

## Reversal of rectification in fullerene-based devices



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### ABSTRACT

Model Al/C<sub>60</sub>/ITO sandwich devices were fabricated, where Al is a magnetron sputtered aluminum layer (top electrode); C<sub>60</sub> is a buckminsterfullerene layer routinely deposited by thermal evaporation in vacuum; and ITO is an indium tin oxide layer (bottom electrode). These devices demonstrate weak rectification in the dark and almost negligible photovoltaic activity under illumination, if polyethyleneterephthalate (PET) is used as substrate. If the substrate is glass, inversion of rectification occurs, accompanied by a rather more pronounced photovoltaic effect (in the reverse direction, too) than in their Al/C<sub>60</sub>/ITO/PET counterparts. Secondary ion mass spectroscopy (SIMS) with depth-profiling suggests that this effect is associated with the differences in the chemical composition of the top Al/C<sub>60</sub> interface in devices on PET and on glass. Such differences result from migration of admixtures from the substrate towards the top electrode. Since (photo)electrical properties of the devices reflect the dominating contribution of one of the two interfaces (top Al/C<sub>60</sub> and bottom C<sub>60</sub>/ITO), rectification can be reversed by amending either interface. This fact is to be taken into account when comparing efficiency of multilayer photovoltaic cells (e.g., with a heterojunction) on different substrates.

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## 1. Introduction

Fullerenes are the most frequently used n-type layers in functional organic-based and hybrid heterostructures, such as photovoltaic cells [1–15] or field-effect transistors [16,17]. And still, there is not enough reliable information on the actual structure of an interface between the fullerene layer and the low work function metallic contact, primarily aluminum. It is generally recognized that the hot metal atoms reaching the surface of fullerene during deposition of top electrode may react, diffuse and/or form defects in the uppermost molecular layer, thus modifying its initial structure [1–8]. This makes the interfacial region indeterminate, in both composition and geometry. Further modifications, often uncontrolled, may occur through interaction with admixtures coming from the adjacent layers or ambient [1–3,9,10,16]. In this work we consider

the simplest case when a fullerene layer is sandwiched between ITO on the substrate and top sputtered aluminum electrode. We will show that through changing the substrate material from glass to PET it is possible to reverse the rectification in these devices. Analysis of the chemical composition of interfacial regions in the Al/C<sub>60</sub>/ITO cells by means of secondary ion mass spectrometry with depth profiling provides an explanation for this effect. Results for the thermally evaporated Al are discussed in [5], but the effect is more pronounced with sputtered Al due to better quality and adhesion of the top electrode.

## 2. Materials and methods

Double indium–tin oxide (ITO) coated rectangular glass slides (sheet resistance 70–100 ohm/sq, ITO thickness 15–50 nm) and polyethylene terephthalate (PET) sheets with resistance of 100 ohm/sq (ITO thickness 100 nm) were purchased from Aldrich. Both slides and sheets were cut into 25 × 25 mm<sup>2</sup> pieces, and a 5 mm wide ITO strip was etched off from one side of each piece for further electrical clamping. All substrates were pretreated under similar conditions: first by thorough wiping in dimethylformamide (DMFA) and isopropyl alcohol (IA), then by successive sonication

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using deionized water, DMFA and IA (10 min each, in that order), and, finally, by drying under a strong Ar flow.

Buckminsterfullerene  $C_{60}$  (99.5%) was synthesized and purified at IOMC RAS ([18] and references therein). Fullerene films were deposited on substrates by thermal evaporation under residual pressure of  $5 \times 10^{-3}$  Pa using a VUP-5M facility. The deposition rate was  $\leq 1$  nm/s; the resulting thickness of  $C_{60}$  layer was 75 nm. Top electrode was deposited by a DC magnetron sputtering method from a  $\varnothing 60$  mm aluminum target (99.999%) at 0.32 Pa of Ar, with anode voltage and current being 0.7–1.5 kV and 200 mA, respectively. The metallic layer thickness was 40 nm. Our preliminary experiments have shown that at given conditions this technique can effectively be applied for depositing contacts on thin molecular films without serious distortion or overheat of any component of a heterostructure ([4] and references therein). The effective device area was defined by rectangular metallic strips (i.e., top Al electrodes, 3–4 in array) having dimensions of  $500 \times 6000 \mu\text{m}$  each, which have been left on the surface of fullerene after removal of the shadow mask. Immediately after fabrication, the samples were placed in either vacuum for analysis or inert atmosphere for photoelectrical measurements, within minimum required contact with laboratory air (less than a minute).

The surface topology of the bare substrates and deposited layers was controlled by a non-contact method (white-light interferometry, WLI) with a TalySurf CCI2000 microscope from Taylor & Hobson. At least three different points across the area of interest on the sample surface were measured and the results were compared. The same instrument was used to observe the craters after SIMS profiling [13,19]. The window size for surface analysis by WLI was  $300 \times 300 \mu\text{m}$  (set by the lens type), which is comparable with both the cell's size and the raster size in ToF-SIMS measurements—see below. Alternatively, atomic force microscopy (AFM) in semi-contact mode was used to evaluate the surface relief in more detail. Reliability of the latter technique is, however, limited for analysis of macroscopic substrates, since the scanned area has maximal dimensions to  $10 \times 10 \mu\text{m}$  (Proton-MIET CMM-2000 microscope (see Supplementary materials)). Meanwhile, the ITO coating on PET has spikes that are spaced apart at distances often reaching  $10 \mu\text{m}$  or more. Besides, plastic substrate is always slightly bent, and bending tends to increase after deposition of multilayered photovoltaic cell on substrate surface. Therefore, WLI results are basically taken into account hereinafter.

