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Photoinduced degradation of organic solar cells with different microstructures*

Lu Chun-Xi(路春希)[a)b)], Yan Peng(闫 鹏)[b)], Wang Jin-Ze(王金泽)[b)], Liu Ai-Min(刘爱民)[a)c)], Song De(宋 德)[d)], and Jiang Chao(江 潮)[b)†]

[a)] *College of New Energy, Bohai University, Jinzhou* 121013, *China*

[b)] *CAS Key Laboratory of Standardization and Measurement for Nanotechnology, National Center for Nanoscience and Technology, Beijing* 100190, *China*

[c)] *School of Physics and Optoelectronic Engineering, Dalian University of Technology, Dalian* 116024, *China*

[d)] *Department of Physics, Science College, Changchun University of Science and Technology, Changchun* 130022, *China*

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An *in situ* measurement setup is established to investigate the photoinduced degradation effects in a controllable inert gas ambient environment for the two different microstructures of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyricacid methyl ester (PCBM) bulk-heterojunction organic solar cells. The two devices are fabricated with the solvent vapor drying process followed by a thermal annealing (vapor drying device) and only a normal thermal annealing process (control device), respectively. Their power conversion efficiencies (PCEs) and aging features are compared. Their different degradation behaviors in light absorption are confirmed. In addition, irradiation-induced changes in both nanostructure and surface morphology of the P3HT:PCBM blend films treated with two different fabrication processes are observed through scanning electron microscopy and atomic force microscopy. Aggregated bulbs are observed at the surfaces for control devices after light irradiation for 50 h, while the vapor drying devices exhibit smooth film surfaces, and the corresponding device features are not easy to degrade under the aging measurement. Thus the devices having solvent vapor drying and thermal annealing show better device stabilities than those having only the thermal annealing process.

Keywords: organic solar cells, photodegradation, solvent vapor drying, stability

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1. Introduction

Organic solar cells (OSCs) are promising for the next generation photovoltaic devices due to their excellent characteristics of low cost, low weight, mechanical flexibility, and easy fabrication.[1–3] However, enhancement of OSC efficiency and stability is still a challenging task for the commercial applications. Power conversion efficiency (PCE) has been increased to more than 10% over the last decade, but instability of the cell is still one of the key issues to tackle. Previous reports reveal that organic solar cells tend to degrade due to their limited resistances to moisture,[4] temperature,[5–7] and light,[8–11] thus the clarification of the degradation mechanisms becomes the focus of recent research.

Experiments conducted by Manceau *et al.*[8] indicated that light exposure would rearrange the structure of the active layer, which leads to slight disorganization of the P3HT domains. PCBM molecules diffuse through the polymeric matrix to become PCBM aggregates, and at the same time large P3HT-rich domains are formed. Therefore, most of the excitons are "lost" because the donor and the acceptor domains are too large to be transferred across when compared with the exciton diffusion length ($\sim$ 10 nm). Kawano and Adachi[12] discovered that the photodegradation could be attributed to the carrier accumulation, and that the degraded organic solar cell manifested a close relationship with the number of accumulated charge carriers.

In this paper, we investigate the photodegradations in two different microstructure OSC devices, and particularly focus our attention on the aging stabilities for devices with different fabrication processes. Two sets of devices are made to perform experiments of 50 hour photodegradation, the two devices being a solvent vapor drying device made by thermal annealing (hereafter called the vapor drying device) and a normal device made by a conventional thermal annealing process (called the control device). *I–V* characterization, atomic force microscopy (AFM), scanning electron microscopy (SEM), and ultraviolet visible light spectrophotometry are used to observe and analyze the OSC microstructures. AFM investigation indicates that the vapor drying device exhibits a smooth film surface, and is not easy to degrade under light irradiation. Spherical aggregates are observed at the surface of the control device by SEM, but not detected in the vapor drying device. The mechanism that leads to the above different microstructures is analyzed. The vapor drying device has better stability than the control one. All results may help us better understand the

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†Corresponding author. E-mail: jiangch@nanoctr.cn

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stabilities of organic solar cells with different microstructures.

