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Citation	Journal Of Applied Physics, 2003, v. 93 n. 9, p. 5472-5479
Issued Date	2003
URL	http://hdl.handle.net/10722/42357
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Indium–tin–oxide surface treatments: Influence on the performance of CuPc/C_{60} solar cells

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(Received 2 October 2002; accepted 14 February 2003)

In this work, we investigate the influence of different indium tin oxide (ITO) surface treatments on the performance of organic solar cells. ITO substrates have been characterized by Hall measurements, Seebeck coefficient measurements, surface sheet resistance measurements, and surface probe microscopy. Single layer (ITO/copper phthalocyanine (CuPc)/Al) and double layer (ITO/CuPc/C_{60}/Al) solar cells were fabricated. It was found that the surface treatments changed the parameters of the ITO (work function, carrier concentration, sheet resistance, surface roughness) and significantly influenced the solar cell performance. The AM1 power conversion efficiency of the ITO/CuPc/C_{60}/Al cell with optimal surface treatment ($\sim$0.1%) is 1 order of magnitude larger than the power conversion efficiency of the solar cell fabricated on untreated ITO substrate ($\sim$0.01%). The AM1 power conversion efficiency can be further enhanced with improved device structures. Obtained AM1 power conversion efficiency for a three layer structure ITO/CuPc/CuPc:C_{60} (1:1)/C_{60}/Al was measured to be 0.16%. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1565824]

I. INTRODUCTION

Indium–tin–oxide (ITO) is frequently used as an electrode in flat panel displays, solar cells, and organic light emitting diodes (OLEDs) due to its high conductivity and transparency in the visible spectral region. ITO is a highly degenerate *n* type semiconductor with a wide band gap and relatively high work function. The effect of various surface treatments [plasma, chemical, ultraviolet (UV) ozone, etc.] to the ITO properties and the OLED performance was extensively studied.[1–22] Surface treatments have an effect on ITO parameters such as the work function, surface roughness, carrier concentration, mobility, and surface sheet resistance, so that with appropriate surface treatment significant improvement in the OLED performance can be achieved. Kim *et al.*[1–4] studied the influence of the oxygen plasma, aquaregia, and combinations of these two treatments to the parameters of the ITO surface. They have found that the oxygen plasma treatment results in increased work function,[1] increased carrier concentration and slightly decreased mobility resulting in overall decrease in sheet resistance,[1–4] and decreased surface roughness.[1] On the other hand, aquaregia treatment and combination treatments including aquaregia produced only slight increase in the work function,[1] increase in the sheet resistance due to decrease in carrier concentration,[1–4] and increased surface roughness except for oxygen plasma followed by aquaregia.[1] The best OLED performance in their work was obtained with oxygen plasma treatment.[1–4] The proposed reason for the observed improvements in the device performance with oxygen plasma treatments in their work is increased work function and hence improved hole injection. It was also reported that plasma treatments remove an insulating overlayer from ITO surface.[14] This assumption was confirmed by conducting atomic force microscopy study of local conductance of ITO films before and after oxygen plasma treatment.[23] The thin insulating layer is most likely organic hydrocarbons.[23] Local variations in surface potential on ITO surface were also reported.[24] This observation can possibly explain the observed influence of the ITO morphology to the performance of organic devices. It was found that the devices fabricated on ITO substrates with similar work functions but different surface morphology exhibit markedly different performance.[16,17] The lowest turn on voltage was obtained with ITO exhibiting granular structure with very rough surface.[16,17] Contrary to that result, improvement with mechanical polishing of ITO which resulted in smoother surface was reported.[19] The relationship between oxidative surface treatments (oxygen plasma, UV ozone) and ITO parameters (work function, sheet resistance, carrier concentration and mobility, surface roughness) and OLED performance is not well understood. It was established that oxidative treatments

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of ITO surface improve the OLED performance. Exact nature of physical processes contributing to this improvement still requires further study.

Unlike oxidative surface treatments, reported results with acid treatments[1–3,5–7,20] are somewhat contradictory. Kim *et al.*[1–3] studied the influence of aquaregia treatment and combined oxygen plasma and aquaregia in different order. Oxygen plasma treatment alone was recommended as the best treatment in their study as the best compromise between device efficiency and stability.[1] On the other hand, Li *et al.*[20] and Nuesch *et al.*[5–7] found significant improvement in OLED performance with acid treatments, which was attributed to improved injection due to rougher surface[20] and increased work function of the ITO.[5–7] It was also shown that the acid treatment of the ITO surface (performed after oxygen plasma cleaning) changes the growth mode of N, N′-bis-(1-naphtyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine from island growth on untreated substrate to layer-by-layer growth on the treated one.[25,26] The differences between reported works are possibly due to different acids used, different acid concentrations, different treatment times, and different device structures. Different acids result in different work function and sheet resistance values, as well as different rms surface roughness and surface morphologies.[18] It was also demonstrated that optimal surface treatment/ITO parameters are dependent on the material used.[1,20] Therefore, it is difficult to make any general recommendations concerning ITO surface treatments other than that oxidative (oxygen plasma or UV ozone) treatment will result in better OLED performance compared to OLEDs fabricated on untreated ITO. Optimal treatment, however, may depend on the materials used and it is also likely to depend on the starting properties of ITO. Exact nature of the physical processes responsible for the influence of surface treatments to the OLED performance is still not entirely clear.

