Effects of Humidity During Formation of Zinc Oxide Electron Contact Layers from a Diethylzinc Precursor Solution

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Abstract

This work focuses on the role of humidity in the formation of ZnO thin films from a reactive diethylzinc precursor solution for use as the electron contact layer (ECL) in organic photovoltaic (OPV) devices. This method is well suited for flexible devices because the films are annealed at 120 °C, making the process compatible with polymer substrates. ZnO films were prepared by spin coating and annealing at different relative humidity (RH) levels. It is found that RH during coating and annealing affects the chemical and physical properties of the ZnO films. Using x-ray photoelectron spectroscopy it is found that increasing RH during the formation steps produces a more stoichiometric oxide and a higher Zn/O ratio. Spectroscopic ellipsometry data shows a small decrease in the optical band gap with increased humidity, consistent with a more stoichiometric oxide. Kelvin probe measurements show that increased RH during formation results in a larger work function (i.e. further from vacuum). Consistent with these data, but counter to what might be expected, when these ZnO films are used as ECLs in OPV devices those with ZnO ECLs processed in low RH (less stoichiometric) had higher power conversion efficiency than those with high-RH processed ZnO due to improved open-circuit voltage. The increase in open-circuit voltage with decreasing humidity was observed with two different donor polymers and fullerene acceptors, which shows the trend is due to changes in ZnO. The observed changes in open-circuit voltage follow the same trend as the ZnO work function indicating that the increase in open-circuit voltage with decreasing humidity is the result of improved energetics at the interface between the bulk-heterojunction and the ZnO layer due to a vacuum level shift.

Keywords: Organic Photovoltaics, Zinc Oxide, Processing, Humidity, Contact Layer

1. Introduction

Organic photovoltaics (OPV) remains a technology of interest due to its unique attributes such as solution processability, flexibility, and multiple discrete absorption bands. Solution processability allows for OPV modules to be fabricated using high-throughput roll-to-roll coating methods such as slot-die coating and gravure printing. Based on recent estimates, modules produced using slot-coating with 5% power conversion efficiency (PCE) and a 3-5 year lifetime will have a comparable levelized cost of electricity (LCOE) to a coal power plant.[1] Lab-scale devices have achieved PCE's above 10%, with submodules reaching 6.8% at an area of almost 400 cm². [2] Additionally, fully-printed modules have recently been shown to maintain 95% of their initial efficiency after one year in outdoor testing experiments.[3] These results show that a module

meeting the efficiency and lifetime requirements for grid parity may soon be attainable. Discrete absorption bands allow the color of a OPV module to be tuned for light management or aesthetics – an important consideration for building integrated applications.

For optimal stability, OPV devices are fabricated in an inverted architecture (also known as superstrate configuration) because they use more stable metal electrodes than conventional architecture devices.[4, 5] The inverted architecture requires a transparent, n-type material for the electron contact layer (ECL). Transparent oxides have been extensively used as carrier-selective contacts in OPV, with ZnO and TiO_x commonly used as the ECL.[6, 7] ZnO thin films can be formed from nanoparticle, sol-gel, or reactive precursor solutions.[8, 9, 10] Here, ZnO thin films formed from a reactive precursor solution of stabilized diethylzinc (DEZn) are studied to understand the effect of relative humidity during film formation. This DEZn method was initially developed for ZnO-polymer hybrid solar cells,

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but has since been applied to ZnO thin films for OPV devices.[10, 5] It is well suited for roll-to-roll processing because it requires annealing at only 110 °C, which is at or below the glass transition temperature (T_g) of polymer films such as polyethylene terephthalate (PET), polyethylene naphthalate (PEN) and polyimide. In contrast, a sol-gel route using zinc acetate (ZnAc) usually requires annealing up to 300 °C, which is well above T_g for many polymer films[9, 11], although reports indicate it is possible to fabricate efficient OPV devices with ZnAc-based ZnO annealed at only 100-110 °C.[12, 13]

