

Photoconductivity in Disordered Organic TPD Films

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Abstract – The steady state photoconductivity in disordered tri-methylphenyl diamine (TPD) films has been studied at relatively high temperatures (200 – 300 K). Hopping transport of holes occurs through localized centers with a Gaussian energy distribution. The steady state photoconductivity is proportional to $G^\gamma \exp[-(\sigma/(kT))^2/2]$ (with $\gamma \approx 0.5$) where G is the number of absorbed photons and σ ($= 0.067$ eV) is the standard deviation of the Gaussian distribution. We have formulated the hopping photoconductivity and reasonable physical parameters, such as the hopping relaxation time, recombination time, and diffusion coefficient (and hence mobility) of the charge carriers, are estimated for the TPD films. The photoconductivity increases with exposing air and this is a reversible effect.

Keywords: organic TPD films, photoconductivity, hopping of photocarriers, bimolecular recombination, exposing air

1. Introduction

It is now well known that charge carriers in disordered low molecular weight organic solids are highly localized with the Gaussian energy distribution and the hopping transport near room temperature occurs through localized centers which are molecules or molecular subunits [1],[2]. The drift mobility of charge carriers has been extensively studied theoretically [1],[3],[4] and experimentally using the time-of-flight (TOF) technique [2]. However, steady-state carrier transport in disordered organic films has not yet been fully discussed. To our knowledge there is no formulation of photoconductivity in this class of material.

We have measured the steady state photoconductivity of disordered tri-methylphenyl diamine (TPD) films at relatively high temperatures (200 – 300 K), under photo-generation rates of $10^{19} - 10^{23} \text{ cm}^{-3}\text{s}^{-1}$. We formulated the hopping photoconductivity, and reasonable physical parameters, such as hopping relaxation time, recombination time, and diffusion coefficient (and hence mobility) of charge carriers, are estimated for the TPD films. The effects of exposure air on photoconductivity have been also examined.

2. Experimental

TPD films (thickness 0.5 μm) were deposited onto glass substrates by usual thermal evaporation, and Au was evaporated as the planar electrodes (100 μm gap).

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Photo-carriers were produced by illumination of a He-Cd laser (325 nm) and photo-generation rate G was varied in the range of $10^{19} - 10^{23} \text{ cm}^{-3}\text{s}^{-1}$. The steady state photoconductivity was measured in both vacuumed and air atmospheric conditions.

3. Experimental Results

Fig. 1 shows the temperature variation of the photoconductivity, in vacuum, of the TPD films in the temperature range of 200 – 300K, as a function of light intensity (mW/cm^2).

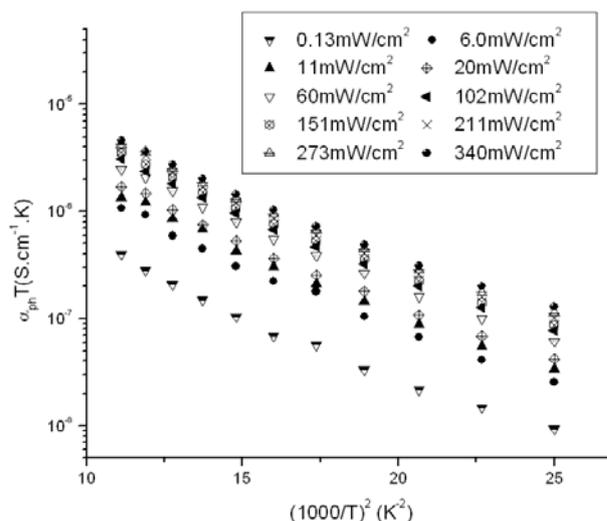


Fig. 1 Temperature variation of photoconductivity of TPD films, plotted as $\sigma_{\text{ph}}T$ vs. $(1000/T)^2$, as a function of light intensity.

Note that the light intensity 1mW/cm^2 corresponds to $1.3 \times 10^{20} \text{ cm}^{-3}\text{s}^{-1}$ (the number of absorbed photon G). The almost straight lines for various light intensity on the $\ln \sigma_p T$ vs. $(1000/T)^2$ curve indicate that the steady-state photoconductivity σ_p is proportional to $\exp[-(\sigma^2/kT)]/2kT$. σ -value deduced is 0.067 eV which is almost independent of light intensity.

The G -dependent photoconductivity as a function of temperature, is plotted in Fig.2. Above 200 K , the photoconductivity is proportional to G^γ ($\gamma \approx 0.5$). The value of γ increases with decreasing temperature and seems to be approaching unity. Low temperature behavior of photoconductivity can be interpreted in terms of the downward hopping of photocarriers, which has been well established in terms of an Exponential DOS [3].

