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Optimized ITO-free tri-layer electrode for organic solar cells

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ABSTRACT

The optical properties of ZnO/Ag/ZnO (ZAZ) multilayer structures were numerically modeled and calculated by a FDTD method. Such tri-layers were also manufactured using an ion beam sputtering plant. A good agreement is obtained between modelizations and realizations. The impact of the oxide thicknesses on the optical properties of the ZAZ structures were experimentally and numerically investigated, and allow us to adjust the spectral position of the transmission maximum. The transmission of these structures is optimized up to around 74%, on the whole absorption spectral range of the photoactive P3HT:PCBM bulk heterojunction. The best electrode design is glass/ZnO (30 nm)/Ag (14 nm)/ZnO (30 nm), which presents a sheet resistance of 7 Ω/□. The optimized ZAZ structure was successfully integrated in an organic solar cell as anode. A photovoltaic efficiency of 2.58% is obtained and is compared to an organic solar cell integrating a traditional ITO anode with an efficiency of 2.99%. Numerical calculations of the intrinsic absorption inside each layer of the organic solar cells are performed. Alternative ITO-free electrodes for organic solar cells are demonstrated.

1. Introduction

Transparent conducting oxides (TCOs) are widely used as electrodes in a large variety of optoelectronic devices due to their unique combination of optical and electrical properties (high transparency in the visible range and high electrical conductivity). Nowadays, indium tin oxide (ITO) is the most popular commercial TCO, having superior stability, transparency and conductivity. However, with the current rate of global consumption of ITO in many applications and the limited supply of indium, the use of the latter became a barrier to low-cost manufacturing. Moreover, in order to achieve the required properties of ITO, the substrate must be maintained at high temperature during the deposition process (>300 °C). With the focus being more on flexible and lightweight optoelectronic devices, high temperature processes are not compatible with flexible, most often polymeric substrates. As it is difficult to extract indium, as it is a rare material and as mechanical properties of ITO are not compatible with flexible substrates, there is an urgent need to replace the ITO by alternative TCOs deposited at low-temperature and based on abundant and relatively inexpensive materials. Various approaches [1–31] were suggested to replace ITO.

Zinc oxide (ZnO) has attracted much attention as a promising candidate in optoelectronic devices such as solar cells [1] and organic light-emitting diodes (OLEDs) [2], because of its lower production cost, lower toxicity and comparable properties with those of ITO. In addition, the material is easier to etch [3] as this is often needed during device fabrication. To improve its conductivity, Zn-based electrode is often doped by metals such as Aluminum (Al) [4] and Gallium (Ga) [5] or halogens such as Fluorine (F) [6]. However, relatively high thickness values and high substrate temperatures are needed to obtain the necessary optical transmittance and electrical conductivity in most metal-doped ZnO films [7–11] which increase its

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fabrication cost. Other ITO-free conductive transparent materials have been studied such as the widely used poly(3,4-ethylene dioxythiophene)poly(styrenesulfonate) (PEDOT:PSS) [12,13], alone or in conjunction with a metal grid embedded in it [14]. Other studies focused on nano-carbon materials [15,16] such as fullerenes, carbon nanotubes, carbon nanofibers and graphite oxides with graphenes being the most promising ones [17]. Other recent research efforts [18,19] focused on metal nanowires as well.

Another viable alternative approach recently proposed consists of oxide/metal/oxide (O/M/O) heterostructures. In order to improve the transparency and durability of the TCO, a thin transparent metal layer is embedded between two oxide layers. This multilayer structure has many advantages compared to a single-layered TCO. High processing temperatures are no longer needed, because optimum optical properties can be obtained without substrate annealing, and even improved in the case of the electrical conductivity. Many oxides and metals have been investigated for the fabrication of O/M/O multilayers such as molybdenum trioxide (MoO_3) [20], vanadium pentoxide (V_2O_5) [21], tungsten trioxide (WO_3) [22], ZnO [23], silver (Ag) [24], copper (Cu) [25] and gold (Au) [26], obtained using low temperature deposition processes such as pulsed laser deposition (PLD) [27], magnetron sputtering [28,29] and ion beam sputtering (IBS) [23,30,31].

