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## Characterization of ZnS-layer-inserted bulk-heterojunction organic solar cells by ac impedance spectroscopy

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A fluorine-doped tin oxide (FTO)/zinc sulfide (ZnS)/[6,6]-phenyl C<sub>61</sub> butyric acid methyl ester (PCBM): regioregular poly(3-hexylthiophene) (P3HT)/poly(3,4-ethylenedioxythiophene): poly(4-styrene sulfonic acid) (PEDOT:PSS)/Au type organic solar cell (FTO/ZnS/PCBM:P3HT/PEDOT:PSS/Au, ZnS cell) with a 1 cm<sup>2</sup> active area was first developed using transparent ZnS prepared on a FTO electrode by a chemical bath deposition method. The ZnS inserted solar cells were investigated by photocurrent-voltage (*I-V*) and ac impedance spectroscopy (IS) measurements. In photo *I-V* measurements, the ZnS cell exhibited scattered power conversion efficiencies ( $\eta$ ) of 0.7%–1.2% when the FTO/ZnS electrode was not immersed in various aqueous solutions before the fabrication of the ZnS cells. In contrast, the solar cells with a surface-modified FTO/ZnS electrode by immersing in 0.1M Na<sub>2</sub>S solutions at pH 7–9 containing hydrosulfide ions (HS<sup>-</sup>) exhibited reproducible  $\eta$  of 1.5%–1.7%. The electric resistance components in the cell consisting of five layers were separately estimated by the IS measurement. The larger  $\eta$  of the solar cell using HS<sup>-</sup> modified ZnS was explained by the fact that the charge transport resistance at the ZnS/PCBM:P3HT interface became smaller due to this surface modification. When a continuous light irradiation was carried out for the modified cells, the resistance at the ZnS/PCBM:P3HT interface increased, being accompanied by the decrease in the  $\eta$ . That is, the cell performance was controlled mainly by charge transport velocity at the ZnS/PCBM:P3HT interface. © 2009 American Institute of Physics. [DOI: 10.1063/1.3153970]

### I. INTRODUCTION

Organic thin-film solar cells have attracted much attention as a clean and safe energy source instead of the fossil fuel since they were expected to provide low-cost and environment-friendly energy-conversion devices. In recent years, the power conversion efficiency and the durability of the solar cells have rapidly improved by extraordinary efforts of many researchers. The solar cells are edging closer to practical use. However, the behavior for electron or hole transport at interfaces existing in organic solar cells is not understood sufficiently yet despite its analysis is very important to improve the cell performance.

Alternating current impedance spectroscopy (IS) is an electric technique to monitor the current response when an ac voltage is applied as a function of the frequency. This method is possible to observe the electric properties of the bulk and the interface that we cannot observe by a dc method, because the electric response speed for each component is different on the microscopic time scale. The IS method has been widely employed to study on the electric properties of organic electronic device such as dye-sensitized solar cells<sup>1–4</sup> and organic light emitting diodes.<sup>5,6</sup> In order to accelerate the development of practical photovoltaic devices, it is similarly necessary to estimate electric parameters such

as resistance and capacitance by evaluating equivalent circuits of organic thin-film solar cells. However, few instances have been reported on the IS measurement of the organic thin-film solar cells compared to that of other devices. This is probably that reasonable accuracy was not obtained for its IS measurement because of rapid performance degradation under light irradiation.

In organic solar cells sandwiching the photoactive layer between the front indium tin oxide (ITO) electrode and the back Al electrode, which are termed “normal type solar cells,” the Al electrode has acted as the electron collection electrode because of its low work function. However, their performance quickly degraded when the Al electrode was not deposited under ultrahigh vacuum condition and further the cells were not completely sealed for moisture and oxygen, because the Al surface is easily oxidized to insulator Al<sub>2</sub>O<sub>3</sub> by slight residue of the moisture and the oxygen. Therefore, in order to improve the cell durability, it is crucially important to develop the solar cells using a noncorrosive electrode instead of the Al. In organic solar cells sandwiching the photoactive layer between the ITO electrode and the noncorrosive Au electrode, the photogenerated electrons flow from the ITO electrode to the Au electrode through an external circuit. The organic solar cells are called “inverted type solar cells” because the electrons flow in reverse against normal type solar cells.

