



Organic tandem Schottky junction cells with high open circuit voltage



Vlad V. Travkin^a, Pavel A. Stuzhin^b, Andrey I. Okhapkin^{a,c}, Sergey A. Korolyov^a,
Georgy L. Pakhomov^{a,c,*}

^a Institute for Physics of Microstructures, Russian Academy of Sciences (IPM RAS) GSP-105, Nizhny Novgorod 603950, Russian Federation

^b Ivanovo State University of Chemical Technology, 7 Sheremetyevsky Ave., Ivanovo 153460, Russian Federation

^c Lobachevsky State University of Nizhny Novgorod (UNN), 23 Gagarina Ave., 603950 Nizhny Novgorod, Russian Federation

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ABSTRACT

In our previous work [Synth.Met.200(2015)99], we demonstrated dye-based tandem photovoltaic cells with vertically stacked Schottky junctions that generate open circuit voltage $U_{oc} = 1.0$ V. In present work, using the same concept we reached $U_{oc} = 1.92$ V. Such a progress is basically associated with optimization of the anode material in both subcells. Two axially substituted phthalocyanine complexes were used as absorbers: boron chloride subphthalocyanine SubPc in the bottom subcell and indium chloride phthalocyanine InClPc in the top subcell. Inorganic semiconducting oxide MoO_x was introduced twice. First, MoO_x layer was deposited over the ITO anode in the bottom subcell. This largely increases U_{oc} as compared to the archetypal Schottky-type cell ITO/SubPc/Al. For the bottom subcell with bilayer LiF/Ag cathode $U_{oc} = 1.23$ V. Second, MoO_x was used in the composite intermediate layer (LiF/Ag/ MoO_x) that assembles subcells in stack, thus acting as anode buffer in the top subcell.

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1. Introduction

The interest in organic Schottky-type photovoltaic cells was recently revived [1–4]. This new generation of cells should be regarded as layered multijunctions, since they contain cascade organic/inorganic (organic/organic, inorganic/inorganic) semiconductor interfaces in addition or instead of classical organic semiconductor/metal junction [4–8]. In previous work [9] we used a very simple scheme to get $U_{oc} = 1$ V in the tandem cells by serially connecting two conventional ‘phthalocyanine dye/Metal’ Schottky junctions through dye-based interlayer. Despite the strong photon capturing in such cells, their output parameters remain very low, basically due to the negative contributions from the encumbering anode/phthalocyanine junctions in both subcells. Besides, the photocurrent suffers from a very thick (and resistive) dye layer that impedes optically generated excitons from reaching the interface for dissociation into free carriers [5–7].

In this work, we will show that thinning of the dye layers with simultaneous modification of the anode/phthalocyanine interface by MoO_x interlayer in each subcell results not only in the reduction

of parasitic resistances in the tandem structure, but also in nearly doubling of photovoltage.

2. Experimental

Experimental techniques and measurements conditions were described earlier in [9–11]. The schematic of cell is given in Fig. 1. Here, boron chloride subphthalocyanine SubPc absorbs photons mostly from the middle part of the visible spectrum (500–650 nm) [1,4,9,11–17], while indium chloride phthalocyanine is responsible for the red and near infrared regions (600–900 nm) [11,16,18,19]. SubPc and InClPc are complementary to each other in their optical absorption so that the visible range of the solar spectrum is fully covered (Supplementary material).

All components were purchased from Aldrich and used as received. Molybdenum(VI) oxide ($\geq 99.5\%$) and lithium fluoride ($\geq 99.99\%$) powders were thermally evaporated in standard vacuum at 550/600 °C and 700/750 °C respectively to obtain thin interlayers. Thickness and roughness of the layers were ex-situ analyzed by white-light interferometry and scanning microscopy, the deposition regimes were adjusted to obtain smooth and continuous layers [10,20]. Although photoelectrical measurements were carried out in an inert atmosphere, the samples were briefly exposed to air during transfer from the vacuum chamber.