In spite of recognized critical importance of the ITO surface in performance improvement of OLEDs, studies of the relationship between ITO surface properties and organic solar cell performance have been scarce. At most, UV ozone or oxygen plasma would be used as a part of ITO cleaning procedure[27,28] in order to remove carbon from the interface without studying the implications of such surface treatments to the solar cell performance. In this work, we have studied the properties (work function, sheet resistance, carrier concentration and mobility, and surface topography) of ITO surface after different surface treatments (UV ozone, acid treatment, mechanical treatment and their combinations) and the performance of single layer (ITO/copper phthalocyanine (CuPc)/Al) and double layer (ITO/CuPc/fullerene (C_{60})/Al) solar cells fabricated on ITO substrates subjected to different surface treatments. Studies of metal phthalocyanine and metal Pc/C_{60} based organic solar cells have been reported in the literature.[27–31] There exists significant variation of the reported power conversion efficiencies. Reported white light conversion efficiencies in these devices vary from 0.002% for ITO/C_{60}/OTiPc/CrAu cell[31] over 0.2% for CuPc/C_{60} double layer cell with optimized thickness[28] to 3.6% for a double heterostructure device.[27] Since the materials used are known to yield promising results, solar cells based on these materials can serve as a model devices for studying the influence of the ITO surface treatments to the organic solar cell performance. The article is organized as follows. In the following section, experimental details are given. In section III, obtained results are presented and discussed. Finally, conclusions are drawn.

II. EXPERIMENTAL DETAILS

The devices were made using high purity CuPc powder which had been purchased from Strem Chemicals and C_{60} which had been purchased from Materials and Electrochemical Research Corp. (Tucson, AZ). ITO glass substrates with surface sheet resistance $\sim 10\ \Omega$/square were supplied by China Southern Glass Holding Co. Ltd., Shenzhen, China, while ITO glass substrates with surface sheet resistance $\sim 23.5\ \Omega$/square were supplied by Varitronix Limited, Hong Kong. Unless otherwise specified, ITO glass substrates with surface sheet resistance $\sim 10\ \Omega$/square were used. Prior to evaporation, ITO substrates were cleaned, first by rubbing with cotton and acetone, cotton and ethanol, then in ultrasonic bath for 10 min in acetone, ethanol, and de-ionized water consecutively and blow dried in nitrogen. If no surface treatment other than cleaning with organic solvents as described above is performed, ITO substrates will be referred to as untreated or as-cleaned substrates. Acid treatment was performed by dipping the substrate into 4% aqueous acid solution for 1 min. The acid used was HCl since it produced the best results for organic light emitting diodes.[18] UV ozone treatment was done for 10 min, with 12 cm distance between 20 W UV light source and the sample. Mechanical treatment has been performed using clean room wiper rubbing. The samples were ultrasonically cleaned with deionized water after mechanical treatment. The films were evaporated in high vacuum. Pressure during evaporation was of the order 10^{-4} Pa. The evaporation rate was 1–2 Å/s. The distance from source to film was about 23 cm to ensure uniformity of film thickness, and the substrate holder was rotating. The thickness of the films was controlled using quartz thickness monitor.

After evaporation, film thickness was verified using step profiler Dektak 3. For the comparison of different ITO surface treatments, the substrates treated in a different manner were placed on the sample holder and all the devices on four different substrates were fabricated during the same deposition process. Eight cells were fabricated on each substrate. Absorption spectra were measured using Hewlett Packard 8453 UV-Vis spectrometer. The current–voltage ($I-V$) characteristics were measured using Keithley 2400 sourcemeter. For white light efficiency measurements, Oriel 66002 xenon arc lamp with AM1 filter was used. Hall measurements were performed using Bioradhl 5500 PC. Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) measurements were performed using Digital Instruments Nanoscope III and Autoprobe CP. The work function change for different surface treatments has been estimated from the tunneling current in STM measurement. The effect of the work function on the tunneling current at barrier width s is determined by[32]

