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SCIENCE DIRECT

Materials Chemistry and Physics 95 (2006) 94–98

MATERIALS CHEMISTRY AND PHYSICS

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Effect of electrode modification on organic photovoltaic devices

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Received 30 November 2004; received in revised form 8 May 2005; accepted 5 June 2005

Abstract

Photovoltaic (PV) devices, in which 4,4′,4″-tris-(2-methylphenylphenylamino)triphenylamine (*m*-MTDATA) and neodymium (dibenzoylmethanato)$_3$(bathohenanthroline) (Nd(DBM)$_3$bath) were used as electron donor and acceptor, respectively, have been fabricated. The PV performance of the diode has been affected largely by two techniques that one is inserting a thin LiF layer between Nd(DBM)$_3$bath and Al electrode and the other is treating the ITO surface through ultraviolet light (254 nm). The short current (I_{sc}) of the PV diode has been increased from 0.057 to 0.145 mA cm^{-2} through the two techniques together. It is interesting to find that the power conversion efficiency can also be increased two-fold compared with that simple double layer diode without any treatments.

Keywords: Thin films; Evaporation; Photovoltaic

1. Introduction

Organic photovoltaic (PV) devices have attracted considerable interests since the letter was reported by Tang in 1986 [1] due to their excellent property such as light weight and low cost. Most research interesting has been mainly focused on improving the efficiency because it is very important to the practical PV devices. However, the efficiency needs to be increased further before these PV cells become practical, which at the moment looks still far away.

About the study of the PV efficiency, some researchers considered that the limiting factors of organic PV devices mainly came from the fundamental nature of charge photogeneration, transport in organic materials [2] and optical absorption characteristic of organic thin film materials [3–5]. While some people thought the important key is the interface properties between the organic films [6,7]. And others demonstrated that the crucial reason is the work functions of metal electrodes [8]. Therefore, many kinds of methods have been adopted to improve the PV performance of organic PV diodes including materials choice, device fabricated techniques, and so on [2,9].

It has been reported that the performance of organic light-emitting diodes (OLEDs) could be significantly improved through inserting a LiF layer between organic layer and aluminum cathode in the devices fabrication [10–13]. This technique has also been used to enhance the performance of plastic solar cells by Brabec et al. [14], and found that can increase both the open circuit voltage (V_{oc}) and the fill factor (FF) of the PV diodes. Whereas, the report of LiF effect on the organic small molecule PV device was not found. We report here is the effect of LiF on the organic small molecule PV device instead of the conjugated polymer/fullerene one. On the other hand, indium tin oxide (ITO) has been widely used as the anode for OLEDs device as well as PV device due to its high transparency and conductivity. It is well known that the surface properties, especially work function and the surface state of ITO directly affect the electroluminescent (EL) characteristics of the OLEDs device. Recently, research concerning improving the efficiency of OLEDs through surface modification of ITO has been widely reported [15–19]. However, few reports about organic PV properties related with ITO surface treatments were found [20]. Here, the effect of ITO surface treated

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doi:10.1016/j.matchemphys.2005.06.033

through UV light on the PV diodes was also discussed in this article.

In this article, PV devices were fabricated in which *m*-MTDATA and $Nd(DBM)_3$bath were used as electron donor and acceptor, respectively. The effect of LiF thin film on the PV performance was investigated, and the effect of ITO surface treatment with UV light was also investigated. It was found that the PV performance was significantly improved through inserting a thin LiF film between $Nd(DBM)_3$bath and aluminum cathode or treating the ITO surface by UV light in the fabrication process. The I_{sc} and the overall powder conversion efficiency of the PV device can be increased 1.5- and 2-folds, respectively, when the PV device has been fabricated though the above two techniques together.

2. Experiment

$Nd(DBM)_3$bath was synthesized according to the traditional method reported in 1964 [21]. LiF and *m*-MTDATA are commercial products from Aldrich Corporation.

A prepatterned indium tin oxide (ITO) coated glass substrate, with a sheet resistance of 100 Ω/□, was cleaned by detergent sonication and deionized water successively. Then it was treated in acetone by ultrasonic for 15 min. The ITO surface was or was not treated by UV-radiation according to the experiment requests before it was loaded into a vacuum chamber.

