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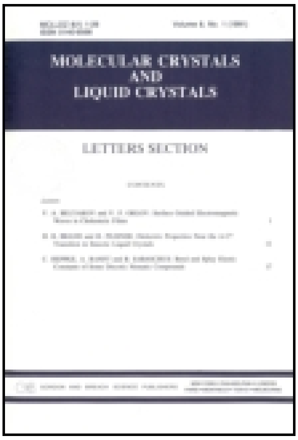

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A Comparative Study of the V_{OC} in CuPc and SubPc Organic Solar Cells

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A Comparative Study of the V_{OC} in CuPc and SubPc Organic Solar Cells

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The open-circuit voltage (V_{OC}) with respect to the reverse dark saturation current density in planar CuPc/C_{60} and non-planar boron subphthalocyanine chloride (SubPc)/C_{60} organic solar cell (OSCs) devices is compared in the present study. The fabricated OSCs devices were: ITO/CuPc/C_{60}/BCP(90Å)/Al(1000Å) and ITO/SubPc/C_{60}/BCP(90Å)/Al(1000Å) organic solar cells. We observed that the dark saturation current and the V_{OC} values vary in the CuPc/C_{60} solar cells, whereas almost no variation of the dark saturation current and V_{OC} values in SubPC/C_{60} solar cells occur. All SubPC devices show almost similar value of dark current. These differences may be attributed to the surface morphologies of planar CuPc and non-planar SubPC donor layers.

Keywords Dark current; open circuit voltage; organic; power conversion efficiency; solar

Introduction

In recent years, organic materials based solar cells to convert solar photon energy into electrical energy are acquiring the center stage, primarily due to the significantly reduced manufacturing costs and facile processing [1,2]. Substantial efforts to improve the key factors such as, power conversion efficiency (PCE) of organic solar cells (OSCs) have been made in recent days owing to their growing demand for the low cost power sources [3,4]. Recent reports show that the PCE is dependent on both photocurrent and photovoltage [5–8]. The open-circuit voltage (V_{OC}), one of the key parameters, is still a debatable issue in the OSCs. Until now, the models of V_{OC} based on the energy difference between the highest occupied molecular orbital (HOMO) or ionization potential of the donor and the lowest unoccupied molecular orbital (LUMO) or electron affinity of the acceptor materials [9], the choice of electrode materials [10], work function difference between the two electrodes [11–13], active layer thickness [14], light intensity and temperature dependent generation of free charge carriers have been considered [15]. Furthermore, the V_{OC} dependence on the various fabrication conditions, such as variation in morphology and packing density of

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*Address correspondence to Prof. Jang Hyuk Kwon and Ramchandra Pode, Department of Information Display and Department of Physics, Kyung Hee University, 1, Hoegi-dong, Dongdaemun-gu, Seoul, 130-701, Korea. Tel.: +(82) 2-961-0948; Fax: +(82) 2-968-6924. E-mail: jhkwon@khu.ac.kr or rbpode@khu.ac.kr the active layer, [14,16,17], and buffer layers at contacts [18,19] have also been reported. Although several factors account for the V_{OC} including the HOMO-LUMO energy level difference between the donor and acceptor, the adequate information is still required to understand the V_{OC} dependence in these devices. Indeed extensive understanding of the V_{OC} is desirable for further development of new materials. Recently, there has been a focus on the role of dark saturation current density in controlling the V_{OC} in various materials [16], because of weak intermolecular interactions, which leads to a low dark current resulting in a high V_{OC}. The magnitude of the dark saturation current density depends on material properties determining the carrier generation, recombination rate, etc. Furthermore, Placencia et al. have demonstrated the Voc dependence on the reverse saturation current in the annealed TiOPc/C60 solar cells [20]. Potscavage et al. have predicted the reduction of dark saturation current in planer pentacene/C60 heterojunctions solar cell and increase of the HOMO value of donor materials always improves the V_{OC} [21]. All these previous studies have shown the logarithmic dependence of V_{OC} on the dark saturation current based on this empirical relation [16].

$$Voc = \frac{nKT}{q} \ln\left(\frac{Jsc}{Jso}\right) + \frac{\Delta\, E_{DA}}{2q}$$

where J_{SC} is the short-circuit current, J_{SO} is the reverse saturation dark current, n is ideality factor, ΔE_{DA} is the thermal activation energy for charge separation at the donor-acceptor interface. This model of V_{OC} based on the reduction of reverse saturation current density has been proven for several donor materials.

