Photovoltaic Properties of Polythiophene: Fullerene Derivative Solar Cell Using Annealing due to Anode Joule Heating

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A hot-plate annealing is often used as the anneal process of a regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT): [6,6]-phenyl-C60-butyric acid methyl ester (PCBM) thin-film solar cell. In laboratories, the anneal procedure is carried out by putting the substrates on a hot plate. We tried to anneal the specimens using the Joule heat due to applying current to ITO electrode. The configuration of ITO electrode is 29mm-length and 2mm-width. The current flowing in ITO is from 60 to 80 mA. The temperatures corresponding to these currents are ~95 and ~140°C. The temperature change of the specimen on a hot plate can be restaged by the Joule heating. Although the photovoltaic properties of non-annealing specimen are the poorest of the three, those of Joule heat annealing specimen are the same as those of hot-plate annealing specimen. The absorption spectra of three specimens are same. The IPCE spectrum of non-annealing specimen is 70% lower than the other specimens. This result shows the carrier transport in the active layer and the carrier ejection from the active layer to both electrodes. The Joule heat anneal is found to give the P3HT:PCBM device performance similar to the hot plate anneal.

Keyword: organic solar cell, P3HT, PCBM, anneal process, Joule heat

1. Introduction

Organic solar cells (OSCs) have some advantages as flexibility, easy processability, especially the use of solution process. In recent, the power conversation efficiency (PCE) of OSCs increases rapidly and is beyond 12%[1]. However, since the panel efficiency of Si solar panel is beyond 20%, it is not easy that OSCs substitute for Si solar panel on electric power source. The incentive of the use of OSC is light-weight and low-cost. A regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) is widely known as a donor material. The OSC with bulk hetero junction[2] consists of P3HT and fullerene. The OSCs with the active layer of P3HT: [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) are reported to have the PCE of 2-5%[3]. The P3HT:PCBM solar cells are popular but their PCE is lower than the OSCs with advanced materials. For example, Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT), 6.1% [4], Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H- cyclopenta [2,1-b:3,4-b']dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT), 7.7% [5], Poly[4,8-bis [(2-ethylhexyl)oxy]benzo[1,2-b :4,5-b']dithiophene -2,6-diyl-alt-3-fluoro-2-[(2-ethylhexyl)carbonyl]thi eno[3,4-b ]thiophene-4,6-diyl] (PTB7), 7.4% [6]. The chemical structure of the latest donor materials with the PCE of >10% are not clarified in the reports. rrP3HT shows the molecular alignment by an annealing. The alignment of P3HT are reported by the X-ray diffraction patern [7,8], Raman spectroscopy [9], transmission electron microscope...
transmission electron diffraction [11] and spectral ellipsometry [12]. The thiophene ring of \( r\)P3HT molecules are vertically aligned to the substrate. The annealing is very effective for the vertical alignment. Generally, the annealing is carried out by putting on a hot-plate. Our groups have studied and proposed on dye-sensitized solar cells[13-18] and organic thin-film photovoltaic cells[19,20]. In this paper, we propose a direct annealing due to the Joule heat by flowing current to ITO electrodes without a hot-plate.

2. Experimental

2.1. Materials and fabrication

Donor and acceptor materials were a regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) and \([6,6\)-phenyl-C61-butyric acid methyl ester (PCBM), respectively. The organic materials were obtained from Luminescence Technology Co. The organic materials were shown in Fig.1.

![Figure 1 Chemical structure of our organic materials.](image)

The PEDOT:PSS thin film was spun on the 2-mm-line-etched ITO substrate. The PEDOT:PSS thin film was annealed at 200 °C, 10 min in an electric oven. The weight ratio of P3HT:PCBM is 1:0.7 and the mixture was dissolved in chlorobenzene. The active layer was spun on the PEPDT:PSS thin film from the solution. Finally aluminum top electrode was vacuum-deposited on the organic layer. After all fabrications, the specimen was annealed in vacuum. We carried out a vacuum-deposition with EO-55 (EIKO Co.).

