]

$$\varepsilon_t=3\varepsilon_o\ln[\frac{3\varepsilon_o}{kT}\frac{a}{2}N^{1/3}] \tag{9}$$

rises with increasing T and passes the filling level ε_{fe}.[11] According to Eq. (8) this occurs near the temperature

$$T_c=3\varepsilon_o/kL \tag{10}$$

or T_c~60K for the particular example of our n-type a–Si:H. The transport energy ε_t is of particular significance because at this energy the probability of upward hops equals that of downward hops. Above ε_t (i.e. $\varepsilon<\varepsilon_t$) downhops predominate. The electron occupation below ε_t is essentially thermal with ε_f playing the role of an effective Fermi energy. As the temperature is raised the non-equilibrium distribution of photocarriers can be considered to unfreeze from the bottom up, becoming thermal at energies below ε_t (i.e., $\varepsilon>\varepsilon_t$ because we chose to count ε positive from the conduction band toward the gap). The major contribution to the conduction occurs in an energy range of width $W=(6kT\varepsilon_o)^{1/2}$ around ε_t. Because of this finite width, σ_P becomes temperature dependent already before T_c of Eq. (10) is reached. Conduction in extended states will begin to dominate when ε_t reaches the mobility edge, i.e., when $\varepsilon_t=0$. We are aware that the simple form Eq. (4) for $g(\varepsilon)$ ceases to be valid near the mobility edge. However, using this simple form for $g(\varepsilon)$ we find that ε_t reaches zero near 130K for a=1nm, ε_o=0.025eV and $N=3\times10^{19}\text{cm}^{-3}$.

The energy states around ε_t not only provide the dominant conduction path but also the major recombination channel.[11] Therefore, as ε_t rises with increasing T, the recombination rate increases. As a consequence, the steady state photocarrier concentration n decreases with increasing T, moving ε_f of Eq. (8) deeper into the gap. Despite this decrease in n (and p), the value of σ_P/eG increases rapidly in this temperature range. The results of our calculations[11] shown by asterisk in Fig. 1 agree quite well with the results on n-type a–Si:H considering that we made no adjustments in $g(\varepsilon)$ and the value of ε_o to achieve a better fit.

Until now we assumed that photoexcited electrons recombine with holes. However, as these concentrations decrease with increasing T above T_c, other centers will become the dominant radiative and nonradiative recombination centers even in the best materials. This causes the photoluminescence to decrease with rising temperature. Although only outlined briefly, this model of transport of photocarriers at low temperatures may help us understand the drift mobility measurements which will be discussed in the following.

4. DRIFT MOBILITY OF PHOTOCARRIERS

We extended the traveling wave technique to low temperatures to explore the new transport regime discovered by Cloude et al.[1,2] This technique consists of the following.[5–7] A semiconductor film of thickness

d and width w is placed a distance h above a piezoelectric crystal which carries a surface acoustic wave (SAW) of frequency ω. The electric wave accompanying the SAW penetrates the film and moves with the sound velocity v_s. A fraction of the charge induced by the traveling electric wave is transported by the wave and gives rise to the short circuit dc current[5–7]

$$I=\frac{\mu_d}{v_s}\sigma E_{rms}^2 dw \tag{11}$$

E_{rms} is the average longitudinal field component in the propagation direction at the film surface a distance h above the piezoelectric crystal. Its value is given by the SAW power. The drift mobility μ_d and conductivity σ correspond to the frequency ω. It is convenient to measure the open circuit voltage between electrodes separated by l in the wave direction

$$V=\frac{\mu_d\sigma}{\sigma_{dc}}\frac{l}{v_s}E_{rms}^2 \tag{12}$$

In Fig. 2 the effective mobility $\mu_{eff}=\mu_d\sigma/\sigma_{dc}$ is plotted as a function of T for intrinsic a–Si:H as well as for films doped with $8\times10^{-4}PH_3$ and $10^{-4}B_2H_6$, respectively, in the gas phase. Above 200K, the effective mobility agrees with the TOF drift mobility if the latter is evaluated for times $t=2\pi/\omega=54$ns. This agreement suggests that the ratio of the ac to the dc conductivities, σ/σ_{dc} in Eq. (12), is close to unity in the multiple trapping regime. The mobility μ_d is independent of light intensity as long as the trap quasi Fermi level does not rise above the demarcation energy $\varepsilon_d=kT\ln(\nu_o/\omega)$.[14]

While the mobility at higher T can be measured with or without illumination, the data below 100K represent μ_{eff} of steady state photocarriers because the dark conductance is too small to obtain measurable currents by the traveling wave technique.

