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Invited Lecture

Dynamics of photoconductivity in organic TPD films

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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 upon exposure to air and this is a reversible effect.

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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 a 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 [1,3-5] 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 [6].

We measured the steady state photoconductivity of disordered tri-methylphenyl diamine (TPD) films at relatively high temperatures (200 – 300 K), under photo-generation rates of $10^{19} - 10^{23}$ $cm^{-3}s^{-1}$. 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 charge carriers, are estimated for the TPD films. The effects of exposure to air on photoconductivity have also been examined.

2. Experimental

TPD films (thickness 0.5 μm) were deposited onto glass substrates by conventional thermal evaporation, and Au was evaporated as the planar electrodes (100 μm gap). Photo-carriers were produced by illumination with a He-Cd laser (325 nm) and the photo-generation rate G was varied in the range $10^{19} - 10^{23}$ $cm^{-3}s^{-1}$. The steady state and residual photoconductivity were measured in both vacuumed and air atmospheric conditions (and also in O_2 and N_2 gases, separately).

3. Experimental results

Fig. 1 shows the temperature variation of the photoconductivity of the TPD films in the temperature range 200 – 300 K, as a function of light intensity (mW/cm^2). Note that the light intensity $1mW/cm^2$ corresponds to 1.3×10^{20} $cm^{-3}s^{-1}$ (the number of absorbed photons G). The almost straight lines for various light intensities on the $ln\ \sigma_p T$ vs. $(1000/T)^2$ curve indicate that the steady-state photoconductivity σ_p is proportional to $\exp[-(\sigma^2/kT)]/2kT$. The 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. The low temperature behavior of the photoconductivity can be interpreted in terms of the downward hopping of photocarriers, which has been well established in terms of an exponential DOS [3]. Details of the recombination kinetics will be discussed in the following section.

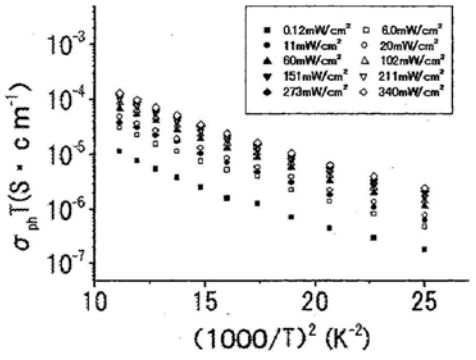


Fig. 1 Temperature variation of the photoconductivity of TPD films, plotted as $\sigma_{ph}T$ vs. $(1000/T)^2$, as a function of light intensity.

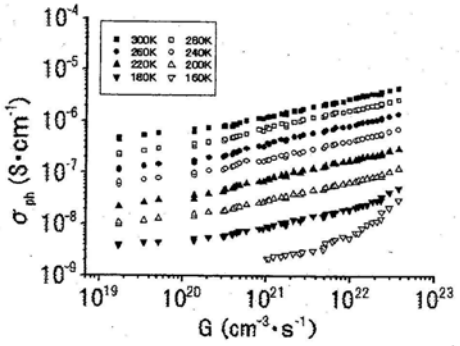


Fig. 2. G-dependent photoconductivity of the TPD films as a function of temperature.

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 residual decay of the photoconductivity as a function of temperature, after stopping illumination. The decay is very slow and all curves approximately fit to a power law, i.e. $\propto t^{\beta}$ with $\beta \approx$ 0.25. Details of the recombination kinetics will be discussed in the following section.

Fig. 5 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.

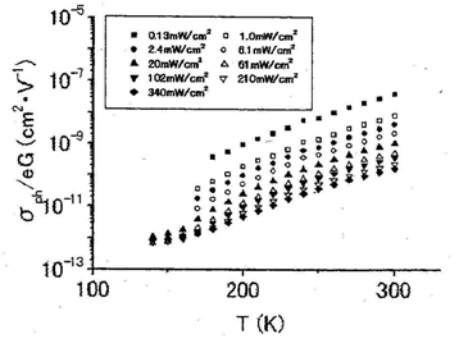


Fig. 3 Temperature variation of the normalized photoconductivity, σp/eG (= ημτ) as a function of light intensity.

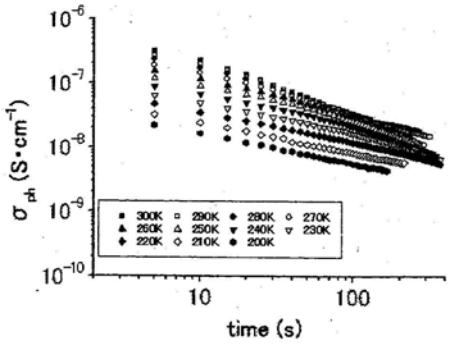


Fig. 4. Residual decay of the photoconductivity after stopping illumination, as a function of temperature.

