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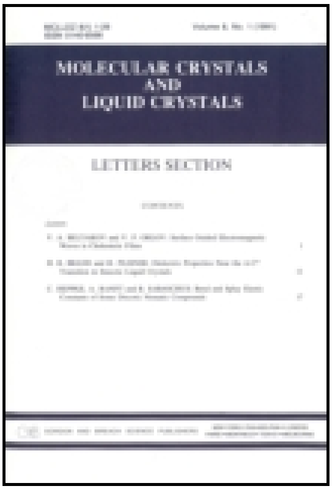

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The Effect of a Substrate on the Current-vs-Voltage Characteristics of Thin-Film Sandwich Structures Based on Buckminsterfullerene

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The Effect of a Substrate on the Current-*vs*-Voltage Characteristics of Thin-Film Sandwich Structures Based on Buckminsterfullerene

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*We analyze the current-*vs*-voltage (*J-V*) characteristics of ITO/C_{60}/Al sandwich cells, where ITO is the double indium tin oxide, C_{60} is the buckminsterfullerene and Al is the thermally evaporated top aluminum electrode. These cells were obtained on either glass/ITO or polyethyleneterephthalate/ITO substrates (or, optionally, on glass/ZnO substrates) in a parallel process under identical conditions. However, the *J-V* dependences in each series behave very differently. The results are discussed in terms of the migration of admixtures from a bulk substrate material toward the top metallic electrode, thus modifying the photovoltaic properties of cells.*

Introduction

Buckminsterfullerene C_{60} is the most widely used acceptor material in organic-based photovoltaic cells (OPVCs) made from low-molecular weight compounds. In a typical OPVC with planar or bulk heterojunction, it adjoins the *p*-type (donor) layer and thermally evaporated aluminum, since this metal is believed to form a quasi-Ohmic contact with *n*-type fullerenes [1–4]. The insertion of an additional ultrathin layer of a certain organic (*e.g.,* bathocuproine, Alq3) or inorganic (*e.g.*, LiF, metals) material at the C_{60}/Al interface improves the efficiency of devices [4–13]. Simultaneously, more than one reason appear for such an improvement. Some are connected with the desired "physical" effects: the interlayer acts as an exciton blocker or optical spacer, or both [8]. The others are assigned to the inhibition of unwanted "chemical" effects, like the interaction of metal atoms with the intact fullerene surface, or the diffusion of a metal from the top electrode (cathode) toward the bulk of a cell [2, 4–6, 9, 10]. Meanwhile, the role of the substrate material underlying the electrode, as a source of oppositely migrating admixtures, is much less elucidated. This is likely because the substrate itself is located far from the C_{60}/cathode interface and is separated by the donor layer (and, frequently, also by the bottom organic or oxide buffer interlayer) and by an inorganic anode, typically a magnetron-sputtered double indium-tin oxide In_2O_3:SnO_2, ITO.

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This work addresses the question of how the current-*vs*-voltage (*J*-*V*) characteristics of OPVCs are affected by the substrate material. Here, the C_{60}/Al interface (intact or inserted with *tris*(8-hydroxyquinolinato) aluminum Alq3) in single-layer sandwich-type cells employing the C_{60} semiconductor is the same, while the substrate material (beneath the ITO anode) changes.

Experimental

The samples were fabricated and tested as described earlier [13]. For the sake of comparison, OPVCs with SubPc/C_{60} heterojunction were also made, *i.e.*, they differ by the presence of a SubPc layer (SubPc is boron chloride subphthalocyanine, the well-known *p*-type material). ITO coated glass slides (70-100 Ω/sq) or ITO covered polyethyleneterephthalate, PET pieces (100 Ω/sq) were used as substrates, all purchased from Aldrich. As claimed by the supplier, the thicknesses of ITO layers were 15–30 and 75 nm, respectively. The substrates were etched and cleaned by the routine procedures [10, 13]. In some cases, we used glass substrates covered with a boron-doped zinc oxide layer (ZnO:B) using a low-pressure chemical vapor deposition process (LPCVD, Oerlikon). This material serves as a transparent contact in commercial silicon-based solar modules. The polycrystalline ZnO layer was etched in argon plasma at a pressure of about 10 mbar during 17 min in order to smooth the surface, so that the initial root-mean square roughness of about 60 nm has decreased by half.