In the present study, we have studied the role of dark saturation current density in controlling the V_{OC} and compared the dependency of open-circuit voltage (V_{OC}) with respect to the reverse dark saturation current density in planar CuPc/C60 and non-planar boron subphthalocyanine chloride (SubPc)/C60 organic solar cell devices. Earlier a good performance in the SubPc/C60 OSC device was demonstrated [22] but detail information about its Voc dependence in relation to the reverse saturation current is still lacking. Here we have shown that the Voc values vary with the dark saturation current in CuPc/C60 solar cells, whereas almost no variation in the dark saturation current in SubPc/C60 solar cells occurs. These differences may be attributed to the surface morphologies of planar CuPc and non-planar SubPc donor layers.

Experimental

To fabricate organic photovoltaic devices (OPV), a clean glass substrate precoated with a 150-nm ITO layer with a sheet resistance 15 Ohm/square was used and the substrate size was 2 cm × 2 cm. The patterns of 2 × 2 mm2 were formed by photolithography and wet etching processes. The glass substrate was cleaned by sonification in an isopropyl alcohol, acetone, and methanol, rinsed in deionized water, and finally irradiated in a UV-ozone chamber. The ozone gas was generated using UV light to excite the oxygen in the air inside the chamber. The organic materials CuPc, SubPc (Lumtech)), buckminsterfullerene (C60 (Alfa Aesar) and C70 (Lumtech)), and bathocuproine (BCP) (Lumtech) were sequentially deposited onto ITO. All the organic materials were deposited by the vacuum evaporation technique under a pressure of $\sim 3.0 \times 10^{-7}$ Torr with a deposition rate of ~ 0.5 Å/s. Subsequently, Al (100 nm) with a deposition rate of ~2.5 Å/s was deposited in vacuum chamber without breaking the vacuum and used as a cathode. The current density–voltage (J–V) characteristics of the

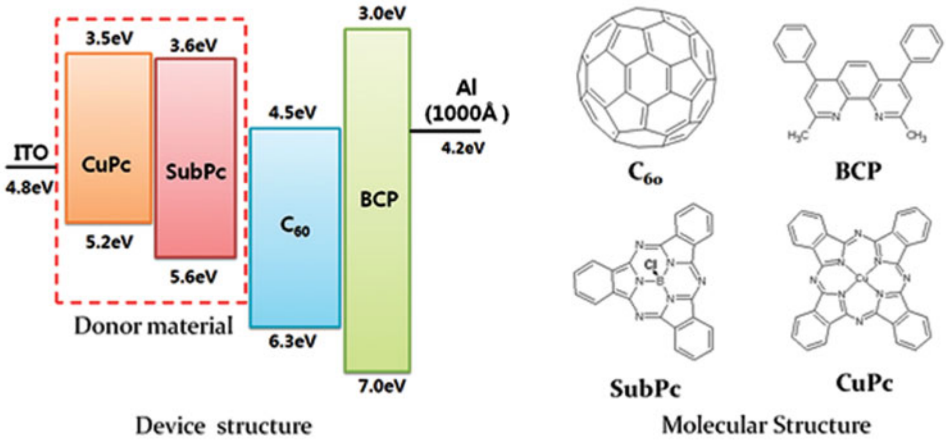


Figure 1. Device structure of fabricated solar cell devices.

fabricated devices were measured using a computer controlled Keithley 2400 source-meter, in the dark and under illumination intensity of 100 mW/cm^2 with calibrated AM 1.5G sun simulator (Asahi Japan, Model HAL-302) in ambient conditions. A xenon light source was used to give simulated irradiance of 100 mW/cm^2 (equivalent to an AM1.5G irradiation) at the surface of the device. The J-V characteristic measurements under illumination were carried out in a dark chamber with a window slit of 5 mm^2 area for illumination.

The device structure of fabricated devices is shown Fig. 1. The fabricated OPV devices have a structure:

ITO/CuPc(xÅ)/C60(yÅ)/BCP(90Å)/Al(1000Å) and
ITO/SubPc(xÅ)/C60(yÅ)/BCP(90Å)/Al(1000Å)

where x and y are thicknesses of donor (CuPc or SuPc) and acceptor (C60), respectively.