To examine which gas, O_2 or N_2, dominates the changes in the photoconductivity, O_2 and N_2 gases are independently exposed to the TPD films. Figure 6 (a) shows the photocurrent in vacuum and the changes in the photocurrent under exposure to O_2 (~10^3 Pa) is shown in Figure 6(b). The photocurrent increases with exposure to O_2 compared to vacuum. Similar behaviours are observed under exposure to N_2 (~10^3 Pa) as in Fig. 6(c).

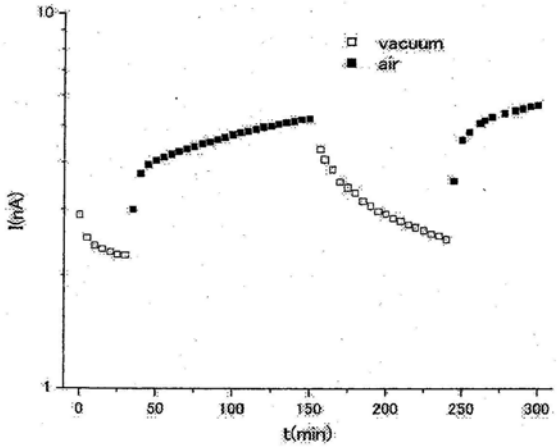
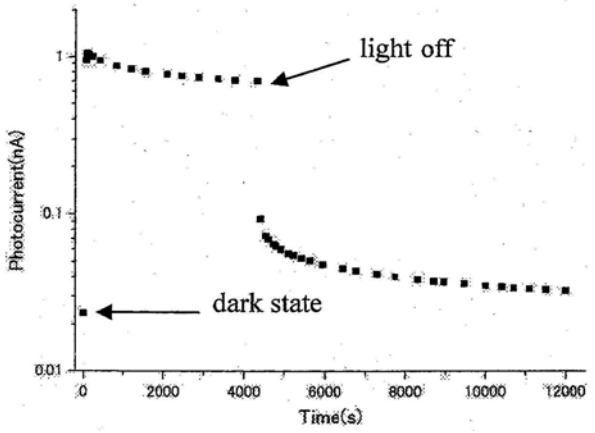
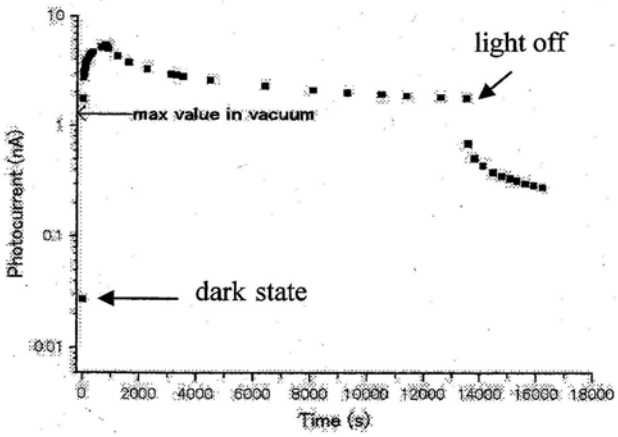


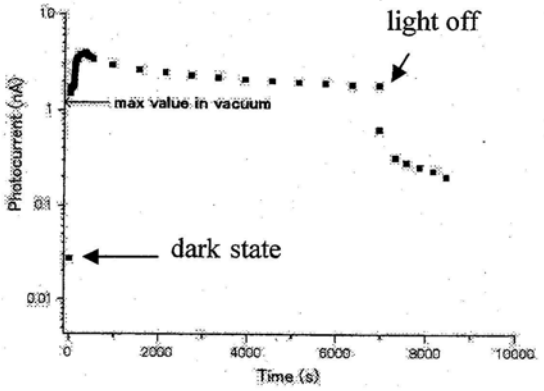
Fig. 5. Effects of exposure to air on the photocurrent.



(a) *Vacuum*



(b) O_2



(c) N_2

Fig. 6. Effects of exposure to O_2 and N_2 on the photocurrent, compared to vacuum.

The decay of the photocurrent under these atmospheric conditions, after stopping illumination, is also shown in Fig.6. The decay times, for example, the time required to reach half of the initial value, are of the order of 10, 400, 400 s, in vacuum, O_2, and N_2 conditions, respectively. This indicates that O_2 or N_2 affects also the decay of photocurrent significantly.

4. Discussion

Fig. 7 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

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

where N is the total concentration of states and σ is the standard deviation of the Gaussian DOS. Note that the 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 [7]. In an exponential DOS, the *transport energy* dominates the hopping conductivity at relatively high temperatures, i.e. carriers hop through a transport energy level [7]. The concept of a transport energy has been extended to systems with a Gaussian DOS, and the positions of the 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 the Gaussian DOS (see Fig. 7) [1,8].

