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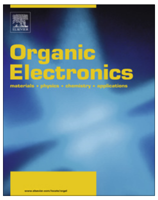

Percolative charge transport in a co-evaporated organic molecular mixture

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Understanding the charge transport in molecular semiconductor mixtures remains challenging, largely due to the lack of a universal dependence of carrier mobility upon doping concentration. Here we demonstrate that it is feasible to use the percolation theory to explain the change of charge mobility in a model system of 4,4′-bis(carbazol-9-yl)-biphenyl (CBP) and tris-(8-hydroxyquinoline) aluminum (Alq_3) with various doping concentrations. As the fraction of CBP within the mixtures increases, the charge mobility initially firstly shows a reduction at low CBP fraction due to the scattering effect, and then increases well following a percolation model. Electron microscopy and atomic force microscopy analysis suggest that CBP and Alq_3 are homogeneously mixed in their co-evaporated amorphous films, which meets the precondition for using percolation theory. We describe the possible microcosmic percolating mechanism with a model combining bond percolation with charge transfer integral calculation. Based on this model, the percolation threshold in molecular semiconductor mixtures can be predicated. For the hole and electron transport in our system, the predicated percolation thresholds are very close to the experimental values.

1. Introduction

Organic molecular semiconductor mixtures have enabled improved performance and novel functionalities in organic devices [1–10]. In organic light emitting diodes (OLEDs), mixing of the transporting host materials would improve charge transport balance and extend the recombination zone, thus enhancing the device efficiency and lifetime [2–5]. Donor–acceptor mixtures in the organic solar cells have created the morphology necessary for efficient photocurrent generation and charge separation, and sequentially high external quantum efficiency [6,7,9,10]. Despite the recent advances in the performance of the above mentioned devices, it remains a challenge to fully describe the optoelectronic properties of organic semiconductor mixtures.

The difficulty in describing the effect of mixing on the performance of the organic optoelectronic devices illustrates the need for further exploration of the role of mixing on the charge transport within organic molecular semiconductor mixtures [11–18]. However, transporting in these materials has been found to be very complicated, and a generally accepted description for the dependence of carrier mobility upon concentration of the transporting phase has not been achieved. Considerable research has suggest that, a small amount of doping would often lead to a reduction of the mobility owing to the introduction of trapping or scattering centers [16–18], and the degree of the reduction can depend strongly on the energy level difference between the compositions [18]. While for the mixtures with various ratios, results have shown that the carrier mobility generally increases monotonically as the concentration of carrier phase increases [12–15], and consequently, the

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expectant ambipolar transport via mixing is only achieved in a limited and system specific range. The lack of a general and quantitative law of the charge mobility makes it a big challenge to expound the transporting mechanism in the molecular semiconductor mixtures.

In the past decades, research of charge transport in organic materials has greatly benefited from the concepts and findings in their inorganic counterparts. For the inorganic semiconducting mixtures, percolation theory has successfully explained the power-law dependence of the carrier mobility upon concentration [19–22]. Since percolation theory holds true only when the transporting phase in the mixture is randomly distributed, analysis of the microscopic configuration of the compositions is needed. Recent evidences have shown that percolation theory may be feasible for carrier transport in polymer based organic mixtures [9,23,24]. Gomez et al. [9] used energy filtered transmission electron microscopy (EF-TEM) to demonstrate that amorphous poly(3-hexylthiophene)(P3HT)/phenyl-C61-butyric acid methyl ester (PCBM) mixtures were miscible when ϕ_{PCBM} (the fraction of PCBM) <0.58, and separated to two phases when $\phi_{PCBM} > 0.58$ due to the formation of a pure PCBM phase. As a result, the electron mobility of the mixtures well followed the percolation theory in the miscible region. The percolative conductivity of graphene and single wall carbon nano-tubes has also been reported in their mixtures with polymers [23,24]. For molecular semiconductor mixtures, Grover et al. [12] recently reported conductivity in the tetracyanoquinodimethane (TCNQ) mixed 4,7-diphenyl-1,10-phenanthroline (Bphen) films were percolating dominated. They used atom force microscopy analysis to find a randomly distributed, separated crystalline TCNQ phase against the amorphous Bphen phase. Nevertheless, the effect of percolating on carrier mobility, a more significant parameter to evaluate charge transport in the molecular semiconducting mixtures, has not been discussed. And the transporting mechanism through percolating in molecule based semiconductors is yet to be understood.