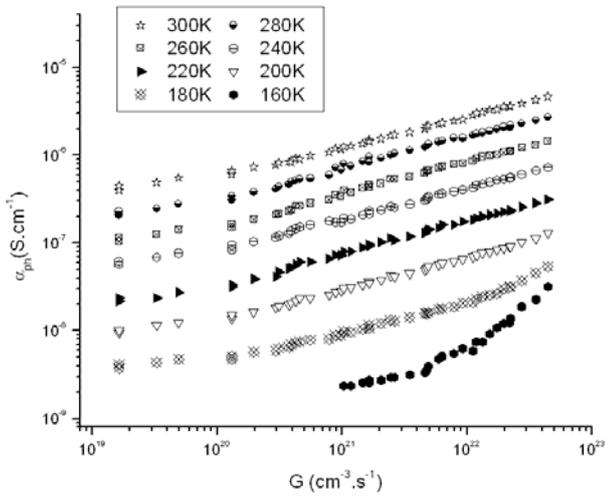


Fig. 2 G -dependent photoconductivity of the TPD films as a function of temperature

Fig. 3 shows the normalized photoconductivity, σ_p/eG ($= \eta\mu\tau$), which depends on G , where η is the quantum efficiency, μ is the mobility, and τ is the life time.

Fig. 4 shows the effects of exposure to air on the photoconductivity. The photoconductivity increases with exposure to air and returns back to the original value (before exposure to air) after removing air (vacuum condition), indicating a reversible effect.

4. Discussion

Fig. 5 shows the expected energy diagram for disordered TPD films, together with the structural unit. A Gaussian energy distribution (hereafter Gaussian DOS) of localized states is usually assumed for low molecular weight organic films and is written as

$$g(\varepsilon) = \frac{N}{\sqrt{2\pi}\sigma} \exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right) \quad (1)$$

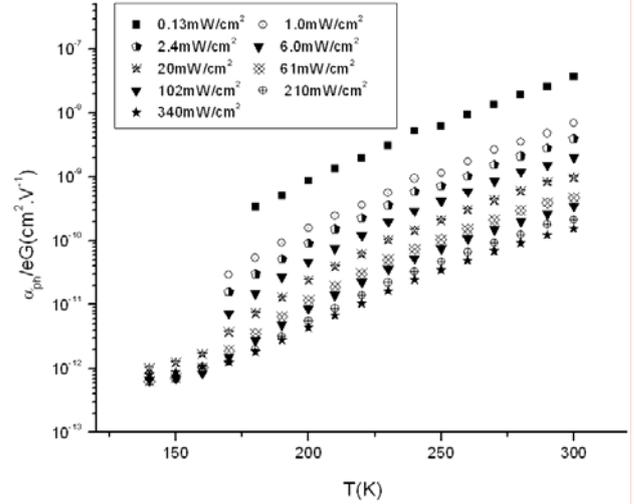


Fig. 3 Temperature variation of normalized photoconductivity, σ_p/eG ($= \eta\mu\tau$) as a function of G

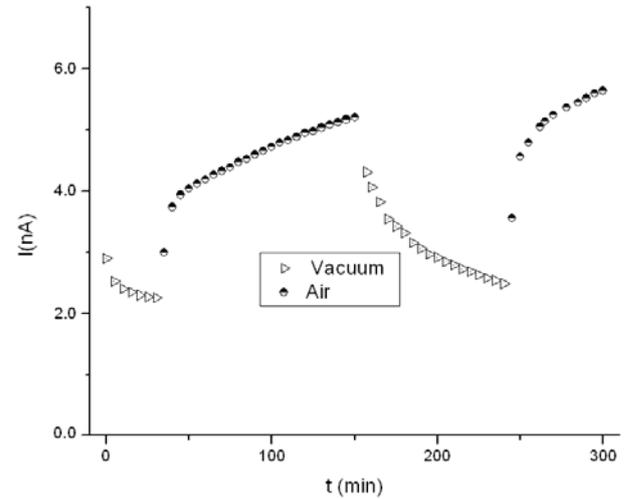


Fig. 4 Effects of exposing air on the photoconductivity.

where N is the total concentration of states and σ is the standard deviation of Gaussian DOS. Note that localized centers are molecules or molecular subunits [1]. Hopping transport of electrons in localized states with an *Exponential* energy distribution (Exponential DOS) has been well established, in particular at low temperatures, and has been successfully applied to the electronic transport in amorphous semiconductors [5]. In an exponential DOS, *transport energy* dominates the hopping conductivity at relatively high temperatures, i.e. carriers hop through a transport energy level [5]. The concept of transport energy has been extended to systems with Gaussian DOS, and the positions of transport energies, ε_{th} in HOMO (for holes) and ε_{te} in LUMO (for electrons), respectively, are temperature dependent and are located in the central part of Gaussian DOS (see Fig.5) [1],[5].