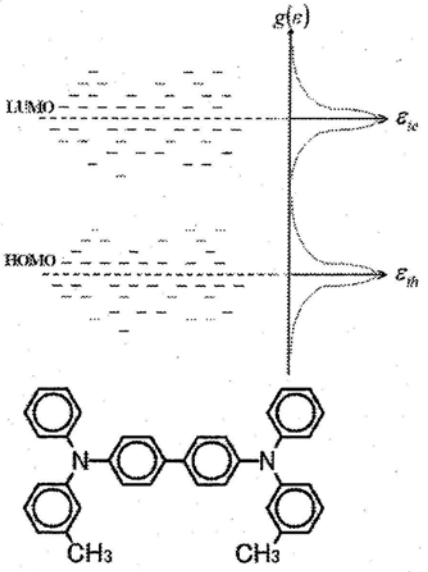


Fig. 7 Expected energy diagram for TPD films, together with the structural unit.

Let us formulate the hopping photoconductivity near room temperature in a Gaussian DOS. Holes are the dominant photo-carriers for TPD films and hence transport near the transport energy ε_{th} plays an important role. During illumination, most of the photoinduced holes and electrons are localized in the deeper tail of the 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 the Gaussian DOS is taken to be $\varepsilon = 0$ [1,3]. For holes, the (HOMO),ε_m is therefore located at an energy of σ^2/kT above the center of the 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 Miller-Abrahams type hopping [9], 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 of $2R_h(\varepsilon_{th})/a + \varepsilon_{th}/kT$ weakly depends on the temperature, the last term $(\sigma/kT)^2/2$ dominates 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 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. The 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 [10]

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

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

$$n = \eta G\tau, \qquad (5)$$

where η is the quantum efficiency, G the number of absorbed photons ($cm^{-3}s^{-1}$), 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 involved in the equations. From the temperature dependence of the 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 the 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 [8], and hence we take $a = 0.3$ nm for the TPD films. The total number of sites N for the present TPD films is 6×10^{20} 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 8×10^7 s^{-1}, by taking $\sigma = 0.067$ eV and $\nu_0 = 1 \times 10^{12}$ 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 $G = 1 \times 10^{21}$ $cm^{-3}s^{-1}$ (8 mW/cm^2) and $\eta = 10^{-3}$, n and τ using eqs.(3)-(5) are estimated to be 1×10^{18} cm^{-3} and 1 s, respectively. The photoconductivity, on the other hand, is given as $\sigma_p = en\mu$, where μ is the mobility. As the value of σ_p at 300 K is 8×10^{-7} Scm^{-1} for $G = 1 \times 10^{21}$ $cm^{-3}s^{-1}$, $\mu = 5 \times 10^{-6}$ $cm^2V^{-1}s^{-1}$ is deduced, which is smaller than the value (1×10^{-3} $cm^2V^{-1}s^{-1}$) 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 1.3×10^{-7} cm^2s^{-1}.

It is of interest to discuss the so called "lifetime-mobility ($\mu\tau$) product" which is a measure of the quality of photoconductors. As σ_p is given by $en\mu$ ($= e\eta G\tau\mu$), 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 $\eta\mu\tau$ $= 1 \times 10^{-9}$ cm^2V^{-1} for $G = 1 \times 10^{21}$ $cm^{-3}s^{-1}$ near 300 K is smaller than that 4×10^{-8} cm^2V^{-1} for $G = 4 \times 10^{20}$ $cm^{-3}s^{-1}$ near 300 K for hydrogenated amorphous silicon (a-Si:H) [11]. However, the $\mu\tau$ product itself for TPD films may be greater than that for a-Si:H, since the quantum efficiency η $= 10^{-3}$ near 300 K is very much smaller than ~1 for a-Si:H.

The photoconductivity increased in air and decreased in vacuum with time, as is clearly seen in Fig. 5. This repeated result shows a reversible effect [12]. We therefore expect that this reversible effect is attributed to a physical reaction (i.e. adsorption of oxygen or nitrogen). As O_2 is expected to be more reactive than N_2, we expect that O_2 in air dominates the increase in the photoconductivity. However, as shown in Fig. 6, both O_2 and N_2 are active gases for the increase of the photoconductivity. It should be noted that both O_2 and N_2 are inactive for the dark conductivity, i.e. the dark conductivity is unchanged under exposure to O_2 or N_2. This suggests that the observed change in the photoconductivity is attributed to *photochemical reactions*.

If O_2 or N_2 is attractive for electrons ($O_2 + e \rightarrow O_2^-$ or $N^2 + e \rightarrow N_2^-$), the number of photo-created electrons may decrease with the oxygen or nitrogen content, leading to an increasing recombination lifetime of holes, which are the dominant carriers in TPD films. More detailed experiments and discussion will be made in a future publication.

5. Conclusions

The steady-state hopping photoconductivity at relatively high temperatures has been studied for low molecular weight organic TPD films. Bimolecular recombination of photocarriers occurs near room temperature. Important physical parameters, such as the

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 was increased by exposure to oxygen and/or nitrogen.

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