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# Development of Inverted Organic Photovoltaics with Anion doped ZnO as an Electron Transporting Layer

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## Abstract

In this study, 3-dimensional ripple structured anion (chlorine) doped ZnO thin film are developed, and used as electron transporting layer (ETL) in inverted organic photovoltaics (I-OPVs). Optical and electrical characteristics of ZnO:Cl ETL are investigated depending on the chlorine doping ratio and optimized for high efficient I-OPV. It is found that optimized chlorine doping on ZnO ETL enhances the ability of charge transport by modifying the band edge position and carrier mobility without decreasing the optical transmittance in the visible region, results in improvement of power conversion efficiency of I-OPV. The highest performance of 8.79 % is achieved for I-OPV with ZnO:Cl-x ( $x=0.5\text{wt}\%$ ), enhanced  $\sim 10\%$  compared to that of ZnO:Cl-x ( $x=0\text{wt}\%$ ).

*Keywords* : Chlorine, ZnO ripple, Organic photovoltaics, Electron transporting layer, Doping, Sol-gel

## 1. Introduction

Using of solar light as unlimited energy resource has been attracted increasing interest, especially, solar cells that convert solar energy into electrical energy [1]. The inverted organic photovoltaics (I-OPVs) are using organic polymer materials as photoactive layer, which are cost-effective, portable, and applicable to the flexible substrates [2-8]. Generally, in I-OPVs, n-type materials such as zinc oxide (ZnO) [9,30,31], titanium dioxide (TiO<sub>2</sub>) [10,30], and cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>) [11,12] have been widely used as hole blocking layer (HBL) [1,13] and electron transporting layer (ETL) [4,9-14]. Among them, ZnO is an

intrinsic n-type semiconductor, which has high optical transparency, wide band gap energy (3.2 eV), large exciton binding energy (60 meV), high electron mobility, and conductivity. And it has been widely used as optoelectronic device, chemical sensor, and photovoltaic application. For improving the conductivity and mobility of ZnO thin film, n-type doping process with group III metallic cation elements such as Al [15,17,20,24], Ga [16,20], and In [17,20] is widely used and that substitute the zinc atoms in ZnO lattice [20,24]. Furthermore, it is also well known that group VII non-metallic anion elements doping such as F [18,29], Cl [19-29], Br [29], and I [29] can also improve the conductivity and mobility. These anion elements can substitute the oxygen atoms in ZnO lattice [20,24,28]. Generally, the oxygen atoms as vacancies can act as an electron-hole recombination sites in I-OPVs [10,30,31], and results in decrease the performance of I-OPV. Among the various methods to reducing the recombination sites of ZnO ETL, anion doping can be one of the ideal concepts, because the ionic radius of group VII anion is almost similar to the oxygen atom as well as their

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excess electrons can help to achieving the high mobility [23,26] and conductivity [21,24,26] while maintaining high optical transparency [20,21,23,27], compared to group III cation metallic elements. Above all, anion element doping into ZnO ETL has been conducted by various deposition techniques such as electrochemical deposition [19,21,22,24,25], atomic layer deposition [26], radio frequency-magnetron sputtering [29], metalorganic chemical vapor deposition (MOCVD) [20,28], and pulsed laser deposition [23,27]. However, these previously used deposition techniques need complicated fabrication process, vacuum system, high price, and difficult to install. Compared to, the fabrication of ZnO thin film using sol-gel method has several advantages. It is cost-effective non-vacuum process, and stable in room temperature. Moreover, it is more easy to control the doping concentration, and solution volume. In this work, chlorine doped ZnO ETL are fabricated using sol-gel method with various chlorine doping ratio. Especially, chlorine-doped ZnO ETL thin film has 3-dimensional ripple structure and firstly applied in inverted organic photovoltaics as an ETL. The ripple structured chlorine-doped ZnO ETL has several advantages: high optical transparency in visible region without affecting the change of nano-morphology of active layer, high electrical conductivity as well as these properties can be adjusted by changing the chlorine doping ratio. We systematically demonstrate the role of chlorine-doped ZnO ETL on the performance of I-OPVs depending on the chlorine doping ratio.