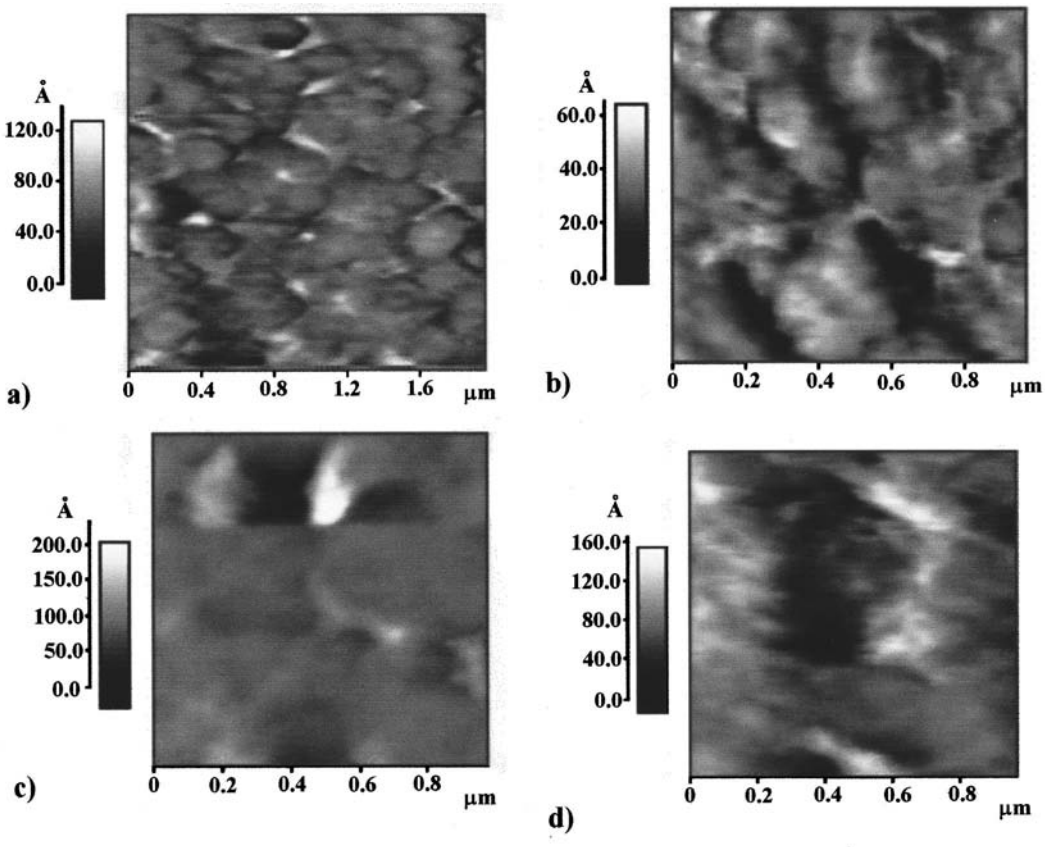

FIG. 1. AFM images of ITO substrates: (a) untreated, (b) UV ozone treated, (c) UV ozone and HCl treated, and (d) mechanical and UV ozone and HCl treated.

$$\frac{I(\varphi_1,s)}{I(\varphi_2,s)}=\exp\left[-\frac{4\pi s\sqrt{2m}}{h}(\sqrt{\varphi_1}-\sqrt{\varphi_2})\right], \tag{1}$$

where m is the electron mass and h is the Planck's constant, and φ_1 and φ_2 are the work functions of materials compared. The comparison was performed for fixed distance $s=5$ nm. The work function change was calculated by averaging the results obtained for ten samples. Obtained results showed good reproducibility, with work function differences between different substrates in the range of ± 0.2 eV. These small variations among the samples are likely due to inherent local variations in surface potential of ITO.[24] The trends in the work function change, such as, for example, increase of the work function with UV ozone treatment, are highly reproducible. Surface sheet resistance was determined from four point probe measurements (Signatone) and Hall measurements. Seebeck coefficient measurements were performed using a home-built apparatus consisting of heating element and thermoelectric cooler with independent power supplies to ensure stable and independent control of the temperature of the two measurement points. Temperature was measured using thermocouples, and Seebeck voltage V_s was measured using Keithley 2400 sourcemeter. Samples for Seebeck coefficient measurements consisted of ITO substrates with different surface treatments. The electrode spacing was 2.0 cm. The temperature difference between two measurement points was 5 K. Seebeck coefficient measurements represent useful characterization technique for determination of the Fermi level position.[33–35] Seebeck coefficient is defined as[33,34]

$$S(T)=\lim_{\Delta T\to 0}\frac{V_s(T,\Delta T)}{\Delta T}=\frac{k}{e}\left(\frac{\Delta E}{kT}+A\right), \tag{2}$$

where k is the Boltzmann constant, T is the temperature in K, ΔE is the difference between Fermi level and top of the valence band (bottom of the conduction band), while A is a factor dependent on the scattering parameter and the Fermi level.[36,37] In some materials, such as organic materials[34] and CdO,[36] A can be considered a constant.

III. RESULTS AND DISCUSSION

Figure 1 shows the AFM images of the ITO substrates: as cleaned, after UV ozone treatment, after UV ozone followed by HCl, and after combination of mechanical, UV ozone and HCl treatments. Untreated ITO substrate exhibits flakes resulting in rather flat surface with low rms roughness. UV ozone treatment results in the reduction of surface roughness, while UV ozone followed by HCl results in significant increase of the surface roughness. Lowest surface roughness is obtained for the mechanical treatment followed by UV ozone and HCl. Results obtained on the ITO substrates from the same supplier show good reproducibility. However, if we compare the results obtained for substrates obtained from different suppliers, we can observe similar trends but different magnitude of changes (i.e., changes in sheet resistance, work function, and surface roughness). This is most likely due to significant differences in surface mor-

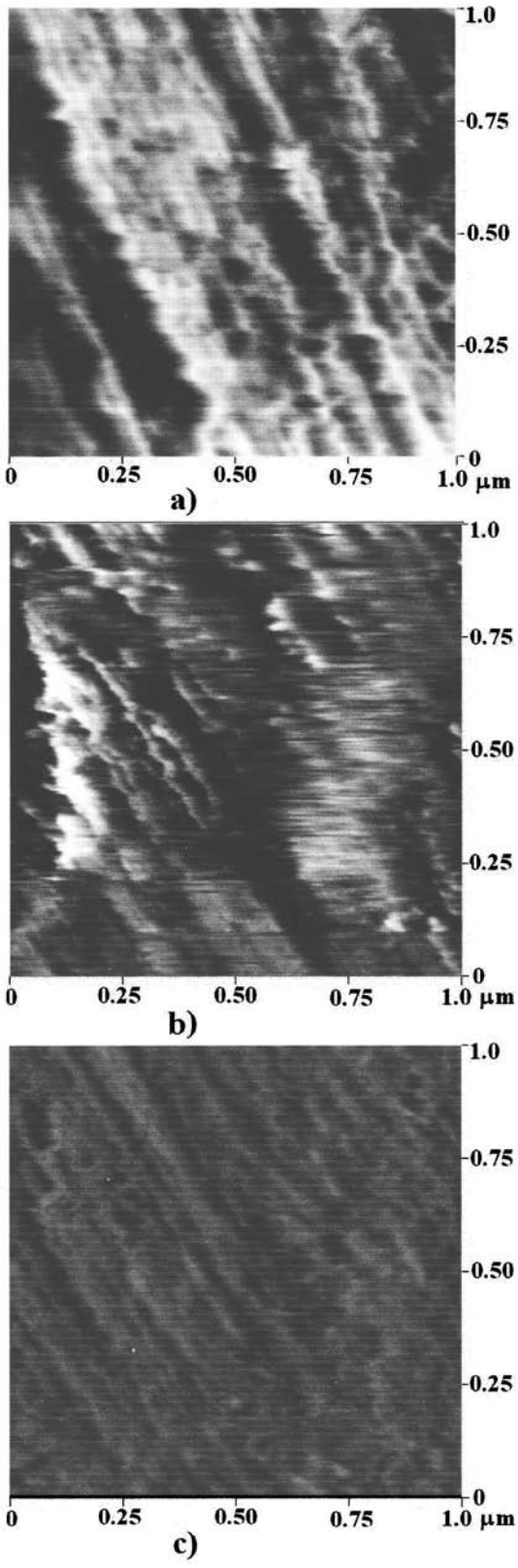

FIG. 2. STM images of ITO substrates: (a) untreated (rms roughness 2.9 nm), (b) oxygen plasma treated (rms roughness 1.9 nm), and (c) HCl treated (rms roughness 1.3 nm).