On its own, pyrophoric DEZn is too reactive to be useful for film formation from solution, so it is diluted and stabilized with toluene and tetrahydrofuran (THF). Once stabilized, DEZn can be processed in air via standard solution-processing techniques, such as spin coating. The conversion of DEZn to ZnO occurs in a two step process. For chemical vapor deposition (CVD) of ZnO from DEZn, molecular orbital studies have shown two reaction pathways..[14] The first reaction pathway is initiated by single hydrolysis

which is followed by the elimination of ethane

to form ZnO. The alternative pathway is initiated by double hydrolysis

and ZnO is formed by the elimination of water

A study of the reaction in ether showed single hydrolysis (Eqn. 1) is the dominant reaction mechanism.[15] However, in all of the reaction conditions studied the $\text{H}_2\text{O}:\text{DEZn}$ ratio was never greater than 1:1, so this may have excluded double hydrolysis as pathway since it would need a ratio of 2:1. Hydrolysis is exothermic, where as elimination is endothermic, thus thermal annealing is necessary to convert the intermediate hydroxide to ZnO. Since hydrolysis of DEZn is initiated by water, it likely that relative humidity (RH) during coating and annealing will impact the formation of ZnO. This was found to be the case in hybrid ZnO:MOMO-PPV (poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene]) solar cells, where the most efficient devices were made when the hybrid bulk heterojunction (BHJ) was spin coated and annealed in a nitrogen environment with 45-60 % RH.[16] For these devices the objective was to form ZnO within the polymer matrix to create an intimately mixed network for efficient free-carrier generation. However, for

ZnO ECLs in polymer:fullerene OPV devices the objective is to create a dense, smooth layer with high optical transparency, thus the optimal humidity conditions may be different than for hybrid structures. A previous study on the solution formation of ZnO from DEZn showed that higher annealing temperature and humidity produces higher field-effect mobilities.[17]

There are also previous reports quantifying the role of processing conditions on the chemical composition of ZnO formed from DEZn through solution and atomic layer deposition (ALD). In ALD-grown films it was found that increasing temperature during formation resulted in a higher Zn:O ratio and more stoichiometric oxide.[18] Solution processing results showed that ZnO films formed from DEZn are less stoichiometric than films formed from ZnAc and it was suggested that the fast decomposition of DEZn could be the cause.[11] Although, the effects of humidity and annealing temperature on the properties of ZnO films formed from DEZn has been previously studied,[17] this report focuses on the role of relative humidity during the formation of ZnO from a DEZn precursor solution. A wide range of humidity, from 10 - 75 %RH, was explored during spin coating and annealing. The results show that relative humidity impacts the chemical composition of the ZnO film. Contrary to what was shown for hybrid devices and the previous study of OPV devices, polymer:fullerene OPV devices are found to be most efficient when the ZnO layer is formed in low humidity. In OPV devices with multiple donor:acceptor BHJ systems, the highest PCE is achieved when the ZnO layer is spin coated in low RH (10-15 %RH) and annealed in a dry nitrogen glovebox. The improvements in PCE are primarily due to increases in the open-circuit voltage (V_{oc}). These improvements are attributed to observed changes in work function that result from changes in chemical composition.

2. Materials and Methods

All substrates were cleaned in ultrasonic baths of acetone and deionized water for 30 min followed by rinsing with deionized water and drying with compressed N_2 . For ellipsometry, the substrates were single-side polished Si wafers with 100 nm of thermal oxide. For Kelvin probe and x-ray photoelectron spectroscopy, the substrates were unpatterned indium tin oxide (ITO) coated glass (15 $\Omega/\square$). For OPV devices, the substrates were patterned ITO (15 $\Omega/\square$) on glass. Humidity was measured using a VWR Traceable Temperature and Humidity Meter.