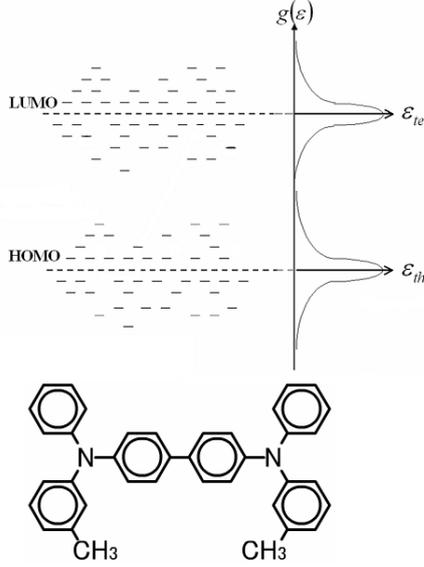


Fig. 5 Expected energy diagram for disordered TPD films, together with the structural unit.

Let us formulate the hopping photoconductivity near the room temperature in a Gaussian DOS. Holes are dominant photo-carriers for TPD films and hence the transport near the transport energy ε_{th} plays an important role. During illumination, most of the photoinduced holes and electrons are localized in deeper tail of Gaussian DOS (toward midgap between the HOMO and LUMO). Bimolecular recombination (tunneling) between these deeply localized electrons and holes may dominate the lifetime of carriers (holes). These localized holes will reach thermal equilibrium and the mean energy location of holes is calculated to be

$$\varepsilon_m = \frac{\int_{-\infty}^{\infty} \varepsilon \exp(-\varepsilon/kT) g(\varepsilon) d\varepsilon}{\int_{-\infty}^{\infty} \exp(-\varepsilon/kT) g(\varepsilon) d\varepsilon} = -\frac{\sigma^2}{kT} \quad (2)$$

where the peak energy of Gaussian DOS is taken to be $\varepsilon = 0$ [1],[3]. For holes the (HOMO), ε_m is therefore located at an the energy of σ^2/kT above the center of Gaussian DOS.

As long as the hopping transport occurs via thermal activation to the transport energy, the relaxation time is determined by the activated transitions from the equilibrium level ε_m to the transport energy ε_{th} . This activated energy should be σ^2/kT . By assuming simple Miller-Abrahams type hopping [1], the hopping relaxation rate ν_h through the transport energy in a Gaussian DOS is given by [1]

$$\nu_h = \nu_0 \exp \left[\frac{-2R_h(\varepsilon_{th})}{a} - \frac{\varepsilon_{th}}{kT} - \left(\frac{\sigma}{kT} \right)^2 / \frac{1}{2} \right] \quad (3)$$

where ν_0 is the characteristic frequency, $R_h(\varepsilon_{th})$ the average nearest-neighbor distance which is calculated for all states deeper than ε_{th} [1], and a the decay length of the localized

holes. As long as the sum $2R_h(\varepsilon_{th})/a + \varepsilon_{th}/kT$ weakly depends on the temperature, the last term $(\sigma/kT)^2/2$ dominate the temperature dependence of ν_h . As the transport level is located at $\varepsilon \approx 0$ (the center of the Gaussian DOS), the term ε_{th}/kT can be actually ignored. The number of hopping sites should be $N/2$ and hence the hopping length $R_h(\varepsilon_{th})$ is taken to be $[3/4\pi(N/2)]^{1/3}$. Although molecules cannot be considered as being randomly distributed in three dimensions (3D), we apply the 3D approximation for simplicity, and a percolation theory is not taken into consideration. It is worth noting that the hopping relaxation time ν_h is the time required for a system to reach thermal equilibrium. Detailed nature of these parameters will be discussed later.

The simplest form of the hopping photoconductivity at temperature T in 3-dimensional (3D) space can be given as [6]

$$\sigma_p = n \frac{[eR_h(\varepsilon_{th})]^2 \nu_h}{6kT} \quad (4)$$

where n is the carrier density being located at ε_m (on average) and is given by

$$n = \eta G \tau \quad (5)$$

where η is the quantum efficiency, G the number of absorbed photon ($\text{cm}^{-3}\text{s}^{-1}$), and τ the recombination time between localized electrons and holes. When the bimolecular process dominates the recombination time, τ should depend on $G^{-\gamma}$ ($\gamma \approx 0.5$) and therefore n can be proportional to G^γ .