Fullerene and top aluminum contact were thermally evaporated using a vacuum evaporation system VUP-5M at a residual pressure of 10^{-5} Torr. A special care was taken on maintaining the identical conditions of the deposition process for all samples. The thickness of C_{60} was 75 nm on the glass/ITO or PET/ITO substrates. On the glass/ZnO substrate, the thickness of C_{60} was 120 nm since the still high surface roughness of ZnO leads to a short circuiting in thinner C_{60} films after the deposition of the top electrode. The top Al layer thickness was ~70–80 nm, and the effective device area was ~0.03 cm^2.

All (photo-)electrical experiments were carried out on the cells transferred into a shielded measuring box filled with pure argon gas (99.99%) immediately after the fabrication, at room temperature, in strictly the same instrumental setup. Bias was applied to the transparent (bottom) electrode, whereas the top metallic electrode was always grounded.

Results and Discussion

Figure 1 demonstrates that the *J*-*V* dependences are affected by the underlying substrate material. No rectification is observed for ITO/C_{60}/Al cells on glass substrates, the curves are symmetric and close to linearity, both in dark and under illumination. In contrast, the same cells on PET substrates act as diodes: under the forward bias, the current density is by 4×10^1 times greater than that under the reverse bias (at $U = \pm0.5$ V) and grows exponentially with applied voltage.

When the light is ON, the current density in the III quadrant strongly increases (see, Fig. 1). Irrespective of whether the substrate material is glass or PET, some little displacement of the *J*-*V* curves from the point of origin toward the II quadrant is seen under illumination, as shown in Fig. 2 in more details.

As follows from Fig. 1, for ITO/C_{60}/Al cells on glass substrates, both the top and bottom contacts appear to be nearly Ohmic. This is in accordance with Refs. [1, 3, 4, 14], where C_{60}/Al contact is regarded as quasi-Ohmic, if the cells were not kept in air

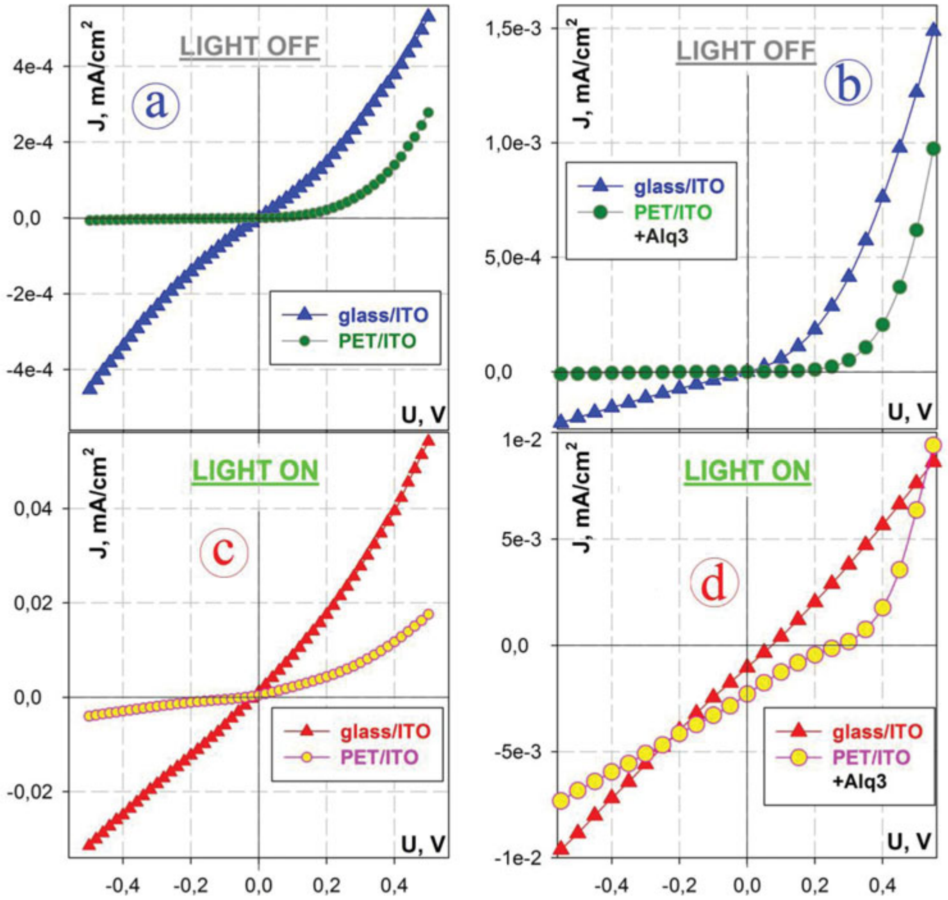

Figure 1. **(a—d).** *J-V* plots measured in dark (**a—b**) and under illuminations (**c—d**) for ITO/C_{60}/Al cells without (**a—c**) and with (**b—d**) 7 nm buffer Alq3 layer.

intentionally. Simultaneously, this is in conflict with Refs. [2, 5, 6, 9–11], where the C_{60}/Al interface is considered as a more complicated case (rectifying, barrier, or composite).