The conventional annealing method was carried out by the following procedure: the specimen whose top electrode is vacuum-deposited, is put on a 100°C hot plate. After the temperature of 100 °C is kept for 8 min, it increases up to 140 °C and is kept for 10 min. And the specimen is removed from the hot plate. Our proposed annealing method was carried out by the follows: the current is flowed between both terminals of ITO electrodes. The current gave the Joule heat to ITO electrodes. The heat annealed the organic layers on the ITO electrodes.

![Figure 2 The appearance of Joule heating method](image)

Figures 3 (a) the current program and (b) the temperature of ITO electrode.

Figs. 3a and 3b show the temperature program and the real substrate temperature change, respectively. The temperature of the specimen can be controlled by the appropriate current distribution. When the current flow is stopped, the temperature of the specimen decreases rapidly. The temperature response is fast and moves on with the change of current. Fig. 4 shows the temperature...
distribution of the substrate. The temperature of the area around two ITO electrodes is thought to be uniform. Although the appropriate current to a desired temperature must be estimated previously, the desired temperature pattern can be obtained by the current control.

Figures 4 The heat distribution of ITO substrate by the Joule heating method

2.2. Measurements
The work functions of ITO and organic materials are measured with the photoemission yield spectroscopy in air (AC-2, Riken Keiki Co.). Absorption spectra were measured by spectrophotometer (U-3000, Hitachi Co., Ltd.). The temperature of ITO electrodes was measured with a thermography (FSV-2000, Apiste). The $\theta - 2\theta$ XRD was measured with Smart Lab X-ray diffractionmeter (Rigaku). Current-voltage characteristics were measured using a source measure unit (2400 Source Measure Unit, Keithley). Photocurrents were measured with the mask (2x2 mm$^2$, equal to device area) under a quasi-solar simulator of AM1.5G, 100 mW/cm$^2$ (XIL-03E, Seric Ltd.). The measurements of luminance-current-voltage characteristics were carried out under vacuum of ~0.1 Pa.

3. Results and Discussion
3.1. PV characteristics
Figure 5 shows the PV properties for three specimens, i.e. non-annealing, hot-plate annealing, and Joule heat-annealing specimens. Table 1 summarizes the PV parameters, a short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor ($FF$), power conversion efficiency (PCE) and the thickness of active layer. The non-annealing specimen has the lowest PV parameters. On the other hand, the PV performance of the Joule heat-annealing specimen is same as that of the hot-plate annealing specimen.

Figure 5 Photocurrent – voltage curve of non-annealing, hot-plate annealing, and Joule heat annealing specimens, the thickness of active layer is ~90 nm.

Figures 6 Comparison of photocurrent vs. dark current curves: (a) Joule heating specimen, (b) hot-plate annealing specimen, (c) non-annealing specimen.
### Table 1: Photovoltaic Properties of Different Annealing Processes

| Process         | $J_{sc}$ [mA/cm²] | $V_{oc}$ [V] | FF  | PCE [%] |
|-----------------|-------------------|--------------|-----|---------|
| non-ann.        | 5.1               | 0.45         | 0.26| 0.62    |
| hot-plate       | 8.1               | 0.55         | 0.48| 2.2     |
| Joule-heat      | 7.7               | 0.61         | 0.48| 2.3     |

The fact of poor FF and low $V_{oc}$ in the non-annealing specimen is caused by the absence of appropriate interface for carrier generation and effective path for carrier transport. Figures 6 show the comparison of photo and dark currents. If good interface between donor and acceptor domains is formed and the leakage current is lower, the photocurrent will almost agree with the dark current at the range of $V > V_{oc}$. The hot plate specimen is the best characteristics of the three specimens but the non-annealing specimen is the worst. This Joule heat specimen is regarded as an unsatisfactory performance.