Here, we examined a model system composed of 4,4′-bis(carbazol-9-yl)-biphenyl (CBP) and tris-(8-hydroxyquinoline) aluminum (Alq_3) and show that it is feasible to apply percolation theory to charge mobility in this system. According to the transmission electron microscopy (TEM) and the atom force microscopy (AFM) analysis, we find co-evaporated films of these two materials at varies ratios are amorphous. Moreover, energy diffraction spectrum (EDS) analysis suggests the two constituents are homogeneously distributed in these films. By fabricating time of flight (TOF) devices, we have examined both the intrinsic hole and electron transport properties of amorphous CBP/Alq_3 mixtures. At low CBP concentrations, CBP molecules are dispersed in Alq_3 as scattering centers, leading a reduction in charge mobilities. When CBP fraction exceeds 10%, continuous CBP transporting areas are formed and lead to more efficient charge transport by promoting percolating pathways throughout the layer. We demonstrate that a 3-dimensional bond percolation model based on charge transfer calculation can better describe the carrier transport in this system than a 3-dimensional site percolation model that is often used in the inorganic counterparts. And the percolation thresholds predicated based on this model fit well with the experimental values. Therefore, our results suggest that charge transport in organic molecular semiconducting mixtures can be described by percolation theory.

2. Experimental methods

As a model system for the amorphous molecule semiconductor mixtures, we mix CBP, which is an ambipolar material with mobilities at the level of 10^{-3} cm^2/V s [25], with Alq_3, of which the electron mobility is around 10^{-5} cm^2/V s [26], at various ratios. Both of the two materials are widely used, and their mixtures as light emitting layers showed higher efficiencies than the control device with Alq_3 as the emitting layer [27]. The TOF devices had a structure of ITO/Alq_3:CBP (ϕ_{CBP}) (2 μm)/Mg:Ag (100 nm), where ϕ is the volume fraction of CBP. The mixtures were created through co-evaporating inside a high vacuum evaporator at 10^{-6} torr onto ITO glass, with a coating rate of about 2 Å/s. Thicknesses of the organic layer were monitored in situ with a quartz crystal sensor. A nitrogen pulsed laser (pulse width 10 ns, wavelength 337.1 nm, beam size 3.14 mm^2) was used as the excitation light source, which is directed from the ITO side to generate a thin sheet of excess carriers near the ITO/organic interface. The transient photocurrent signals were recorded by a digital storage oscilloscope with a current sensor resistor (R) of 50 Ω–1 kΩ, and then the transit time (t_T) was measured from the double-logarithmic plot of the transient photocurrent [16–18,25,26]. With the applied bias V and the thickness L, the charge mobility could be calculated as L^2/t_TV. All the TOF experiments were done at the temperature of 298 K. AFM images of the films were tested by SPA 400 (Seiko Instruments Inc.). The AFM samples (100 nm) were also prepared by co-evaporating in the same condition with the TOF samples. High resolution TEM graphs, EDS spectra and selected area electron diffraction (SEAD) of the mixtures were tested by JEOL-JEM 2010. In order to obtain the nano-scale high contrast graphs, high angle annular dark field (HAADF) imaging was measured by FEI-Titan 2010. The X-ray diffraction (XRD) samples (200–300 nm) were evaporated on ITO substrate and the XRD patterns were measured by Rigaku D/max-2500.

3. Results and discussions

Morphology measurement of the Alq_3:CBP co-evaporating films indicate that the mixtures with various compositions are amorphous. The TEM images and SEAD images shown in Fig. 1(a)–(f) clearly suggest the non-crystalline structure of the pure CBP films and pure Alq_3 films, as well as the mixtures. The amorphous morphologies of the films have reconfirmed by the AFM analysis (Fig. 1(g)–(j)). The images exhibit typical amorphous properties, with RMSs from 1.47 nm to 2.19 nm. XRD patterns of the mixed films also show no significant differences from that of the bare ITO substrate (Fig. 1(m)), with no peaks in the small-angle region. Hence, we could conclude that in the CBP:Alq_3

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