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Application of copper oxide CuO layers as a support layer in binary and ternary organic cells

***Abstract**. This article presents a study of copper oxide (CuO) used as a booster layer in binary and ternary organic solar cells, with the aim to determine its effect on performance and efficiency of the cells. CuO layers were deposited by DC reactive magnetron sputtering, resulting in a film thickness of 23 nm. The cells were fabricated, and tested, and their parameters were determined.*

***Streszczenie.** Artykuł przedstawia badania dotyczące warstw tlenku miedzi (CuO) stosowanych jako warstwa wspomagająca w organicznych ogniwach słonecznych z warstwą dwu i trójskładnikową aby określić jego wpływ na wydajność i efektywność. Warstwy CuO były osadzane metodą reaktywnego rozpylania magnetronowego DC, co pozwoliło uzyskać warstwę o grubości 23 nm. Ogniwa wykonano i przetestowano oraz wyznaczono ich parametry. (**Zastosowanie warstw tlenku miedzi CuO jako warstwy nośnej w dwu- i trójskładnikowych ogniwach organicznych**)*

Słowa kluczowe: ogniwa organiczne, tlenek miedzi, fotowoltaika, cienkie warstwy, tlenek miedzi (II)
Keywords: organic cells, copper oxide, photovoltaics, thin films, copper oxide (II)

Introduction

In 2023, for the first time, more than a quarter of the EU's electricity (27 %) will come from wind and solar power, up from 23 % in 2022. The demand for clean energy from the sun is on an upward trend. As a result, research on photovoltaic cells is constantly being developed. Silicon-based technologies [1, 2] dominate the market and are a popular source of energy for households, while thin-film cell-based panels [3] are being increasingly used. The latest photovoltaic technologies, such as organic cells and perovskite cells, have shown the fastest growth in performance in the recent years [4]. Organic cell research similarly revolves around performance optimization through the use of new materials in cells, new architectures, new support layers, encapsulation methods, and also new manufacturing technologies.

This paper will present a study of copper oxide thin film used as a booster layer in binary and ternary organic solar cells. A scheme of the cell is shown in Figure 1.

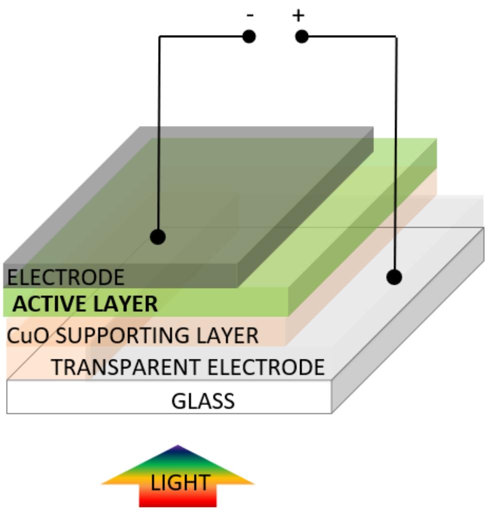

Fig. 1.OPV scheme

Ternary organic cells

A rising trend in organic cell research is ternary organic solar cells [5, 6, 7]. Organic cells of the volumetric heterojunction type do not have the p-n junction typical of first- and second-generation cells. The active layer in these cells is a mixture of donor and acceptor material. The introduction of an additional, third component is intended to increase absorption in the active layer of the cell and facilitate movement between energy levels for electrons and holes. An improvement in the transport of charge carriers in the form of cascade transport is also observed [8, 9]. Depending on the role of the third component, we classify ternary cells as donor1:donor2:acceptor (DDA) [10, 11, 12] or donor:acceptor1:acceptor2 (DAA) [13, 14].

Cupric Oxide

CuO is an intrinsic p-type semiconductor with band gap between 1.0 eV to 1.5 eV depending on deposition method. It crystalizes in monoclinic C2/c space group structure (Fig.2) [15]. Thin film of CuO was deposited using DC reactive magnetron sputtering. The parameters of process were as follows, pressure during deposition was at 1.4 x 10^{-2} mbar, ratio of oxygen partial pressure to argon partial pressure was equal to 3.28, power of discharge was 330 W, current of discharge was 690 mA. The deposition process lasted for 7.5 minutes, with aim to obtain about 30 nm film thickness.