All the organic layers, LiF and aluminum cathode were sequentially deposited onto the ITO substrates by thermal evaporation at a pressure of 8×10^{-4} Pa without breaking the vacuum. Deposition of all layers was monitored by quartz oscillators and controlled at a rate of 0.2–0.4 nm s^{-1} for the organic layers, 0.05–0.1 nm s^{-1} for the LiF layers and 1.0 nm s^{-1} for the cathode. The active area of typical devices was about 0.15 cm^2. All PV diodes were illuminated by 365 nm UV light of 4 mW cm^{-2} through the ITO side.

The molecular structures of the organic materials used and the configuration of the PV diode were shown in Fig. 1. In the PV device, ITO/*m*-MTDATA (20 nm)/$Nd(DBM)_3$bath (20 nm)/LiF (*x* Å): Al(100 nm), ITO and Al were used as hole-collecting electrode and electron-collecting electrode, respectively.

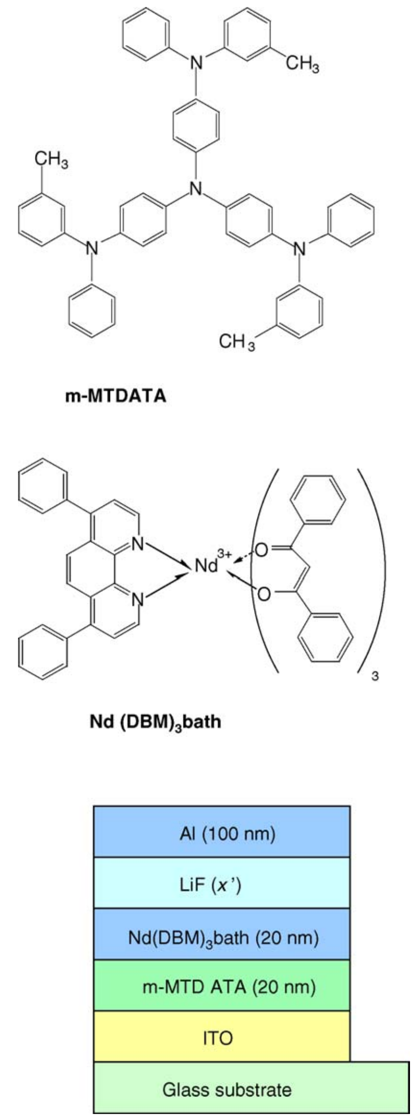

Fig. 1. Configuration of the PV diode and the molecular structure of the materials used.

3. Results and discussion

3.1. Effect of LiF thin layer

A series of PV devices have been fabricated through varying the thickness of LiF layer in which *m*-MTDATA and $Nd(DBM)_3$bath were used as electron donor and acceptor, respectively (the configuration of the PV diodes was shown in Fig. 1). The relation between I_{sc} of the PV device and the thickness of inserted LiF layer was shown in Fig. 2. The I_{sc} first increased and then decreased with increasing the thickness of inserted LiF layer as shown in Fig. 2. The value of I_{sc} of the PV diode reached 0.108 mA cm^{-2} when the thickness of inserted LiF layer was 6 Å. While the I_{sc} value is only 0.057 mA cm^{-2} in the PV diode without LiF. All the ITO glass substrates were not treated with UV-radiation and only the thickness of LiF layers were changed in the fabrication process.

It is well known that the electron state of interface between organic layer and the metal electrode plays an important role in the OLEDs devices. For example, the performance can be enhanced largely through depositing a thin LiF layer on the Al metal electrode, which can form a better ohmic contact and lower the serial resistivity, in many OLEDs fabrication process [22,23]. It has also been reported that a monomolecular layer of LiF can cause a significant vacuum level offset [24] which is well known for the deposition and adsorption of molecules on metal surfaces [25,26] because of the strong

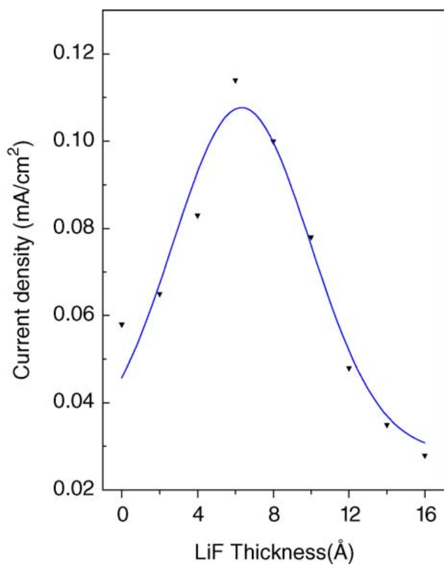

Fig. 2. The relation between short-circuit photocurrent and the thickness of LiF layer.