The precursor DEZn solution was made by mixing one part of a stock solution of diethylzinc (15 wt%) in toluene (Sigma Aldrich, 220809) with three parts of uninhibited tetrahydrofuran (THF, Sigma Aldrich, 401757) in a glove box. The diethylzinc/toluene mixture was injected into the THF using a syringe and nee-

dle to minimize exposure of DEZn to water. The films were deposited by spin coating. To control the humidity during spin coating a large piece of expanded polystyrene was used to cover the spin coater. Three holes were made in the cover to accommodate the gas line, humidity meter, and micropipet for solution dispensing. For relative humidity below the ambient humidity, compressed nitrogen was used to purge the spin coater. For relative humidity above the ambient humidity, compressed nitrogen was bubbled through deionized water en route to the spin coater. For both situations, the nitrogen flow rate was manually adjusted to achieve the desired relative humidity. ZnO films were cast by dispensing 250 μL of solution onto the substrate and spinning at 7000 rpm for 60 s with a 7000 rpm/s ramp. This produced films that were approximately 40 nm thick. For annealing a large expanded polystyrene box was used to cover a hot plate. It also had holes for the gas line and humidity meter and humidity was controlled in the same way as it was for spin coating. Selected samples were annealed in a nitrogen-filled glove box with less than 1 ppm water. All samples were annealed for 20 minutes on a hot plate set to 120 °C.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos AXIS Nova XPS system. Following completion of annealing, the samples were sealed in vials in a N_2 -filled glove box. Ambient exposure during loading of the samples was less than 5 min. Photoelectrons were generated using monochromatic Al $\text{K}\alpha$ X-rays at 1486.6 eV. Pass energy was 10 eV. Base pressures were better than 1×10^{-9} torr. Binding energy calibration was performed by shifting the adventitious C 1s peak to 284.6 eV. Analysis was performed using Vision Processing Software.

Spectroscopic ellipsometry measurements were made using a M2000 variable angle spectroscopic ellipsometer from the J.A. Woollam Co., Inc. The data was analyzed and modeled using the WVASE32 software (J.A. Woollam Co., Inc.). The Si wafers were measured prior to coating with zinc oxide for accurate measurement of the oxide layer thickness. The thickness of the oxide was determined using a model with the `ntve.jaw.mat`, `sio2.jaw.mat`, and `si.jaw.mat` material files found in the software. The thickness of the ZnO films was determined by fitting a Cauchy layer to the measured Ψ and Δ values at energies below the band gap of ZnO. Once the thickness was determined, it was fixed and a point-by-point fit was performed to estimate the refractive index and extinction coefficient at each point. The point-by-point fit does not enforce Kramers-Kronig consistency, so an oscillator model is necessary to ensure a physical model. Next, using the `genosc.mat` layer multiple oscillators were used to model the complex dielectric function of ZnO generated from the saved optical constants. This model incorporated a Tauc-Lorentz oscillator and three Gaussian oscilla-

tors that were fit to the data. Additionally, an energy offset term and a pole at 11 eV were included as fit parameters to better fit the real part of the dielectric function. The energy offset and pole terms are used to account for contributions from oscillators that are outside of the measured wavelength range. Finally, the oscillator model was fit to the measured Ψ and Δ data.

Kelvin Probe measurements were made using an Ambient Kelvin Probe from KP Technologies, Inc. The tip was enclosed in a Faraday box, which was purged with N_2 . The ZnO films were prepared as described above. Reference measurements were made on samples of aluminum with a native oxide and gold, to ensure proper function of the system. For measurement of the ZnO films the samples were continuously measured under UV illumination. Due to the transient nature of ZnO work function the measurement was allowed to stabilize for at least 30 min before a value was recorded. The reported values are the average of at least 26 measured values.

X-ray diffraction (XRD) measurements were performed on a Rigaku D-max system, with Cu $\text{K}\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$. ZnO films were measured on quartz substrates.