All three samples show nearly the same relatively high value of μ_{eff} at low temperatures. The effective mobility is constant to about T=10K and then decreases approximately as T^{-2} between 20 and 100K. It may seem surprising that μ_{eff} of all three samples are similar in magnitude in the low T regime. This is because the photocarriers are electrons below 100K for both n-type and p-type a–Si:H films. The sign of the current of Eq. (11), positive for flowing in the traveling wave direction, is that of the dominant carriers, and the sign changes in p-type samples from positive above 200K to negative below 100K.

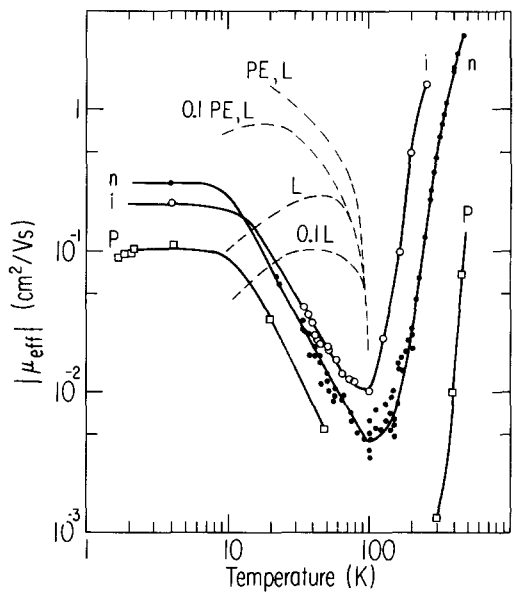

Figure 2
Effective mobility of a-Si:H measured by traveling wave method. Dashed lines are TOF measurements of Ref. 1 and 2.

The dashed curves in Fig. 2 show the electron TOF results of Cloude et al.[1,2] for different transit pulse intensities L and pre-excitation pulse strengths PE. The low temperature transport regime starts in both our experiments near the same temperature. However, one notes important differences between the TOF and traveling wave results. The TOF mobility depends on light intensity as shown and its temperature dependence differs from that of μ_{eff} measured by the traveling wave method. We find that μ_{eff} does not depend on light intensity. Furthermore, it does not depend on photon energy for $h\nu >$ band gap. It is evident that the two techniques measure different parameters of the same conduction process. In the following we try to explain what is measured by the traveling wave method.

5. TRAVELING WAVE MOBILITY

The electric field pattern above the piezoelectric transducer can be obtained from the static field produced by the positive and negative charge packets that are associated with the longitudinal surface acoustic wave as illustrated in Fig. 3. This 'static' field moves with the sound velocity v_s in the x-direction. The normal component E_y in the film produces a current density $j_y=\sigma(\omega)E_y$. The current divergence produces space charge densities $\delta=-i\,\sigma(\omega)E_y/\omega$ of opposite sign at the top and bottom film surfaces. These space charges interact with the longitudinal field E_x giving rise to currents in the x-direction $I_i \propto \mu_d(\omega)\sigma(\omega)E_{yi}E_{xi}/\omega$. Since E_y and E_x are $\pi/2$ out of phase, δ and E_x are in phase yielding two currents I_1 and I_2 flowing in the x-direction near the film surfaces at h and $h+d$ above the piezoelectric crystal, respectively. Eq. (11) is the net dc component of the current I_1+I_2. This current is obtained by considering that those carriers that move with the drift velocity $\mu_d E_x$ along the wave remain in the same field direction a fraction of time $\mu_d E_x/v_s$ longer than those carriers that find themselves in the opposite field direction and hence drift against the wave. The dc current of Eq. (11) is therefore proportional to $\mu_d E_x/v_s$.[5–7]

In connection with Eq. (12) we mentioned that μ_{eff} contains the ratio of ac to dc conductivity and the drift mobility. In the multiple trapping regime above 200K one is familiar with the physical meaning of the drift mobility μ_d: Only a fraction of the charge δ is free, the rest is trapped during the period $2\pi/\omega$. This fraction multiplied with the free carrier mobility is the drift mobility μ_d. In the low temperature hopping regime our interpretation of μ_d follows the same line of reasoning: Only that fraction of δ is transported by E_x with a mobility $\mu(\omega)$, that does not recombine before making a hopping transition under the influence of E_x in the period $2\pi/\omega$. This fraction multiplied with $\mu(\omega)$ is the drift mobility $\mu_d(\omega)$. This fraction is constant at very low temperatures. As the temperature is increased, the transport path ε_t rises, thereby accelerating recombination and decreasing $\mu_d(\omega)$. Part of the observed temperature dependence of μ_{eff} may be caused by the factor

