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PHOTOCONDUCTIVITY OF DOPED AMORPHOUS SEMICONDUCTORS AT LOW TEMPERATURES

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Abstract Low-temperature photoconductivity of doped amorphous semiconductors is calculated using the energy-loss hopping model developed previously for intrinsic materials. It is shown that even at very low temperatures, when carriers from impurities are frozen in, the doping can strongly influence the magnitude of the photocurrent. It can even change the sign of the dominant carriers as has been recently observed experimentally.

Keywords: *photoconductivity, hopping, amorphous semiconductors*

INTRODUCTION

Investigation of photoconductivity plays a central role in the study of amorphous semiconductors. Experiments on such different amorphous materials as a-Si:H, a-Ge, CVD a-Si, alloy glasses, a-As₂Se₃, a-B:H, a-Se, a-BC:H show very similar temperature dependences of the photoconductivity¹. At low T the photoconductivity is temperature-independent, while at higher temperatures it steeply rises with T in all these systems. The relatively simple and universal behaviour of the photoconductivity at low temperatures suggests that the conduction process is related to very general features of amorphous semiconductors². The most studied amorphous material with respect to the photoconductivity is a-Si:H and below we discuss data obtained for this material.

Hoheisel et al.³ suggested that the low-T photoconductivity σ_{ph} is due to photocarriers passing through extended states before they become trapped into lo-

calized band tail states. This model, however, fails to explain the observation that σ_{ph} (normalized by the generation rate G) is independent of the photon energy $h\nu$ above the gap and decreases very slowly when $h\nu$ is smaller than the mobility gap⁴. Furthermore, σ_{ph} begins to rise with temperature above $T \approx 40$ K, which is too small for reexcitation of carriers from localized tail states into the extended states².

An alternative model of the low-temperature photoconductivity has been suggested by Shklovskii et al.⁵ and is widely accepted now. According to this model, the photoconductivity at low T is due to energy-loss hopping of electrons and holes through localized tail states. The problem of hopping diffusion and recombination of photocarriers in localized tail states has been solved rigorously for intrinsic amorphous semiconductors^{5,6}. The solution agrees well with experimental data and explains, in particular, why electrons are the dominant photocarriers in intrinsic materials.

Recently experiments were carried out on doped samples of a-Si:H in order to reveal the sign of dominant photocarriers^{1,7}. In these experiments the energy-loss hopping photoconductivity was excited at low T once by subgap light, $h\nu < 1.1$ eV, which excites only one or the other mobile carrier in n-type or p-type samples respectively, and then with bandgap light, $h\nu \approx 2$ eV, which creates mobile electrons and holes at equal rate. Knowing the sign of photocarriers with $h\nu < 1.1$ eV excitation allowed Fritzsche et al.¹ to determine the sign of the photocarriers under $h\nu \approx 2$ eV excitation, because electrons and holes yield different values of photoconductivity σ_{ph} at low T . Two samples were investigated, one doped with 1000 ppm B_2H_6 , the other with 800 ppm PH_3 . For each sample, the σ_{ph} curves for subgap and bandgap lights agree perfectly, manifesting that electrons are the dominant photocarriers in the n-type and holes in the p-type sample.

This observation has been considered as surprising¹ with respect to the p-type sample. Indeed, as has been mentioned above, electrons dominate the photocurrent in the intrinsic material. Since the concentrations of photogenerated electrons and holes in the intrinsic material are equal, this obviously means that the electrons have the higher mobility. The holes at impurities in the p-type sample are immobile at low temperatures. How can these immobile holes then influence the photocurrent? In other words, if electrons hopping through tail states yield a larger value of σ_{ph} than holes, as they apparently do in intrinsic and n-type samples, why are there no electrons hopping through tail states in p-type samples when they are excited by 2

eV light to the mobility edge? We address this question below in a theoretical analysis of the energy-loss hopping photoconductivity. Preliminary results of our study have been recently published⁸. We first recall some results for intrinsic materials^{5,6} and then develop a theory in order to describe the photoconductivity in doped amorphous semiconductors.