In our previous studies, we have developed organic thin-film solar cells using a noncorrosive Au metal as the back

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electrode, and an ITO/In or a fluorine-doped tin oxide (FTO)/titanium oxide ( $\text{TiO}_2$  or  $\text{TiO}_x$ ) as the front electrode.<sup>7–11</sup> For example, we reported that the ITO/amorphous  $\text{TiO}_x$ /PCBM:P3HT/PEDOT:PSS/Au inverted type cell showed the power conversion efficiency of 2.47% and the performance of the cells with sealing was about the same after continuous light irradiating for 120 h in an ambient atmosphere.<sup>12</sup> Even without sealing, this solar cell maintained the performance after continuous light irradiation for 20 h. Thus, we have the techniques required to fabricate the organic thin-film solar cells with reasonable performance and stability.

An *n*-type semiconductor  $\text{TiO}_2$  (Refs. 12–16) or ZnO (Refs. 17 and 18) has worked as an electron collection layer as well as a hole blocking layer in the organic thin-film solar cells. ZnS is also an important inorganic semiconductor with bandgap of 3.7 eV at 300 K,<sup>19</sup> being expected as one of the promising electron collection layer. However, the *n*-type semiconductor ZnS has not been applied to the organic solar cells so far. We first developed the inverted type bulk-heterojunction organic solar cells (FTO/ZnS/PCBM:P3HT/PEDOT:PSS/Au, ZnS cells) using a ZnS layer prepared on a FTO plate by a chemical bath deposition (CBD) method as the electron collection layer. Furthermore, we found that the performance of the ZnS cells was improved by immersing the FTO/ZnS electrode in sodium sulfide aqueous solution at *pH* 7–9. Herein, we present the *I*-*V* and IS characteristics of the surface-modified ZnS cells. The presented solar cells are significantly different in the cell performances and the IS profiles from nontreated ZnS cells without immersing the FTO/ZnS electrode in sodium sulfide aqueous solution before the cell fabrication.

## II. EXPERIMENTAL

### A. Materials

Zinc acetate ( $\text{Zn}(\text{OAc})_2$ ), thioacetamide (TAA) ( $\text{CH}_3\text{CSNH}_2$ ), sodium sulfide ( $\text{Na}_2\text{S}$ ), regioregular P3HT (Mw ~ 87,000), PEDOT:PSS 1.3 wt % dispersion in water, and chlorobenzene were purchased from Sigma-Aldrich Chemical Co., Inc. PCBM was purchased from Frontier Carbon Corporation. All the chemicals were used as received. FTO substrates (Asahi Glass A110U80, sheet resistance;  $12 \Omega/\square$ ) and Au wires were purchased from Asahi Glass Co., Inc. and Furuuchi Chemical Corporation, respectively.

### B. Fabrications of organic thin-film solar cells using chemical bath deposited ZnS thin film

The FTO electrode was ultrasonicated in 2-propanol, and then cleaned in boiling 2-propanol, and subsequently dried in air. A ZnS film on the FTO electrode was deposited by the CBD method described by Yamaguchi *et al.*<sup>20</sup> The step reactions can be explained as follows:

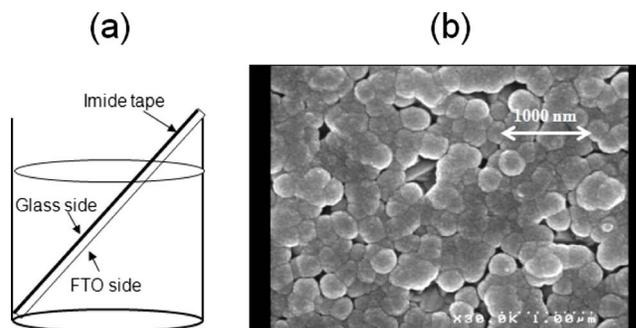


FIG. 1. (Color online) Illustration of the chemical ZnS-deposition apparatus (a) and surface SEM image of ZnS film (b) deposited onto a FTO electrode by immersing in  $0.1M \text{Zn}(\text{OAc})_2 + 0.1M \text{TAA}$  at  $80^\circ\text{C}$  for 120 min.



