

Method of determining the exciton diffusion length using optical interference effect in Schottky diode

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(Received 24 March 2009; accepted 4 May 2009; published online 1 June 2009)

A general model of calculating the short circuit photocurrent and exciton diffusion length from Schottky diode is given here using optical interference method. This method of estimating the exciton diffusion length can be very useful for those materials that do not give photoluminescence. It also serves as an accurate and simple method to determine the exciton diffusion length, which is an important material property to design devices such as organic solar cells. Our model is verified with the spectral response of indium tin oxide (ITO)/copper phthalocyanine (CuPc)/Al and ITO/CuPc/Ag Schottky diodes. © 2009 American Institute of Physics. [DOI: 10.1063/1.3142869]

Organic devices have gained much interest nowadays because of their low cost and large area applications such as displays and solar cells. To be able to design efficient devices, it is important to understand its optoelectrical properties. In the case of organic materials optical excitation is excitonic in nature, i.e., after absorbing light, bound electron hole pairs called excitons form in these materials. These excitons typically have a binding energy ranging from hundreds of meV to a few eV.¹ After its creation, the exciton diffuses and dissociates at the structural inhomogeneities such as a metal-semiconductor junction. This exciton diffusion length (L_D) is an important material property as it plays a critical role in designing efficient devices. There are several authors reporting various measurement techniques to measure L_D .^{2,3} While calculating L_D , not considering optical interference effect can give misleading result.⁴ Pettersson *et al.*⁵ and Peumans *et al.*³ measured L_D of poly(3-4'-(1'',4'',7''-triox-aocetyl)phenyl)thiophene, copper phthalocyanine (CuPc), 3,4,9,10-perylene-tetracarboxylic bis-benzimidazole and fullerene (C_{60}) using optical interference effect from the spectral response of heterojunction solar cells. Although this procedure is quite prevalent,^{6,7} it is very difficult to measure L_D on a routine basis through this procedure. Moreover, several other authors reported L_D values by not considering optical interference effect from the spectral response of Schottky diode.^{2,8} In this article, we focused our attention to measure L_D using optical interference effect in Schottky diodes. For this purpose, indium tin oxide (ITO)/CuPc/Al and ITO/CuPc/Ag Schottky diodes were made and their spectral responses were studied. A general model to calculate the L_D of the active organic material from the spectral response of Schottky diodes is proposed here. Finally L_D is estimated by fitting the model in the experimentally determined spectral response. This method is simpler and can be done on a routine basis which will be helpful to device designing.

In this section, we shall describe the mechanism of photoconductive behavior of a Schottky diode. The absorption in organic molecular crystals leads to exciton generation. The photogenerated excitons then diffuse through the device, and when they find structural inhomogeneity such as an organic-metal interface in the case of Schottky diodes, they dissociate into electrons and holes or they may recombine. The local electric field present in the device carries the electrons or holes to the cathode and anode, respectively, and results in a photocurrent. Now the external quantum efficiency of the device η_{EQE} is defined as the number of electrons collected at the external circuit for every incident photon. This is dependent on several other efficiencies and can be modeled as

$$\eta_{EQE} = \eta_A \times \eta_{ED} \times \eta_d \times \eta_{CC}, \quad (1)$$

where η_A is the absorption efficiency (efficiency of exciton creation), η_{ED} is the diffusion efficiency (efficiency of excitons to reach the junctions), η_d is the dissociation efficiency (efficiency of exciton dissociation leading to free electron and holes), and η_{CC} is the collection efficiency (efficiency of carrier collection at the electrodes). Here η_A is dependent on the material properties of the devices such as their optical constants. Using optical constants of these materials, we simulate the exciton generation profile inside the device using transfer matrix approach given elsewhere.^{3,5} This generation term is then included in a steady state diffusion equation to calculate η_{ED} for the active layer,

$$L_D^2 \frac{\partial^2 \Phi}{\partial x^2} - \Phi + \tau \frac{\lambda}{hc} Q = 0, \quad (2)$$