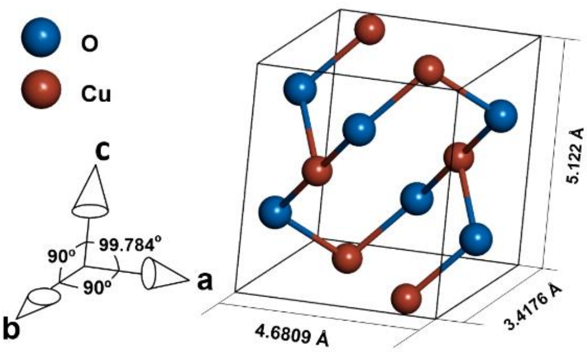

Fig. 2. CuO crystal structure [16]

Materials

In this study, cells with active layers based on compounds: PTB7-Th (poly([2,6′-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,3-b]dithiophene]{3-fluoro-2[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}), Y5 ((2,2'-((2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro[1,2,5]thiadiazolo[3,4e]thieno[2'',3'':4',5'] thieno[2',3':4,5]pyrrolo[3,2-g] with thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene))bis(3-oxo-2,3-dihydro1H-indene-2,1-diylidene))dimalononitrile) Y6 (BTP-4F, Y6, PCE 157)and PCBM ([6,6]-phenyl-C71-butyric acid methyl ester) were prepared. All chemical formulas are shown in Figure 3.

As a binary active layer the popular mixture of donor material PTB7-Th and two non-fullerene acceptors Y5 and

Y6 were used. The third used component was PCBM. Compounds under consideration are a good reference because of their proven effectiveness and proven performance in organic solar cells [17, 18, 19].

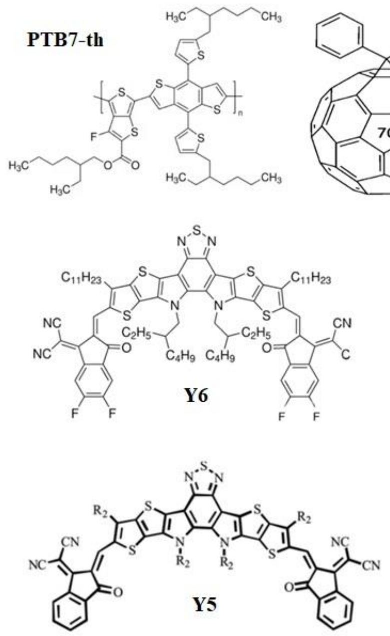

Fig. 3. Chemical formulas of compounds under investigation

Materials properties

To confirm that CuO was deposited, we used grazing-incidence X-ray diffraction. The diffractogram with peaks assigned using ICDD card # 01-080-1268 is presented in Figure 4. We determined the thickness of the film with X-ray reflectivity technique. The thickness calculated by Fourier transform of interferences is 22.5 nm, while the thickness calculated by measuring distance between fringes is 24 nm.

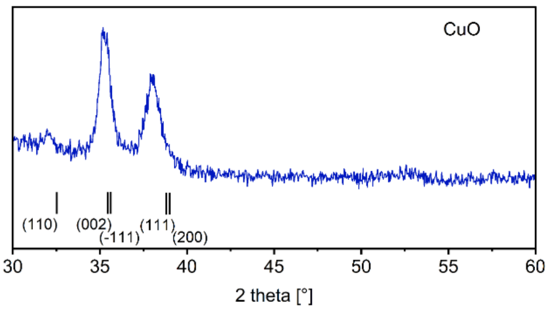

Fig. 4. X-ray diffractogram of CuO thin film

Both X-ray diffraction and X-ray reflectivity measurements were performed with Panalytical Empyrean diffractometer equipped with a Cu Kα radiation source.

Sheet resistivity of the film measured with four point probe method (MDC Four Point Probe Resistivity Measurements Set) was 1.75 x 10^6 Ohm/sq.

Absorption studies were performed using an Avantes spectrometer Avantes Sensline Ava-Spec ULS-RS-TEC fibre. The materials used exhibit the absorption spectrum shown in Figure 5.

The materials from which the active layer is made are characterized by an absorption spectrum mainly in the visible range. The CuO layer covers the range of 250-400 nm.

Binary & ternary solar cells

The cells were fabricated in two architectures - with and without a CuO support layer for two types of binary layers and two types of ternary layers. Indium tin oxide (ITO) and aluminum (Al) electrodes were applied.

The CuO layer was deposited on the ITO substrate (120 nm, 12 Ω/sq). The active layers were applied from the liquid phase (the weight ratio of PTB7-Th:Y5/Y6 was 1:0.8, and for PTB7-Th:Y5/Y6:PCBM 1:0.5:0.5, the solvent was spectral chloroform) using spin coating method (rate of 1000 rps/min). On this system it was sputtered in vacuum Al thin layer (about 100 nm). Chemical compounds, dissolvers (spectrometric grade) and ITO sheet were provided by the Merck KGaA.