$\text{H}_2\text{S}$  is produced by the reaction of  $\text{CH}_3\text{CSNH}_2$  and  $\text{H}_2\text{O}$  [Eq. (1)], then the  $\text{H}_2\text{S}$  almost dissociates into  $\text{HS}^-$  ions at a neutral *pH* range of the chemical bath solution [Eq. (2)]. Finally, a ZnS solid film is deposited on the FTO plate by the reaction of  $\text{Zn}^{2+}$  and  $\text{HS}^-$  ions [Eq. (3)]. The CBD method was experimentally carried out as follows. A TAA aqueous solution was added in a  $\text{Zn}(\text{OAc})_2$  aqueous solution, then the mixed solution was diluted just to 50 ml. The solution was transferred to a 100 ml beaker being used as a reaction bath for the film deposition.  $xM \text{Zn}(\text{OAc})_2 + yM \text{TAA}$  mixed solution was tested as the content of the chemical deposition bath, where *x* and *y* were changed from 0.05 to 0.2. The glass side of the FTO substrate was covered with an imide tape to prevent an extra deposition of ZnS, and then the FTO was immersed for 80–120 min in the bath at  $60$ – $90^\circ\text{C}$  as shown in Fig. 1(a). The as-deposited ZnS film on the FTO was ultrasonicated for 10 min in water and dried in a dry oven at  $130^\circ\text{C}$  overnight. Figure 1(b) shows the surface scanning electron microscopic (SEM) image of the ZnS film, which was deposited in  $0.1M \text{Zn}(\text{OAc})_2 + 0.1M \text{TAA}$  chemical bath for 120 min at  $80^\circ\text{C}$ . The FTO electrode was densely covered with ZnS particles of  $\sim 150$ – $200 \text{ nm}$  size. The thickness of the ZnS film was  $\sim 110 \text{ nm}$ , being estimated by atomic force microscopic (AFM) measurement.

A chlorobenzene solution containing  $25 \text{ g l}^{-1}$  of P3HT and  $20 \text{ g l}^{-1}$  of PCBM was spin coated onto the FTO/ZnS substrate; further a PEDOT:PSS aqueous solution was spin coated onto its blend film. Finally, a Au metal as the top electrode was vacuum deposited on the PEDOT:PSS solid film. The film thicknesses of the PCBM:P3HT, the PEDOT:PSS, and the Au were about 250, 80, and 200 nm, respectively. The device was heated at  $150^\circ\text{C}$  for an annealing treatment. The effective area of the solar cell was restricted to  $1.0 \text{ cm}^2$  by depositing the Au electrode using a mask substrate.

### C. Measurements

In order to observe the ZnS surface and its cross section, SEM and AFM data were recorded using a Hitachi S-4500 SEM apparatus and an SII SPI3800N AFM apparatus, respectively. The photocurrent-voltage (*I*-*V*) curves of the solar cells were measured by linear sweep voltammetry (LSV)

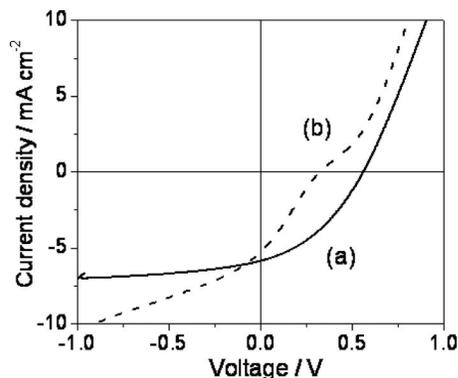


FIG. 2.  $I$ - $V$  curves of inverted type solar cells with (a) and without a ZnS layer (b) under light irradiation.

with a scan rate of  $5 \text{ V min}^{-1}$  under an AM 1.5G simulated sunlight with  $100 \text{ mW cm}^{-2}$  intensity. The light source was from a Kansai Kagakukikai XES-502S solar simulator, its intensity being calibrated by an EKO MS-601 pyranometer equipped with a silicon diode. Durability test of the solar cells was carried out by an interval LSV measurement in combination with a rest voltage measurement under continuous irradiation of the AM 1.5 G– $100 \text{ mW cm}^{-2}$  light. All the dc electric measurements were implemented using a Hokuto Denko HZ-5000 electrochemical analyzer. The IS measurements were implemented using a Hewlett-Packard precision LCR meter 4284A for solar cells in the dark and under light irradiation of AM 1.5 G– $100 \text{ mW cm}^{-2}$ . The frequency range is from 20 Hz to 1 MHz and the magnitude of the alternative signal is 5 mV. The obtained data were fitted with Scribner Associate Z-VIEW software v2.6 in terms of appropriate equivalent circuits. All measurements were carried out in an ambient atmosphere, that is, at room temperature of  $15\text{--}30 \text{ }^\circ\text{C}$  and under relative humidity of 40%–60%.