$$Q(x, \lambda) = \frac{4\pi c \epsilon_0 k(\lambda) n(\lambda)}{2\lambda} |\bar{E}(x)|^2, \quad (3)$$

where Φ is the exciton density, L_D is the exciton diffusion length of the active material, τ is the exciton lifetime in the active material, h is the Planck's constant, c is the speed of light, ϵ_0 is the free space permittivity, $Q(x, \lambda)$ is the averaged absorbed power at position x and wavelength λ , $n(\lambda)$ and $k(\lambda)$ are the real and imaginary parts of the complex index of

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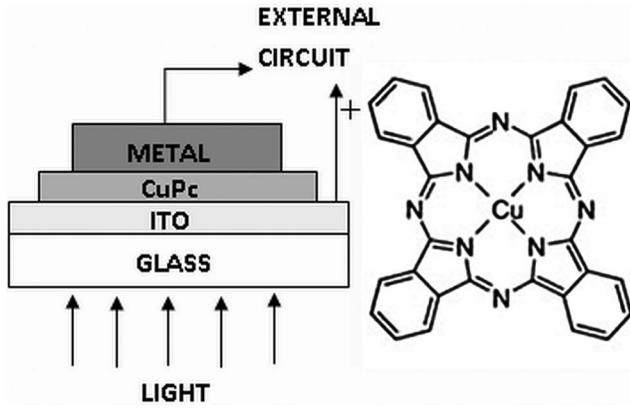


FIG. 1. Schematic diagram of the device structure fabricated for characterization. The molecular structure of CuPc is also shown in the figure.

refraction, and $\vec{E}(x)$ is the electric field at position x in the device, which is calculated by the transfer matrix approach. Now in the case of ITO/CuPc/metal devices exciton dissociates at ITO/CuPc and CuPc/metal junction leads to a photocurrent. In our calculation we assumed $\eta_{CC}=1$.³ For the zero bias case, it is assumed that η_d can be different for the different junctions considered here, as at the metal/organic junctions the metal forms nanoclusters, which can act as efficient quenching sites⁹ for excitons. So the total current density is calculated as

$$j = \eta_d^{\text{ITO}} q \frac{L_D^2}{\tau} \left| \frac{\partial \Phi}{\partial x} \right|_{x=x_{\text{ITO}}} + \eta_d^{\text{metal}} q \frac{L_D^2}{\tau} \left| \frac{\partial \Phi}{\partial x} \right|_{x=x_{\text{metal}}}, \quad (4)$$

where q is the electron charge, η_d^{ITO} and η_d^{metal} are the exciton dissociation efficiencies at the ITO/CuPc and CuPc/metal junctions, respectively, and x_{ITO} and x_{metal} are the positions of the ITO and metal interface inside the device. The external quantum efficiency of the full device is then calculated by normalizing the diffusion current by the incident photon flux

$$\eta_{\text{EQE}} = \frac{j/q}{\frac{1}{2} \epsilon_0 c |\vec{E}_0|^2 / (hc/\lambda)}. \quad (5)$$

Experimentally wavelength dependent external quantum efficiency is measured. L_D is then estimated by fitting the above model to the experimental data.

For experimental verification of the model described above devices were fabricated as described below. ITO coated glass substrates were prepared by cleaning in soap and organic solutions and then patterned. Thin films of CuPc were deposited on these substrates at 5×10^{-6} mbar pressure. Metal deposition was done on top of it using a shadow mask. CuPc and metal deposition rates were 1 and 0.2 Å/s, respectively. After metallization, the samples were exposed to air as briefly as possible before encapsulation in N_2 atmosphere. Two metals were used for the device fabrication. Final device structure was 140 nm ITO/110 nm CuPc/200 nm Al and 140 nm ITO/110 nm CuPc/200 nm Ag for the devices, respectively. Schematic diagram of the sample structure is shown in Fig. 1.