phology of ITO from different suppliers and with different initial properties. This is illustrated in Fig. 2, which shows scanning tunneling microscopy (STM) images of the ITO substrates with surface sheet resistance 23.5 Ω/square.

ITO substrates after different surface treatments were characterized with STM, Hall measurements, surface sheet resistance measurements, and Seebeck coefficient measurements. The results are summarized in the Table I. It can be observed in Table I that only UV ozone followed by HCl treatment leads to increased surface roughness. As expected, UV ozone yields increase in the obtained work function. Increase in the work function of ITO with oxidative treatments (oxygen plasma, UV ozone) has been attributed to carbon removal from ITO surface,[8,12,13] larger number of states created close to and possibly below the edge of the conduction band,[2,3] or shift of the Fermi level.[21,22] It should be noted that the work function and sheet resistance values are dependent not only on type of treatment but also on treatment time.[1,2] This was explained by interplay between different mechanisms responsible for the work function change.[1] Three possible causes for the shift of the Fermi level with ITO surface plasma treatments have been identified: surface states created by plasma treatment, change in the ratios of surface constituents (In, Sn, O), and formation of surface dipoles.[22] Most likely the contributions of these causes are combined to produce the observed work function shift. The possible role of surface states created by plasma treatment is not entirely clear since Ar plasma, unlike oxygen plasma, does not result in the increase of the work function.[12,22] Also, Ar plasma treatment yields lower carbon contamination compared to oxygen plasma, yet the obtained work function is lower for Ar plasma treatment.[1] It was suggested that the influence of carbon contamination removal is far less significant contribution to work function change compared to the band bending and Fermi level shift.[21] However, it was also found that the changes in carrier concentration do not correlate in a simple way with the changes in surface composition.[21] This indicates that, indeed, there are multiple mechanisms contributing to the observed phenomena.

Contrary to results of aquaregia and oxygen plasma treatments reported by Kim *et al.*[2,3] all the treatments employed in this work result in increase in the surface carrier concentration with the largest increase obtained by UV ozone treatment which also corresponds to the lowest mobility. Obtained increase with combination treatments in our work is also significantly higher compared to combination treatments used by Kim *et al.*[1–4] This is not surprising since the results reported in the literature for acid surface treatments of ITO are to some extent contradictory. Kim *et al.*[1–3] have found that aquaregia and combination treatments increased sheet resistance and decreased carrier concentration,[1,2] while work function showed nonmonotonous dependence on the time of aquaregia treatment and surface roughness was increased.[1] The lowest turn on voltage and highest luminance was obtained for oxygen plasma treatment, though oxygen plasma followed by aquaregia yielded higher efficiency. Aquaregia treatment alone resulted in better performance than aquaregia followed by oxygen in ITO/poly(*p*-phenylene vinylene (PPV)/Ca devices, while in ITO/poly(4,4′-diphenylene diphenylvinylene)/Ca aquaregia followed by oxygen plasma shows the best performance.[1] Lowest carbon contamination of ITO surface out of oxygen plasma only, aquaregia only, and two combined treatments

TABLE I. ITO parameters for different surface treatments.

ITO treatment	$\Delta\Phi$ (eV)	$N_s(10^{17}$ $cm^{-2})$	μ ($cm^2/V/s$)	R_s ($\Omega/\square$) Hall	R_s ($\Omega/\square$) 4pp	rms roughness (nm)
Untreated	—	0.54	14.3	8.02	15.8	1.28
UV ozone	0.75	1.48	6	7.03	16.5	1.10
UV ozone+HCl	0.5	0.73	11	7.76	16.6	2.63
Mech.+UV ozone+HCl	0.19	0.85	10	7.37	15.0	1.06

was obtained for aquaregia followed by oxygen plasma, while oxygen plasma followed by aquaregia resulted in highest sheet resistance and lowest surface roughness.[1] Li *et al.*[20] found significant improvement in the device performance with aquaregia treatment. The optimal treatment time and resulting sheet resistance was dependent on the material used for hole transport layer.[20] Observed improvements were attributed to improved hole injection due to increased surface roughness with acid treatment.[20] Nuesch *et al.*[5–7] studied acid and base treatments of ITO surface (the surface was cleaned with oxygen plasma prior to acid treatment). The devices treated with H_3PO_4 exhibited lower turn-on voltage and higher efficiency compared to oxygen plasma only treated devices.[5] The improvement in the device performance was attributed to the increase in work function due to protonation of ITO surface and the formation of the surface dipole.[5–7] The differences among the reported results most likely arise from the use of different acids, different solution concentrations and treatment times, and different initial ITO parameters.

