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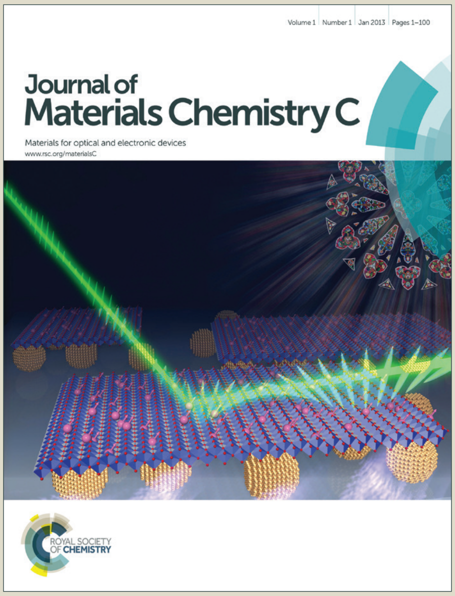

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ARTICLE

Enhancing the Efficiency of the Opto-electronic Devices by the Cathode Modification

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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A non-conjugated polymer with polar hydroxyl group as a side group, poly(vinyl alcohol) (PVA), is applied to polymer solar cells (PSCs) and polymer light-emitting diodes (PLEDs) as a buffer layer at the active layer/cathode interface. The best power conversion efficiency (PCE) of PSC with the PVA film as a cathode buffer layer exhibits 3.27%, which is a 27% increase compared to that of PSC without the PVA film (2.58%). The PCE improvement is due to enhancement of the short circuit current, the fill factor, and the open circuit voltage, simultaneously. Also, the performances of polymer light-emitting diode with the PVA film as a cathode buffer layer are improved than those of the device without PVA. Improvement of the performances of the devices is due to that the PVA film reduces a Schottky barrier by the formation of favorable interface dipoles and improves the interface properties.

Introduction

The opto-electronic devices such as solar cells and light-emitting diodes based on π-conjugated polymers have been receiving attention in the past decades.[1-4] The charge transporting and injecting/collecting properties are crucial factors for improving the performances of the devices. Among them, the charge injecting/collecting properties are related to the interfacial properties between the semiconducting layer and the cathode or the anode.[5] Insertion of an interfacial (or a buffer) layer at the interfaces was used to optimize the properties between the semiconducting layer and the both electrodes. A thin layer of PEDOT:PSS,[6] thermally curable triarylamine derivatives,[7-12] self-assembled monolayers (SAMs) modification,[13-15] or metal oxides such as WO_3[16,17] and MoO_3[18-20] were mainly used for improving the hole injecting/collecting properties between the semiconducting layer and the anode to achieve highly efficient devices. Water or alcohol soluble conjugated polymer electrolytes (CPEs) such as cationic[21-24] π-conjugated polymer electrolytes (cCPEs), anionic[25-26] π-conjugated polymer electrolytes (aCPEs), and alcohol-soluble neutral conjugated polymers (NCPs)[27-29] have been mainly applied to solution processible cathode interface layer for opto-electronic devices. Solution processible n-type metal oxides such as TiO_x[33] and ZnO[34] have been used as solution processible cathode interface layer to improve the electron injecting/collecting properties of the opto-electronic devices. The photovoltaic parameters of the devices such as the open circuit voltage (V_{oc}), the short circuit current (J_{sc}), and the fill factor (FF) with these materials as an interface layer (IFL) at the active layer/metal cathode interface were dramatically improved by the formation of favorable interface dipole and the reduction of contact resistance. Recently, non-conjugated cationic and anionic polymer electrolyte such as dialkylviologen (PVs)[32], zwitterionic conjugated polymer electrolytes and non-conjugated small-molecule elecrolytes[33] and non-conjugated anionic poly(sodium 4-styrenesulfonate) (PSS-Na),[34(a)] also have been demonstrated for a cathode interface layer to improve the performances of the opto-electronic devices. Non-conjugated polymer with high dielectric constant such as poly(ethylene oxide) (PEO)[34(b)] and poly(4-vinyl pyrrolidone) (PVP)[34(c)] also have been used for a cathode interface layer. Even though the polymers consist of non-conjugated back bone, these polymers can be used as electron transporting and injecting/collecting layer for PSCs. These reduce a Schottky barrier at the interfaces leading to improvement of the J_{sc} and the FF. In addition, enhancement of the V_{oc} of the devices was explained in terms of the formation of interface dipole between the active layer and the cathode.