It should be noted that, despite numerous publications, the actual structure of the C_{60}/Al interface is not fully understood [10]. Hot vaporized Al atoms landing on the C_{60} surface may cause the formation of a carbide-like interlayer [6, 10] or interface dipole [2, 11, 15], which increases the work function of Al or shifts the vacuum level [2, 9]. Furthermore, the conflicting results are obviously due to circumstances in the sample history. Particularly, the admission of oxygen (and water) molecules is very critical, because the oxide barrier layer AlO_x can readily be formed at the C_{60}/Al interface. As shown recently [12], the lateral diffusion of oxygen in fullerene-based cells in dark is quite fast. Moreover, it accelerates under external irradiation and leads to irreversible reactions. Therefore, in the samples fabricated and tested with interruption of oxygen-free conditions (ultra-high vacuum or high-purity glove box), a barrier-free C_{60}/Al interface is hardly possible.

Views on the second, ITO/C_{60} interface are opposite, too. According to Refs. [4, 15], ITO is a Schottky contact to fullerene, the photogenerated excitons dissociate due

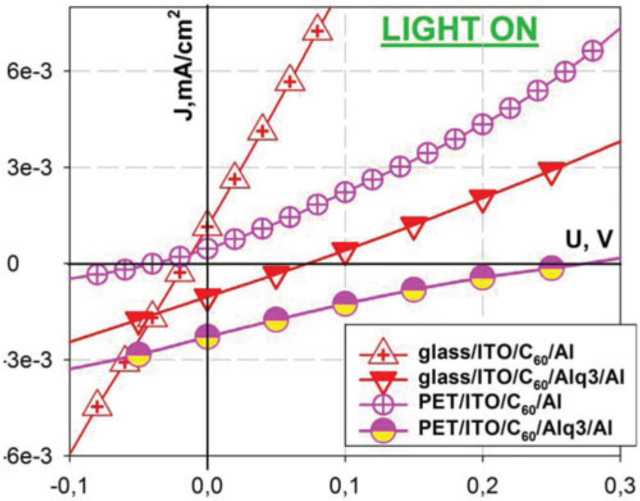

Figure 2. I and IV quadrants of *J-V* plot for the cells under illumination.

to the built-in potential at this interface [2]. According to Refs. [11, 14–16], there is no or little barrier between fullerenes and ITO. Hence, the quasi-Ohmic behavior should be observed.

Summarizing the published data, there is no established meaning on the photoelectrical properties of both interfaces. Even the direction of rectification in dark does not coincide in various works. In addition, the polarity of the photovoltage in the single-layer cells, where C_{60} is interfaced with Al and another electrode (ITO, Au), can be changed by the incident light intensity or by applying external bias [2, 3] (not revealed for the phthalocyanine/Al interface).

The work function range of ITO depends on the pretreatment, manufacturing process, *etc*. and lies in the range of 4.5–5.1 eV. The energy levels of C_{60} are reported between 6.2–6.4 eV for the ionization potential and 3.6–4.1 eV for the electron affinity. The work function of Al is about 4.2–4.3 eV, but as said above, this value is most probably irrelevant for the real C_{60}/Al interface. For instance, the value as high as 5.2 eV is used in Refs [2, 9]. So, the construction of a relevant diagram depicting a mutual arrangement of energy levels in such cell becomes problematic. Presumably, the equivalent scheme of the ITO/C_{60}/Al heterostructure is a superposition of two, top and bottom, low-barrier diodes. These diodes may work oppositely, *i.e.*, set off the effect (including photovoltaic) of each other. Under certain conditions or due to a modification (*e.g.*, by an interlayer), one of them turns into an injecting contact, and the cell is getting asymmetric.

The appearance of rectification in Cu/C_{60}/Al cells was observed in [9] after the annealing of the completed device at 120°C either in vacuum or in air. This was assigned to the efficient electron injection from the Cu/C_{60} contact that became Ohmic in the annealed device, in contrast to the rectified Cu/C_{60} contact in the device before a heat treatment. The C_{60}/Al contact remains rectifying (in varying degrees). Authors used different substrates for the device fabrication (Si, glass, and polymer polysterin), and the devices showed similar characteristics [9].