The lowest sheet resistance in our work was obtained for UV ozone treatment as determined by Hall measurements, while for four point probe technique mechanical treatment followed by UV ozone and HCl gave the lowest resistance. The difference between the two measurement techniques is most likely due to the fact that Hall measurement was performed immediately after the treatment, while four point probe measurement was performed approximately 15 min after the treatment. The obtained results indicate lower reactivity of the surface of ITO with mechanical treatment followed by UV ozone and HCl. We have not investigated mechanical treatment alone since in our previous work it resulted in very smooth surface but inferior OLED performance,[18] which is also in agreement with results of Fujita *et al.*[11] Decrease in mobility found in oxygen plasma treatments of ITO surface[2,3] are easy to explain due to defects induced by ions. However, reduction in mobility with UV ozone treatment observed in our work is more difficult to explain. It is possible that removal of organic carbon contamination from the ITO surface would result in existence of dangling bonds and surface states which may result in the decrease of mobility. Increased reactivity of ITO surface cleaned by UV ozone or oxygen plasma is another indication in favor of this assumption. However, observed phenomenon requires further study before definite explanation can be found.

It should also be pointed out that the obtained results are most likely strongly dependent on the initial ITO used. From

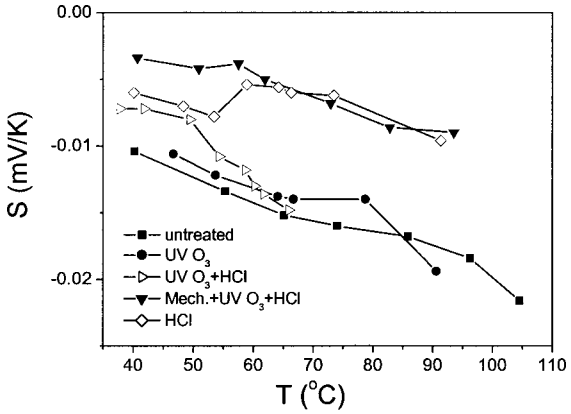

FIG. 3. Seebeck coefficient vs temperature for different surface treatments of ITO.

comparison of the Figs. 1(a) and 2(a) large difference in the surface morphology of ITO glass substrates with surface sheet resistance $\sim 10\ \Omega$/square and substrates with surface sheet resistance 23.5 Ω/square is obvious. More importantly, these two types of ITO substrates produce different results with surface treatments. In the latter case, we observed a more significant increase in sheet resistance with treatments using HCl, as well as smaller changes in work function with oxidative treatments, and more significant reduction of surface roughness in all cases.[18] Therefore, final results of the surface treatments are dependent on the initial properties and surface morphology of the untreated ITO. We have also performed Seebeck coefficient measurements on ITO substrates treated with different treatments. Seebeck coefficient dependence on the temperature is shown in Fig. 3. Our experimental Seebeck coefficient value for untreated ITO is in good agreement with a previous study of Hall mobility and Seebeck coefficient of pyrolytic ITO (16 μV/K for carrier concentration $\sim 10^{21}$ cm^{-3}).[38] It can be observed that Seebeck coefficient exhibits nonlinear temperature dependence, which is markedly nonmonotonous in the case of HCl treated ITO. The largest value of the Seebeck coefficient is obtained for the untreated ITO, while surface treatments result in the lower values of the Seebeck coefficient. In a degenerate semiconductor, Seebeck coefficient can be expressed as[37]

$$S = \frac{\pi^2}{3}\frac{k}{e}\frac{(r+3/2)}{\eta^*}, \tag{3}$$

where r is the scattering parameter, and η^* is the reduced Fermi energy E_F/kT, where E_F is measured from the bottom of the conduction band. From Eq. (3), it can be observed that the Seebeck coefficient is inversely proportional to the separation between the Fermi level and the conduction band. However, scattering parameter r is also dependent on the carrier concentration,[38,39] so that it would be difficult to estimate the position of the Fermi level based on the Seebeck coefficient measurement only. Also, we cannot observe any direct correlation between the Seebeck coefficient, carrier concentration changes, and the obtained work function changes. It should be pointed out that previous study on surface treatments of ITO[1] also did not reveal any simple relationship between the work function, sheet resistance, and the

chemical composition of ITO. The work function shift and carrier concentration changes with the ITO surface treatments are still not well understood and the explanations commonly proposed in the literature for the work function change with the surface treatments of ITO (carbon contamination removal,[8,12,13] Fermi level shift,[21,22] and the surface dipole formation[5–7,9,10,22]) do not fully explain all the experimental data. Carbon removal hypothesis is in contradiction with Ar plasma treatment, which significantly reduces carbon[1] but does not yield increase in the work function. Fermi level shift hypothesis[22] is in contradiction with the carrier concentration results. From the change in donor concentration determined in their work, Fermi level shift should be ~ 0.04 eV which was much smaller than the measured experimental value of ~ 0.3 eV.[22] Increased surface carrier concentration with oxygen plasma treatment obtained from Hall measurements[1–4] does not support the hypothesis of the formation of depletion region on the surface. Large work function changes reported in the literature for various plasma treatments, including increase in the excess of 1 eV,[8] are not likely to be explained by the Fermi level shift only since the carrier concentration data do not support such large Fermi level shift. Also, the carrier concentration changes cannot be fully explained with the changes in indium/tin ratio and oxygen content. There is no simple correlation between the changes in surface composition of ITO and the carrier concentration.[21] Furthermore, some electrically active Sn species can be deactivated by forming complexes with interstitial oxygen.[10] Surface dipoles hypothesis, which was used to explain the work function increase with acid treatments,[5–7] represents another possible explanation for the work function shift with UV ozone[10] and plasma treatment.[9,10,22] This hypothesis represents a very likely explanation for the work function increase with the surface treatments of ITO. However, this hypothesis does not clarify carrier concentration and mobility changes with surface treatments. Further work is necessary to conclusively establish whether formation of surface dipoles causes the work function change due to vacuum level shift[5–7] or due to formation of surface depletion region and Fermi level shift,[22] and elucidate a relationship between the changes of different ITO properties. Most likely the combined influence of different phenomena plays a role in the observed behavior of ITO with different surface treatments. A variety of possible physical processes in addition to variation of initial properties of ITO and nonlinear dependence of the change of properties on the treatment time[1] contribute to the complexity of the problem of establishing mechanisms responsible for the observed changes with ITO surface treatments.