Poly(vinyl alcohol) (PVA) is well known water soluble non-conjugated polymer with polar hydroxyl (-OH) group, which is widely used as a binder for light-emitting electrochemical cells and solar cells based on small molecule because of their excellent film forming and adhesive properties.[35] Like CPEs, complicated synthetic procedures are not necessary at all. Also, this has the advantage of being very cheap prices. As depicted in Fig. 1, like the other materials such as conjugated or non-conjugated polymer electrolytes, PVA also might be used as a cathode buffer layer in polymer solar cells (PSCs) and polymer light-emitting diodes (PLEDs). Because the hydrophobic semiconducting layer surface will push away the hydrophilic hydroxyl side groups from a surface of the semiconducting layer. Consequently, the interface dipoles will be generated at the interface between the active layer and the cathode by the permanent dipole moment of hydroxyl groups. To the best of our knowledge, PSCs and PLEDs with the PVA film as a cathode buffer layer has never been tested and reported before. In this paper, we report and demonstrate the application of PVA as an IFL in PSCs (and PLEDs) in terms of the formation of interface dipoles and wetting property on the active layer.

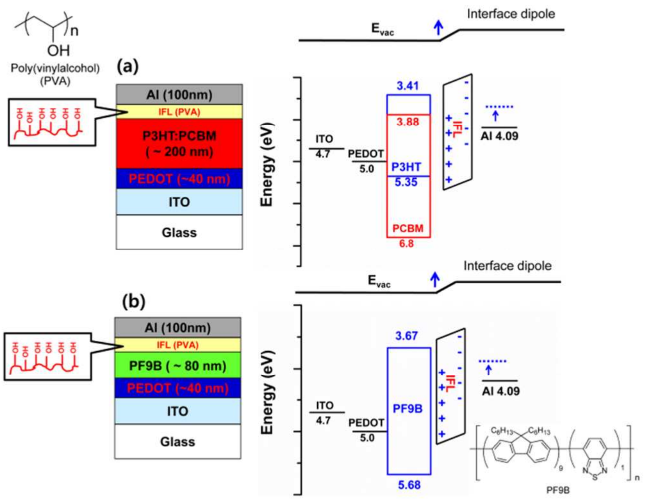

Fig. 1. The device structures and the chemical structures of materials used in the device fabrications. The proposed work function reduction scheme by the formation of favorable interface dipole between the organic layer and the cathode, (a) PSC and (b) PLED.

Experimental

Materials

Chemicals were purchased from Aldrich Chemical Co. and Alfa Aesar and were used as received unless otherwise described. PVA (99+% hydrolyzed, Cat. No. 41243, Mw = 88000-97000 g/mol) was purchased from Aldrich. Regioregular P3HT (Cat. No. 4002-EE) and PCBM (Cat No. nano-cPCBM-BF) were purchased from Rieke Metals Inc. and nano-C, Inc., respectively. A PF9B was used as an emissive layer (EML) and synthesized according to the literature procedures.[36]

Measurements

The work function measurements were carried out using a UPS (VG Scientific Co.) with a He I source (hν= 21.2 eV) at a pressure of 1 x 10^{-8} Torr. A -3 V was applied to a sample during the measurements to distinguish between the analyzer and sample cut-off. The thickness of film was measured by Alpha-Step IQ surface profiler (KLA-Tencor Co.). As for the PVA film, we measured the thickness of the PVA film on silicon wafers by using an ellipsometry (J. A. Woollam Co., Inc., M-2000D).[21(a)] The PVA films were prepared under the same spin-coating condition as in the device fabrications. Atomic force microscope (AFM) images were taken on a Digital Instruments (Multi ModeTM SPM). AFM images were obtained by the tapping mode and a scan rate of 2 Hz. The surface energy (γ) of the layer with and without the PVA thin film was evaluated by the measurements of the static advancing contact angle with deionized water and diiodomethane (CH_2I_2). The contact angles (KRUSS, Model DSA 100) were entered in the Wu model (harmonic mean) for the calculation of the dispersive and polar components of the surface energy[37] The J–V measurements under 1.0 sun (100 mW/cm^2) condition from a 150 W Xe lamp with an AM 1.5G filter were performed using a KEITHLEY Model 2400 source-measure unit. A calibrated Si reference cell with a KG5 filter certified by National Institute of Advanced Industrial Science and Technology was used to confirm 1.0 sun condition.