Devices were fabricated on patterned ITO substrates. The ZnO films were coated as described above. For the P3HT:ICBA bulk heterojunction, P3HT (BASF P200) and ICBA (Plexcore OS 2500) with an 1:1 mass ratio were codissolved in 1,2-dichlorobenzene. The total solids concentration was 50 mg/mL. The solution was stirred on a hot plate at 60 °C overnight. The solution was cooled for 10 min on the floor of the glove box before use. The bulk heterojunction was cast by dispensing 60 μL of solution on the substrate and spreading it with the pipet tip, followed by spinning at 600 rpm for 60 s with a 300 rpm/s ramp. The still wet substrate was then transferred to a petri dish and covered and allowed to slowly dry for 2 hours. Following drying, the samples were annealed for 5 minutes on a hot plate set to 150 °C. Devices were also fabricated with poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}):[6,6]-phenyl- C_{71} -butyric acid methyl ester (PTB7:PC₇₁BM) BHJs. PTB7 (1-Material) and PC₇₁BM (Nano-C) with a mass ratio of 1:1.5 were codissolved in chlorobenzene with 1,8-diiodooctane (97:3 by volume) at a total solids concentration of 25 mg/mL. This solution was stirred and heated at 60 °C for 20 hours. The solution was spin coated at 1400 rpm for 40 s. Devices were dried for 30 min in covered petri dishes. For all OPV devices, the electrodes were deposited by thermal evaporation. The chamber was pumped down to a base pressure of 8×10^{-8} torr. 8 nm of MoO_3 was thermally evaporated at a rate of 0.2 $\text{\AA}/\text{s}$ through a shadow mask. Then, without breaking vacuum, 100 nm of Ag (99.99 %) was evaporated at 0.5 $\text{\AA}/\text{s}$ for the first 10 nm and then

Table 1: Calculated values of the ratio of stoichiometric (O_i) to non-stoichiometric oxygen (O_{ii}) and Zn to O from x-ray photoelectron spectroscopy measurements. These data show that as humidity during formation increases so does the amount of stoichiometric oxygen and Zn content.

Spin Hum. (%RH)	Annealing Hum. (%RH)	O_i/O_{ii}	Zn (at%)	O (at%)
13	0	0.76	48.15	51.15
45	0	0.95	48.74	51.26
45	45	1.08	49.05	50.95
75	75	1.16	50.45	49.55

increased to 2.0 Å/s. The devices were measured in a glove box with a Newport 3A solar simulator. The intensity of the lamp was adjusted to using a KG5-filtered Si reference cell, which has a mismatch of less than 1 % with P3HT:ICBA. The samples were illuminated through an aperture with an area of 0.061 cm². Current-voltage sweeps were measured with a Keithley 2420 digital multimeter. Device performance metrics were calculated using Igor Pro (Wavemetrics). Statistics were calculated from between 6 and 12 individual cells. Cells with anomalous performance due to defects in films were removed from calculations.

3. Results and Discussion

Atomic force microscopy (AFM) and contact angle measurements (Supporting Information Table S1) were used to determine if the humidity impacted the surface of the ZnO films, since a previous report of ZnO films from a zinc acetate sol-gel solution showed that the surface roughness of ZnO had an effect on OPV device performance.[19] Here, both measurements showed only small differences between the surfaces of the films (Table S1). The ZnO films were also measured using x-ray diffraction (XRD), which showed no measurable difference between the samples (Fig. S1). Also, the XRD data do not show any evidence of crystallinity in these films (no crystalline peaks), which is likely due to the low annealing temperature. Together, the AFM and XRD indicate the different formation conditions result in films with similar structure.

3.1. X-ray Photoelectron Spectroscopy

In order to quantify the chemical composition of the surfaces of the ZnO films, x-ray photoelectron spectroscopy (XPS) was used to measure the ratios of stoichiometric oxygen to non-stoichiometric oxygen, and zinc to oxygen. Fig. 1 shows the normalized O 1s spectra for the films coated and annealed under different RH conditions. The spectra all display two peaks: the O_i peak at 530.0 eV (full width at half maximum (FWHM) 1.17 eV) corresponds to stoichiometric oxygen (Zn–O) within the lattice and the O_{ii} peak at 531.5 eV (FWHM 1.61 eV) corresponds to non-stoichiometric

Figure 1: O 1s spectra measured by x-ray photoelectron spectroscopy of ZnO films formed under different relative humidity conditions (Legend: % RH coating/% RH annealing). The stoichiometric (O_i) and non-stoichiometric (O_{ii}) oxygen peaks are labeled for comparison of the ratio of stoichiometric to non-stoichiometric oxygen in the ZnO films. These spectra show that as RH is increased during formation the film becomes more stoichiometric.

oxygen (Zn–O–H).[20] It is clearly seen that as humidity increases the intensity of the O_{ii} peak decreases relative to the O_i peak, which indicates an increase in stoichiometry of the oxide. The ratio of stoichiometric to non-stoichiometric oxide can be calculated by comparing the areas of two Gauss/Lorentz (70/30 ratio) oscillators fit to the peaks. These ratios are summarized in Table 1 and O 1s spectra with peaks and fits are shown in Fig. S2. The atomic percentages of Zn and O in the films can also be found Table 1. These percentages show that as % RH is increased during film formation the Zn/O ratio increases.