After characterizing ITO substrates after different treatment, we fabricated Schottky barrier ITO/CuPc/Al and heterojunction ITO/CuPc/C_{60}/Al. In heterojunction devices, CuPc was doped with C_{60} in ratio 20:1, while Schottky barrier cells were not intentionally doped. Figure 4 shows the $I-V$ characteristics of the CuPc Schottky cells with different ITO treatments under AM1 illumination. The inset shows current-voltage characteristics in the dark. It can be observed that the HCl treatment whether alone or in combination with UV ozone increases short circuit current. UV ozone treatment alone also increases short circuit current, but for a very small amount. HCl treatment alone reduces open circuit voltage, significantly worsens rectification ratio, and increases the dark current. If acid treatment is performed without previous cleaning of the surface with oxygen plasma or UV ozone to remove carbon contamination, it is possible that the residue from chemical reactions between acid and surface contaminants would modify the growth of organic layer and contribute significantly to impurities and pinhole defects, thus causing higher current both in the light and in the dark, and lower open circuit voltage for HCl only treated cell. In combination with UV ozone, however, open circuit voltage is increased from $V_{oc}=0.94$ V for the untreated cell to $V_{oc}=0.99$ V for the UV ozone+HCl treated one, while short circuit current density increases from 23.5 to 28.9 μA/cm^2. The best efficiency for a Schottky barrier structure, 0.005%, was obtained with UV ozone+HCl treatment.

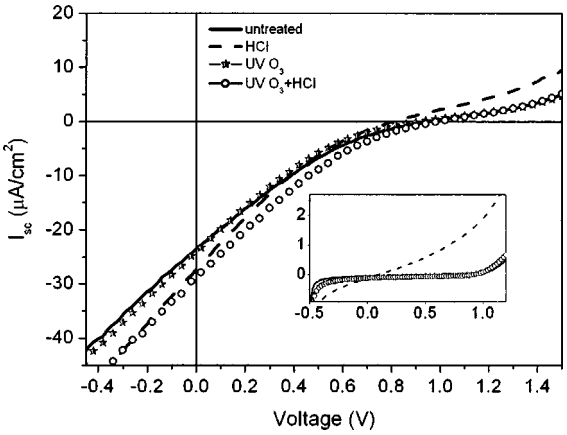

FIG. 4. The current–voltage characteristics of CuPc Schottky barrier cells with different ITO treatments under AM1 illumination: (solid line) untreated, (dashed line) HCl treated, (dash-dot line) UV ozone treated, and (dash-dot-dot line) UV ozone +HCl treated. The inset shows $I-V$ characteristics in the dark.

$I-V$ characteristics of a heterojunction cell under AM1 illumination is shown in Fig. 5, while the performance parameters are summarized in Table II. We can observe that in this case UV ozone followed by HCl results in inferior per-

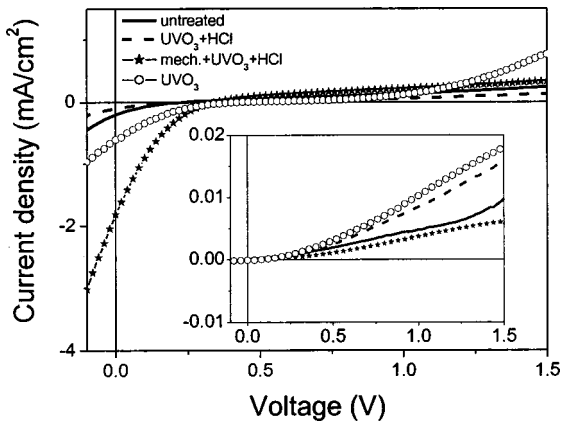

FIG. 5. The $I-V$ characteristics of ITO/CuPc/C_{60}/Al cells with different ITO surface treatments under AM1 illumination. The inset shows the dark current.

TABLE II. Comparison of the ITO/CuPc/C_{60}/Al solar cells parameters for different ITO treatments for AM1 98 mW/cm^2 excitation.

Treatment/ parameter	Untreated	UV ozone	UV ozone+ HCl	Mech.+UV ozone+HCl
I_{sc} (mA/cm^2)	0.20	0.60	0.10	1.81
V_{oc} (V)	0.22	0.44	0.34	0.34
FF	0.17	0.13	0.13	0.15
η (%)	0.008	0.035	0.004	0.093

formance, while the best results are obtained with mechanical treatment followed by UV ozone and HCl. The best treatment results in order of magnitude larger efficiency compared to untreated cell and about three times larger efficiency compared to UV ozone only treated cell, which is mainly due to larger short circuit current. There are several factors which affect solar cells performance that can be influenced by ITO surface treatments. It is possible that the surface treatments affect the Fermi level alignment. Nuesch *et al.*[40] investigated CuPc layers grown on untreated, argon plasma, and oxygen plasma treated substrates and found that work function becomes practically pinned at the highest occupied molecular orbital level of CuPc after 10 nm thick layer regardless of the surface treatment, which they explained with *p* doping of CuPc due to reaction with oxygen from ITO. Fermi level pinning at the ITO/polymer interface was also demonstrated and attributed to a high density of deep defect states at the interface.[41] Both mechanisms, i.e., surface states and oxygen doping of interfacial region can contribute to the Fermi level pinning on ITO/phthalocyanine interfaces. Small changes in Fermi level alignment of CuPc can affect the open circuit voltage of the cell. Another possible contributing factor is the change in surface state density. Reduction in the density of surface states which can act as traps would contribute to the increase in the short circuit current density. From the obtained results, the short circuit current density increase is the main contributing factor to the overall improvement in the cell efficiency. The only significant distinguishing factor, which we can identify among ITO parameters from Table I and Figs. 1 and 3, is the surface roughness and morphology of ITO. The surface of UV ozone+HCl treatment exhibits highest roughness, with all other parameters very similar to the results obtained with additional mechanical treatment. Therefore, we conclude that surface roughness and ITO morphology play a significant role in the solar cell performance. The difference between optimal treatment between single layer and two layer devices is most likely due to different operational principles in terms of where exciton dissociation occurs (depletion region at metal electrode versus organic/organic interface). Since ITO roughness and morphology influence the subsequent growth of organic layers, the interfaces in fabricated devices and hence exciton dissociation will depend on the substrate used. ITO interface will also play a role in the carrier collection. Therefore, interplay between multiple mechanisms will influence the performance of the solar cells fabricated on different ITO substrates. Further studies of the ITO/CuPc interface are needed in order to fully explain the obtained results.