On the strength of their transmittance, we will denote the SubPc-based cell as red subcell, and InClPc based cell as blue

* Corresponding author at: Institute for Physics of Microstructures of the Russian Academy of Sciences (IPM RAS), 7 Akademicheskaya St., Afonino vill., Kstovo Dist, Nizhny Novgorod Region, 607680, Russian Federation. Fax: +7 831 417 94 64.

E-mail address: pakhomov@ipmras.ru (G.L. Pakhomov).

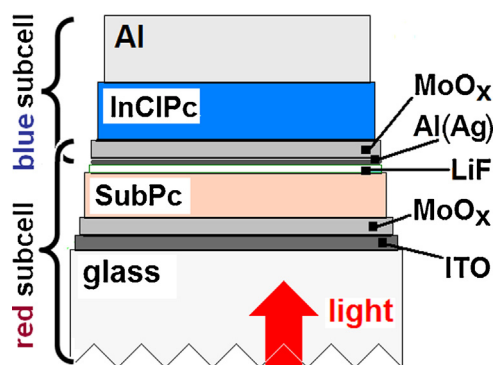


Fig. 1. Schematic of cells.

subcell (Supplementary material). At first, archetypal red 'glass/ITO/SubPc/Al' and blue 'glass/ITO/InCIPc/Al' subcells were individually fabricated and tested. The characteristics of the red cell were optimized by depositing MoO_x over the ITO anode and ultrathin lithium fluoride LiF layer under the cathode. Then, the blue cell was adapted for tandem structure by replacing ITO with Ag/ MoO_x or Al/ MoO_x anode, since in the proposed scheme the red subcell was located at the bottom, while the blue subcell was formed on top—Fig. 1. Finally, tandem structures were fabricated, in which the thickness of photoabsorbers, buffers and the composition of intermediate layer was step-by-step optimized to electrically couple the subcells in stack [21].

3. Results and discussion

3.1. Optimization of the red subcell

Optimum thickness of SubPc layer in heterojunction-based photovoltaic cell corresponds typically to 13 ± 2 nm being limited by the short exciton diffusion length L_D [4,11,15,17]. We faced two problems when attempting to maintain similar thickness in archetypal red subcell ITO/SubPc/Al. First, thinning of the SubPc layer from 100 to 25–30 nm is accompanied by a decrease in U_{oc} from about 0.80 ± 0.5 to 0.60 ± 0.5 V (some deviation was found in recurrent measurements on samples in the batch). Such a decrease is known for both Schottky junction cells with a single phthalocyanine layer [5–7] and for heterojunction-based cells with SubPc as a donor layer [4,20]. Alterations in photovoltage are mostly attributed to the morphological evolution in the vacuum deposited molecular films with decreasing thickness. Second, short circuit current J_{sc} and fill-factor FF of archetypal ITO/SubPc/Al cells increase as the thickness of SubPc layer decreases, but the risk of shorts becomes very high. The single-layer devices with SubPc < 25 nm are practically unstable and poorly reproducible, obviously owing to bare (unsmoothed) ITO [13,22].

To overcome these problems we used inorganic buffer layers: LiF under the metallic cathode and MoO_x over the ITO anode—Fig. 1. Introduction of ultrathin LiF layer between SubPc layer and thermally deposited metal, Al or Ag, allows us to further reduce the thickness of SubPc layer from 25–30 to 13–15 nm. There is no dark rectification in such devices, but photovoltages are maintained at their minimum level of 0.50 ± 0.5 V (Supplementary material). It is worth mentioning that L_D in SubPc may be underestimated, it may amount to 28 nm for a film thickness ≥ 40 nm [17].