A 100 W tungsten halogen lamp coupled with a monochromator (Acton Spectrapro 275) was used as a light source. High pass filters of 320 and 590 nm cutoff were used for the wavelength range considered here. Light was me-

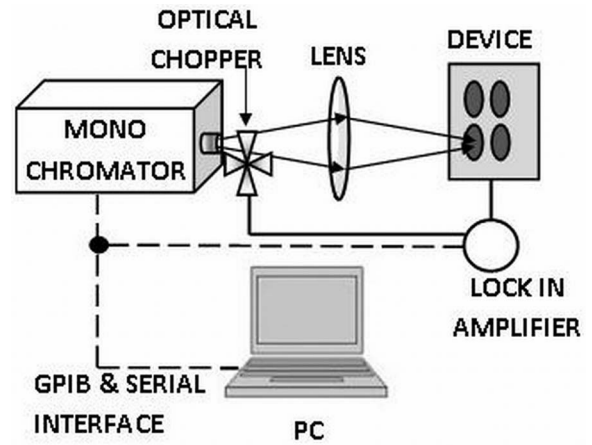


FIG. 2. Schematic diagram of the experimental set up is used for the spectral response characterization.

chanically chopped at 23 Hz and shined from the ITO side. Modulated photocurrent measurement was done using lock-in amplifier (Stanford Research model no 830). A calibrated Si photodiode (Acton Si440) was used for measuring the absolute intensity of light falling on the sample to get the external quantum efficiency. Schematic diagram of the experimental set up is shown in Fig. 2.

We have fitted the model described above to the experimental data for the zero bias condition. In this model L_D , η_d^{ITO} and η_d^{metal} are the free parameters used for the least-square fitting. The optical constants of the model are taken from literature.¹⁰⁻¹³ The boundary conditions used to solve the diffusion equation are $\Phi(x)=0$ at ITO/CuPc and CuPc/metal junction. The best fitted parameters are $L_D=9.6$ nm, $\eta_d^{\text{ITO}}=0.5\%$ and the exciton dissociation efficiency at the CuPc/Al junction $\eta_d^{\text{Al}}=0.03\%$ for the case of Al device. Here, contribution to photocurrent from Al is so small that we can ignore it. In Fig. 3, a comparison between experimental observation and the fitted model is shown. Although this model fits the experimental data very well the slight discrep-

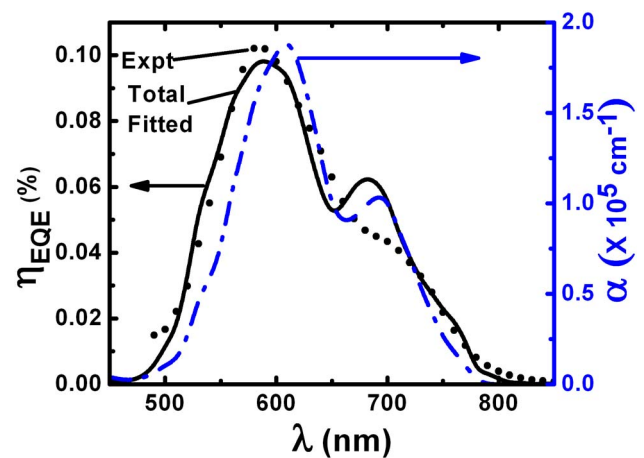


FIG. 3. (Color online) Model fitted to the experimental data. The black line is showing total response of the ITO/CuPc/Al Schottky diode. From the model fitting it seems that Al junction has 100 times lesser contribution than ITO junction. So here we have only shown the total response found from the model which is practically same as ITO's contribution to the photocurrent. Al's contribution is so small that it is not shown here and neglected. The response found from this device is symbatic. Absorption spectrum of CuPc (blue dash dot line) is also shown for comparison.