Results and Discussion

The fabricated CuPc/C60 devices are summarized in Table 1. The J-V characteristics of fabricated devices 1 to 6 were measured under the dark and illumination condition 1.5G AM, 100 mW/cm^2 sun simulator to investigate the factors controlling the V_{OC}. Figures 2(a)

Table 1. The fabricated CuPc/C60 organic photovoltaic devices

Device	ITO Thickness (Å)	CuPc Thickness (Å)	C60 Thickness (Å)	BCP Thickness (Å)	Al Thickness (Å)
1	1500	175	425	60	1000
2	1500	175	450	60	1000
3	1500	175	375	60	1000
4	1500	200	375	60	1000
5	1500	200	400	60	1000
6	1500	200	300	100	1000

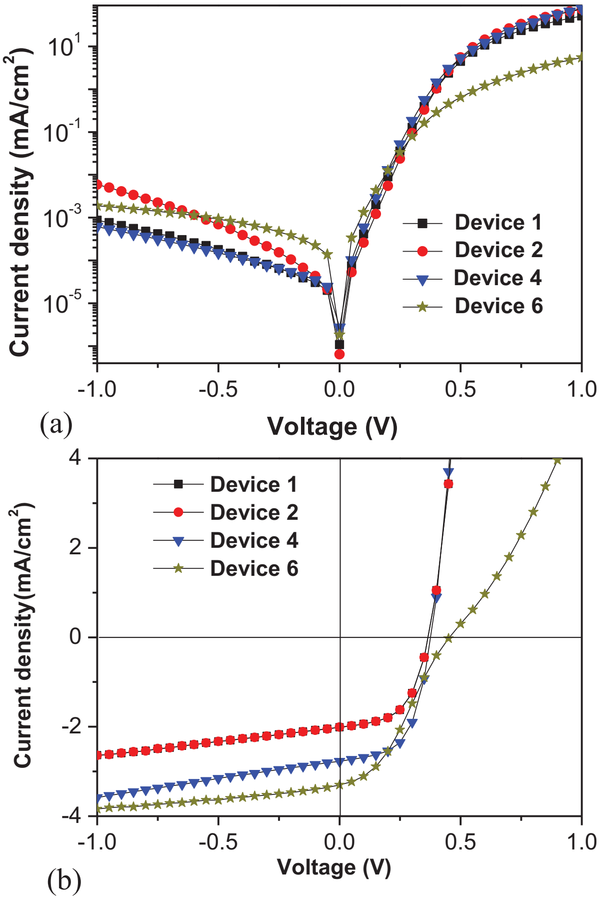


Figure 2. (a) J-V characteristics of CuPc/C60 solar cells under the dark condition, (b) J-V characteristics of CuPc/C60 solar cells under the illumination condition 1.5G AM, 100 mW/cm2.

and (b) show the photovoltaic characteristics of the described devices. Table 2 lists key factors such as V_{OC}, Jsc and power conversion efficiency, η, in these devices. At first, the CuPc thickness was fixed to 175Å and the C60 thickness was varied from 375 to 450Å. Subsequently, the CuPc thickness was increased to 200Å and the C60 thickness was varied

Table 2. Parameters and device performances of CuPc/C60 solar cells

Device/ parameters	1	2	3	4	5	6
CuPc thickness (Å)	175	175	175	200	200	200
C60 thickness (Å)	425	450	375	375	400	300
V_{OC} (V)	0.36	0.36	0.39	0.37	0.3	0.45
Jsc (mA/cm^2)	2.01	2.01	2.68	2.77	2.8	3.30
F.F.	55.27	55.27	56.74	56.45	53.5	34.46
Efficiency, η (%)	0.40	0.40	0.59	0.58	0.56	0.51

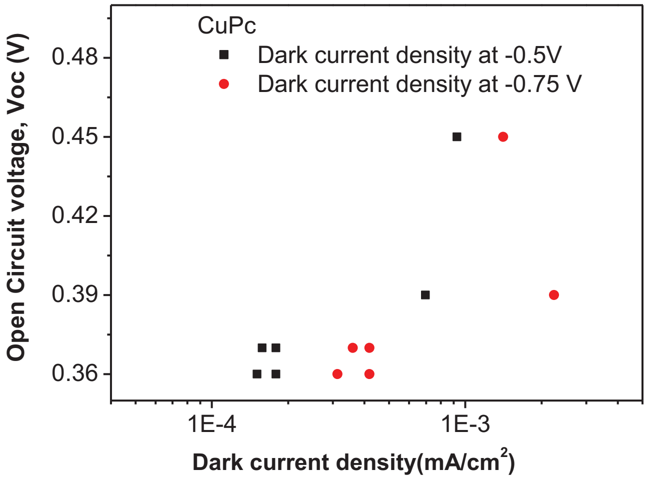


Figure 3. Variation of open circuit voltage, V_{OC} with the dark current density in CuPc/C60 solar cells devices.