These results give insight to where in the formation process the hydrolysis and elimination reactions occur. Given that films coated in a humid environment and annealed in 0 % RH form ZnO films (with varying degrees of stoichiometry), it can be concluded that, to a large extent, hydrolysis occurs during coating. This is not surprising given that the hydrolysis of DEZn is highly exothermic. Comparing the two films spin coated at 40 % RH it is found that the oxide is more stoichiometric and the Zn/O ratio is higher for the film annealed at 40 % RH than at 0 % RH. This suggests that hydrolysis also occurs during annealing. With water present, any DEZn that was not reacted during coating can be converted to $Zn(CH_2CH_3)OH$ and then to ZnO. This result supports the hypothesis of MacLeod et al. that the formation of ZnO from DEZn is kinetically limited.[11] Annealing in a more humid environment allows more of the trapped species to be fully reacted.

Table 2: Kelvin probe measurements of the contact potential difference (CPD) relative to a gold alloy tip of ZnO films formed under different humidity conditions during spin coating and annealing. Values are reported with one standard deviation. The estimated work function of ZnO films (ϕ) were calculated relative to a native aluminum oxide sample. The results show that as humidity is increased, so is ϕ .

Spin Hum. (%RH)	Annealing Hum. (%RH)	CPD (mV)
12	0	-678 $\pm$ 4
12	11	-594 $\pm$ 2
48	0	-584 $\pm$ 2
48	54	-523 $\pm$ 2
75	75	-495 $\pm$ 2

Elimination is endothermic and occurs during annealing. However, it is unclear how the elimination reaction affects the stoichiometry of these films since it cannot be isolated from hydrolysis, which appears to be occurring during coating and annealing.

3.2. Kelvin Probe

In light of the XPS results that show differences in the chemical composition of the surfaces of ZnO films formed under different RH, it is important to quantify how this affects the electronic properties of these films. The work function (ϕ) is the most relevant measurement given that it is a surface electrical property. The contact potential difference (CPD = $\phi_{tip} - \phi_{sample}$) of the ZnO films was measured after UV light soaking in nitrogen. Previous results have shown that UV light soaking results in a slight decrease in work function due to desorption of chemisorbed oxygen.[21] Light soaking of the ZnO mimics conditions that are most relevant to OPV devices given the correlation between UV effect on charge extraction and current-voltage characteristics.[22] Five processing conditions were measured and the results are displayed in Table 2. The data show that decreasing humidity during ZnO formation leads to a more negative CPD, which translates to a smaller ϕ (closer to vacuum). The changes in ϕ are likely due to changes in composition and stoichiometry of the surface. These observed differences in ϕ have implications for OPV device efficiency. A shift in ϕ is indicative of a shift in the vacuum level relative to the energy levels of ZnO. This shift should result in improved energy level alignment between ZnO and the fullerene and a larger built-in field.

3.3. Spectroscopic Ellipsometry

Spectroscopic ellipsometry is a powerful technique to characterize the optoelectronic properties of thin films. Using a collection of oscillators the dielectric function of thin films can be modeled. For solution-deposited ZnO thin films, the dielectric function from 300 - 1700 nm has been successfully modeled using Gaussian oscillators and a Tauc-Lorentz (TL) oscillator.[23] The

Figure 2: Extinction coefficient of ZnO films formed under different humidity conditions (Legend: % RH coating/% RH annealing) generated from oscillator model fits to spectroscopic ellipsometry data. Reducing humidity during film formation results in a larger band gap and a decrease in the extinction coefficient near the onset of absorption.