In our case, however, the rectification appears if the substrate material, not electrode, was changed, without heat (or other type) treatment. The work function of ITO sputtered on glass is only 0.2 ± 0.1 eV higher, so that the interface dipole of the same magnitude may be formed [17]. Its absence is unlikely to cause diode characteristics in ITO/C_{60}/Al cells on PET (Fig. 1). Another, more likely reason is a different chemical composition of the substrate. From Ref. [18], the glass/ITO surface is more affected by air contamination, though the ratio Sn/In remains constant in both substrates. Differences are in the presence of a larger amount of $In(OH)_3$, probably as an amorphous species, in ITO films on glass and in increased amount of O^{2-} ions in ITO films on PET. Migration of vacancies and ions (mainly oxygen) is possible in the ITO layer [18]. So, the diffusion of impurities in working devices from (or through) ITO may be different for two types of bulk substrate materials.

To verify which interface is responsible for rectification, the insulating Alq3 interlayer (bandgap 2.9-3.2 eV [5, 11]) was inserted between C_{60} and Al. Now, the cells on both glass and PET substrates demonstrate diode properties (Fig. 1). On glass, the rectification is poorer: under the forward bias, the dark current density is only by 6 times greater than that under the reverse bias (at $U = \pm 0.5$ V). On PET, this ratio is 7×10^1. When the light is OFF, the current density under the forward bias increases by a factor of three in both cases with respect to the cells without Alq3 ($U>0.5$ V). Notably, the current density under the reverse bias is lower. Taking into account that the direction of rectification does not change, one can assume that the conductivity in our cells is limited by the top interface C_{60}/Al.

Another important feature is the appearance of short circuit current J_{sc} and open circuit voltage U_{oc} in ITO/C_{60}/Alq3/Al cells (see, Fig. 2). Small values of J_{sc} would be explained by the C_{60} layer thickness (exciton diffusion length in C_{60} is 10-40 nm) and/or by the optical screening. For the cells on PET, U_{oc} is 0.26 V. It is known that the insertion of an interlayer between fullerene and a thermally evaporated metal can substantially modify the structure of the interface and the built-in field in devices [4-13]. Moreover, the insertion of a modification layer may enhance the exciton dissociation at the interface [11].

Next, we examined what happens if ITO is substituted by another transparent conductive oxide ZnO (Fig. 3). Although the intrinsic absorbance of ZnO partly suppresses the light penetration to C_{60} at wavelengths shorter than 400 nm, this material provides a negligible energy barrier for electrons at the interface with fullerene [7] (work function of ZnO is smaller than that of ITO). As follows from Fig. 3, the *J-V* dependences for cells on the glass/ZnO substrate are strongly asymmetric. The current densities in the forward bias direction are more than one order of magnitude higher as compared to the cells with ITO bottom contact (*cf.,* Fig. 1). The rectification ratio at 0.5 V reaches 9×10^1 and 6×10^2 in the cells with and without Alq3 layer, respectively, with the current densities in the reverse bias direction being smaller than those in cells on glass/ITO. Consequently, the serial resistance due to a barrier at the conductive oxide/fullerene interface is lower in the cells with the ZnO bottom electrode. Importantly, the insertion of the Alq3 layer results in the same trend for the illuminated cells, as in their ITO/C_{60}/Al analogs: the *J-V* curve slightly shifts down from the point of origin, as seen from Fig. 3. The shift amplitude is very small, probably due to highly increased current densities in the cells on ZnO. Nevertheless, it is fully consistent with the assumption on the controlling role of the top C_{60}/Al interface in the photovoltaic effect.

As known, fullerene can easily be doped [4, 6, 9, 11], which tunes its conducting and interfacial properties. If the arrival of admixtures from the bulk substrate is admitted, they will dope C_{60} in different ways when coming from glass and from PET. Our preliminary data obtained by secondary ions mass spectrometry with depth profiling display the different