to optimize the device performance. The optimum values (FF = 56.74 and h = 0.59%) are reported in device 3 with CuPc = 175Å and C60 = 375Å (Table 2). Figure 3 shows the relation between the open-circuit voltage and the dark current density at applied voltage values of −0.5 and −0.75 V. The Voc is varying with the dark saturation current in planar CuPc/C60 and results are in agreement with the earlier reported results in organic solar cells [9].

To investigate the validity of our argument in other type of phthalocyanine such as nonplanar SubPc, the SubPc/C60 solar cells were fabricated and studied. At first, the SubPc donor layer thickness was varied from 85 to 130Å while C60 acceptor layer was fixed to 315Å. With the optimization of SubPc donor layer thickness to 115Å, the C60 acceptor layer thickness was changed from 315 to 275Å. The fabricated SubPc/C60 devices are summarized in Table 3.

Figures 4(a) and (b) show the photovoltaic characteristics of the described devices under the dark and illumination intensity of 100 mW/cm^2 with a calibrated AM 1.5G sun simulator. Table 4 lists the J-V characteristic of all the devices. The optimized values of

Table 3. The fabricated SubPc/C60 organic photovoltaic devices

Device	ITO Thickness (Å)	SubPc Thickness (Å)	C60 Thickness (Å)	BCP Thickness (Å)	Al Thickness (Å)
1	1500	85	315	90	1000
2	1500	100	315	90	1000
3	1500	115	315	90	1000
4	1500	130	315	90	1000
5	1500	115	340	90	1000
6	1500	115	290	90	1000
7	1500	115	275	90	1000

Table 4. Parameters and device performances of SubPc/C60 solar cells

Device/ parameters	1	2	3	4	5	6	7
SubPc thickness (Å)	85	100	115	130	115	115	115
C60 thickness (Å)	315	315	315	315	340	290	275
V_{OC} (V)	0.94	0.95	0.98	0.95	0.95	0.94	0.93
Jsc (mA/cm^2)	3.94	4.37	4.53	4.32	4.31	4.67	4.14
F.F.	51.18	52.27	54.48	51.69	53.79	52.77	53.15
Efficiency, η (%)	1.89	2.16	2.41	2.11	2.21	2.31	2.05