Details of the photoelectrical measurements can be found elsewhere [4,5,11]. The current–voltage ( $I$ – $V$ ) characteristics were recorded by using a Keithley 4200 SCS parameter analyzer in a dual sweep mode.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) with depth profiling was used to characterize the chemical composition of the sample surfaces, inner interfaces, bulk layers and substrates [2,4,8,10,12,13,19,20]. The experiments were done in TOF-SIMS5 (ION-TOF GmbH, Germany) spectrometer on freshly made samples that were stored in high vacuum ( $<10^{-5}$  Pa) overnight before measurements. The bare vacuum in the analytical chamber was  $<5 \times 10^{-8}$  Pa. Heavy primary ions  $\text{Bi}_3^+$  with energy of 25 keV were used in the probing beam. The probing beam current was  $\sim 1$  pA with pulse time of 1 ns. Negative secondary ions in the mass range of 1–1100 amu were registered using the time-of-flight (ToF) technique with a mass resolution  $M/\Delta M > 10,000$ .

At first, the secondary ion mass spectra from pure fullerene surface were recorded (static SIMS mode). Characteristic fragmentation of  $C_{60}$  molecules on the film surface under ion bombardment was carefully analyzed [13]. For depth profiling, static SIMS was combined with the dynamic layer-by-layer sputtering of surface by low-energy  $\text{Cs}^+$  ions. The raster size of the sputtering beam was  $200 \times 200 \mu\text{m}$ , with that of the probing beam being typically about 20 per cent of this value [19]. It was shown in previous study

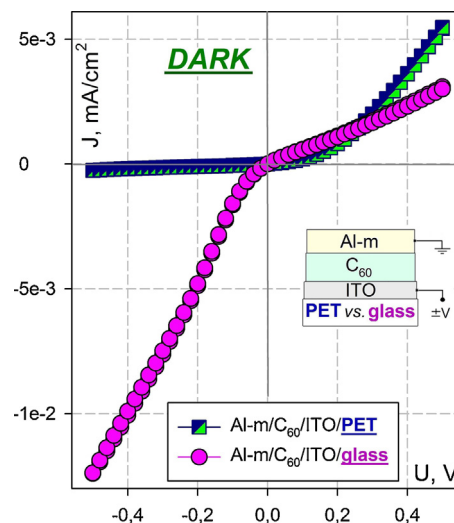


Fig. 1.  $I$ – $V$  characteristics of Al-m/ $C_{60}$ /ITO cells on PET (squares) or glass (circles) substrates in the dark.

[13], that by lowering of the sputter ion energies from 2.0 down to 0.2 keV one makes it possible to observe unbroken molecular ions  $^{12}\text{C}_{60}^-$  in the ToF-SIMS spectra. This, however, increases the time required to complete the depth profiling process (which is often unwanted for subtle multilayer organic structures). In this study, energy of the sputter ion beam was 1 keV.

Sample holder in our experiments was always grounded. Low-energy flood gun (20 eV) was switched on to neutralize the electrical charge accumulated during analysis of poorly conductive samples. Preliminary tests were performed to prove that the electrons hitting the surface do not significantly damage molecular layers [4,13].

### 3. Results

#### 3.1. Photoelectrical testing

The  $I$ – $V$  characteristics measured in the dark for Al/ $C_{60}$ /ITO sandwich cells manufactured on either PET or glass substrates are shown in Fig. 1. Top metal electrode was always grounded, whereas bias was applied to ITO electrode (see insets). Here, aluminum is marked as Al-m, so as not to be confused with the data for the cells with thermally evaporated aluminum top electrode published elsewhere [1,2,5–7,9,11,14–16].

When on PET, the Al/ $C_{60}$ /ITO device behaves as typical diode, with forward bias corresponding to positive voltage applied to the ITO electrode—Fig. 1. The current rectification (the ratio of the forward-to-reverse bias current densities) of the device at  $\pm 0.5$  V is equal to 21.

When on glass, the current in quadrant III of  $I$ – $V$  plot increases dramatically—Fig. 1. It is 51 times higher than in the devices on PET (at 0.5 V), while the current densities in quadrant I remain at the same level. So, the device exhibits rectification with forward bias corresponding to negatively biased ITO electrode. Rectification is now equal to 4 only but its direction is reversed in the Al/ $C_{60}$ /ITO cells on glass with respect to the same cells on PET.

The  $I$ – $V$  plot for the Al/ $C_{60}$ /ITO cells exposed to light is shown in Fig. 2. When on PET, a weak but distinguishable displacement of the  $I$ – $V$  curve from the point of origin is seen. The values of open circuit voltage ( $U_{oc}$ ) and short circuit current ( $J_{sc}$ ) are equal to +0.05 V and  $-7 \times 10^{-4}$  mA/cm $^2$ , respectively. For the Al/ $C_{60}$ /ITO cells on glass, the  $I$ – $V$  curve shifts to quadrant II of the plot when the light is on (Fig. 2), so that  $U_{oc}$  becomes equal to -0.075 V with

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