### III. RESULTS

#### A. Photo $I$ - $V$ properties

The photo  $I$ - $V$  curves of the inverted type solar cells with and without a ZnS layer are shown in Fig. 2. In the case of the cell without ZnS, the performance showed the short-circuit photocurrent ( $J_{sc}$ ) of  $5.28 \text{ mA cm}^{-2}$ , the open-circuit voltage ( $V_{oc}$ ) of 0.32 V, the fill factor (FF) of 0.26, and consequently the power conversion efficiency ( $\eta$ ) of 0.45%; see curve (b). Whereas, the best properties of the cells with a CBD-ZnS layer showed  $J_{sc}=5.86 \text{ mA cm}^{-2}$ ,  $V_{oc}=0.56 \text{ V}$ ,  $\text{FF}=0.37$ , and  $\eta=1.23\%$ , see curve (a), although the ZnS cells exhibited scattered  $\eta$  values of 0.7%–1.2%. This performance increment is from an improvement of the rectification properties. It is known that the  $n$ -type semiconductor such as  $\text{TiO}_2$  and ZnO acts as an electron collection layer as well as a hole blocking layer in the organic thin-film solar cells. The ZnS thin layer may have the same function.

In order to control the charge transport property at the ZnS/PCBM:P3HT interface, we have tried to modify the ZnS surface by immersing the FTO/ZnS electrode in various solutions. Figure 3 shows the photo  $I$ - $V$  curves of the surface-modified ZnS cells under light irradiation of AM

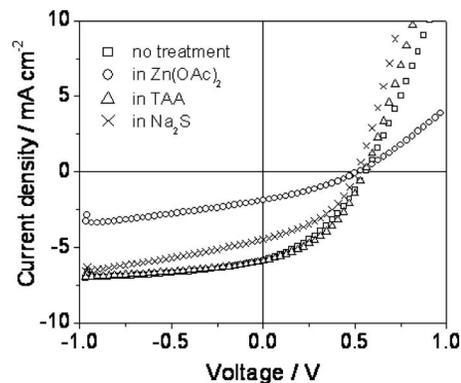


FIG. 3.  $I$ - $V$  curves of inverted type solar cells with ZnS layers treated by immersing in various solutions under light irradiation. Immersing solutions: no treatment (open square), 0.1M  $\text{Zn}(\text{OAc})_2$  (open circle), 0.1M TAA (open triangle), and 0.1M  $\text{Na}_2\text{S}$  at pH 13.5 (cross mark). All solutions were not pH adjusted.

1.5 G– $100 \text{ mW cm}^{-2}$ , and the cell performance is summarized in Table I. When the FTO/ZnS electrode was immersed in a 0.1M  $\text{Zn}(\text{OAc})_2$  aqueous solution after the ZnS deposition, the  $\eta$  of the ZnS cell decreased down to 0.39% (open circle). This value is considerably lower than that of the non-treated ZnS cell. This result suggested that an energetically disfavored ZnO thin layer was formed on the ZnS surface, preventing the interfacial electron transport between the PCBM:P3HT and ZnS layers. However, when the FTO/ZnS electrode was immersed in a 0.1M TAA solution supplying  $\text{HS}^-$  ions [see Eqs. (1) and (2)], the  $\eta$  of the surface-modified ZnS cell increased up to 1.37% (open triangle). In addition, the reproducible photo  $I$ - $V$  characteristics were obtained in several other independent runs. However, when the FTO/ZnS electrode was immersed in a non-pH-adjusted 0.1M  $\text{Na}_2\text{S}$  solution (pH 13.5) supplying  $\text{S}^{2-}$  ions, the  $\eta$  of the surface-modified ZnS cell was 0.97% (cross mark). We presumed that both of  $\text{S}^{2-}$  ions and hydroxide ions ( $\text{OH}^-$ ) contained in the non-pH-adjusted 0.1M  $\text{Na}_2\text{S}$  solution were adsorbed on the ZnS surface, and the adsorbed  $\text{OH}^-$  ions offered an inferior interface for the charge transport.