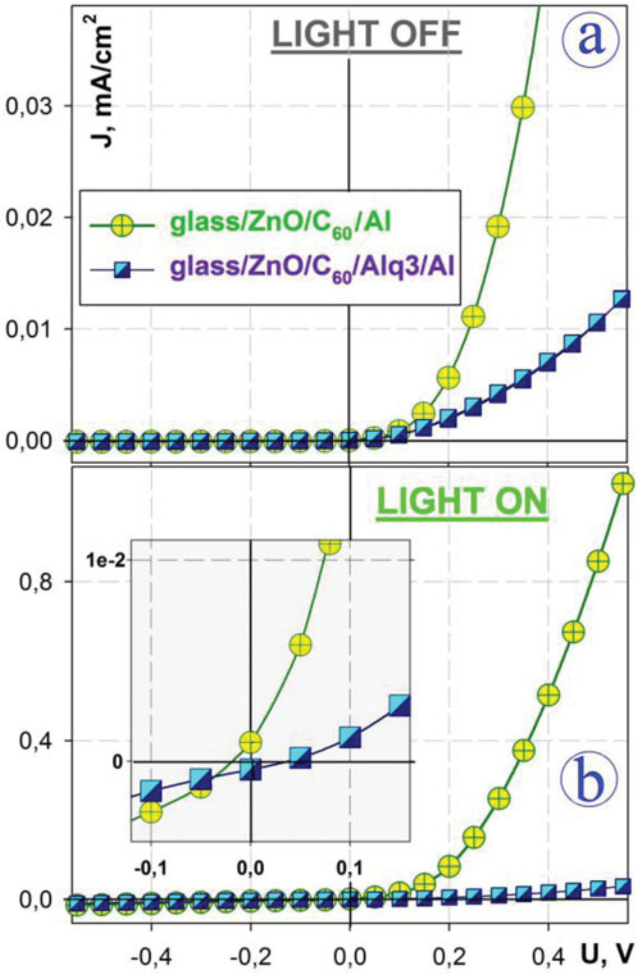

Figure 3. **(a, b).** *J*-*V* plots for the cells on glass/ZnO substrates in dark (**a**) and under illumination (**b**), zoomed area at the point of origin is given in inset.

chemical compositions of uppermost C_{60} layers, in a vicinity of the Al contact. This means that some species may diffuse from the bulk substrate, through ITO and fullerene, up to the C_{60}/Al interface and alter its properties (to be published).

Finally, OPVCs with planar (not optimized) *p*-SubPc/*n*-C60 heterojunction were tested. As expected, the diode quality of such cells is much better, and the photovoltaic effect is much more pronounced (Fig. 4). Without Alq3 layer, the *J*-*V* plots suffer from the well-known "kink" effect caused by parasitic resistances in thin-film devices (not shown here). With inserted Alq3 interlayer, J_{sc} remains weakly affected, but U_{oc} increases by 0.2 V in the cells on PET, as seen from Fig. 4. Here, the ITO/C_{60} interface is replaced by the ITO/SubPc interface, which is inactive, and the charge separation basically occurs at the SubPc/C_{60} interface. The advantage of the PET substrate for the photovoltaic activity of a cell, however, holds. Again, this indirectly points to the assisting role of a (second) diode describing the C_{60}/Alq3/Al interface.

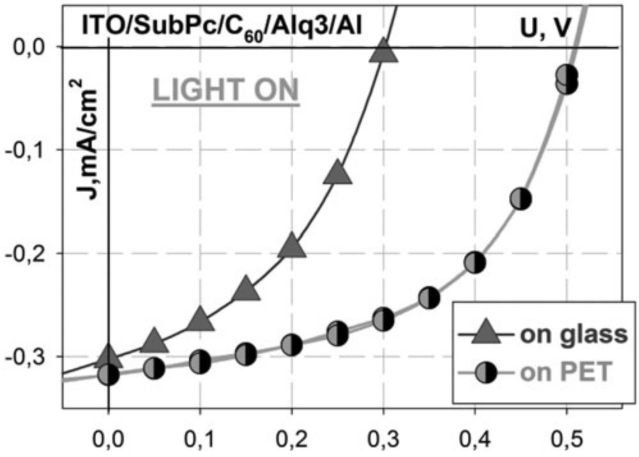

Figure 4. *J*-*V* plots for the heterojunction based cells under illumination.

Concluding Remarks

Analyzing the obtained results, we conclude that the equivalent scheme of a multilayer OPVC, based on a planar donor/acceptor heterojunction, comprising two or more diodes seems to be more adequate (see, *e.g.*, [5]). In this scheme, the properties of the diode related to the top (acceptor/metal) interface depend on the choice of a bulk substrate material, from which various chemical species (through the basic C_{60} layer) reach the top interface. This diode may have its own photovoltaic activity. For instance, in the cells on the glass substrate, it is "back-to-back" connected with respect to the main heterojunction diode of OPVC, thus worsening the overall photovoltaic efficiency. By contrast, on the PET substrates, the synergistic effect is realized, similarly to the tandem OPVC.

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