The photocurrent density-voltage characteristics for prepared photovoltaic cells were measured with Enlitech SS-X200R sun simulator under 1000 W/m^2 Am1.5 irradiation. The current-voltage characteristics for cells with a binary active layer are shown in Figure 6(a) and with a ternary active layer in Figure 6(b).

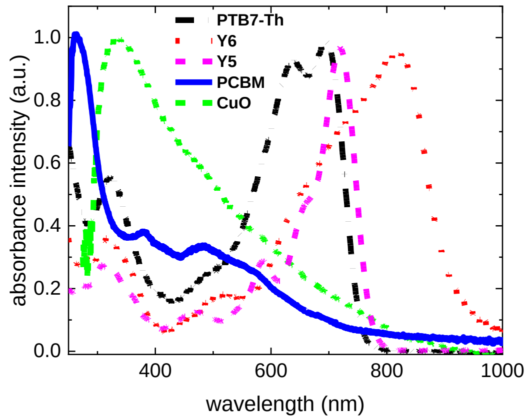

Fig.5. Absorption spectra for materials used in OPV

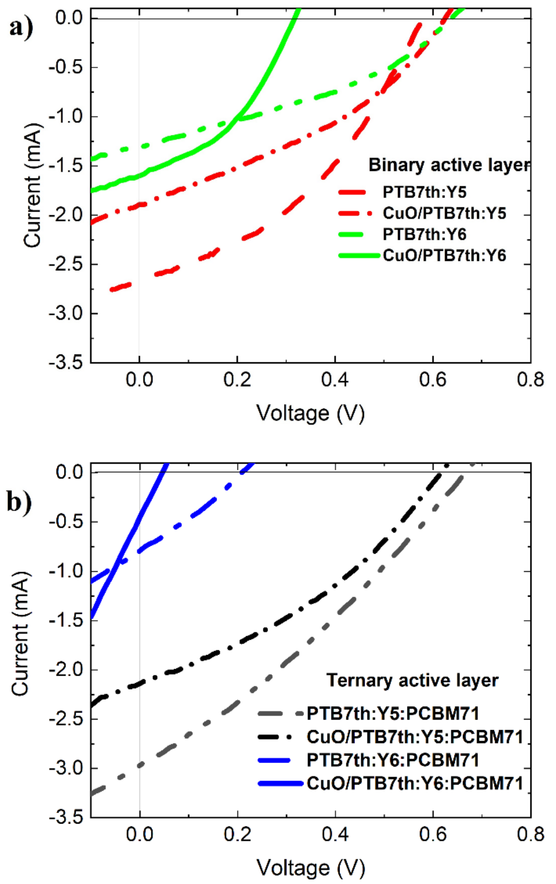

Fig. 6. Current-voltage characteristics of investigated ITO/active layer/Al and ITO/CuO/active layer/Al cells

Based on experimental data, polynomial curves were fitted and the critical parameters of photovoltaic cells were determined (Tab. 1). Parameters describing the photovoltaic cells are short current density (J_{sc}),open circuit voltage (U_{oc}) , fill factor (FF) and conversion efficiency (η).

Table 1. The parameters of the resulting organic cells

Device architecture	Jsc (mA/cm^2)	Voc (V)	FF (%)	η (%)
ITO/PTB7th :Y5/Al	5.4	0.58	39	1.2
ITO/Cu0/PTB7th :Y5/Al	2.2	0.40	36	0.85
ITO/PTB7th :Y6/Al	2.6	0.64	38	0.59
ITO/Cu0/PTB7th :Y5/Al	3.8	0.63	36	0.85
ITO/PTB7th :Y5:PCBM/Al	5.8	0.67	30	1.2
ITO/Cu0/PTB7th :Y5: Al	4.2	0.62	35	0.93
ITO/PTB7th :Y6:PCBM/Al	1.6	0.21	29	0.095
ITO/Cu0/PTB7th:Y5:PCBM/Al	0.9	0.046	25	0.011

The applicability of copper oxide layers in both ternary and binary organic cells has been demonstrated. In the ternary cell (with PCBM), there was a reduction in cell efficiency, particularly in the case of ternary cells due to overlap of the CuO absorption spectrum with PCBM71. To test the applicability in ternary solar cells, a combination of acceptors absorbing above 500 nm should be used to shift the maximum of the absorption spectrum towards the infrared. In the case of the cell with the PTB7:Y5 binary layer, an increase in V_{oc} was noted, which was related to CuO supporting hole transport. Increase in V_{oc} indicates improvement through elimination of interfacial energy disorder [20]. A similar increase in V_{oc} occurred in cells with aluminum oxide [21].

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