From such speculation, we immersed the FTO/ZnS electrode in 0.1M  $\text{Na}_2\text{S}$  solutions supplying  $\text{HS}^-$  ions at pH 7–9 containing little  $\text{OH}^-$  ions. Figure 4 shows the photo  $I$ - $V$  curves of the ZnS cells treated by 0.1M pH-adjusted  $\text{Na}_2\text{S}$  solutions, and the cell performance is summarized in Table I. By immersing in the solutions at pH 9.0 and 7.0, the  $\eta$  values increased up to 1.52% (filled circle) and 1.45% (open circle), respectively. These results support the above pro-

TABLE I. Device performance of the inverted type solar cells with a ZnS layer treated by immersing in various solutions.

Immersing solution	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	$V_{oc}$ (V)	FF	$\eta$ (%)
No treatment	5.86	0.56	0.37	1.23
0.1M $\text{Zn}(\text{OAc})_2$ aq.	2.40	0.54	0.30	0.39
0.1M TAA aq.	5.89	0.55	0.42	1.37
0.1M $\text{Na}_2\text{S}$ aq. at pH 13.5	4.50	0.51	0.42	0.97
0.1M $\text{Na}_2\text{S}$ aq. at pH 9.0	5.97	0.55	0.46	1.52
0.1M $\text{Na}_2\text{S}$ aq. at pH 7.0	5.94	0.54	0.45	1.45

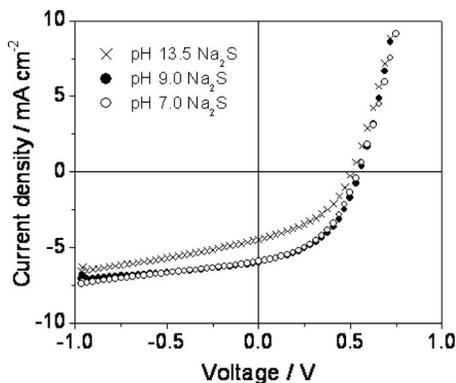


FIG. 4.  $I$ - $V$  curves of inverted type solar cells with ZnS layers treated by immersing in  $0.1M$  pH-adjusted  $Na_2S$  solutions under light irradiation. pH of the  $Na_2S$  solutions: pH 13.5 (not pH-adjusted, cross mark), pH 9.0 (filled circle), and pH 7.0 (open circle). Diluted  $H_2SO_4$  was added to adjust the pH of the solutions.

posal for the effect of the surface modification. The best performance of  $J_{sc}=6.44$  mA  $cm^{-2}$ ,  $V_{oc}=0.55$  V,  $FF=0.48$ , and  $\eta=1.70\%$  was obtained by depositing ZnS on FTO in  $0.05M$   $Zn(OAc)_2+0.2M$  at TAA  $80^\circ C$  for 120 h, by immersing the FTO/ZnS electrode in  $0.1M$   $Na_2S$  solution at pH 9, and by drying the surface-modified ZnS at  $200^\circ C$ . When the FTO/ZnS electrode was immersed in a  $HS^-$  ion-rich solution,  $OH^-$  ions adsorbed on the ZnS may be almost substituted by  $HS^-$  ions. After all, the electron transport from the acceptor PCBM to the electron collection ZnS layer became easily at the ZnS/PCBM:P3HT interface.

## B. ZnS/bulk-heterojunction interface characterized by alternating current impedance spectroscopy

Figure 5 shows the typical Nyquist plots of the ZnS cells treated by immersing in  $0.1M$   $Na_2S$  at pH 9 at zero bias. When the IS measurement of the ZnS cells in the dark and under light irradiation was carried out in the frequency range of 20 Hz–1 MHz, the Nyquist plots were analyzed using an equivalent circuit as shown in Scheme 1, showing reasonable concordance with a simulated curve. The  $R_s$  represents series

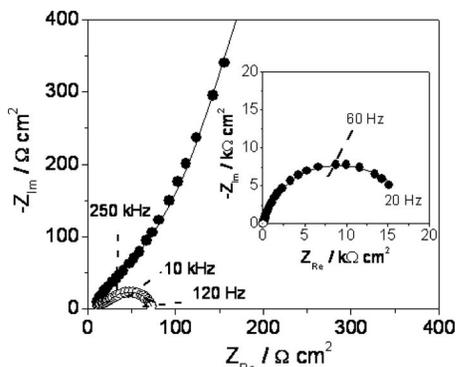
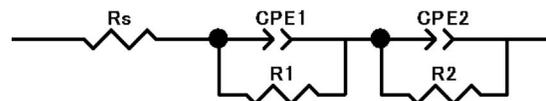


FIG. 5. Typical Nyquist plots for inverted type solar cells with ZnS layers treated by immersing in  $0.1M$   $Na_2S$  solution at pH 9.0. The plots of filled and open symbols were obtained for the cells at zero bias in the dark and under light irradiation, respectively. The solid lines indicate fitting curves calculated by the equivalent circuit shown in Scheme 1. The dashed lines indicate IS measurement frequency. The inset showed the full plots of filled symbols.