LiF is frequently used as cathode modifier in heterojunction-based photovoltaic cells ([1,12,23–26] and References therein). Several scenarios are proposed for n-type semiconductor (e.g., fullerene)/LiF/Al interface, such as enhanced electron injection from Al through thin LiF layer, doping by Li^+ ions, dipole alignment, or shielding of the molecules from detrimental reactions with

metal atoms. The band diagrams show the lowering of the electrode work function from ~ 4.2 eV (Al) to ~ 2.7 eV (LiF/Al). In such a case one would expect an increase of U_{oc} in the single-layer cells with p-type phthalocyanine since this parameter relates to the work function difference. However, it did not occur in our experiments (Supplementary material), nor other researchers reported either absence or negative effect of LiF on the photovoltaic parameters of the phthalocyanine-based Schottky-type cells [6–8]. Therefore, the role of the LiF cathode interlayer appears to be specific for p- or n-type molecular semiconductors, and we will rely on the latter scenario considering LiF as simply protecting layer [12,26]. Here, the upward shift of work function of the metallic cathode will not be taken into account, but free tunneling of charge carriers through LiF to/from the electrode is allowed. Notably, recent studies on the role of LiF interlayer [23] revealed a dramatic impact of the layer thickness and bias history on injecting or ohmic behavior of the contact.

In thus obtained ITO/SubPc/LiF/Al cells with nominal SubPc thickness of 13 ± 1 nm we deposited the MoO_x layer over the bottom ITO electrode—Fig. 1. As known, by introducing the MoO_x anode interlayer, in addition to improvement of the overall device performance, one can increase the photovoltage in heterojunction-based cells or in cells containing cascade inorganic/organic junctions [1–4,12,13,15,16,21–25]. It is generally accepted that MoO_x increases the anode work function, but the details of this mechanism are still under debate [4,12,21]. Within the fixed experimental setup (i.e., deposition method, air admission etc.), the key parameter affecting the photovoltage is the thickness of the MoO_x layer: both the work function and conductivity vary with thickness of substoichiometric oxide.

By inserting MoO_x interlayer with thickness ranging from 2 to 25 nm, the photovoltage in the ITO/ MoO_x /SubPc/LiF/Al cells can be increased up to 1.18 V—Table 1. Apparently, this is due to the downward shift of work function of the modified ITO/ MoO_x anode very closely to the HOMO level of SubPc (~ 5.6 eV). U_{oc} reaches a constant (maximum) value that is determined by the built-in potential at the top Schottky junction arising from the work function difference between SubPc and Al, i.e., ~ 1.3 eV. If we consider the work function of MoO_x equal to 5.4 eV [12], the bottom interface between ITO/ MoO_x and SubPc can roughly be treated as ohmic. Dark rectification is enhanced with the MoO_x anode layer, too (Supplementary material).

More recently, the work function of MoO_x was found to be as deep as 6.4–6.7 eV [1–4,16,21] which suggests that it lies below the HOMO level of SubPc. Then, the observation of high photovoltage in the cells with the MoO_x interlayer would be explained as a contribution from an additional photoactive junction arising at the MoO_x /SubPc interface. Indeed, in Ref. [21] formation of a Schottky junction between MoO_x and SubPc in ITO/ MoO_x /SubPc/Al cells was proposed, this junction being capable of generating its own photovoltage that boosts the output from the cascade. There are two confusing circumstances here. First, authors in [21] analyzed ITO/ MoO_x /SubPc/Al devices completely disregarding the SubPc/Al interface as photoactive component. Second, the MoO_x /SubPc Schottky junction was found to add $U_{oc} < 0.05$ V at room

Table 1
Parameters of subcells^a under 1 sun illumination.

	Red subcell						Blue subcell			
MoO_x , nm	0	2	3.5	5	10	25	0	5	10	
U_{oc} , V	0.49	1.01	1.09	1.16	1.18	1.17	0.30	0.34	0.58	
J_{sc} , mA/cm ²	0.60	0.85	0.81	0.78	0.54	0.24	1.40	0.39	1.55	

^a Red subcell = glass/ITO/ MoO_x = 0, 2, 3, 5, 5, 10, 25 nm/SubPc (13 nm)/LiF (1 nm)/Al (60 nm). Blue subcell = glass/ITO/(MoO_x = 0 nm)/InCIPc (25 nm)/Al (60 nm) and glass/Ag (5 nm)/(MoO_x = 5, 10 nm)/InCIPc (25 nm)/Al (60 nm).

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