

1 Introduction and theoretical part

Energy demands in expanding modern society are constantly growing. Parallel with the industry's permanent search for lower cost energy resources, mankind is also looking for renewable energy, whose exploitation would not affect the fragile nature balance. Earth heat, wind and tide energy are some examples of the potential of renewable sources for the production of energy [1].

With a constantly growing share in renewable energy use is the utilization of Sunlight. So called "solar cells" transform it to electricity with commercial energy conversion efficiencies of 10-15% [1]. The record of solar cell efficiency in present time is being held by single crystalline silicon solar cells, whose highly structured surface, together with some extremely complex light trapping techniques transforms incident light with about 25% efficiency in electricity [2]. These solar high-tech devices are of course very expensive and have, therefore limited use, for example, in space technologies, where very compact and efficient devices are required. On Earth, where space is not a problem, bigger and cheaper devices can be installed. The end cost of silicon panels, even if polycrystalline is quite high, firstly because of material purity requirements and secondly because of the amounts of material used.

1.1 *Organic photovoltaic devices*

In the last two decades a new branch in photovoltaic research was formed. Scientists all over the world have found a new playground in the face of organic ultra-thin film solar cells. Produced from environment-friendly organic materials, on cheap and flexible plastic substrates, semitransparent, cut in various shapes and sizes – those are the dream properties of the organic photodiodes. Some of these are already achieved, but there's still a long path to walk if one wants to combine all these properties in a single device.

The photovoltaic effect in organic materials is known since the mid 70s [3]. Though as the beginning of organic solar cell research scientists tend to point 1986 from the publishing of the well known C. W. Tang article on a "Two-layer organic

photovoltaic cell” [4]. At present time many different organic solar cell device architectures exist. From just an organic substance between two electrodes scientists have expanded the complicated interpenetrating organic mixtures or tandem cells [5]. All these concepts have been developing very intensively in the last years and sooner or later it is expected that organic photovoltaic devices reach compatible efficiencies to eventually compete with their expensive silicon or poisonous inorganic relatives. Also the price of an organic device is many times lower than that of inorganic ones mainly because of the quantities of material used. Even at prices of about 200-300\$ per gram active layer material, a square centimeter of an organic solar cell is much cheaper than one of a silicon single crystal, because in a couple of nanometers thick layer one uses almost invisible quantities of material. Our estimations show that out of 1 kg organic absorber material at 3% organic solar cell efficiency 1 MW electrical power could be yielded.

1.2 Zn-Phthalocyanine - C₆₀ heterojunction cell architecture

In the present work we are dealing with a bi-layer bulk heterojunction, donor acceptor solar cell concept having as an absorber/donor the substance zinc-phthalocyanine (**ZnPc**) and as an acceptor fullerene C₆₀ (Figure 1). Beside the active layers there are also two buffer layers – Bathocuproine (**BCP**) (2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline) and a block copolymer – Poly-Ethylene DioxyThiophene : Poly-Styrene Sulphonate (**PEDOT:PSS**) who's role is to admit only electrons or only holes to the corresponding electrode, respectively. This architecture is sandwiched between two electrodes: Indium-Tin Oxide (**ITO**) - at present the mostly used transparent conducting oxide (**TCO**) and Aluminum (Al).