Fabrication of PSCs and PLEDs

For fabrication of PSCs with a structure of ITO/PEDOT/active layer (P3HT:PCBM)/PVA/Al, a thickness of 40 nm of PEDOT:PSS (Baytron P, diluted with 2-propanol 1:2 by volume) was spin-coated on pre-cleaned indium tin oxide (ITO) glass substrate (sheet resistance = 15 ohm/sq). After being baked at 150 ^{o}C for 10 min under the air, the active layer was spin-cast from the blend solution of P3HT and PCBM (20 mg of P3HT and 20 mg of PCBM dissolve in 1 mL of o-dichlorobenzene (ODCB)) at 600 rpm for 40 s and then dried in covered petri dish for 1 hour. Prior to spin coating, the active layer solution was filtered through a 0.45 μm membrane filter. The typical thickness of the active layer was 200 nm. An IFL prepared by spin coating with a solution of PVA at 4000 rpm for 60 s. The thickness of PVA layer was controlled by the concentration of PVA solution. The Al layer was deposited with a thickness of 100 nm through a shadow mask with a device area of 0.13 cm^2 at 2 × 10^{-6} Torr. After the cathode deposition, the device was thermally annealed at 150 ^{o}C for 20 min in the glove box (N_2 atmosphere). For fabrication of PLEDs with a structure of ITO/PEDOT/emissive layer (PF9B)/PVA/Al, the deposition of a PEDOT:PSS layer is same as the fabrication of PSCs. After being baked at 150 ^{o}C for 10 min under the air of a PEDOT:PSS layer, an emissive polymer solution (15 mg/mL in Toluene) was spin coated on to PEDOT:PSS layer at 2000 rpm for 60 s. Prior to spin coating, the emissive polymer solution was filtered through a 0.45 μm membrane filter. The deposition procedures of the IFL and the cathode were same as the fabrication of PSCs. The typical thickness of the emissive layer was 80 nm.

Results and discussion

Fig. 2 shows current density - voltage curves of devices with and without the PVA film as a cathode buffer layer. The PCE (power conversion efficiency) of the devices with the PVA film spun-coated from the solution in aqueous alcoholic solvent (water:methanol = 2:8 by volume, 20 vol.% of water is minimum amount for dissolving PVA) were 2.67 - 2.70% (See Fig. S1 and Table S1, Supplementary information). The PCEs of the devices were slightly higher than the device without PVA (reference device, PCE = 2.58%). Also, the V_{oc} and FF of the devices with PVA were almost the same as the data of reference device. One possible reason is the poor wetting property of PVA on the active layer. It is known that the amount of water in the solvent for buffer layer is a critical factor for affecting the film quality or the wetting property on the active layer and should be less than 20 vol.%.[32] In order to get highly efficient devices, it is necessary to optimize the processing solvent for PVA coating. As shown in Fig. 2 and Table 1, the devices with the PVA film deposited from the solution in dimethysulfoxide (DMSO)/methanol mixed solvent (DMSO:methanol = 5:95 by volume, found to be optimum solvent composition for deposition of the PVA film on the active layer surface) showed better performances than those of the reference device. In addition, we varied the PVA film thickness to optimize the device performances by varying the concentration of PVA solutions. We refer to the fabricated device with spin-coated the PVA film from the concentration of 0.2 mg/mL, 0.5 mg/mL, and 1.0 mg/mL as PVA0.1, PVA0.5, and PVA1.0, respectively. We could not measure the thickness of the PVA film directly on the active layer by using a thickness monitor (Alpha-Step IQ surface profiler) or an AFM due to the surface roughness of the active layer (Fig. 4) is very similar to the thickness of the PVA film. Thus, we estimated the thickness of the PVA layer by using an ellipsometry. The thickness of PVA film prepared from the concentration of 0.2 mg/mL, 0.5 mg/mL, and 1.0 mg/mL on Si wafer were 1.76 ± 0.06, 2.22 ± 0.03, and 4.16 ± 0.04 nm, respectively. Even though the surface property (i.e. energy) of the active layer is different from that of Si wafer, the thickness of the PVA film on the active layer would be similar to that on Si wafer.[21(a)]