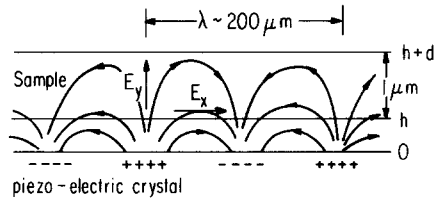

Figure 3
Traveling wave geometry. Note difference in vertical and horizontal scales.

$\sigma(\omega)/\sigma_{dc}$. One normally finds that the ac conductivity is only weakly temperature dependent while σ_{dc} increases with T. This however cannot be the major factor because μ_{eff} decreases by a factor 10 while σ_{dc} increases by less than a factor 2 between 10 and 40 K.

The measurements by Long et al.[15] of the ac dielectric loss appear to be at odds with our results. We find that σ_{dc} is proportional to the light intensity G while μ_{eff} is independent of G. This means that $\mu_d(\omega)\sigma(\omega)$ must be proportional to G. We suspect that $\mu_d(\omega)$ is constant while $\sigma(\omega)\propto G$ because the hops are most likely uncorrelated, so that the dc as well as the ac photoconductivity is proportional to G. Instead, Long et al. find that $\sigma(\omega)$ depends only weakly on G.[15]

6. CONCLUSIONS

The σ_P/eG curves of different semiconductors have very similar shapes, but at low temperatures the highest and lowest values measured by us differ by a factor 10^3 which is too large for a unified theory. The normalizing factor that is still unaccounted for by the present theories appears to be the Coulomb attraction of the photoexcited electron hole pairs that enhances geminate recombination. The Coulomb interaction is larger in materials having a smaller dielectric constant such as Se, As_2Se_3 and $GeSe_2$ in agreement with their small σ_P/eG values in Fig. 1. Geminate recombination reduces σ_P of hopping as well as of extended state conduction because the drift range gained in a field is taken back by the recombination process.

The value $\sigma_P/eG=3\times10^{-12}\text{cm}^2/\text{V}$ estimated for hopping from Eq. (6) agrees well with data on Si and Ge considering the uncertainty in a^2/ε_o. The Coulomb

effect, neglected in this theory, seems not to play an important role in these materials. The calculated temperature dependence for n-type a–Si:H shown by asterisk in Fig. 1 is somewhat less than the experimental one. The hopping theory fails moreover to explain the rapid decay $\tau<10^{-5}$s observed by Hoheisel et al.[3] at a generation rate $G\sim3\times10^{20}\mathrm{cm}^{-3}\mathrm{s}^{-1}$. The theory predicts $\tau\sim10^{-4}$s. This discrepancy may be removed by using instead of Eq. (4) a special form for the density of states $g(\varepsilon)$ such as suggested by Spear.[2]

The extended states transport model[3] for σ_P, on the other hand, fails to explain the factor 10 decrease of μ_{eff} between 10 and 40K where σ_P is constant.

From the fact that μ_{eff} is independent of the generation rate G while $\sigma_P \propto G$, we conclude that $\mu_d(\omega)\sigma(\omega)\propto G$. We suppose that $\sigma(\omega)$ is nearly proportional to G as long as the occupancy factor at the ac transport path for the traveling wave frequency of 18MHz is much less than unity. Long et al. observe[15] instead a very weak dependence of the dielectric loss on G. They however deal with frequencies in the kHz range and hence a transport path close to the occupancy filling energy ε_f. Moreover, according to Pollak and Geballe,[16] isolated close pairs of states contribute to the normal σ_{ac}. It does not seem reasonable that such isolated pairs contribute to the charge $\delta=-i\,\sigma(\omega)E_y/\omega$ which upon interaction with E_x yields Eqs. (11) and (12). The quantities $\sigma(\omega)$ and σ_{ac} are estimated in ref. 11.

ACKNOWLEDGEMENTS

I wish to thank R. Johanson for his traveling wave mobility measurements and him and A. Vomvas for their σ_P/eG data. I gratefully acknowledge many inspiring discussions with B.I. Shklovskii and S.D. Baranovskii. The work was partially supported by NSF DMR-8806197.

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