In order to further improve the efficiency, we have fabricated a three layer ITO/CuPc/CuPc:C_{60} (1:1)/C_{60}/Al cell on ITO substrate with mechanical+UV ozone+HCl treatment. Comparison between three layer and two layer structures is shown in Fig. 6. It can be observed that three layer cell exhibits significantly higher short circuit current and lower series resistance. The obtained cell parameters are: open circuit voltage $V_{oc}=0.2$ V, short circuit current density $I_{sc}=3.58$ mA/cm^2, fill factor FF=0.23, and $\eta=0.16\%$. It should be pointed out that our measurements have been performed on unencapsulated cells in air immediately after fabrication. While oxygen acts as a *p*-type dopant in phthalocyanines,[42,43] in C_{60} oxygen impurities act as carrier traps and increase the resistance of C_{60}.[26] Furthermore, it has been demonstrated that water molecules decrease surface conductivity of ZnPc layers.[44] Negative effects of oxygen and moisture are the most likely cause of the relatively low fill factor obtained in our work. Aging effects in air are very pronounced, indicating strong negative effects of atmosphere exposure. For example, resistance of a double layer cell fabricated on UV ozone treated substrate increases four times after one hour storage in air, while AM1 power conversion efficiency decreases by 2 orders of magnitude, which demonstrates strong effects of the air exposure.

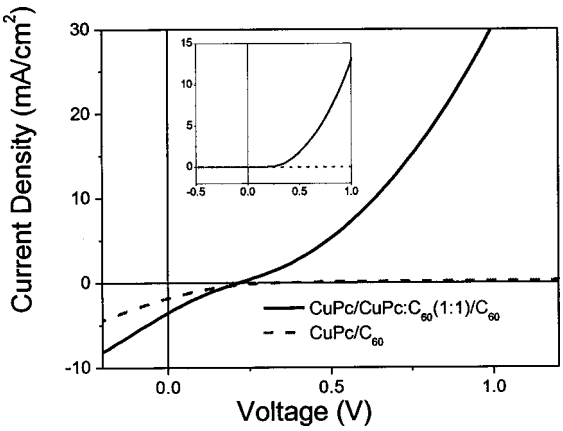

FIG. 6. The comparison between double layer ITO/CuPc/C_{60}/Al and three layer ITO/CuPc/CuPc:C_{60} (1:1)/C_{60}/Al cells under AM1 illumination. The inset shows $I-V$ characteristics in the dark.

IV. CONCLUSIONS

In this work, we investigated influence of surface treatments (UV ozone, UV ozone and HCl, mechanical and UV ozone and HCl) to the ITO properties (work function, carrier concentration and mobility, surface roughness, and morphology) and the performance of the solar cells fabricated on treated ITO substrates. We found that there is a complex relationship between ITO parameters and the solar cell performance. The optimal surface treatment (best result obtained for mechanical treatment followed by UV ozone and HCl) enables a 1 order of magnitude increase in the AM1 power conversion efficiency for CuPc/C_{60} heterojunction cell (0.09% for the best treatment compared to 0.008% for no treatment). Power conversion efficiency can further be increased by using a three layer structure, which results in 0.16% AM1 power conversion efficiency.

ACKNOWLEDGMENTS

This work has been supported by the RGC earmarked grant of Hong Kong (Project Nos. HKU 7096/00P, HKU 7075/01P, and HKU 7056/02E) and the University of Hong Kong University Research Committee seed funding grant. The authors would like to thank Professor K. Y. Chan from the Department of Chemistry, the University of Hong Kong and Dr. A. H. W. Ngan from the Department of Mechanical Engineering for performing the STM and AFM measurements, respectively.