ENERGY-LOSS HOPPING IN UNDOPED MATERIALS

At very low temperatures photoexcited carriers can only lose energy by relaxation to lower energy states or by recombination. We consider photogeneration of carriers with energies near the mobility edges. Hence relaxation to lower energy states occurs by hopping between localized states in the band tails. The rate of the hop to the localized state at a distance r has the form

$$\nu_d(r) = \nu_o \exp(-2r/\alpha_{e,h}), \quad (1)$$

where $\alpha_{e,h}$ is the localization length in the tail states for electrons and holes, respectively, and ν_o is usually taken to be of the order of a phonon frequency, $\nu_o \approx 10^{12} \text{ s}^{-1}$. Due to the localization of carriers, the recombination is a tunneling process as well with the rate

$$\nu_r(R) = \nu_1 \exp(-2R/\alpha_e), \quad (2)$$

where R is the electron-hole separation (we assume that $\alpha_e > \alpha_h$). The prefactor ν_1 for radiative recombination is the typical inverse dipole radiation lifetime $\approx 10^8 \text{ s}^{-1}$, i.e. it is much smaller than ν_o . For non-radiative recombination this prefactor should be much lower than ν_o as well due to the multiphonon character of the recombination process⁹. We will not specify a precise value of this parameter because it always appears in our formulas in the argument of a logarithmic function and its particular value is hence not very important for the calculation of the photoconductivity below.

We consider here the static photoconductivity under continuous generation of carriers with a generation rate G . Those photocarriers which recombine geminately do not contribute to the photocurrent³. Hence, we have to take into account only those photocarriers which recombine non-geminately. The probability $\eta(R)$ that an electron-hole pair avoids the geminate recombination until the electron and the hole escape from each other to a distance R by hopping through localized states has the

form⁵

$$\eta(R) = C(R_o/R)^\beta, \quad (3)$$

where the numerical factors C and β depend on the ratio¹⁰ α_e/α_h and

$$R_o = (\alpha_e/2) \ln(\nu_o/\nu_1).$$

The steady-state concentration n of nonequilibrium electrons is then determined by the equation²

$$G\eta(0.5n^{-1/3}) = \nu_1 n \exp(-n^{-1/3}/\alpha_e) \quad (4)$$

with the solution

$$n(G) = (\alpha_e L(G))^{-3}, \quad (5)$$

where the quantity $L(G)$ is the solution of the equation

$$L = \ln(\nu_1/(GL^2\alpha_e^3 \ln(\nu_o/\nu_1))). \quad (6)$$

The left-hand side of the equation (4) represents the generation rate of those carriers which survive through hopping to the distance $0.5 n^{-1/3}$ and avoid therefore the geminate recombination. The photocurrent density then has the form

$$j \approx G\eta(0.5n^{-1/3})d, \quad (7)$$

where d is the typical field-induced dipole moment of a pair when interpair recombination occurs. From this formula we see that it is the dipole moment d gained by a pair in the energy-loss hopping, which determines the contribution of a pair to the steady-state photocurrent. In order to calculate d in the intrinsic material, Shklovskii et al.⁵ have solved the following problem. They considered the hopping relaxation of an electron at $T=0$ under the influence of the electric field E through the band tail states with the density decreasing into the gap as

$$g(\epsilon) = g_o \exp(-\epsilon/\epsilon_o). \quad (8)$$

It was found that the typical field-induced dipole moment which appears after a jump of the length r has the form

$$d(r) = (1/3)(e^2 E r^2 / \epsilon_o). \quad (9)$$

In the hopping relaxation of a carrier the length of the typical hop increases with the number of hops because the concentration of available states (those which are deeper in energy) decreases and the nearest available site is on the average further apart than those at previous steps. Therefore the dipole moment provided by an electron is dominated by the last step in the relaxation process. For undoped materials the length of this step is close to $0.5 n^{-1/3}$. Hence, for undoped material

$$d \approx d(0.5n^{-1/3}) = (1/3)(e^2 En^{-2/3}/4\epsilon_o). \quad (10)$$

We obtain then for the static photoconductivity $\sigma_{ph} = j/E$ the expression²

$$\sigma_{ph} \approx G\eta(0.5n^{-1/3})(e^2 n^{-2/3}/12\epsilon_o), \quad (11)$$

where the steady-state concentration of electrons n is determined by Eq.(5).

To compare contributions of electrons and holes to the photoconductivity one has to take into account that the value of ϵ_o for the valence band tail is usually larger than that for the conduction band tail. Hence, the contribution of holes must be smaller as was experimentally confirmed¹.

LOW-TEMPERATURE PHOTOCONDUCTIVITY IN A DOPED MATERIAL

In this section we consider the hopping photoconductivity in a p-type amorphous semiconductor. A theory for n-type material can be developed in a similar way by replacing notations for electrons by corresponding notations for holes and vice versa. Let us consider a p-type sample which contains p holes per cubic centimeter in the dark. Under steady-state generation there is an additional concentration of holes p_{ph} , and that of electrons $n_{ph} = p_{ph}$. We assume that the generation rate G is not too high and $p_{ph} \ll p$.

As we have seen in the previous section, the contribution of an electron-hole pair to the photocurrent is determined by the dipole moment gained by the pair during hopping of carriers through localized band tail states. Below we show that in a p-type sample the dipole moments gained by electrons and holes differ considerably from each other, thus providing different contributions of electrons and holes to the photoconductivity.