## 2. Experimental

### 2.1 Fabrication for Chlorine-doped zinc sol-gel

Zinc sol-gel solution of 0.5 M was prepared using zinc acetate dihydrate (1.09 g, JUNSEI), 2-methoxyethanol (10 ml, Sigma Aldrich), and ethanolamine (500  $\mu$ l, Sigma Aldrich) as stabilizer. Zinc acetate was dissolved in 2-methoxyethanol solvent containing ethanolamine. It was stirred at 60°C for 2 hours on hot plate. And, ammonium chloride (SAMCHUN) was dissolved in 0.5 M zinc solution and stirred at 60°C for 1 hour. Finally, chlorine-doped zinc sol-gel solution was filtered using 0.20  $\mu$ m PTFE filter.

### 2.2 OPV device fabrication

Patterned indium tin oxide (ITO) glasses (AMG tech, 4.5  $\Omega$ /sq, and 25 mm  $\times$  25 mm) were cleaned

by using isopropyl alcohol and acetone for 20 minutes each steps. And the substrates were dried in oven (100°C) for 30 minutes. 0.5 M zinc sol-gel solution (pristine, chlorine-doped zinc sol-gel (0.25 wt%, 0.5 wt%, 1.0 wt%, and 2.0 wt%)) was spin-coated on ITO-coated substrates that had been pre-treated with UV-Ozone clean for 60 minutes. After coating, the substrates were dried in room-temperature to 180°C on a hot plate. The prepared doped ZnO electron transporting layer (ETL) in this work are denoted as ZnO:Cl-x (x = 0.25, 0.5, 1.0, 2.0) depending on the doping concentration.

To prepare the active layer, PTB7 and PC<sub>70</sub>BM used as donor and acceptor were mixed with a weight ratio of 1 : 1.5 in chlorobenzene/1,8-diiodooctane (CB/DIO; 970  $\mu$ l : 30  $\mu$ l, Sigma Aldrich). This solution was stirred at 60°C for 24 hours. Continually, the active layer was coated on ZnO ETL by spin-coating method at 1000 rpm for 40 seconds in Argon atmosphere glove box. After drying for 30 minutes in glove box, PEDOT:PSS (Clevios PVP AI4083, Heraeus) as hole transporting layer was diluted in isopropyl alcohol (1 : 10 v/v ratio). Diluted PEDOT : PSS was spin-coated onto the active layer at 5000 rpm for 40 seconds and dried in glove box for 30 minutes. Finally, the Ag electrode (100 nm) was thermally evaporated on the top of the device under  $3 \times 10^{-6}$  Torr. The active area of the device with the shadow metal mask was 0.38 cm<sup>2</sup>. The device architecture of inverted organic photovoltaic (I-OPV) was illustrated in Fig. 1(d).

### 2.3 Device characterization

The current density-voltage (J-V) curves were measured using a Keithley source and solar simulator (MODUSYS, PS-KS2C). The inverted organic photovoltaics (I-OPVs) were measured under AM 1.5G condition simulated with 100 mW/cm<sup>2</sup> intensity. The photoluminescence (PL) spectra were obtained using a Raman/PL spectrometer (LabRam-HR, Horiba Jobin Yvon SAS) excited by 325 nm He-Cd laser for PL. The optical transmittance spectra were obtained with an ultraviolet-visible (UV) spectrometer (Varian Australia Pty., LTD, Cary 5000). The hall mobility of ZnO ETL and chlorine doped ZnO ETL was obtained from Hall Effect measure system (MODUSYS). The work function of ZnO ETL and chlorine-doped ZnO ETL were obtained from using ultraviolet photoelectron spectroscopy (Thermo Scientific, Multilab-2000) with monochromatic He I ( $h\nu = 21.22$  eV) for UPS.