dipole moment of LiF (6.3 D) [27]. In the PV diode fabrication process, when LiF was introduced into the system, the interface between $Nd(DBM)_3$bath and Al electrode was modified and the adsorption of $Nd(DBM)_3$bath on the Al electrode surface was strengthened. And on the other hand, the $Nd(DBM)_3$bath molecule will have a tendency to be stacked with the same orientation on the Al cathode and lowered the serial resistivity. Furthermore, it has also been reported that this technique, which deposit little LiF on the Al electrode, can also lower the Al work function and that was verified by UPS [28]. It is suggested that the increase of I_{sc} should be attributed to all the three factors described above in the PV diode modified with LiF.

About the I_{sc} value of the PV device decrease with the thickness of LiF layer further increasing, we considered that it should be contributed to the resistance of thicker LiF layer. When the LiF layer gets thick, the diffusive electron will be intercepted because of the increasing resistance of LiF and lead to the decrease of I_{sc} value. Both the effects of dipole moment and the resistance of LiF were strengthened simultaneously when the thickness of LiF layer was increased in the fabrication process. Therefore, there should be existed an optimum thickness of LiF layer in the PV diode because of the two contrary factors, dipole moment and resistance. With further increasing the thickness of LiF layer, the influence of resistance of LiF will be the main factor instead of the dipole moment factor in the PV diode then lead to the I_{sc} value decrease through preventing from the electron diffusing in LiF layer. The I_{sc} value of the PV diode was even lower than that without LiF when the thickness of inserted LiF layer is larger than 14 Å as shown in Fig. 2.

Compared our results with that reported by Brabec et al. [14], we found that the optimum thickness of LiF layer in our PV diode is very similar with that report. But the influence of LiF on the PV performance is larger in the device fabricated with organic small molecule than that with polymer because of the size of molecule. The influence of dipole moment of LiF is much on organic small molecule than that on polymer. The maximum value of the I_{sc}, V_{oc}, FF and power conversion efficiency of the PV diode are 0.108 mA cm^{-2}, 1.88 V, 0.32 and 1.6%, respectively, when the inserted LiF layer thickness is 6 Å, as shown in Table 1.

3.2. Effect of UV treatment

To investigate the effect of ITO modified by UV irradiation on the PV performance, the pretreated ITO glass substrates were treated for different time by UV-irradiation before them were put into a vacuum chamber. The UV treatment was carried out in a UV-ozone cleaning chamber with UV emission from low pressure quartz mercury vapor lamps and a 254 nm UV intensity of 10 mW cm^{-2} at a distance of 5 cm from the lamps. The LiF thin film was not inserted between $Nd(DBM)_3$bath and Al cathode in all the experiments for just investigating the effect of UV treatment.

The correlation between I_{sc} of the PV diodes and UV-treating time was shown in Fig. 3. It was found that the I_{sc} of the PV diodes first increased then decreased with prolonging the UV treating time.

The atmosphere oxygen was irradiated through the UV light and was changed to ozone and atomic oxygen which can remove a small amount of contamination on the surface of the ITO, such as surface hydoxyls and carbon atoms remaining on the ITO surface [16,17,19]. On the one hand, oxygen atoms of the ITO were enhanced so that the work function of ITO was increased in this process [18]. On the other hand, there existed different chemical forms of oxygen atoms (O^{2-}, OH^-, organic oxygens and H_2O) which evolve with surface treatment on the ITO [29]. It is suggested that the factors affecting the current density should include the cleansing of

Table 1
PV performance at the different fabricating conditions

Experimental conditions	I_{sc} (mA cm^{-2})	V_{oc} (V)	FF	Power conversion efficiency (%)
LiF (0 Å), UV (0 min)	0.057	1.58	0.32	0.7
LiF (0 Å), UV (10 min)	0.081	1.69	0.31	1.1
LiF (6 Å), UV (0 min)	0.108	1.88	0.32	1.6
LiF (6 Å), UV (10 min)	0.145	1.96	0.32	2.2