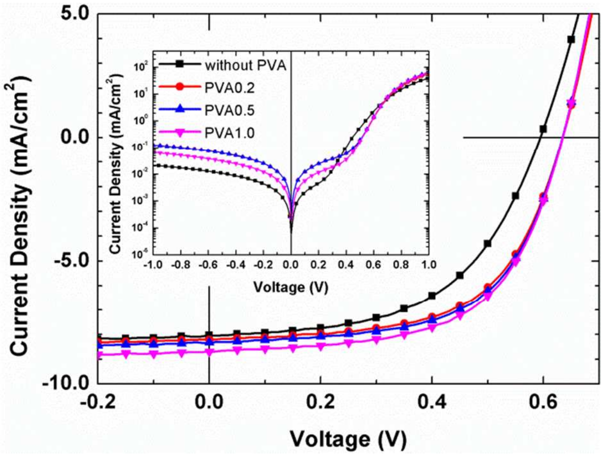

Fig. 2. Current density–voltage curves of PSCs under AM 1.5G simulated illumination with an intensity of 100mW/cm^2 and under the dark condition (inset) without PVA (square) with the PVA film prepared from a concentration of 0.2 mg/mL (circle: PVA0.2), 0.5 mg/mL solution (triangle: PVA0.5), and 1.0 mg/mL solution (inverted triangle,: PVA1.0) in DMSO/methanol mixed solvent.

The PCE of the device with PVA1.0 showed the highest PCE of 3.27%, which is a 27**%** increase compared to that of the device without IFL. The increase in the device efficiency resulted from the 8% enhancement in the short circuit current (J_{sc}) and the 11% improvement in the fill factor (FF), respectively. For the devices with PVA0.2 and PVA0.5, the PCE were 3.10 and 3.17%, respectively, which is a 20% and a 23% of PCE increases, respectively, compared to those of the device without PVA. The performances of PSCs were dependent on the thickness of PVA film. The devices with a PVA1.0 showed a V_{oc} of 0.63 V, a J_{sc} of -8.70 mA/cm^2, and a FF of 59.7%, respectively, which were significantly higher than those of the device without the PVA film. The J_{sc} and FF of the devices with PVA were in the range from -8.21 to -8.70 mA/cm^2 and from 59.9 to 60.4%, respectively, which are higher than those of the device without IFL (J_{sc} = -8.04 mA/cm^2, FF = 54.0%). Also, the V_{oc} values of the devices were higher than that of the V_{oc} of the reference device.

Table 1. The photovoltaic parameters of PSCs with the best PCE value. The averages and mean deviation of the parameters are given in the parentheses.

	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	R_s (Ωcm^2)^a	R_p (kΩcm^2)^b
without PVA	0.59 (0.59 ± 0.01)	-8.04 (-7.89 ± 0.19)	54.0 (54.7 ± 0.9)	2.58 (2.55 ± 0.03)	5.34	46.5
PVA0.2	0.63 (0.63 ± 0.01)	-8.21 (-8.04 ± 0.15)	59.9 (59.4 ± 0.6)	3.10 (3.03 ± 0.03)	2.78	7.84
PVA0.5	0.63 (0.62 ± 0.01)	-8.33 (-8.12 ± 0.18)	60.4 (59.4 ± 0.1)	3.17 (3.11 ± 0.04)	2.46	7.97
PVA1.0	0.63 (0.62 ± 0.01)	-8.70 (-8.36 ± 0.24)	59.7 (59.3 ± 0.9)	3.27 (3.17 ± 0.05)	2.72	15.3

The [a] series and [b] parallel resistance (estimated from the device with the best PCE value).

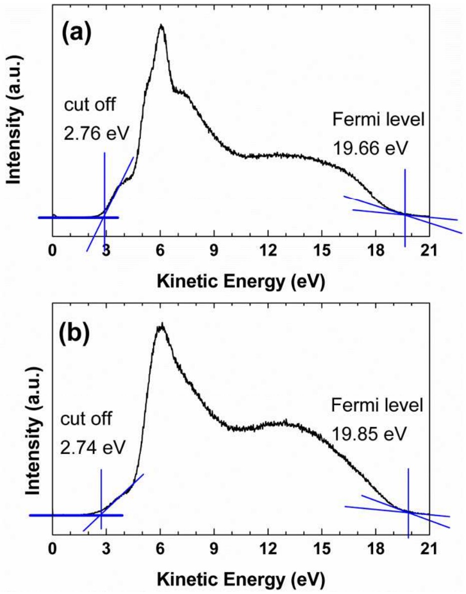

Fig. 3. UPS spectra of (a) Al and (b) PVA coated Al. The work function (eV) was calculated by: 21.2 - ($E_{Fermi\ level}$ - $E_{cut\ off}$).