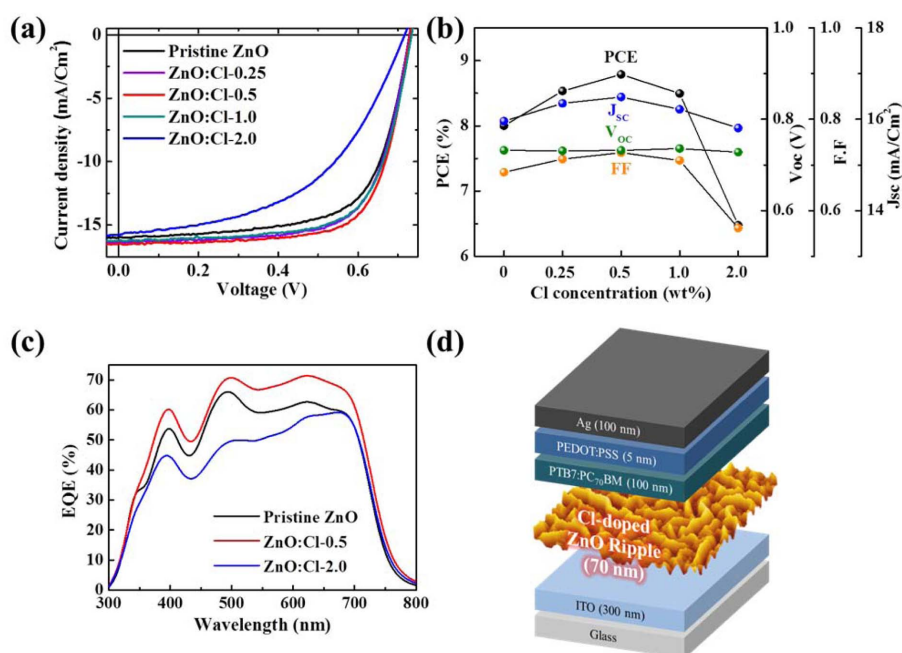


Fig. 1. (a) J-V curves, (b) characteristics, and (c) external quantum efficiencies of I-OPVs with ZnO and ZnO:Cl ETLs. (d) Schematic of an inverted organic photovoltaic structure.

### 3. Results and Discussion

The J-V characteristics of the inverted organic photovoltaics (I-OPVs) including pristine and anion (chlorine) doped ZnO electron transporting layer (ETL) are shown in Fig. 1(a) depending on the doping concentration of chlorine. Device descriptions for all configurations are summarized in Table 1. OPV with pristine ZnO ETL shows the power conversion efficiency (PCE) of 8.002% based on fill factor (FF) of 0.684, an open circuit voltage ( $V_{oc}$ ) of 0.732 V and a short circuit current density ( $J_{sc}$ ) of 15.960 mA/cm<sup>2</sup>. The power conversion efficiencies of I-OPVs with ZnO:Cl-x (x = 0.25, and 0.5) are improved more than ~5% and ~10%, respectively, with respect to the pure ZnO ETL. The improvements are originated from the increasing FF and  $J_{sc}$  values (Fig. 1(b)). Regarding the FF and  $J_{sc}$ , I-OPVs with ZnO:Cl-1.0 ETL resulted in a slightly decrease values of about ~0.5% with respect to the ZnO:Cl-

0.5 ETL which shows the highest device performance. However, as shown in Fig. 1 and Table 1, with increasing the chlorine doping concentration to 2.0 wt%, the device performance, PCE, FF, and  $J_{sc}$  dramatically decrease up to 14%, 13%, and 10%, respectively. It is worth mentioning that the  $V_{oc}$  is almost identical for all devices which means the prepared bulk hetero-junction photoactive layer are very stable and the used ZnO ETL in this work do not affect the field effect of the device. The variation of device performance depending on the doping concentration can be expected due to the change of morphology, transmittance and electrical property of ZnO ETL. However, geometrical effect of ZnO ETL for the deviation of solar cell performance can be excluded. The prepared pristine- and doped- ZnO ETL in Fig. 2(b) show 3-dimensional structure of around 70 nm in thickness, and furthermore peak to peak height and density do not be changed by anion doping. Figure 1(c) shows the external quantum

Table 1. The device characteristics of chlorine doped ZnO ETL based IOPVs with different concentrations.