### 3.2. Characteristics of active layer and discussion

Figure 7 shows the absorbance of three specimens. These absorbance spectra are measured after the incident photon to current conversion efficiency (IPCE) spectra in Fig. 9. The absorptions around 350 nm and 520 nm are derived from PCBM and P3HT, respectively. The shoulder at 580 nm is due to the molecular alignment of P3HT. The shoulder of 580 nm for the non-annealing specimen appears superficially similar to those for the annealing specimens.

Figures 8 show the XRD patterns on P3HT domain for for hot-plate (113 nm) and Joule-heat (118 nm) annealing P3HT:PCBM thin films: (a) original XRD patterns, (b) Lorentz-approximated XRD patterns. Although there is little the absorbance between non-annealing and annealing specimens, the distinct difference is observed in the XRD pattern. The XRD peak becomes larger and narrower, and is shifted to the small angle by the annealing process. This results support the enlargement of P3HT domain and the enhancement of molecular packing (alignment). On the other hand, the annealing effect does not depend on the annealing method.
Figure 9 The IPCE property of the non-annealing, hot-plate annealing, and Joule-heat annealing specimens (ITO/PEDOT:PSS (~60 nm)/P3HT:PCBM active layer: ~90 nm)/Al.

Figure 9 shows the IPCE spectra of three specimens. Fundamentally the peaks of IPCE spectra are caused by the absorption of organic material. The peaks of IPCE at 360 nm and 480 nm are due to PCBM and P3HT, respectively. However, the IPCE peak of P3HT is shifted to the short wavelength region as compared with the absorption of P3HT. The IPCE of the non-annealing specimen is poorer those of the annealing specimens. When the IPCE spectra are normalized by the maximum of peak, the configurations of three specimens are coincided. The configuration of IPCE spectra does not depend on the annealing but the peak of IPCE spectrum for the non-annealing specimen decreases to 70 % as compared with the annealing specimens.

The external quantum efficiency, \( \eta_{\text{EQE}} \), is described as the equation (1),

\[
\eta_{\text{EQE}} = \eta_A \eta_{\text{ED}} \eta_{\text{CT}} \eta_{\text{CC}},
\]

where \( \eta_A \) is the optical absorption efficiency in the active layer, \( \eta_{\text{ED}} \) is the diffusion efficiency of exciton to the donor/acceptor (D/A) interface, \( \eta_{\text{CT}} \) is the generation efficiency of free carrier at the D/A interface, and \( \eta_{\text{CC}} \) is the ejection efficiency to the electrode connected with an external circuit, respectively. Since the absorbance spectra of the three specimens are same, the \( \eta_A \) is thought to be same. The generation efficiency of free carrier at the D/A interface will be mainly controlled by the energy gap between donor and acceptor. The apparent electronic transfer probability from a molecule on the electrode to the electrode does not depend on the fabrication process. However, the area density of the molecule on the electrode and the environmental condition depend on the fabrication condition. Therefore, the \( \eta_{\text{CC}} \) is not same and the \( \eta_{\text{ED}} \) is not same since the configuration and distribution of the D/A interface is different for the bulk hetero type with high facultativity. The low performance of the non-annealing specimen will be caused by the low \( \eta_{\text{CC}} \) and \( \eta_{\text{ED}} \). However, the low performance can be improved by the Joule-heat annealing in the same manner as the hot-plate annealing.

4. Conclusion

We proposed a direct annealing method using the Joule-heat due to applying current to ITO electrodes. ITO electrodes was a part of device structure. The annealing apparatus as hot-plate, halogen lamp etc. was not needed in this annealing method. We used this annealing method to the fabrication of the P3HT:PCBM solar cells. The OSCs’ performance using the Joule-heat annealing was equal to those using the conventional hot-plate annealing. It was suggested that the direct Joule-heat annealing was an effective annealing method.

Acknowledgements

This research is partially obtained by a financial assistance of a MEXT-Supported Program for the Strategic Research Foundation at Private Universities (S1001033, 2010-2014) and the AIT Special Grant for Education and Research.

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