SCHEME 1. A typical equivalent circuit for Nyquist plot containing two semicircles.  $R_s$ , series resistance consisted of the Ohmic components;  $CPE1$  and  $CPE2$ , capacitances; and  $R1$  and  $R2$ , resistances.

resistance consisted of Ohmic components. The  $R1$  and  $R2$  are resistance components forming a parallel circuit with constant phase elements ( $CPE1$  and  $CPE2$ ). Further, the  $CPE1$  and  $CPE2$  are roughly equal to differential electric capacitances because there was almost no depression of semicircles. Two semicircles were observed at a higher frequency of more than 250 kHz and at a lower frequency of less than 250 Hz, being named semicircles 1 and 2, respectively. That is, the ac response of semicircle 2 in the low-frequency range was slower than that of another semicircle 1 in the high-frequency range. Figure 6 shows the dependence of the  $R$  and  $CPE$  values of the ZnS cells treated by immersing in  $0.1M$   $Na_2S$  at pH 9 on the applied dc voltage. In the dark, the  $R2$  estimated from semicircle 2 was much larger than the  $R1$  from semicircle 1; further  $R2$  became remarkably small by light irradiation. Hence, we concluded that the higher frequency semicircle 1 and the lower frequency semicircle 2 originated from ZnS as an  $n$ -type inorganic semiconductor and from PCBM:P3HT as an organic photoconductor and light absorber, respectively.

The  $R2$  in the dark increased rapidly when the applied dc voltage decreased from 0.5 to 0 V as shown in Fig. 6(b); at the same time, the  $CPE2$  also decreased suddenly by applying the dc voltage of less than 0.2 V. This increase in the  $R2$  was ascribed to the fact that the depletion layer with low carrier density was gradually formed at the ZnS/PCBM:P3HT interface by applying the dc voltage of less than 0.5 V. On the other hand, the slight decrease in  $R2$  was observed by applying the dc voltage of less than 0 V because of a leak current of the ZnS cell. Further, this decrease in the

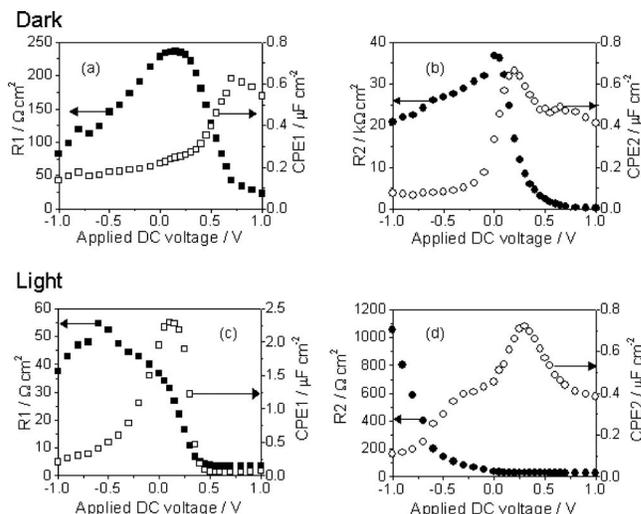


FIG. 6. Dependence of the  $R$  and  $CPE$  values of the ZnS cells treated by immersing in  $0.1M$   $Na_2S$  at pH 9 on the dc applied voltage in the dark [(a) and (b)] and under light irradiation [(c) and (d)]. Plots for higher frequency component: (a) and (c); plots for lower frequency component: (b) and (d).