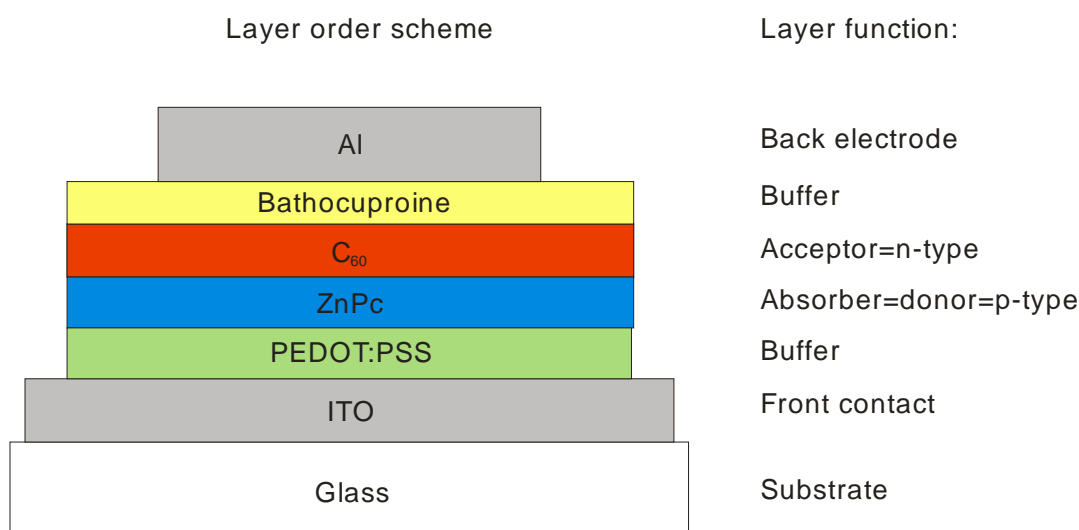


Figure 1. ZnPc/C₆₀ solar cell architecture. The two active layers ZnPc and C₆₀ are sandwiched between the two buffers, which lay next to the electrodes

After a layer thickness optimization procedure, hereby not conducted by the author, but in the same scientific group, the optimum thickness for each layer of this cell was found. Highest cell efficiency (electrical cell parameters described further in 2.8) was produced by a cell with the following configuration: ZnPc – 30 nm, C₆₀ – 30 nm,

BCP – 17 nm and Al – about 150 nm. As concerning PEDOT:PSS thickness, it will be explained later in the experimental section of this work under PEDOT:PSS spin-coating (2.5). Further referenced as a standard cell, this solar cell architecture will be used without the spin-coated PEDOT:PSS buffer, in order to study different chemical ways to manipulate the ITO-organics interface and align the energy band structure for optimum charge carrier transport.

1.3 Theoretical model and energy diagram

After a careful check and comparison of different literature sources, the following energy level diagram for our solar cell could be sketched [6,7,8,9,10,11].

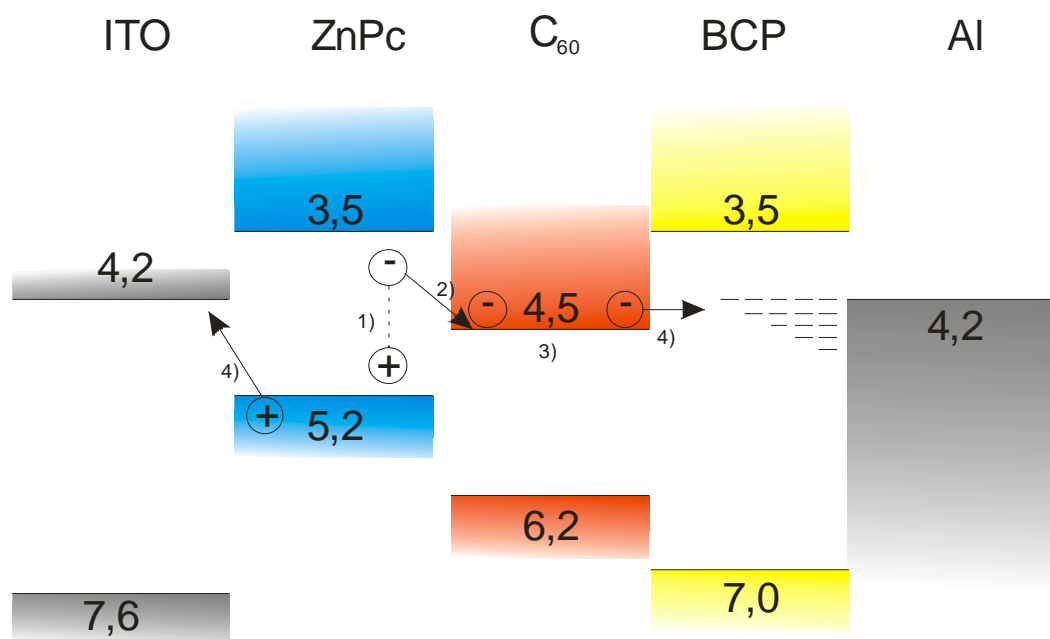


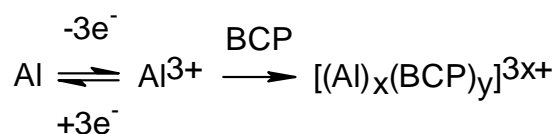
Figure 2. Energy level diagram of the ITO/ZnPc/C₆₀/BCP/Al cell; Values in eV. Process 1) stands for exciton creation in absorber layer; process 2) is charge separation on ZnPc-C₆₀ interface; process 3) is the diffusion of charges; process 4) is charge transfer to contacts through the buffer layers. Work function of ITO can vary up to 4,7 eV, but 4,2 eV is the value, measured on a clean-sputtered ITO surface

Of course the values for each substance in this diagram vary from publication to publication. Particularly for ITO, a work function value from 4,1 up to 4,7 eV can be found. That's why for this band diagram either mean reference values (ZnPc, C₆₀,

BCP), or values measured by us (ITO) were used. Aluminum, as an element has one, precise value in all sources, namely 4,2 eV.