2. Experimental details

2.1. Sample preparation

The device structure was composed of the following structural sequence from bottom to top: indium tin oxide (ITO)–PEDOT:PSS–P3HT:PCBM–calcium (Ca)–aluminum (Al). Solutions (P3HT:PCBM = 1:1 by weight) were prepared using 1,2-dichlorobenzene (DCB) and stirred overnight to promote complete dissolution. The glass substrates coated by patterned ITO (Luminescence Technology Corp. LT-G001, 9–15 Ω/sq) and ITO substrates were cleaned thoroughly in acetone, alcohol, and deionized water sequentially by ultrasonic treatment followed by blow drying with nitrogen gas and 100 °C annealing for 5 h. Glass substrates were treated by UVO for 15 min, then a thin layer (∼ 40 nm) of PEDOT:PSS (CLEVIOS^{TM} P VP AI 4083) was spin-coated to modify the ITO surface, which was dried at 100 °C for 40 min. The active layer (1:1 w/w, photoactive layer thickness 180 nm) was obtained by spin-coating onto the surface of PEDOT:PSS. Two wet films were dried at room temperature for 60 min with one set at glassware and the other set at glassware with DCB vapor. Then the films were thermally annealed at 150 °C in an oven for 10 min. Next, 20 nm Ca and 100 nm Al were evaporated as the cathode. The growth and evaporation of all films were manipulated in a glove box. Testing was operated under simulated AM 1.5 irradiation (100 mW·cm^{-2}) in a xenon-lamp-based solar simulator (NEWPROT).

2.2. Aging

To test the photodegradation of organic solar cells, we carried out an illumination experiment in a home-made aging measurement facility that has a controllable inert gas environment (H_2O< 0.1 ppm, O_2< 0.1 ppm). A fixed testing stage can hold several OSC devices simultaneously and guarantee comparable testing conditions for measurement of device stability. Figure 1 shows the power conversion efficiency (PCE) that has been normalized by the original value of a P3HT:PCBM solar cell as a function of illumination time. All the devices were illuminated by the simulated AM 1.5 irradiation (100 mW·cm^{-2}) using a xenon-lamp-based solar simulator (NEWPROT). The light intensity was calibrated to be 100 mW·cm^{-2} using a crystalline silicon reference cell as a standard cell. Note that the cell temperature during the 50 h illumination was maintained at around 40 °C. Original parameters of electrical performance are shown in Table 1.

Table 1. Original device parameters before photodegradation.

Sample	PCE/%	FF/%	J_{sc}/mA·cm^{-2}	V_{oc}/V
Control devices	3.33	58.67	8.62	0.62
Vapor drying devices	3.70	63.74	8.76	0.62

3. Results and discussion

Figures 1 and 2 show that the PCE and fill factor (FF) of solar cells decline gradually with illumination time, even though the devices are tested in an inert gas ambient glove box where we have eliminated the influence of vapor and oxygen. The relative variations in the power conversion efficiency of the devices under continuous irradiation (AM 1.5 G, 100 mW·cm^{-2}) demonstrate that relatively slow change is obtained for the device treated by solvent vapor drying and thermal annealing compared with the control device. The fill factor of the vapor drying device also decreases more slowly than the control one, as shown in Fig. 2. It is concluded that the solvent vapor drying and thermal annealing improves the stability of the solar cell.

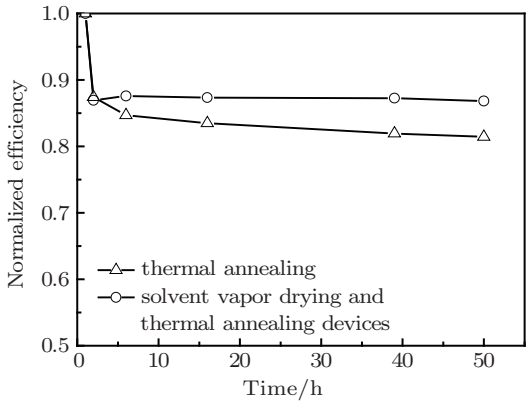


Fig. 1. Variations of normalized efficiency with illumination time for solar cells treated by different processing procedures.

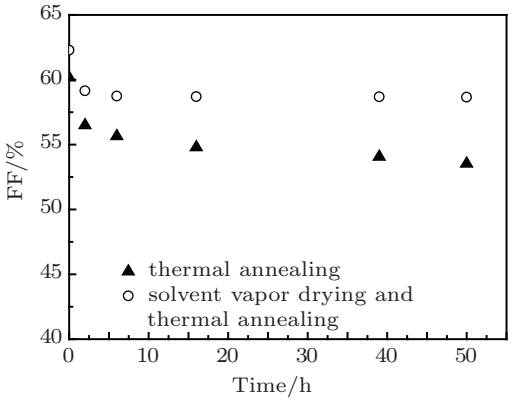


Fig. 2. Evolutions of FF with irradiation duration for solar cells treated by different processing procedures.