[1] J. S. Kim, M. Granström, R. H. Friend, N. Johanson, W. R. Salaneck, and F. Cacialli, J. Appl. Phys. **84**, 6859 (1998).
[2] J. S. Kim, F. Cacialli, A. Cola, G. Gigli, and R. Cingolani, Synth. Met. **111–112**, 363 (2000).
[3] J. S. Kim, F. Cacialli, A. Cola, G. Gigli, and R. Cingolani, Appl. Phys. Lett. **75**, 19 (1999).
[4] J. S. Kim, R. H. Friend, and F. Cacialli, J. Appl. Phys. **86**, 2774 (1999).
[5] F. Nüesch, E. W. Forsythe, Q. T. Le, Y. Gao, and J. Rothberg, J. Appl. Phys. **87**, 7973 (2000).
[6] F. Nüesch, L. J. Rothberg, E. W. Forsythe, Q. T. Le, and Y. Gao, Appl. Phys. Lett. **74**, 880 (1999).
[7] F. Nüesch, K. Kamaras, and L. Zuppiroli, Chem. Phys. Lett. **283**, 194 (1998).
[8] M. Ishii, T. Mori, H. Fujikawa, S. Tokito, and Y. Taga, J. Lumin. **87–89**, 1165 (2000).
[9] D. J. Miliron, I. G. Hill, C. Shen, A. Khan, and J. Schwartz, J. Appl. Phys. **87**, 572 (2000).
[10] M. G. Mason, L. S. Hung, C. W. Tang, S. T. Lee, K. W. Wang, and M. Wang, J. Appl. Phys. **86**, 1688 (1999).
[11] S. Fujita, T. Sakamoto, K. Ueda, K. Ohta, and S. Fujita, Jpn. J. Appl. Phys., Part 1 **36**, 350 (1997).
[12] K. Sugiyama, H. Ishii, Y. Ouchi, and K. Seki, J. Appl. Phys. **87**, 295 (2000).
[13] S. K. So, W. K. Choi, C. H. Cheng, L. M. Leung, and C. F. Kwong, Appl. Phys. A: Mater. Sci. Process. **68**, 447 (1999).
[14] H. Peisert, T. Schwieger, M. Knupfer, M. S. Golden, and J. Fink, J. Appl. Phys. **88**, 1535 (2000).
[15] I-M. Chan, W.-C. Cheng, and F. C. Hong, Appl. Phys. Lett. **80**, 13 (2002).
[16] T. Osada, Th. Kugler, R. Bröms, and W. R. Salaneck, Synth. Met. **96**, 77 (1998).
[17] Th. Kugler, Å. Johansson, I. Dalsegg, U. Gelius, and W. R. Salaneck, Synth. Met. **91**, 143 (1997).
[18] A. B. Djurišić, T. W. Lau, C. Y. Kwong, W. L. Guo, Y. Bai, E. Herbert Li, and W. K. Chan, Proc. SPIE **4464**, 273 (2002).
[19] N. G. Park, M. Y. Kwak, B. O. Kim, O. K. Kwon, Y. K. Kim, B. You, T. W. Kim, and Y. S. Kim, Jpn. J. Appl. Phys., Part 1 **41**, 1523 (2002).
[20] F. Li, H. Tang, J. Shinar, O. Resto, and S. Z. Weisz, Appl. Phys. Lett. **70**, 2741 (1997).
[21] V. Christou, M. Etchells, O. Renault, P. J. Dobson, O. V. Salata, G. Beamson, and R. G. Egdell, J. Appl. Phys. **88**, 5180 (2000).
[22] H. Y. Yu, X. D. Feng, D. Grozea, Z. H. Lu, R. N. Sodhi, A.-M. Hor, and H. Aziz, Appl. Phys. Lett. **78**, 2595 (2001).
[23] Y.-H. Liau, N. F. Scherer, and K. Rhodes, J. Phys. Chem. B **105**, 3262 (2001).
[24] J. N. Barisci, R. Stella, G. M. Spinks, and G. G. Wallace, Synth. Met. **124**, 407 (2001).
[25] Q. T. Le, E. W. Forsythe, F. Nüesch, L. J. Rothberg, L. Yan, and Y. Gao, Thin Solid Films **363**, 42 (2000).
[26] Q. T. Le, F. Nüesch, L. J. Rothberg, E. W. Forsythe, and Y. Gao, Appl. Phys. Lett. **75**, 1357 (1999).
[27] P. Peumans and S. R. Forrest, Appl. Phys. Lett. **79**, 126 (2001).
[28] T. Stübinger and W. Brütting, J. Appl. Phys. **90**, 3632 (2001).
[29] M. Pfeiffer, A. Beyer, B. Plönings, A. Nollau, T. Fritz, K. Leo, D. Schlettwein, S. Hiller, and D. Wöhrle, Sol. Energy Mater. Sol. Cells **63**, 83 (2000).
[30] K. Murata, S. Ito, K. Takahashi, and B. M. Hoffman, Appl. Phys. Lett. **68**, 427 (1996).
[31] H. Yonehara and C. Pac, Thin Solid Films **278**, 108 (1996).
[32] A. A. Marchenko, V. V. Cherepanov, D. T. Tarashchenko, Z. I. Kazantseva, and A. G. Naumovets, Surf. Sci. **416**, 460 (1998).
[33] W. Bücker, J. Non-Cryst. Solids **18**, 11 (1975).
[34] M. Pfeiffer, A. Beyer, T. Fritz, and K. Leo, Appl. Phys. Lett. **73**, 3202 (1998).
[35] M. Rusu, A. Stanciu, V. Bulacovschi, G. G. Rusu, M. Bucescu, and G. I. Rusu, Thin Solid Films **326**, 256 (1998).
[36] R. W. Wright, Proc. Phys. Soc., London, Sect. A **64**, 350 (1951).
[37] K. Kishimoto and T. Koyanagi, J. Appl. Phys. **92**, 2544 (2002).
[38] M. Obaidul Hakim, J. Mater. Sci. **25**, 1455 (1990).
[39] D. L. Young, H. Moutinho, Y. Yan, and T. J. Coutts, J. Appl. Phys. **92**, 310 (2002).
[40] F. Nüesch, M. Carrara, M. Schaer, D. B. Romero, and L. Zuppiroli, Chem. Phys. Lett. **347**, 311 (2001).
[41] S. A. Jeglinski, O. Amir, X. Wei, Z. V. Vardeny, J. Shinar, T. Cerkvenik, W. Chen, and T. J. Barton, Appl. Phys. Lett. **67**, 3960 (1995).
[42] T. G. Abdel-Malik and R. M. Abdel-Latif, Thin Solid Films **286**, 277 (1996).
[43] H. R. Kerp and E. E. van Faassen, Chem. Phys. Lett. **332**, 5 (2000).
[44] H. R. Kerp and E. E. van Faassen, Sol. Energy Mater. Sol. Cells **63**, 15 (2001).