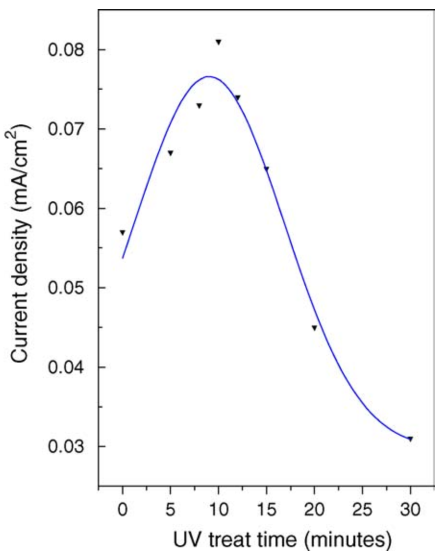

Fig. 3. UV treating time dependence of short-circuit photocurrent.

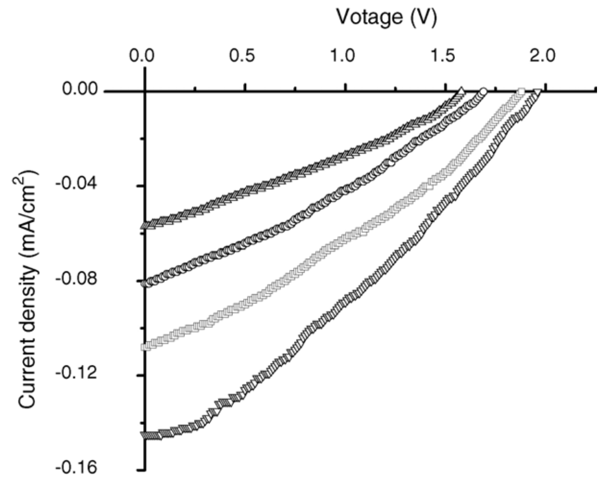

Fig. 4. *I–V* characteristics of the PV diodes fabricated with different techniques, without any treatment (up triangle); UV treat time 10 min (circle); thickness of LiF 6 Å (square); thickness of LiF 6 Å and UV treat time 10 min (down triangle).

the surface of ITO, the work function of ITO and the forms of oxygen atoms on the ITO surface.

First, the contamination on the surface of ITO would be removed and the work function of ITO would be increased with the UV treatment time increasing. And these factors led to the increase of I_{sc} value of the PV diode. With further increasing the UV treatment time, the amount of oxygen atoms (O^{2-}, OH^-, organic oxygens and H_2O) was increased and this would lead to the decrease of the I_{sc} value. Then there would exist an optimum time in the ITO treatment process. The maximum value of the I_{sc}, V_{oc}, FF and power conversion efficiency of the PV diode were 0.081 mA cm^{-2}, 1.69 V, 0.31 and 1.1%, respectively, when the treating time is 10 min as shown in Table 1.

3.3. Effect of both UV treatment and LiF thin film

Considered both the LiF thin layer and UV treatment effects on the PV performance, we fabricated the PV diode at the relative optimum condition and investigated the PV properties of the PV device. The maximum value of the I_{sc}, V_{oc}, FF and power conversion efficiency of the PV diode can be reached 0.145 mA cm^{-2}, 1.96 V, 0.32 and 2.2%, respectively, when the thickness of LiF layer is 6 Å and the UV treating time is 10 min. And other results at different experimental conditions were shown in Table 1. The values obtained through the two techniques together are better than those through the single treatment. The *I–V* characteristics of the PV devices fabricated with different techniques were shown in Fig. 4. The PV performance was significantly improved through the two fabricating techniques together. The further study is under the process to find the most optimum conditions on the PV diode fabricating through the two techniques together. And these techniques can be applied to other PV devices to improve the performance.

4. Conclusions

The effect factors of LiF layer between $Nd(DBM)_3$bath and Al cathode and ITO treated through UV radiation on the PV performance have been investigated and the relative optimum conditions were found, respectively. The reasons of the two fabricating techniques on the PV diodes were investigated, respectively. In view of the two factors that affected the PV performance, we fabricated the PV diode at the relative optimum conditions. And found that both the I_{sc} and power conversion efficiency can be improved significantly compared with that without any modification. It is a new technique to improve the PV performance through inserting LiF thin layer and UV-treatment on ITO together in the fabricating process.

Acknowledgement

The study is supported by the National Natural Science Foundation of China with Grant No. 90201012.

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