Sunlight, after being absorbed in organic molecular crystal semiconductors, does not “immediately” create a free electron, but an exciton [12]. This exciton, being a pair of an electron and a hole, held together by Coulomb forces, has some binding energy of ~1 eV in organic materials [13]. It also can diffuse in the ZnPc bulk not more than 30±10 nm [14]. This is the main reason why this material in our cell has an optimum thickness of 30 nm. If it is thinner less light is absorbed leading to lower currents. If it is thicker, less excitons reach the ZnPc/C₆₀ interface where charge separation occurs [15]. To be separated, excitons need either more energy, or a favorable arrangement of the surrounding molecular orbitals, where the surrounding field forces them to separate. The electron is transferred to the LUMO of C₆₀ and the hole is being transported to ITO. In general, in the transport of charge carriers in organic semiconductors, dominates the so called, hopping mechanism, rather than band-like transport [16].

Further transfer of the electron to the aluminum contact is believed to happen through acquired energetic levels of bathocuproine, which is practically an insulator substance. Its valence band is very low (7,0 eV), thus excluding the possibility of charge transport through its conduction band. The acquired energetic levels in BCP appear after the physical diffusion of the incoming hot aluminum vapor (about 1200°C), during aluminum electrode evaporation. Having a glass point of about 80°C BCP is a “soft” material which allows aluminum to interpenetrate. During this process partially a chemical reaction occurs, which results in an aluminum complex with BCP [17]:



Dispersed in the BCP matrix, this complex creates the additional interpenetrating energy levels which make the transport of electrons to the Al electrode possible. Also the charge of this complex, gathered on the interface C₆₀/BCP blocks holes from proceeding to the aluminum electrode. This way BCP serves as a hole filtering buffer allowing mainly electrons to reach the Al back contact.

1.4 Stability and reproducibility problems

It is a well known fact that organic photovoltaic devices have a much shorter life in comparison with their inorganic or silicon analogues [18,19,20]. It is proven that this is due to the combined effect of light and oxygen traces diffusing in the sample – the so called photo-degradation [21]. One hypothetical explanation of degradation are the aggressive oxygen radicals, generated by UV in ITO, which attack the organics and by chemically modifying the organics, create exciton traps, or lower the electro-conductivity of the materials [22]. In the literature the degradation is reported in different time scale periods: from hours to days and even months, all depending on different production and encapsulation techniques to keep the aggressive oxygen and humidity out of the device.

The standard cell in the present work (see 1.2) had a half-life of roughly 5 hours, under encapsulation in a Plexiglas container, isolated from atmosphere with pressed rubber O-rings. Unprotected the device degraded in much less time.

Reproducibility of the efficiency results of organic solar cells is also a step stone for scientists. Along with different batches of ITO glass, having different properties, also by the evaporation of the active organic layers there are many parameters which can differ from one to another batch. Vacuum quality, thickness measurement accuracy, evaporation rate, substrate temperature – these are some of the parameters that need to be kept constant in order to achieve reproducible results. Of course this is difficult and that is why statistical quantity of experiments has to be conducted in order to say: “This cell now has that defined efficiency”.

Knowing all these difficulties and problems of the organic photovoltaic device that we are dealing with, we can define the topics of the present work.

1.5 Topics and goals of the present work

Analytical studies:

- Study of the ITO substrate and extraction of data about its surface (appearance, roughness, work function), its thickness, temperature behavior (resistance), different substrate types (ITO thickness, resistance);
- Test of the chemical stability of organic cell materials under O₂ and UV irradiance;
- Study of the cell by means of optical simulation;
- Comparison of different methods for layer thickness determination;

Preparative studies:

- Testing different means of ITO passivation in order to avoid the PEDOT:PSS buffer layer, but attaining cell efficiency;
- With all gained experience, engineering and testing of a new chemical passivation on ITO;
- Up-scaling our current standard cell (0,032 cm²) to 1 cm², to be able to conduce space resolved I/V measurements;
- Experimentation with different (from Aluminum) metal counter-electrodes, to observe cell behavior through counter-electrode work function change