Concentration	PCE (%)	FF	$V_{oc}$ (V)	$J_{sc}$ (mA/Cm <sup>2</sup> )
Pristine ZnO	8.002	0.684	0.732	15.960
ZnO:Cl-0.25	8.534	0.713	0.731	16.350
ZnO:Cl-0.5	8.789	0.727	0.732	16.490
ZnO:Cl-1.0	8.497	0.710	0.736	16.220
ZnO:Cl-2.0	6.477	0.562	0.728	15.810

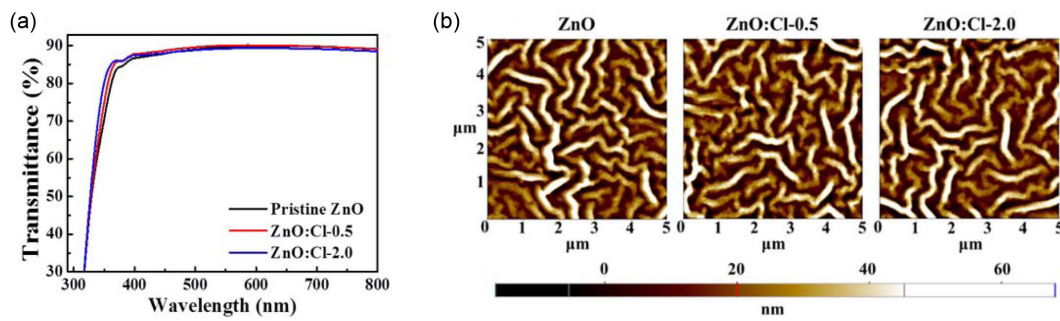


Fig. 2. (a) UV-Vis transmittance spectra, and (b) AFM images of ripple structured ZnO:Cl- $x$  ( $x = 0, 0.5, 2.0$ ) ETLs.

efficiency (EQE) spectra for the I-OPVs with ZnO:Cl- $x$  ( $x = 0, 0.5, 2.0$ ) ETL. The EQE spectra of I-OPVs with ZnO:Cl-0.5 ETL was drastically higher than that of pristine ZnO. However, when the highly doped ZnO ETL, ZnO:Cl-2.0, the value of EQE spectra decreased at 350 nm ~ 700 nm. The value of  $J_{sc}$  difference between the devices with ZnO:Cl- $x$  ETL is consistent with the value originated from the EQE spectra.

In order to figure out the optical influence on performance of I-OPV, optical transmittance spectra of ZnO ETLs with various doping ratio was obtained in Fig. 2(a), which was deposited on pure soda-lime glass. As before mentioned the ripple structured ZnO ETLs have similar thickness regardless of doping ratio. In the region of below 380 nm, the ZnO:Cl- $x$  ETL with more high doping ratio show increased transmittance. However, in the visible region between 380 nm ~ 800 nm, it shows almost similar transmittance of ~90%. It can be described that the incident light is injected from the side of glass, thus same amount of photo-energy is absorbed in the photoactive layers in this work. Based on the result, one can argue that optical transmittance of ZnO ETLs does not influence on the variation of characteristics of I-OPVs.

Another optical characteristic like photoluminescence (PL) spectroscopy has been widely used to determine the optical band structure, and also PL spectra in the high wavelength represents the status of the surface structure kinds of surface defects of ZnO thin film [22,25,26,30,31]. In conventional PL spectra of ZnO thin film, one can detect two major peaks, one is strong emission peaks in the UV region of 380 nm ~ 400 nm which is related to the property of optical band gap. For the pristine ZnO showed a strong emission peak at 386 nm, at 382 nm for the ZnO:Cl-0.5, and at 392 nm for the ZnO:Cl-2.0, respectively. It is well known that PL peak shift is related to the

change of optical band gap energy. Main peak shift to red, and blue can be understood the optical band edge is changed depending on the variation of doping concentration [32], and these results are well agreed with the results of transmittance in Fig. 2 and UPS in figure 4.