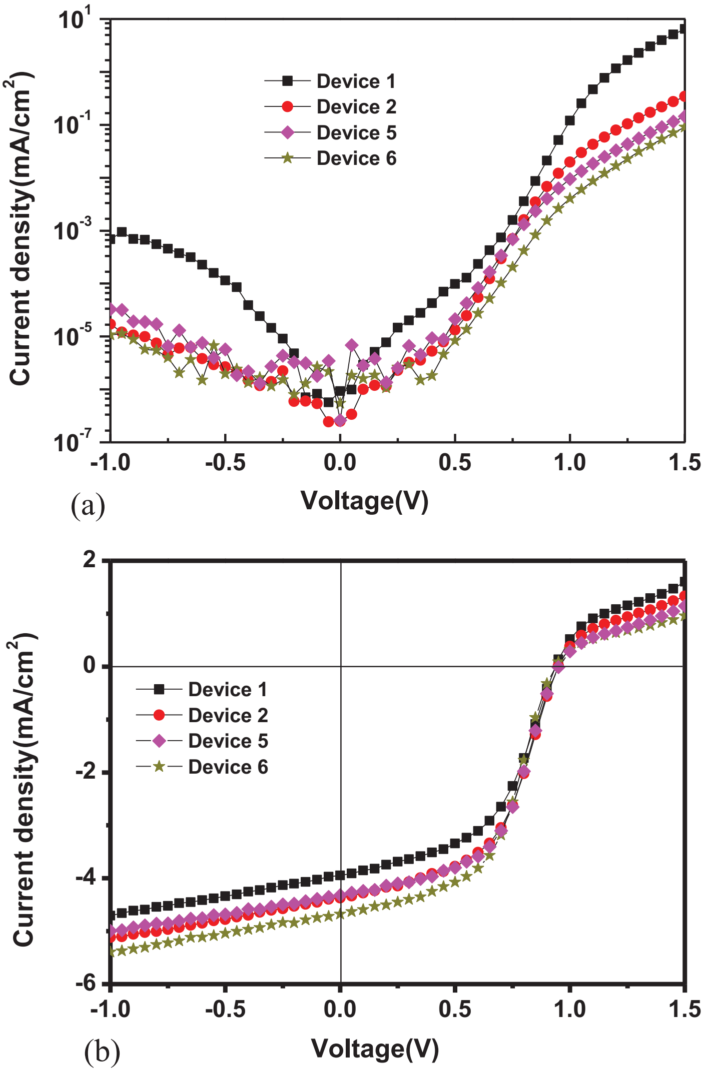


Figure 4. (a) J-V characteristics of SubPc/C60 solar cells under the dark condition, (b) J-V characteristics of SubPc/C60 solar cells from 1 to 7 under the illumination condition 1.5G AM, 100 mW/cm^2.

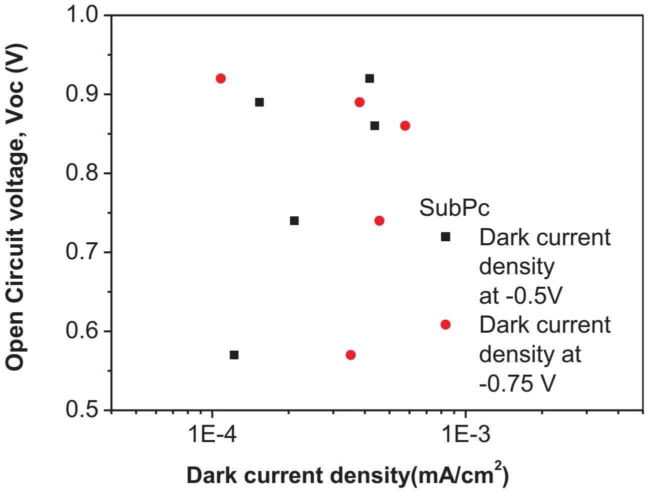


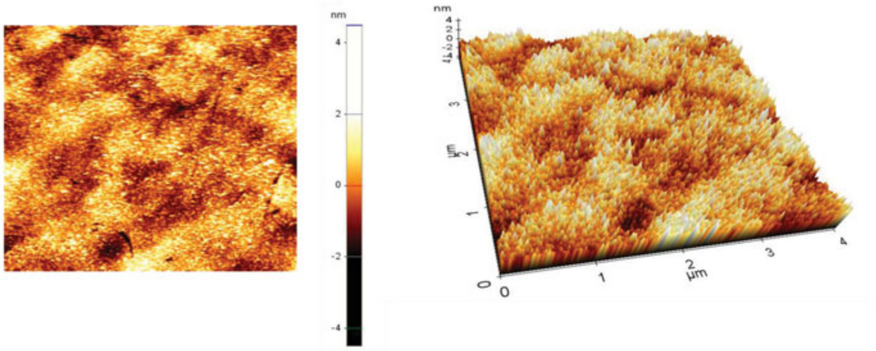
Figure 5. Variation of open circuit voltage, VOC with the dark current density in 1 to 7 SubPc/C60 solar cells devices.

FF= 54.48 and power conversion efficiency $\eta = 2.41$ are observed in SubPc(115Å)/C60(315Å)/ solar cell device. The optimum value of V_{OC} at 0.98 V is also obtained in this device. Further improvement of SubPc thickness to 130Å deteriorates the device performance (Table 4, Device 4). Besides, any change in the C60 donor thickness from 315Å seems to be also not facilitating to improve the device performance (Table 4).

