

Graduate School of Pure and Applied Sciences

Studies on Charge States in Organic Semiconductor Materials and Devices
using Electron Spin Resonance Spectroscopy

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Signature

Abstract

Introduction

Organic semiconductor devices, such as organic light-emitting diodes (OLEDs), organic solar cells (OSCs), have been intensively investigated because they have the potential for low-cost and large-scale production. Moreover, they have properties, which inorganic semiconductors usually do not have, such as light-weight and flexibility.

Although some of the organic semiconductor devices are already being commercialized, there are still many problems that are to be clarified. However, investigating organic devices is not very simple because of the lack of appropriate methods. In this dissertation, I would like to show that

electron spin resonance (ESR) spectroscopy is an effective tool for investigating such organic semiconductor devices and materials. Materials for OLED application and inverted-type organic solar cells (IOSCs) are characterized with ESR.

n-type doped electron transporting material tris(8-hydroxyquinoline) aluminum (Alq_3) and iodine doped hole transporting material N,N' -Di(1-naphthyl)- N,N' -diphenylbenzidine (NPB) were investigated to elucidate the charge carrier state of those materials..

IOSCs are much more durable than normal type OSCs, which makes IOSCs more suitable for commercialization. However, there is a problem called light-soaking phenomenon. IOSCs cells using n-type metal oxides such as TiO_x or ZnO , which are very commonly used materials, requires several tens of minutes of UV-light irradiation to optimize the device performance. This will cause a loss in the daily power generation amount, and UV itself can harm the organic materials inside the cell. Therefore, understanding the mechanism of the light-soaking phenomenon is inevitable. In this work, I used ESR to elucidate the mechanism of the phenomenon.

Experimental

Doped Alq_3 films were prepared in a vacuum chamber under a pressure of lower than 2×10^{-4} Pa by thermally coevaporating Alq_3 and n-type dopants (Mg, Cs_2CO_3 , LiF) on quartz substrates. Subsequently, an additional metal (Al, Au) layer was deposited on the doped Alq_3 layer to protect the radicals from oxygen and water, and to investigate the interaction between cathode metals and the doped layer. Fabricated samples were sealed in ESR sample tubes under vacuum of approximately 1×10^{-4} Pa.

NPB film was deposited on quartz substrate by thermal vacuum evaporation, under the pressure of 4×10^{-4} Pa, Subsequently, the film was doped using iodine vapor under pressure of 1×10^{-1} Pa for 1 h, then sealed in an ESR sample tube. The doping concentration was controlled by additionally exhausting the sample tube.

IOSC cell used in this work has structure of ITO/ TiO_x / regioregular poly(3-hexylthiophene)

(P3HT):phenyl-C₆₁-butyric acid methyl ester (PCBM)/Au. TiO_x layer deposited on ITO coated quartz substrate by chemical bath deposition (CBD) method. P3HT:PCBM (5:4 w/w) chlorobenzene (CB) solution was spin-coated atop the TiO_x film. Au hole-collecting electrode was thermally deposited. The active area of the device was 0.16 cm². Finally, the device was connected with lead wire using Ag paste, then sealed in an ESR sample tube under a nitrogen glove-box atmosphere.

ESR measurements were performed using a JEOL JES-FA200 X-band spectrometer at room temperature. A standard Mn²⁺ marker sample was used to calibrate the *g* value, the ESR linewidth, and the number of spins of the ESR signal. Note that all the samples for low-temperature ESR measurements were sealed in an ESR sample tube with helium gas at 100 Torr.

Device characteristic measurements for the IOSC were carried out using a Keithley 2612A source meter under AM 1.5G 100 mW cm⁻² simulated solar irradiation containing UV region light (“White light”) or simulated solar irradiation excluding UV light shorter than 420 nm using a UV light cut filter (“UV-cut light”).

Density functional theory (DFT) calculations were performed to validate the origin of ESR signals, by calculating their *g* values. Calculations for Alq₃ and NPB molecules are carried out with isolated radical anion and radical cation states, respectively. For IOSC experiment, *g* value for a radical cationic hexamer thiophene (6T) and its monobromide (6T-Br) was calculated.