Another peak in PL spectra shown in the region between 450 nm and 700 nm is giving information about surface defect such as oxygen vacancy and/or point defects of ZnO thin film [22,25,26,30,31]. It is already well known that surface oxygen vacancy of metal oxide film is quite important for the high electrical conductivity of the film. However, these vacancies can be also reacted as an electron-hole recombination centers in OPV when metal oxide film is used as an interfacial layer between photoactive layer and electrode. In order to reduce these recombination sites and enhance the performance of OPV, generally, another ultra-thin metal oxide film or tiny nanoparticle such fullerene deliberates are coated on the metal oxide interfacial layer [35]. In this work, it is found that optimal anion doping in the ZnO ETL also reduce the surface defect. In Fig. 3, photoluminescence of doped ZnO ETLs are shown. PL peak intensity of ZnO:Cl-0.5 film decrease compared to that of pristine ZnO, which means surface defect are reduced by the chlorine doping. But, for the highly doped ZnO ETL, ZnO:Cl-2.0, the intensity dramatically increase again. Conventionally, the group III cation metallic elements (such as Al, Ga, and In) substitute the zinc atoms. On the other hands, group VII anion non-metallic element chlorine can substitute the oxygen atoms in ZnO lattice. The dopant, chlorine atom, can be located on the oxygen vacancy and/or replace the oxygen atoms in the ZnO lattice in this work. As a result, green emission peak of ZnO:Cl-0.5 decrease and the surface defects are cured by chlorine doping process. However, the excessive chlorine doping cause the

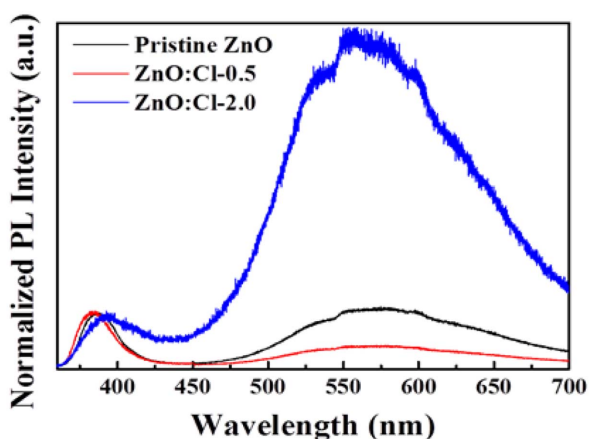


Fig. 3. The normalized photoluminescence (PL) spectra of ZnO ETLs with pristine, ZnO : Cl-0.5 and ZnO : Cl-2.0 chlorine doping at room temperature.

distortion of ZnO lattice, i.e., the excessive chlorines are acted as the interstitial atoms, not substitution. This trend is in line with the results of Hall effects and the variation of power conversion efficiency of I-OPV in Fig. 6 and 1, respectively.

In order to clarify the effect of chlorine doped ZnO ETL on the performance of I-OPV, energy band

diagram based on the band edge position obtained using ultraviolet photoelectron spectroscopy (UPS) are displayed in Fig. 4 and Table 2. The work functions (WFs) were calculated from the cut-off energy which are  $WF = h\nu - E_{\text{cut-off}}$ ;  $21.22 \text{ eV} - 16.45 \text{ eV} = 4.77 \text{ eV}$  (pristine ZnO),  $21.22 \text{ eV} - 16.44 \text{ eV} = 4.78 \text{ eV}$  (ZnO:Cl-0.5) and  $21.22 \text{ eV} - 16.50 \text{ eV} = 4.72 \text{ eV}$  (ZnO:Cl-2.0) [33]. At the low binding energy region of the UPS spectra, we could calculate the valence band maximums (VBMs). In addition, we could calculate the conduction band minimums (CBMs) by using VBMs and optical band gap energy ( $E_g$ ) measured by photoluminescence (PL) spectroscopy. The conventional work function (WF) of ITO glass is determined to be about 4.8~5.0 eV, and upon the surface modification like UV-ozone treatment in this work, the WF of ITO glass decreased to  $\sim 4.3 \text{ eV}$ . For more efficient electron extraction from photoactive layer to ITO glass, energy level of highest occupied molecular orbital (HOMO) should be located between about 4.3 eV and 3.8~4.3 eV, work function of ITO and HOMO level of PC<sub>70</sub>BM, respectively. The detailed values extracted from UPS spectra of ZnO : Cl-x ETL