TL oscillator is a Lorentz oscillator multiplied by the Tauc joint density of states function and was developed to better model the band-edge of amorphous semiconductors and insulators.[24] The imaginary part of the TL oscillator is defined as

$$\epsilon_2^{TL} = \begin{cases} \frac{AE_c B(E-E_g)^2}{(E^2-E_g^2)^2 + B^2 E^2} \cdot \frac{1}{E} & E > E_g \\ 0 & E \leq E_g \end{cases} \quad (5)$$

where A is oscillator amplitude, B is the broadening, E_c is the peak transition energy, and E_g is the optical band gap energy. When characterizing ZnO films, the TL oscillator model makes it possible to directly fit E_g . The Gaussian oscillators are used to model the dielectric function at energies above the band edge. Five ZnO films formed under different coating and annealing humidity conditions were prepared on Si wafers with 100 nm of thermal oxide: 13/0, 13/13/ 45/0, 45/45, and 75/75 %RH. The oscillator parameters obtained from the best fits are reported in Table S2. Two other fit parameters $\epsilon_1(\infty)$ and an unbroadened pole at 11 eV are included for the Kramers-Kronig integration to determine the real part of the dielectric function. Figures showing ϵ_2 for the films with the contributions of each oscillator are shown in Fig. S3.

The extinction coefficients of the films are shown in Fig. 2. The parameters of the Tauc-Lorentz oscillators are reported in Table 3. It is clear from the parameters and extinction coefficient plot that as relative humidity increases during formation, either coating, annealing, or both, E_g decreases. This is consistent with results from RF sputtered and atomic layer deposited ZnO that show E_g decreases as the Zn/O ratio increases.[25, 26] A film was also measured after spin

Table 3: Best-fit parameters for the Tauc-Lorentz oscillators used to fit dielectric function for ZnO films measured by ellipsometry. As the humidity exposure is increased there is an observable decrease in the band gap energy. Values are reported with 90% confidence intervals.

Coating Hum. (%RH)	Annealing Hum. (%RH)	A (eV)	E_c (eV)	B (eV)	E_g (eV)
13	0	16.1 ± 0.15	3.61 ± 0.005	0.390 ± 0.008	3.32 ± 0.004
13	13	19.2 ± 0.11	3.60 ± 0.002	0.42 ± 0.006	3.31 ± 0.002
45	0	31.7 ± 0.07	3.54 ± 0.008	0.40 ± 0.002	3.31 ± 0.001
45	45	36.3 ± 0.06	3.49 ± 0.001	0.38 ± 0.001	3.28 ± 0.001
75	75	23.8 ± 0.07	3.46 ± 0.001	0.50 ± 0.002	3.27 ± 0.001

coating at 13 %RH and without annealing, so it should not be converted to ZnO. Measurement and analysis of the optical properties of the film show that it does not start to absorb until above 5 eV (Fig. S4), well above the band gap of ZnO.

Another trend observed is an increase in extinction coefficient with increasing humidity up to 45 %RH. This can be seen in Fig. 2 and by comparison of the TL oscillator amplitude (A) in Table 3. The 75/75 %RH sample does not fit this trend. However, there were some difference between 75/75 %RH sample and the other ZnO films. First, is that the 75/75 %RH films were about 10 nm thicker than the films cast at lower humidities. This was observed in multiple film preparations and was independent of the order in which the films were prepared. The second difference is that the 75/75 %RH sample required 4 Gaussian oscillators to accurately model the dielectric function where as the other ZnO films only required 3 Gaussian oscillators. This suggests there is physical change in the ZnO films formed at high humidity that is impacting the optoelectronic properties of the film. It is not possible to definitively say what this change is (aside from film thickness) since the Gaussian oscillators have not been ascribed to specific electronic transitions.[23]

3.4. Organic Photovoltaic Devices

To test the effects of ZnO properties on OPV efficiency, inverted devices with a P3HT:ICBA BHJ were fabricated with ZnO ECLs that were formed under different humidity conditions. For these devices the humidities during spin coating were 13, 45, and 75 %RH and for annealing the humidities were 0, 13, 45, and 70 %RH. Spin coating at 0 %RH was not tested because a water source is necessary for the hydrolysis reaction that occurs during the drying of the spin coated solution. As such, spin coating in a 0 %RH environment will not produce useful films. The current density/voltage (JV) curves for devices with the ZnO ECLs spin coated and annealed at different %RH values are shown in Fig. 3(a) and their performance metrics are reported in Table 4. The most efficient devices were fabricated with ZnO coating at 13 %RH and annealing at 0 %RH. These conditions produced an average V_{oc} , J_{sc} , FF , and PCE of 821 mV, 9.25 mA/cm², 68.8 %, and 5.23 %. The least efficient devices had ZnO ECLs

coated at 75 %RH and annealed at 75 %RH. These devices had an average V_{oc} , J_{sc} , FF , and PCE of 764 mV, 9.57 mA/cm², 58.1 %, and 4.25 %.