Figure 3 shows UV–visible absorption curves of P3HT:PCBM films with different treatments before and after aging testing. The device after thermal annealing treatment shows different absorption characteristics from the pristine one, while the device after solvent vapor drying and thermal annealing treatment shows similar absorption characteristics to the pristine device. The absorption evolution of the

control device suggests that the device with merely thermal annealing treatment experiences a rearrangement process for the active layer under light-irradiation exposure. Less change under the light-irradiation exposure indicates a minor molecular structure rearrangement occurring in the active layer for the vapor drying device.

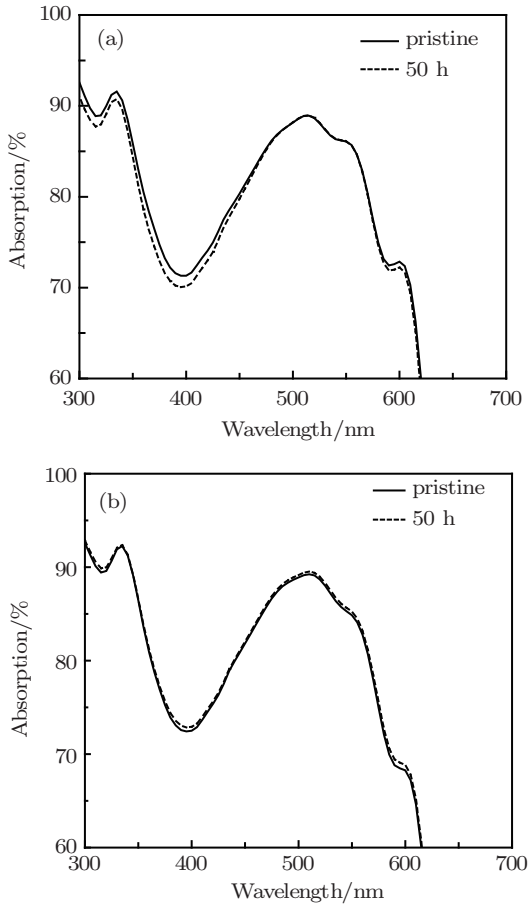


Fig. 3. Modifications of the UV–vis spectra of glass–ITO–PEDOT:PSS–P3HT:PCBM samples during photolysis: (a) thermal annealing treatment, and (b) solvent vapor drying and thermal annealing treatment.

Figure 4 shows the AFM images of the active layer of two devices before and after irradiation for 50 h. The roughness of the solvent vapor drying and thermal annealing film is smaller than that of the thermal annealing film, as indicated in Fig. 4. This is due to the fact that the P3HT molecular chains self-organize and form ordered structure after the DCB vapor treatment, and thus the roughness decreases compared with that of the control device. Figure 4(d) shows an AFM image of the active layer surface treated by solvent drying and thermal annealing after light irradiation for 50 h. The morphological change is relatively small, thus the thin film is barely affected by light irradiation. The surface of the thermal annealing film is significantly influenced by light irradiation, compared with that of the solvent drying and thermal annealing film.

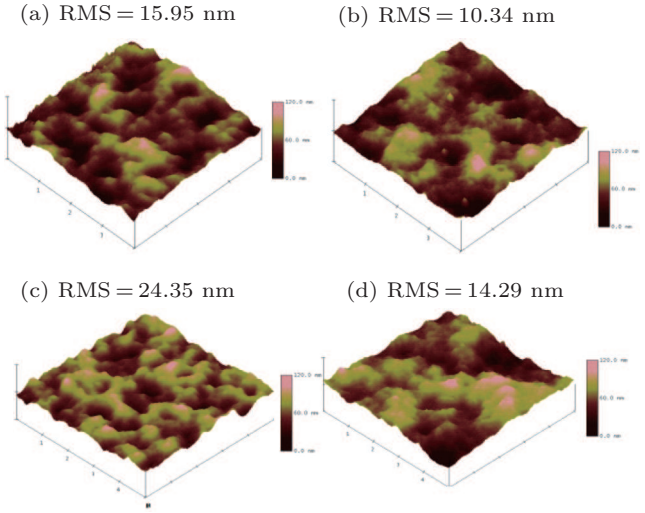


Fig. 4. (color online) AFM phase images of the active layer: (a) and (c) thermal annealing treatment before irradiation and after 50 h photodegradation; (b) and (d) solvent vapor drying and thermal annealing treatment before irradiation and after 50 h photodegradation, respectively.