In this study, we prove the feasibility of ITO replacement by a numerically-optimized ZnO/Ag/ZnO multilayer anode deposited at room temperature using the IBS technology in (poly-3-hexylthiophene):[6,6]-phenyl-C_{61}-butyric acid methyl ester (P3HT:PCBM)-based solar cells. The fabrication and characterization of multilayer electrodes and of the ITO-free highly efficient polymer solar cell, as well as the optical and electrical properties of multilayer electrodes and the photovoltaic parameters of the solar cell are reported in this paper.

2. Experimental details and numerical model

2.1. Experimental details on the realization and characterization of ZnO/Ag/ZnO electrodes

ZnO/Ag/ZnO (ZAZ) multilayer electrodes were sequentially deposited on soda-float glass substrates (purchased from CHEVALLIER Glass & Lux) at room temperature by IBS using two targets (ZnO, 99.999% and Ag, 99.99% pure). Under a pressure around 5×10^{-4} Pa in the vacuum chamber, the targets were bombarded by argon ions accelerated at 6 keV with a current density of about 1 mA/cm^2. The target-substrate distance was fixed at 6 cm and the substrate orientation with respect to its axis was optimized at 60°; in these conditions, the deposition rates are low (0.3 nm/min and 1.6 nm/min for ZnO and Ag, respectively). The thicknesses of ZnO and Ag films were controlled by a quartz crystal monitor and measured using a Bruker DektakXT profiling system; the various multi-layers were characterized using the four-point-probe method to measure the sheet resistance (experimental error of 1 Ω/□), and a SAFAS200 spectrophotometer to measure the optical transmission. Although the deposition rates are low, the IBS technique offers a good control of the stoichiometry to improve the interfacial characteristics of the films. In optimal conditions, IBS does not require any annealing after deposition to recrystallize the layers.

In Fig. 1, it is shown [23] that the best compromise between a low sheet resistance and a high optical transmission is obtained for a 14 nm-thick Ag layer as the intermediate metal layer in the ZAZ tri-layer electrode. Such a thickness corresponds to a continuous layer to limit the diffusion phenomena [32]. The ZnO layers are used to expand the narrow optical window of the metal layer in the visible. Note that the commercial ITO used in this study as a reference has a sheet resistance of 7 Ω/□ for a thickness of 220 nm.

2.2. Numerical model

The optical properties of ZAZ electrodes were calculated via a Finite-Difference Time Domain (FDTD) method. This method is able to rigorously solve the Maxwell's equations and makes it possible to obtain the electromagnetic field versus time and position. Our simulation zone (Fig. 2) presents periodic conditions in x and y directions, and perfectly matched layers (PML) along the z direction, which absorb all waves moving towards the exterior of the simulation area without reintroducing reflection. The light source is a polychromatic plane wave polarized along the x-axis. The space-mesh size is 0.4 nm inside the silver layer, 1 nm at the ZnO/(air or glass) interface and up to 11 nm far away from its interfaces. The time-mesh size is 3.1×10^{-18} second. The values of the silver optical indices are taken from Palik [33] and ZnO optical indices from Li et al [34]. Each layer is considered as a flat surface, i.e. without any roughness. Similar modeling was successfully performed for calculating optical properties of thin film coatings integrating silver nanoparticles [35] or of multilayer electrodes [20].

Organic solar cells integrating ZAZ electrode were also modelized with the same method after adding the active layer, the interfacial layers and the metallic cathode in

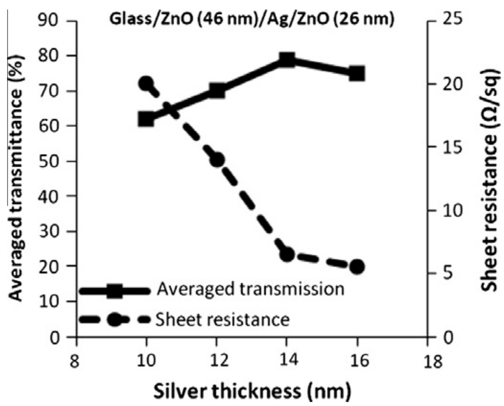

Fig. 1. Sheet resistance and averaged transmission in the 450–650 nm spectral range versus silver thickness of the glass/ZnO (46 nm)/Ag/ZnO (26 nm) electrode.