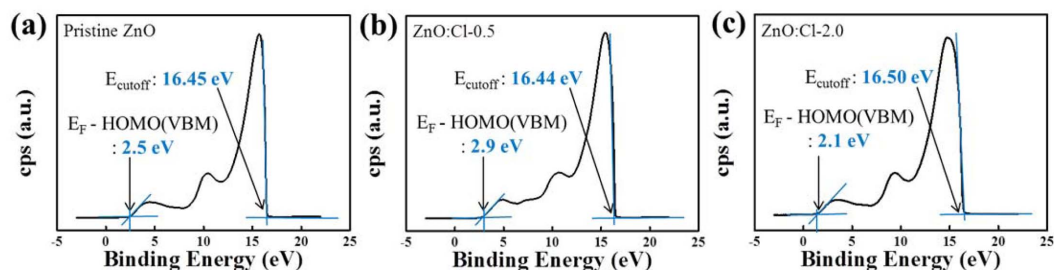


Fig. 4. The ultraviolet photoelectron spectroscopy (UPS) spectra of ZnO ETLs with pristine, ZnO:Cl-0.5 and ZnO:Cl-2.0 chlorine doping at room temperature.

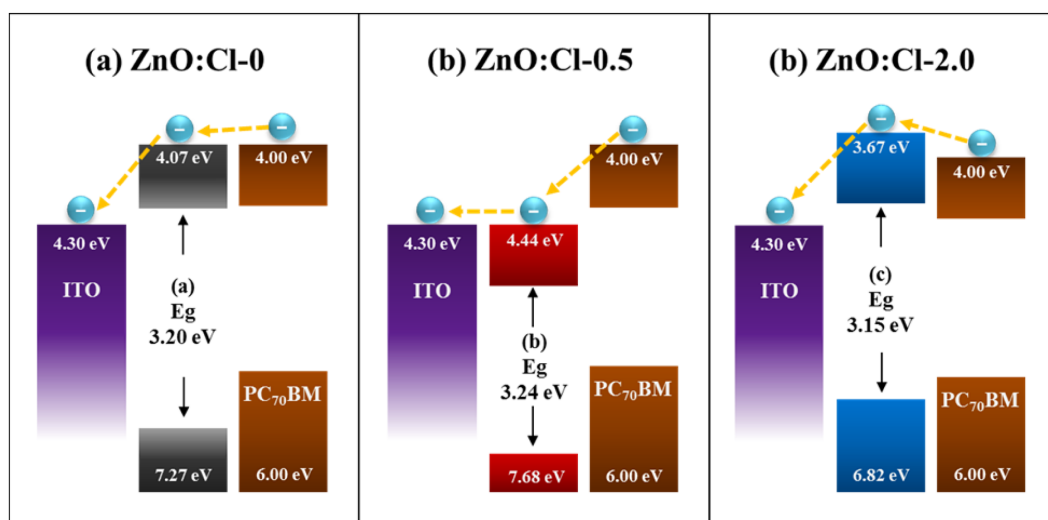


Fig. 5. The energy band diagram of I-OPVs with ZnO:Cl-x ( $x = 0, 0.5, 2.0$ ) ETLs.