Using eqs.(3)-(5) and comparing with the experimental results, we will get the unknown physical parameters being involved in the equations. From the temperature dependence of photoconductivity (Fig.1), $\sigma = 0.067$ eV is obtained and is smaller than that (0.11 eV) estimated from the drift mobility (time-of-flight; TOF) study [2]. This may be due to the fact that the samples studied in the TOF study [2] were 40 wt.% TPD doped polycarbonate, known as molecularly doped polymers: in general, the energetic width of DOS is smaller in evaporated organic materials than in their molecularly doped polymers. $\gamma \approx 0.5$ suggests that bimolecular recombination dominates the photoconductivity at relatively high temperatures. Electrons in Gaussian tails (LUMO) recombine with holes in Gaussian tails near ε_m (HOMO).

The decay length a is also not clear but is usually taken to be around 0.3 nm for localized holes in organic materials [5] and hence we take $a = 0.3$ nm for the TPD films. The total number of sites N for the present TPD films is $6 \times 10^{20} \text{ cm}^{-3}$ [2], yielding the values of $R_h(\varepsilon_{th}) = 0.9$ nm and $\exp(-2R_h(\varepsilon_{th})/a) = 2.5 \times 10^{-3}$. Thus ν_h , for example at 300 K, is estimated to be $8 \times 10^7 \text{ s}^{-1}$, by taking $\sigma = 0.067$ eV and $\nu_0 = 1 \times 10^{12} \text{ s}^{-1}$.

We expect here that the temperature dependence of σ_p is dominated by ν_h and hence n should be independent of temperature (near room temperature); i.e. the recombination time τ is independent of temperature. For example, for

$G = 1 \times 10^{21} \text{ cm}^{-3}\text{s}^{-1}$ (8 mW/cm^2) and $\eta = 10^{-3}$, n and τ using eqs.(3)-(5) are estimated to be $1 \times 10^{18} \text{ cm}^{-3}$ and 1 s , respectively. The photoconductivity, on the other hand, is given as $\sigma_p = e n \mu$, where μ is the mobility. As the value of σ_p at 300 K is $8 \times 10^{-7} \text{ Scm}^{-1}$ for $G = 1 \times 10^{21} \text{ cm}^{-3}\text{s}^{-1}$, $\mu = 5 \times 10^{-6} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ is deduced, which is smaller than the value ($1 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) deduced from the TOF measurement [2]. This discrepancy is not clear and will be discussed in a future publication. The diffusion coefficient D of holes at 300 K, using the Einstein relation ($\mu kT = eD$), is estimated to be $1.3 \times 10^{-7} \text{ cm}^2\text{s}^{-1}$.

It is of interest to discuss the so called "lifetime-mobility ($\mu\tau$) product" which is a measure of quality of photoconductors. As σ_p is given by $e n \mu (= e \eta G \tau \mu)$, σ_p / eG gives the value for $\eta\mu\tau$. Fig. 3 shows the temperature variation of $\eta\mu\tau$ as a function of G in the present TPD films. The recombination time τ decreases with G and hence $\eta\mu\tau$ decreases with G . The value of $\eta\mu\tau = 1 \times 10^{-9} \text{ cm}^2\text{V}^{-1}$ for $G = 1 \times 10^{21} \text{ cm}^{-3}\text{s}^{-1}$ near 300 K is smaller than that $4 \times 10^{-8} \text{ cm}^2\text{V}^{-1}$ for $G = 4 \times 10^{20} \text{ cm}^{-3}\text{s}^{-1}$ near 300 K for hydrogenated amorphous silicon (a-Si:H) [7]. However, the $\mu\tau$ product itself for TPD films may be greater than that for a-Si:H, since the quantum efficiency $\eta = 10^{-3}$ near 300 K is very much smaller than ~ 1 for a-Si:H.

The photoconductivity increased in air and decreased in vacuum with time could be clearly seen in Fig. 4. This repeated result shows a reversible effect. We therefore expect that this reversible effect is attributed to a physical reaction (i.e. *adsorption* of oxygen or nitrogen). As oxygen is attractive for electrons ($\text{O}_2 + e \rightarrow \text{O}_2^-$), the number of photogenerated electrons may decrease with the oxygen contents, leading to an increasing lifetime of holes which are the dominant carriers in TPD films. More detailed experiments and discussion will be made in a future publication.

5. Conclusion

The steady-state hopping photoconductivity at relatively high temperatures has been studied for low molecular weight organic TPD films. Important physical parameters, such as hopping relaxation time, recombination time, and mobility (and hence the diffusion coefficient) of holes, were deduced, and all of these seem to yield reasonable values. We also found that the photoconductivity increased by exposure to oxygen and/or nitrogen.

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