Results and Discussion

1. Alq₃ thin film

Clear ESR signals of radical anions in thin films of tris (8-hydroxyquinoline) aluminum Alq₃ was observed. The *g* values of the Cs₂CO₃, Mg, and LiF doped Alq₃ thin films were obtained as 2.0040, 2.0030, and 2.0028, respectively. Calculated *g* value for an isolated Alq₃ radical anion was 2.0028, which was very close with that of LiF doped film. This feature can be explained by spin-orbit interaction between the spin and dopant atom. A large spin-orbit interaction caused by heavy Cs atoms

resulted in a big shift in the g value (2.0040). While doping of Cs_2CO_3 and Mg did not showed cathode-metal (Al and Au) dependence, LiF doping did not occur without Al.

It was confirmed that the doped charges are localized at deep trapping sites by the lineshape analysis and temperature dependence of the ESR signals. The spin susceptibility of the film was found to obey Curie's law, which indicates that no interaction exists between spins of Alq_3 anions.

The doping concentration of $\text{Alq}_3\text{:Mg}$ (coevaporation ratio 1:3) sample was evaluated to be 4.3%, which was significantly lower than expected. This low doping concentration can be explained by the aggregation of Mg atoms. Assuming that Mg atom is distributed at atomic level and reacts with Alq_3 in the ratio of 1:1, doping concentration should be 100%. Transmission electron microscopy (TEM) observation clarified co-evaporated Mg atoms form “islands” with the diameter of 100~200 nm, depending on the coevaporation ratio. The low doping concentration is reasonable because charge transfer occurs only at the interface between Alq_3 molecules and Mg islands.

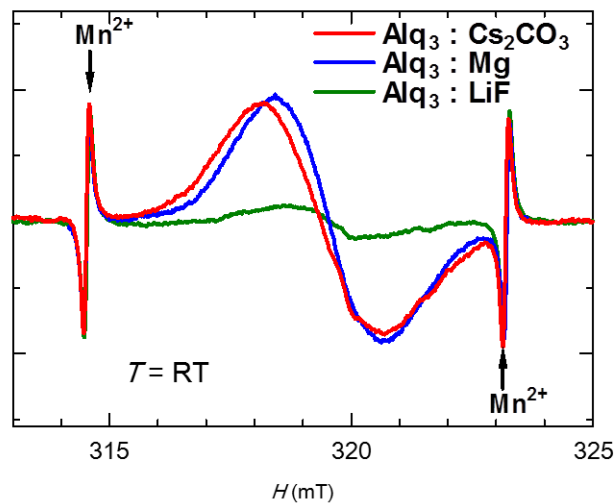


Figure 1. ESR spectra of $\text{Alq}_3\text{:Cs}_2\text{CO}_3$ (red line), $\text{Alq}_3\text{:Mg}$ (blue line), and $\text{Alq}_3\text{:LiF}$ (green line) samples at room temperature. The spectra include those from a Mn^{2+} standard marker. Coevaporation ratio (molecular ratio) for each sample is 1:0.3, 1:0.5, and 1:10, respectively.

2. NPB thin film

ESR signal of radical cations in the iodine-doped NPB thin film were successfully observed. g value of the sample was varied between 2.0036 and 2.0040, depending on the doping concentration. ESR linewidth, ΔH_{pp} , also showed correlation with doping concentration. Calculated g value of an isolated NPB radical cation was 2.0029, which was slightly different from the experimental value. The difference can be explained spin-orbit interaction of iodine atom, similar to that of the Alq₃ thin films discussed above.

ΔH_{pp} gets narrower when doping concentration is increased. In contrary, ΔH_{pp} is broadened when as the temperature is lowered. These observations strongly support the vigorous motion of the observed spins. Its Lorentzian lineshape is also an indication of the moving spins. When their motion gets more active by raising the temperature, ΔH_{pp} will become narrower according to motional narrowing. Also, higher doping concentration could also activate the motion of the spins by trap filling.