Generally, a large Schottky barrier inhibits the facile injection/collection of electron at the organic(or polymer) semiconductor/Al interface. Thus, Ohmic contact by the reduction of a Schottky barrier at the interfaces are required to obtain high J_{sc}.[38,39] Therefore, the more efficient injecting/collecting of electrons are expected in the device with the PVA thin film as a cathode buffer layer. Enhancement of the J_{sc} can be achieved by introducing the PVA film leading to the reduction of a Schottky barrier, which is due to the formation of interface dipoles at the cathode interface. We performed the ultraviolet photoelectron spectroscopy (UPS) to confirm that the reduction of the work function and a Schottky barrier at the interface. As shown in Fig. 3, the work function was calculated from the Fermi level and the secondary cut-off energy in the UPS spectrum. The work function of Al and PVA coated Al figured out from the UPS spectra were 4.30 and 4.09 eV, respectively. The reduction of a Schottky barrier is 0.21 eV, which is very comparable to the case of PEO, PSS-Na, PVP, CPEs, NCPs, and PVs. The V_{oc} value of the devices with the PVA film prepared from the mixed solvent having DMSO were 0.63 V, which is higher than that of the device without PVA (0.59 V) and very comparable to the data of the device with CPE as a cathode buffer layer. However, the V_{oc} values of the device with the PVA film prepared form the solution in water/methanol mixed solvent were the same as the device without PVA (See Fig. S1 and Table S1, Supplementary information). This is also possibly due to that the quality of the PVA film prepared from the mixed solvent having water is poor. Current density - voltage curve under the dark condition (inset of Fig. 2) provides information about the series resistance (R_s) and the parallel resistance (R_p), which were calculated from the inverse slope near high current regime and slope near lower current region in the dark J–V curves, respectively.[41] The devices with the PVA film showed smaller R_s values than that of the device without PVA. Interestingly, the R_p values of the devices with PVA were smaller than that of the reference device, while both the J_{sc} and the FF are increased. Regardless of smaller R_p values were observed in the device with PVA, the devices with PVA exhibited better both the J_{sc} and the FF than those of the device without PVA.

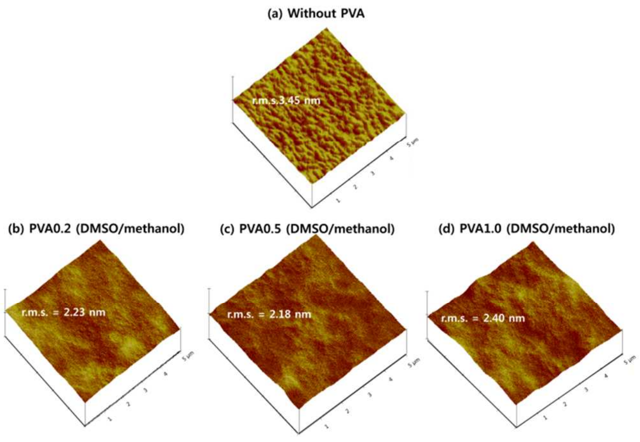

Fig. 4. AFM topographies of the active layer (a) without PVA, (b) - (d) with the PVA film spin-coated from the DMSO/methanol mixed solvent (x, y = 1 μm/division, z =100 nm/division).