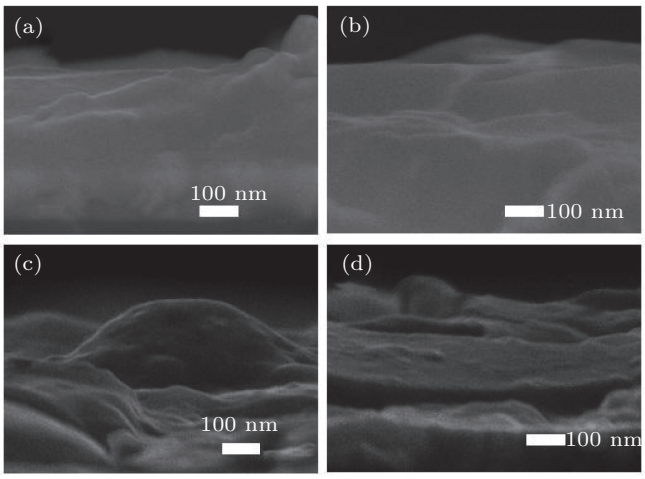


Fig. 5. SEM images of the cross section of the active layers: (a) and (c) thermal annealing treatment before and after irradiation, respectively; (b) and (d) solvent vapor drying and thermal annealing treatment before and after irradiation, respectively.

Different phases are observed in the SEM analyses, as shown in Fig. 5. After 50 h exposure under the sun simulator irradiation, the P3HT:PCBM blends with only thermal annealing treatment show spherical aggregates. The aggregates are on average 500 nm in diameter and 80 nm high and are attributed to the formation of large PCBM concentrated areas. PCBM molecules are mobile and can diffuse through the polymeric matrix, leading to the formation of PCBM aggregates. At the same time, large P3HT-rich domains are created. The observation results suggest that most of the excitons are 'lost' because the donor and acceptor domains become too large after the samples immersed in light irradiation have been crossed because of a limited exciton diffusion length (around 10 nm). The structures observed are similar to those reported by Manceau *et al.*[8] and Hoppe and Adachi.[13] On

the other hand, the morphology of the nanostructure for the P3HT:PCBM blends with solvent vapor drying and thermal annealing treatment is not significantly changed after the 50-h irradiation (see Figs. 5(b) and 5(d)), which is a major reason why the vapor drying device possesses a better stability.

4. Conclusions

Effects of photodegradation for organic solar cells are compared within two devices fabricated with different treatment processes using an *in situ* aging measurement facility. The UV–visible absorptions of different aging devices are recorded. Compared with the control devices having only the thermal annealing process, the vapor drying devices treated by solvent vapor drying and thermal annealing show much better degradation behavior within an aging time of 50 h. Minor microstructure change proves to be the reason for improving the stability of the organic solar cell. This means that much better device stability may be achieved by further optimizing the device fabrication processes.

References

[1] Helgesen M, Søndergaard R and Krebs F C 2010 *J. Mater. Chem.* **20** 36

[2] Dennler G, Scharber M C and Brabec C J 2009 *Adv. Mater.* **21** 1323

[3] Krebs F C, Tromholt T and Jørgensen M 2010 *Nanoscale* **2** 873

[4] Hauch J A, Schilinsky P, Choulis S A, Rajoelson S and Brabec C J 2008 *Appl. Phys. Lett.* **93** 103306

[5] Lin C, Lin E Y and Tsai F Y 2010 *Adv. Funct. Mater.* **20** 834

[6] Bertho S, Janssen G, Cleij T J, Conings B, Moons W, Gadisa A, Haen J D, Goovaerts E, Lutsen L, Manca J and Vanderzande D 2008 *Sol. Energy Mater. Sol. Cells* **92** 753

[7] Conings B, Bertho S, Vandewal K, Senes A, Haen J D, Manca J and Janssen R A J 2010 *Appl. Phys. Lett.* **96** 163301

[8] Manceau M, Rivaton A, Gardette J L, Guillerez S and Lemaître N 2011 *Sol. Energy Mater. Sol. Cells* **95** 1315

[9] Reese M O, Nardes A M, Rupert B L, Larsen R E, Olson D C, Lloyd M T, Shaheen S E, Ginley D S, Rumbles G and Kopidakis N 2010 *Adv. Funct. Mater.* **20** 3476

[10] Tromholt T, Madsen M V, Carlé J E, Helgesen M and Krebs F C 2012 *J. Mater. Chem.* **22** 7592

[11] Bhattacharya J, Mayer R W, Samiee M and Dalal V L 2012 *Appl. Phys. Lett.* **100** 193501

[12] Kawano K and Adachi C 2009 *Adv. Funct. Mater.* **19** 3934

[13] Hoppe H and Sariciftci N S 2006 *J. Mater. Chem.* **16** 45