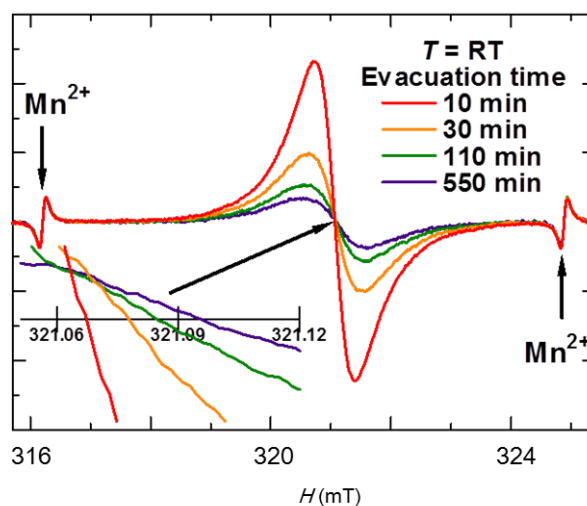


Figure 2. ESR spectra of iodine-doped NPB thin film with different doping concentration at room temperature. Doping concentration is controlled by evacuating the ESR sample tube. Inset shows the change of resonance center with respect to the doping concentration.

3. IOSC device

Direct correlation between charge accumulation and device performance was observed. Before the device was soaked with white light, the device showed poor short-circuit current (J_{sc}) and

did not show significant change in ESR signal. When the device was irradiated with white light, the number of spins (N_{spin}) was increased, and J_{sc} was dramatically improved. The ESR signal increased by white light irradiation is identified to be holes trapped at the bromine chain-end of P3HT polymer. These holes are supplied from band excitation of TiO_x layer. Because TiO_x has a large bandgap, it requires UV-light for band excitation. Counterpart electrons are speculated to be filling the traps of TiO_x layer, however in ESR inactive form. Possible ESR free electron traps are OH groups of TiO_x layer. Thus, passivation of OH groups of TiO_x layer is required to avoid light-soaking phenomenon in IOSCs using TiO_x as electron collecting layer.

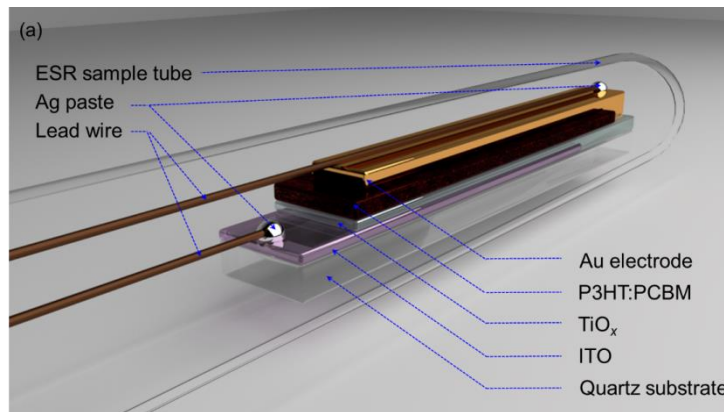


Figure 3. A schematic device structure of an inverted-type polymer solar cell of indium tin oxide (ITO)/ TiO_x /poly(3-hexylthiophene) (P3HT):phenyl C₆₁-butyric acid methyl ester (PCBM)/Au for electron spin resonance (ESR) measurements.

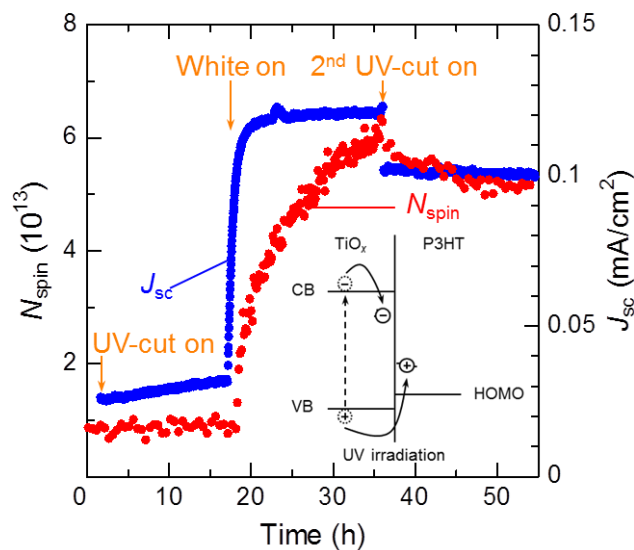


Figure 4. Transient response of N_{spin} (red circles) and J_{sc} (blue circles) of an ITO/ TiO_x /P3HT:PCBM/Au cell to UV-cut and white light irradiation. Inset shows charge trapping scheme with respect to UV-light irradiation.