To more clearly illustrate the trends V_{oc} , FF , and PCE are plotted as a function of annealing humidity for all of the spin coating and annealing humidities (Fig. 4). The average device metrics for all measured samples are also tabulated in Table S3. Humidity does not appear to affect J_{sc} . For a fixed coating humidity, decreasing the annealing humidity increases V_{oc} and FF . The same trend is observed for decreasing coating humidity at a fixed annealing humidity. These data clearly show that reducing humidity during spin coating and annealing increases V_{oc} and FF .

Since the P3HT:ICBA BHJs were thermally annealed to improve the morphology of the BHJ, it is possible that the improvements in efficiency could be due to some unknown thermally-induced interactions between the BHJ and ZnO and not the intrinsic properties of the ZnO. To test this possibility, devices were also fabricated with a PTB7:PC₇₁BM BHJ, which achieves maximum efficiency without thermal annealing. Devices were fabricated with the ZnO coated and annealed at different humidities (Fig. 3 and Table 4). These device data show that reducing humidity either during coating or annealing increases V_{oc} , consistent with what is seen in the P3HT:ICBA devices. Unlike the P3HT:ICBA devices, there does not appear to be a trend in FF with humidity.

Taken in aggregate with the Kelvin probe data, the device data suggests the observed improvements in V_{oc} follows a vacuum shift as evidenced by the change in ϕ . This same relationship between V_{oc} and ϕ has previously been reported where ϕ of ZnO has been manipulated using organic additives for nanoparticle ZnO ECLs or phosphonic acid SAMs for ZnO from DEZn.[27, 28, 22] Similar to what has been previously observed, the change in V_{oc} is smaller than the change in ϕ , which has been attributed to Fermi-level pinning.[28, 29, 30, 31, 32] The shift in ϕ of ZnO would increase the built-in field within the device, therefore increasing V_{oc} . ZnO formation humidity did not affect the series resistance of the devices, which indicates that potential changes in ZnO conductivity due to changes in stoichiometry are not responsible for changes in V_{oc} and FF .

Table 4: Average device performance metrics for P3HT:ICBA and PTB7:PC₇₁BM BHJ devices with ZnO layers that were spin coated and annealed under different humidity conditions. These results show that decreasing humidity during coating and annealing increases V_{oc} , and for P3HT:ICBA, FF .

	Spin Hum. (%RH)	Annealing Hum. (%RH)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
P3HT:ICBA						
	13	0	821 ± 7	9.25 ± 0.2	68.8 ± 0.7	5.23 ± 0.2
	13	13	811 ± 6	9.63 ± 0.1	65.4 ± 1.9	5.11 ± 0.2
	45	0	796 ± 8	9.68 ± 0.3	65.4 ± 3.7	5.05 ± 0.5
	45	45	789 ± 5	9.56 ± 0.3	63.1 ± 1.7	4.76 ± 0.2
	75	75	764 ± 11	9.57 ± 0.2	58.1 ± 2.7	4.25 ± 0.3
PTB7:PC₇₁BM						
	13	0	752 ± 4	13.6 ± 0.2	68.3 ± 0.9	7.01 ± 0.1
	45	0	733 ± 5	13.8 ± 0.5	70.1 ± 0.3	7.08 ± 0.3
	45	45	715 ± 6	13.5 ± 0.3	67.4 ± 0.4	6.50 ± 0.2

Figure 3: Average current density-voltage (JV) curves for (a) P3HT:ICBA and (b) PTB7:PC₇₁BM BHJ OPV devices with ZnO ECLs that were spin coated and annealed under different humidity conditions (spin/anneal). The J - V curves show that reducing the humidity during ZnO formation leads to improvements in V_{oc} , and FF for P3HT:ICBA. (c) Energy level diagram for ZnO, P3HT, ICBA, PTB7, and PC₇₁BM. The energy difference between the fullerene LUMO and ZnO CB is illustrated as ϕ_B .