The surface morphology of the active layer (Fig. 4) with the PVA film showed quite different features with that of the active layer without the PVA film. This is due to that the PVA film covers the roughness of the active layer surface. As shown in Fig. 4 (b) - (d), the r.m.s. surface roughness of the active layer with the PVA were 2.23, 2.18, and 2.40 nm, respectively, which were smaller than that of the active layer without PVA (Fig. 4 (a), 3.45 nm). The surface roughness of the PVA coated active layer were smoother than that of the active layer without the PVA film, indicating that the PVA film can form uniformly on the active layer. The r.m.s. surface roughness of the active layer reflects the quality of the PVA film deposited from the solution in methanol/water is poor (See Fig. S2, Supplementary information). We measured the surface energy of the active layer with and without the PVA layer to investigate the change of the property of the active layer surface. The surface energy (See Fig. S3 and Table S3, Supplementary information) of the active layer with PVA0.2, PVA0.5, an PVA1.0 prepared from the solution in DMSO/methanol solvent were 27.2, 26.8, and 26.8 mN/m, respectively, which were higher than that of the active layer without PVA (23.6 mN/m). The surface energy (Fig. S2 and Table S2, Supplementary information) of the active layer with the PVA film prepared by using a mixed solvent containing 20 vol.% of water was 24.0 mN/m, which was almost the same as the surface energy of the active layer without the PVA film (23.6 mN/m), indicating that the surface property was not much changed by poor quality of the PVA film. The surface morphology and energy data indicate that the performances of the device depend on the quality of the PVA film. The processing solvent is also very important parameter for affecting the efficiency of the devices.

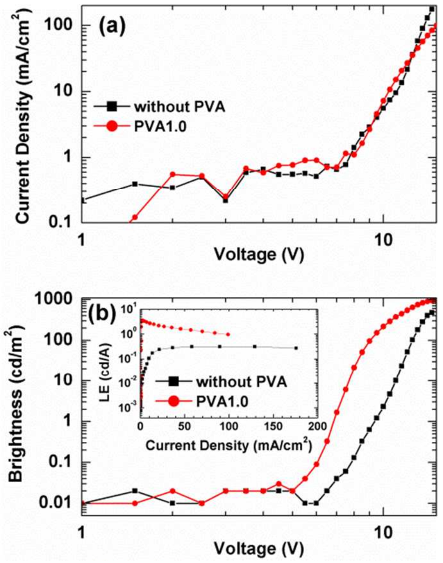

Fig. 5. (a) Current density-voltage and (b) brightness-voltage curves (square: without PVA, circle: with PVA coated from the solution of 1.0 mg/mL in DMSO/methanol mixed solvent, inset: luminance efficiency (LE) -current density curves).

We also fabricated the PLED with PVA1.0 at the cathode interface to investigate the effect of the PVA film on the device.

As shown Fig. 5 (a), the devices showed the typical diode characteristics. The device without the PVA film (ITO/PEDOT/PF9B/Al) showed a turn on voltage of light (V_{on}, defined as the literature procedure[40]) of 6.5 V, a maximum luminance efficiency (LE_{max}) of 0.316 cd/A at 89.7 mA/cm^2, and a maximum brightness (B_{max}) of 476 cd/m^2, respectively. Contrarily, the device with PVA1.0 exhibited a V_{on} of light of 5.0 V, a LE_{max} of 3.612 cd/A at 2.68 mA/cm^2, and a B_{max} of 961 cd/m^2, respectively, which are improved than those of the device without IFL. PLEDs in this research seem to need to be optimized further because of lower performances than previously reported data.[36] However, one can easily noticed that the performances of PLED with the PVA film were improved than those of the device without IFL.

Conclusions

A non-conjugated polymer with polar hydroxyl group, PVA, has been demonstrated as a cathode buffer layer for PSC to modify the contact property at the semiconducting layer/Al interface. The performances of PSCs were dependent on the thickness of the PVA film and the processing solvent. The increase in the PCE resulted from enhancement of the J_{sc}, the FF, and the V_{oc}, simultaneously. The surface roughness of the active layer with the PVA film was smaller than that of the active layer without the PVA film and the surface energy of the active layer with the PVA film was higher than that of the active layer without PVA, indicating that the hydrophilic PVA layer is well coated on the surface of the active layer. The results support that enhancement of the J_{sc} and FF are related with the contact property and the surface morphology as well as the surface energy at the interface. Also, a Schottky barrier between the semiconducting layer and the Al cathode was reduced by the formation of favorable interface dipole by insertion of the PVA film. As a result, the performance of the opto-electronic devices with the PVA film as a cathode buffer layer was improved than that of the devices without the PVA film. This research provides a very simple, facile, and cheap strategy for the enhancement of efficiency of the opto-electronic devices.

Acknowledgements

This research was supported by Converging Research Center Program through the Ministry of Education, Science and Technology (2013K000196) and Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2013020225).

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Electronic Supplementary Information (ESI) available: [The photovoltaic properties of the device with PVA film deposited from the solution in aqueous alcoholic solvent and the surface energy data are available in supplementary information]. See DOI: 10.1039/b000000x/

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