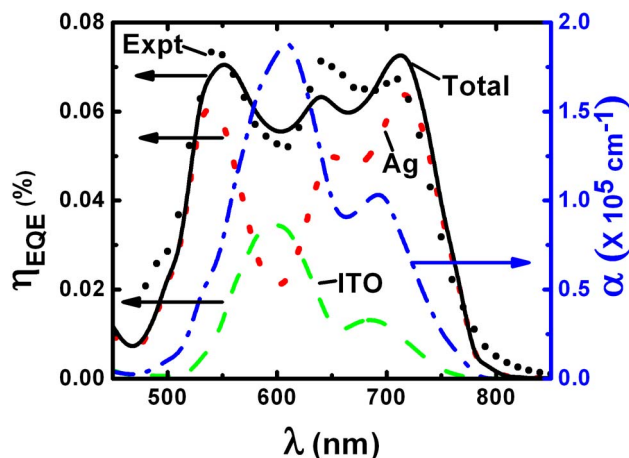


FIG. 4. (Color online) Model fitted to the experimental data of spectral response obtained from ITO/CuPc/Ag device. Black line is showing total response of the ITO/CuPc/Ag Schottky diode. The ITO/CuPc (green dashed) and CuPc/Ag (red dotted) junction's contribution are also shown here. It can be clearly seen that ITO/CuPc junction's contribution is sybatic where as CuPc/Ag junction's contribution is antibatic. Absorption spectrum of CuPc (blue dash dot line) is also shown for comparison.

ancy between the model and experimental data especially around 680 nm can be attributed to the possibilities of inaccuracies in optical constant taken from literature for our devices. From the fitted model it can also be concluded that ITO/CuPc junction is more efficient exciton dissociation center than CuPc/Al junction. In Fig. 4, we have compared the experimentally determined spectral response with the model for ITO/CuPc/Ag device. The best fitted parameters for this device are $L_D = 9.5$ nm, $\eta_d^{\text{ITO}} = 0.2\%$, and exciton dissociation efficiency at the CuPc/Ag junction $\eta_d^{\text{Ag}} = 0.5\%$. In the case of Al devices we get sybatic response and we find from the model that ITO/CuPc junction is playing the crucial role for exciton dissociation. Also Ghosh and Feng¹⁴ assumed that merocyanine/Al junction is the exciton dissociation center as they got sybatic response when light was shined from the Al side for their Al/merocyanine/Ag devices. It appears possible that the ITO/CuPc junction is more efficient for exciton dissociation as when light shined from the ITO side, at the absorption maxima more light will be absorbed close to the ITO/CuPc junction, which is the active dissociation center of the device. So more exciton dissociation will take place because of the presence of dissociation site nearby leading to more photocurrent. By the same argument less photocurrent will be generated for the absorption minima, which will attribute to the sybatic response. If the other junction is the

only efficient dissociation center then we would expect antibatic response. Several other authors^{14,15} also concluded that the distant electrode is an exciton dissociation center as they got antibatic response in their single layer organic devices. This observation can also be analyzed by our model. As shown in Fig. 4, it can clearly be observed that CuPc/Ag junction's (distant electrode's) contribution is antibatic while ITO/CuPc junction's contribution is sybatic, supporting both the observations of Ghosh and Feng¹⁴ and Ray *et al.*¹⁵ In general both the junctions can contribute to the photocurrent and is better to consider the photoactivity of each junction.

In this letter, we have discussed a method for determining the exciton diffusion length by using a simple device structure, especially useful for the materials which do not show photoluminescence. Using a CuPc based Schottky diode, its exciton diffusion length is determined by analyzing the photogenerated current using optical interference effect. This method allows for a quick evaluation of the parameter in any new material. In our sample the exciton diffusion length was found to be 9.5 ± 0.5 nm. The analysis method used also showed the relative exciton dissociation efficiencies of the CuPc/Al, CuPc/Ag, and ITO/CuPc junctions.

We are grateful to the Indian and Swiss governments for funding this research (Project No. SNSF/PHY/20050356).

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