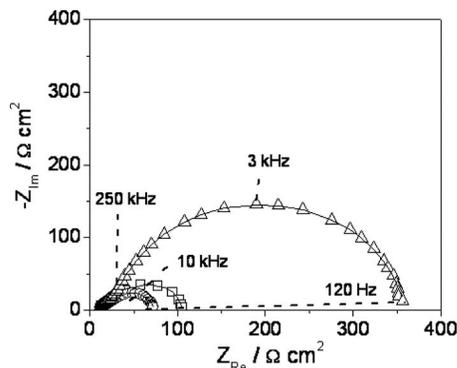


FIG. 7. Typical Nyquist plots for inverted type solar cells with ZnS layers treated by immersing in  $0.1M$   $Na_2S$  solution at  $pH$  9.0 (circles), no treatment (squares), and  $0.1M$   $Zn(OAc)_2$  solution (triangles). All plots were obtained for the cells at zero bias under light irradiation. The solid lines indicate fitting curves calculated by the equivalent circuit shown in Scheme 1. The dashed lines indicate IS measurement frequency.

*CPE2* was explained from a lowering of polarizability of the PCBM and P3HT molecules in the depletion layer, because an electric field generated in the depletion layer was allowed to polarize these organic molecules previously. On the other hand, the *CPE2* decreased slightly by applying the dc voltage of more than  $0.2$  V, probably because of a dielectric polarization of the organic molecules. The same explanation was possible for the dependence of the *R1* and *CPE1* corresponding to ZnS in the dark on the applied dc voltage as shown in Fig. 6(a).

However, since charge carriers were produced in the PCBM:P3HT and ZnS layers under light irradiation and as a result the electric-field profile of these depletion layers changed somewhat, the dependence of the *R1*, the *CPE1*, and the *CPE2* on the applied dc voltage shifted to slightly negative direction as shown in Figs. 6(c) and 6(d). On the other hand, the peak observed for the *R2*-dependence in the dark disappeared under irradiation; see Figs. 6(b) and 6(d), because the leak current of the ZnS cell was negligible compared to the photocurrent. Thus, it was proved from this IS measurement that the rectification interface was formed at the ZnS/PCBM:P3HT interface. This exhibits that the ZnS layer functions as the electrode to form an electric field for charge-separating photogenerated excitons in the PCBM:P3HT as well as the electron collection and hole blocking layers.

Figure 7 shows the typical Nyquist plots of the surface-modified ZnS cells at zero bias under light irradiation. It was estimated from Fig. 7 that the *R2* at zero bias for the cell with a ZnS layer immersed in  $0.1M$   $Na_2S$  solution at  $pH$  9 was  $40 \Omega cm^2$  under light irradiation, and the *R2* values for the cells with the nontreated ZnS layer and with the ZnS layer immersed in  $0.1M$   $Zn(OAc)_2$  solution were  $63$  and  $325 \Omega cm^2$ , respectively. On the other hand, the *R<sub>s</sub>* and *R1* values were nearly equal even when the ZnS layer is immersed in various solutions,  $R_s \approx 8 \Omega cm^2$  and  $R1 \approx 30 \Omega cm^2$ . This dependence of *R2* suggested that the charge transport resistance at the ZnS/PCBM:P3HT interface, maybe the resistance for transporting photoproduced electrons from the lowest unoccupied molecular orbital of acceptor PCBM to conduction band of ZnS, was observed in

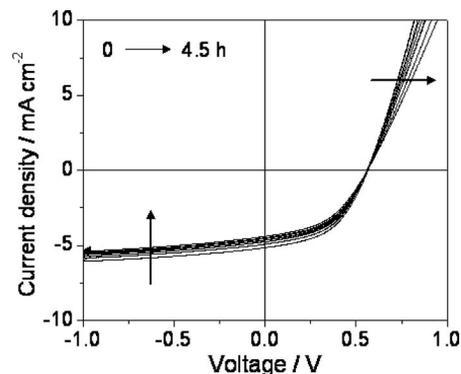


FIG. 8. Irradiation time dependence of the photo *I-V* curves for inverted type solar cells with ZnS layers treated by immersing in  $0.1M$   $Na_2S$  solution at  $pH$  9.0 in air under continuous irradiation of the simulated sunlight AM 1.5 G– $100 mW cm^{-2}$ .

the IS measurement at the lower frequency. That is, the charge transport became considerably easy by covering the ZnS surface with chemically adsorbed  $HS^-$  ions. This was the most important factor for improving the photovoltaic property of the ZnS cells.