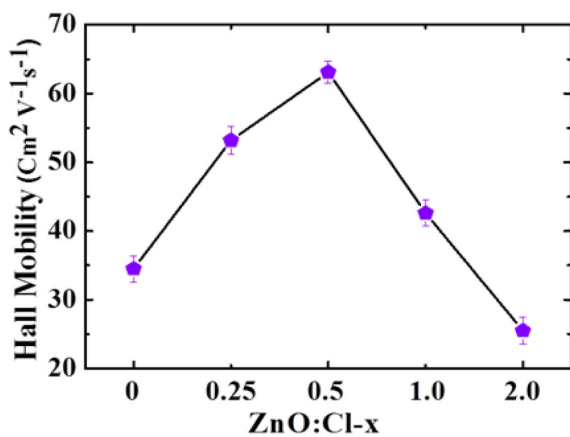


Fig. 6. Hall effects of ZnO:Cl ETLs depending on the chlorine doping ratio (The error bars: 5 measurements standard deviation).

depending on the doping concentration are 4.07 eV and 4.44 eV for the  $x = 0$ , and 0.5 wt%, respectively. Obviously, this cathode modification, chlorine doping in ZnO ETL, reduces the energy barrier between ITO and PC<sub>70</sub>BM, resulting in facilitating electron transport from photoactive layer to ITO electrode. Thus I-OPVs with ZnO:Cl-0.5 is showing the highest PCE. However, HOMO level of the ZnO:Cl-2.0 is shifted into more lower energy level, 3.67 eV, which increase the electron injection barrier. The reduced electron transportation from PC<sub>70</sub>BM to ITO causes the reduced PCE of I-OPV.

Beside the band edge position of ZnO ETL, electrical property of barrier layer such as carrier mobility is one of the important properties for efficient charge separation and transport from photoactive layer to electrode. Generally, the ZnO thin film with the high optical transparency has been widely used as transparent conductive oxide (TCO), and their mobility and conductivity can be improved through cationic doping of group III metallic elements such as Al, Ga, and In. In addition, group VII anion non-metallic elements (F, Cl, Br, and I) can be also used for modifying the electrical property of ZnO thin film. Figure 6 shows the electrical characteristic of ripple structured ZnO ETL depending on the doping ratio, which was obtained by using the Hall Effect measurement. The mobility

of pristine ZnO is about 35 Cm<sup>2</sup>V<sup>-1</sup>S<sup>-1</sup>. The samples of ZnO:Cl-0.25 and ZnO:Cl-0.5 is showing high Hall mobility of 54 Cm<sup>2</sup>V<sup>-1</sup>S<sup>-1</sup> and 63 Cm<sup>2</sup>V<sup>-1</sup>S<sup>-1</sup>, respectively. On the other hand, the Hall mobility is dramatically decreased for the sample with over than 0.5wt% doping concentration. Highly doped chlorine causes the lattice distortion of ZnO and results in the interruption of carrier mobility [34]. The trend of Hall mobility of doped ZnO ETL is similar to the change of PCE, J<sub>sc</sub>, and FF of I-OPV cells. That means electrical characteristic, especially mobility in this work, of ZnO ETL is strong influencing on the performance of I-OPVs.

#### 4. Conclusions

In summary, group VII non-metallic element, chlorine (Cl), is easily doped into ripple structured ZnO thin film using simple sol-gel method and which are applied as an electron transporting layer (ETL) in inverted organic photovoltaics. The highest performance of I-OPV is achieved with ZnO:Cl-0.5 ETL of 8.79%, enhanced ~10% compared with that of pristine ZnO. Optical property of ZnO:Cl-x ETL are influenced by the chlorine doping ratio that change the band edge position. Furthermore, chlorine doping can heal the surface defect of ZnO ETL, results in more enhancing electrical conductivity.

#### Acknowledgment

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Table. 2. Energy levels of (a) pristine ZnO, (b) ZnO : Cl-0.5, and (c) ZnO : Cl-2.0.

	Conduction Band Energy (eV)	Valence Band Energy (eV)	Band Gap Energy (eV)
(a) Pristine ZnO	4.07 eV	7.27 eV	3.20 eV
(b) ZnO:Cl-0.5	4.44 eV	7.68 eV	3.24 eV
(c) ZnO:Cl-2.0	3.67 eV	6.82 eV	3.15 eV

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