The increase in V_{oc} may also be attributed to a changes in energy barrier between the fullerene LUMO and the ZnO conduction band (CB), as illustrated by ϕ_B in Fig. 3c. These offset between these transport levels is significant because electrons are injected from the fullerene LUMO to the ZnO CB. An offset between these levels is will cause the electron to lose voltage when it is injected to the ZnO. The change in ϕ should result in a shift in the alignment between the fullerene LUMO and the ZnO CB. As ϕ moves towards the vacuum it will push CB closer to the fullerene LUMO. This decreases the energetic loss of an electron injected to the ZnO CB from the fullerene LUMO. Decreasing this loss, as humidity is decreased, will increase V_{oc} .

Differences between the LUMO energies of the fullerenes could also explain the different trends in FF between the two BHJs. $PC_{71}BM$'s LUMO is further from the vacuum level than ICBA's LUMO, making it is closer to the ZnO CB, as illustrated in Fig. 3c.[33, 34, 35] Because ϕ_B is smaller for $PC_{71}BM$ than ICBA, thus making it smaller and moving ZnO's CB closer to $PC_{71}BM$'s LUMO may have a negligible effect of FF . But with ICBA, ϕ_B is larger, so moving CB closer to the LUMO of ICBA appears to have a larger effect on FF .

Our OPV device results differ with the results of Bao Foong, et al.[17] They report that the most efficient P3HT: $PC_{61}BM$ devices are obtained with the ZnO layer coated and annealed at 75 %RH. However, in their study, annealing conditions were variable (110 - 350 °C) when comparing the ZnO formation at different humidities, so the changes in device efficiency they observe may be due to differences in annealing temperature not humidity. It should also be noted that when comparing ZnO formation conditions, their devices utilized un-annealed P3HT: $PC_{61}BM$ BHJs, which have poor exciton separation. Their devices had measured FF below 40 % suggesting their results may be confounded by low free-charge generation in the BHJ. Only PCE values at one %RH are reported for OPV devices with annealed (optimized) P3HT: $PC_{61}BM$, so it is not possible to directly compare their results to ours. The results presented here use two optimized BHJs (one annealed and one unannealed) and a consistent ZnO annealing temperature. Also, BHJs presented here have been optimized with and without thermal annealing thereby providing results free of deficiencies in exciton separation or charge transport in the BHJ. Our results show reducing humidity during ZnO ECL film formation from stabilized DEZn results in the most efficient OPV devices.

4. Conclusions

The effects of humidity during the formation of ZnO from a diethylzinc precursor solution were quantified using XPS, Kelvin probe, and spectroscopic el-

Figure 4: Plots of V_{oc} , FF , and PCE as a function of annealing humidity during ZnO ELC formation. The spin coating humidity is indicated by the color of the markers and lines: 13 %RH (black circles), 45 %RH (red squares), 70 %RH (blue triangles). Regardless of the spin coating humidity, these data show that decreasing the humidity during annealing has a positive effect on these three parameters. J_{SC} is not shown because it is not affected by the ZnO formation conditions.

lipsometry and OPV device studies. Decreasing humidity during coating and annealing is shown to decrease the oxide stoichiometry and Zn/O ratio. Kelvin probe measurements show that the films formed under lower humidity exhibit lower work function. When incorporated into OPV devices, ZnO ECLs formed in reduced humidity result in higher V_{oc} and, in most cases, FF . The improvements in V_{oc} follow the observed shifts in ϕ measured by Kelvin probe. These improvements in V_{oc} are attributed to: 1) improved alignment between the energy levels of the fullerene and ZnO, and 2) increased built-in field in the devices, both of which are derived from decreasing ϕ . These results highlight the need for a controlled environment during ZnO formation. It also indicates that obtaining the highest quality (stoichiometric) ZnO does not necessarily result in the most efficient OPV devices.

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