Let us calculate first the contribution of electrons to the photocurrent. An

electron recombines once the hopping rate becomes smaller than the recombination rate. Without any correlation in the distribution of holes in space the recombination occurs at a distance $0.5 p^{-1/3}$ provided this distance is larger than R_o from Eq.(3), which we assume to be the case. The corresponding recombination rate is

$$\nu_r(0.5p^{-1/3}) = \nu_1 \exp(-p^{-1/3}/\alpha_e). \quad (12)$$

Electrons contribute to the photocurrent with

$$j_{ph}^e \approx G\eta(0.5p^{-1/3})d_e, \quad (13)$$

where d_e is the typical field-induced dipole moment gained by an electron just before it recombines non-geminately. This dipole moment is determined by the longest hop r which is usually the last one before the recombination event. Equating the hopping rate (1) with the recombination rate (12) we find that

$$r \simeq 0.5p^{-1/3} + (\alpha_e/2) \ln(\nu_o/\nu_1). \quad (14)$$

Assuming that r is dominated by the first term in Eq.(14) we obtain from Eqs.(9) and (14) the typical dipole moment gained by electrons

$$d_e = \frac{e^2 E p^{-2/3}}{12\epsilon_o^g}. \quad (15)$$

Substituting this expression into Eq.(13) we obtain the contribution of electrons to the photoconductivity

$$\sigma_{ph}^e \simeq G\eta(0.5p^{-1/3}) \left(\frac{e^2 p^{-2/3}}{12\epsilon_o^g} \right). \quad (16)$$

We calculate now the contribution of holes to the photocurrent

$$j_{ph}^h \approx G\eta(0.5p^{-1/3})d_h. \quad (17)$$

As long as the hole does not recombine it contributes to the photocurrent. Again we are interested in the non-geminate recombination only. Let us consider a hole which has escaped the geminate recombination and hops through the valence band tail states. A non-geminate recombination event happens when a new electron is created by light so that the considered hole is the nearest one to the electron. Hence, this electron has to be generated at a distance r relative to the hole with $r < 0.5p^{-1/3}$. The

average time τ necessary for the generation of such electron to occur is determined by

$$G\tau(0.5p^{-1/3})^3 \approx 1 \quad (18)$$

or

$$\tau \approx \frac{8p}{G} \quad (19)$$

During the time τ the hole can hop to a distance r determined by the equation

$$\nu_o \exp\left(-\frac{2r}{\alpha_h}\right) \simeq \tau^{-1}. \quad (20)$$

Using Eq.(19) we obtain for the typical longest hop of a hole the distance

$$r \simeq (\alpha_h/2) \ln\left(\frac{8p\nu_o}{G}\right). \quad (21)$$

Then the typical dipole moment d_h gained by a hole in the energy-loss hopping is

$$d_h = \frac{e^2 E \alpha_h^2}{12\epsilon_o^h} \ln^2\left(\frac{8p\nu_o}{G}\right). \quad (22)$$

We see that the dipole moment gained by a hole (Eq.(22)) is determined by the different set of parameters than the dipole moment gained by an electron (Eq.(15)). This provides the different contributions of holes and electrons to the photoconductivity in doped amorphous semiconductors.

Using Eqs. (17) and (22) we obtain for the photoconductivity of holes

$$\sigma_{ph}^h \simeq G\eta(0.5p^{-1/3}) \frac{e^2 \alpha_h^2}{12\epsilon_o^h} \ln^2\left(\frac{8p\nu_o}{G}\right). \quad (23)$$

Taking the typical values of parameters involved $\nu_o = 10^{12} s^{-1}$, $p = 10^{18} cm^{-3}$, $\alpha_h = 10 \text{\AA}$, $G = 10^{19} cm^{-3} s^{-1}$, $\epsilon_o^e = 0.025 eV$, $\epsilon_o^h = 0.042 eV$, one obtains that σ^h is approximately an order of magnitude larger than σ^e .

For n-type a-Si:H a similar consideration leads to the larger contribution of electrons than that of holes, in agreement with experimental data.

CONCLUSIONS

A theory of energy-loss hopping photoconductivity is developed in order to describe the low-temperature photocurrent in doped amorphous semiconductors. It is shown that in spite of the fact that carriers at impurities are immobile at low temperatures,

they influence drastically the behaviour of photogenerated carriers via recombination processes. As a consequence, the contributions of electrons and holes to the photocurrent are determined by different sets of material parameters, so that in p-type (n-type) samples holes (electrons) dominate the photoconductivity in good agreement with experimental data.

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