Evaluating the durability of the solar cells in an ambient atmosphere was carried out by the *I-V* and IS measurements under continuous light irradiation. The *I-V* curves and the Nyquist plots of the ZnS cell treated by immersing in  $0.1M$   $Na_2S$  solution at  $pH$  9 against the elapse time of the light irradiation in air are shown in Figs. 8 and 9, respectively. The photo *I-V* curves exhibited a decrease by 20% of the maximum  $\eta$  and an increase in the series resistance at the forward bias under light irradiation for 4.5 h. Meanwhile, the Nyquist plots exhibited twice increase in the *R2* although the *R<sub>s</sub>* and *R1* were almost constant. Figure 10 shows the plots of  $\eta$ , *R1*, and *R2* at zero bias against irradiation time. The  $\eta$  decreased following the increase in the *R2*. We recently reported that the ITO/TiO<sub>x</sub>/PCBM:P3HT/PEDOT:PSS/Au type solar cells maintained the performance even under light irradiation for 20 h in an ambient atmosphere.<sup>12</sup> That is, the photodegradation of the PCBM:P3HT bulk is not responsible for increasing the *R2* of the ZnS cell or for lowering of the performance in this time scale. This suggests that the charge

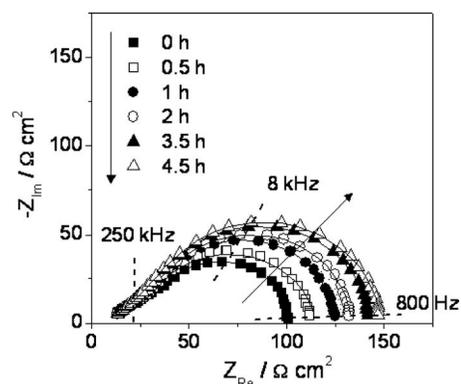


FIG. 9. Irradiation time dependence of the Nyquist plots for inverted type solar cells with ZnS layers treated by immersing in  $0.1M$   $Na_2S$  solution at  $pH$  9.0 in air under continuous irradiation. The measurement was carried out for the cells at zero bias. The dashed lines indicate IS measurement frequency.

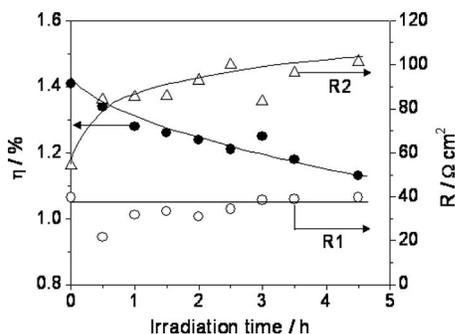


FIG. 10. Plots of the  $\eta$  and the resistance components  $R_1$  and  $R_2$  against the irradiation time.

transport between the ZnS and PCBM:P3HT layers became gradually difficult with light irradiation perhaps because of a photocatalytic effect.

#### IV. CONCLUSION

The present work was focused on the photoelectric properties of the inverted type organic thin-film solar cells with ZnS as an electron collection layer. The characteristics were evaluated by photo  $I$ - $V$  curves as well as photo IS plots. The performance ( $\eta=1.70\%$ ) of the cell with the ZnS layer treated by immersing in the  $\text{Na}_2\text{S}$  solution at pH 9 was improved at least by 30% compared to that ( $\eta=1.23\%$ ) with a nontreated ZnS layer. This suggested that adsorbed  $\text{OH}^-$  ions on the ZnS surface were substituted by  $\text{HS}^-$  ions, introducing to a superior interface for charge transport at the ZnS/PCBM:P3HT interface. The IS measurements of the organic thin-film solar cells with a ZnS layer in the dark and under light irradiation were carried out in air, the Nyquist plots consisting of two components. According to this result, it was proved that the rectification interface was formed at the ZnS/PCBM:P3HT interface, and further the  $R_2$  estimated from the slower ac response was ascribed to the charge transport resistance at the ZnS/PCBM:P3HT interface. A decrease in the  $\eta$  was observed with an increase in the  $R_2$  resistance under continuous light irradiation, indicating that the performance degradation was caused mainly by the lowering of the charge transport velocity at the ZnS/PCBM:P3HT interface. In this way, photoelectric properties of the organic thin-film solar cells were analyzed more apparently by introducing the photo IS measurement. Applying the IS method to under-

stand the properties of organic thin-film solar cells in detail will give highly useful insights toward the performance improvements; however, we have not used this excellent method completely yet. We are under investigating extensively on organic solar cells using other  $n$ -type semiconductors to develop high performance and long lifetime device toward the practical use.

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