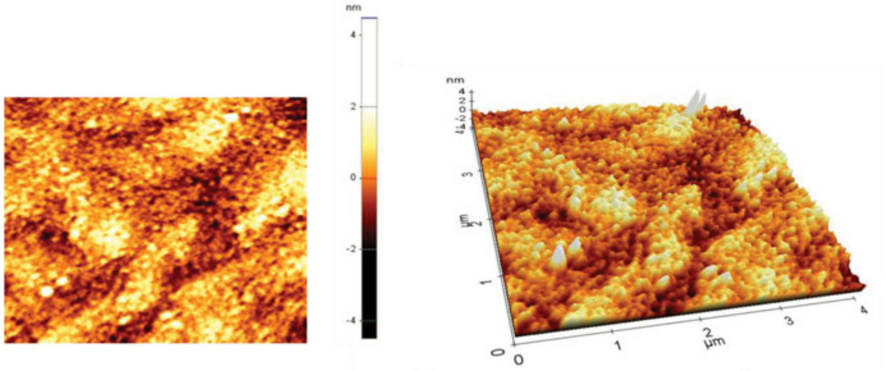
Figure 5 shows the relation between the open-circuit voltage and the dark current density at applied voltage values of −0.5 and −0.75 V. The V_{OC} value increases from 0.93 to 0.98 V without much change in the dark current value. It is clearly seen from the results that the dark current (or leakage current) in the voltage range from 0.0 to −1.0V is not changing much in all these devices. Results indicate that the V_{OC} is independent of the dark current in non-planar SubPc solar cells. Similar type of findings were discussed in amorphous silicon p-i-n solar cells where no correlation between Voc and dark current was noticed [23].

Results of Figs. 3 and 5 gave experimental evidences of V_{OC} dependence on the dark saturation current. In all SubPC/C60 devices, the value of dark saturation current is contributing by the same amount to the V_{OC} values as it is all most same in all these devices and V_{OC} is uniformly increasing due to other factors. Whereas, the degree of dark saturation current contribution to the V_{OC} in CuPc/C60 devices varies as it is not the same in these devices which is also reflected in scattered (or random) behavior of V_{OC} as displayed in Fig. 3. These differences in dark saturation current contributions to V_{OC} in CuPc/C60 and SubPc/C60 devices seem to do something with the morphologies of CuPc and SubPc films.

To understand the exact origin of the observed results, we performed surface morphology studies of CuPc and SubPc films deposited ITO glass substrate. Figure 6 shows the AFM images of 130Å thick CuPc and SubPc films deposited on ITO glass. The CuPc film shows the surface roughness value of 7.61Å, while the SubPc film exhibits a smooth morphology without needle like structure. The measured surface roughness RMS value of 6.79Å in this film indicates that the morphology of SubPc film is uniform and smooth and is within acceptable limit in organic devices. The formation of uniform amorphous



(a) ITO / CuPc (130Å), RMS value : 7.61 Å



(b) ITO / SubPc (130Å), RMS value : 6.79 Å

Figure 6. AFM images of 130 Å thick CuPc (a) and SubPc (b) films deposited on ITO glass.

SubPc film favors no variation in the leakage current. Obviously, the observed variation in the V_{OC} values in fabricated SubPc/C60 devices is certainly not related to the leakage current.

Since the optical as well as the electrical properties of the molecular material are highly anisotropic, the knowledge of film morphologies is essential for successful application. Surface morphology of CuPc depends on the deposition conditions. The CuPc film surface of amorphous structure is more porous [24]. Earlier, small islands representing columnar growth of the crystallites in the CuPc thin films deposited at room temperature (295 K) was reported [25,26]. Whereas, it was shown that the SubPc forms a smooth and amorphous film with considerably lower mobility of the order of 10^{-5} $cm^2/(V.s)$ [27] which is not the case with the planar CuPc. For multijunction solar cells, the thin and smooth films absorbing over a limited spectral window are desirable [28]. The low value of dark saturation current in smooth and uniform amorphous film is expected. However, the annealing of donor film enhances the dark current due to the formation of ordered crystallites, which help to percolate electrons via the large crystallites towards the electron-collecting electrodes [17]. Since almost similar dark current value was observed in all the fabricated devices, we have investigated the surface morphology of SubPc films in order to establish that the smooth and uniform amorphous film of SubPc is formed in these devices.

Conclusions

In this paper we have studied the V_{OC} in planar CuPc/C60 and non-planar SubPc/C60 solar cells. We have observed that the degree of contribution of the dark saturation current density to the V_{OC} values in case of all non planer SubPc/C60 organic solar cells is same and does not hold any relationship, and V_{OC} varies uniformly due to other factors, different from CuPc/C60 solar cells. The observed difference may be attributed to the surface morphology of donor films. In conclusion, the V_{OC} value and hence efficiency in fabricated solar cells is significantly dependent on the surface morphology of the donor film.

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