Tailored ZnS/Ag/TiO\textsubscript{x} transparent and conductive electrode for organic solar cells

Mohamed Ahmed Cherif\textsuperscript{1,3}, Amina Labiod\textsuperscript{1}, Damien Barakel\textsuperscript{1}, Saad Touihri\textsuperscript{2}, and Philippe Torchio\textsuperscript{1,*}

\textsuperscript{1} Aix-Marseille Université, Institut Matériaux Microélectronique Nanosciences de Provence–IM2NP, CNRS-UMR 7334, Domaine Universitaire de Saint-Jérôme, 13 397 Marseille Cedex 20, France
\textsuperscript{2} UPDS, Faculté des Sciences de Tunis, Université de Tunis El Manar, Tunis, Tunisia
\textsuperscript{3} École Nationale d’Ingénieurs de Tunis ENSIT, Université de Tunis, Tunis, Tunisia

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Abstract. Organic photovoltaic cells (OPVCs) attract high interest for solar energy harvesting. They are based on organic thin films sandwiched between two electrodes, one of them being transparent and conductive. Nowadays, ITO remains the most widely used transparent conductive electrode (TCE) because of its excellent optical and electrical properties compared to other TCEs. However, it has some drawbacks such as scarcity of indium, high fabrication cost, and mechanical properties poorly adapted to use as flexible substrates. To keep these performances without indium, several materials can replace ITO such as MoO\textsubscript{3}, ZnO, ZnS, TiO\textsubscript{2},... as dielectric and Ag, Cu,... as metal inside a dielectric/metal/dielectric three-layer structure. A Transfer Matrix Method (TMM) based numerical model is used to predict the optical behavior of the considered electrodes. ZnS/Ag/TiO\textsubscript{x} electrodes are manufactured by a vacuum electron beam evaporator on glass substrates, then characterized by UV-Visible spectrophotometer for obtaining transmittance and reflectance and by a four-point method for the measurement of sheet resistance. It is found that the simulation and experimental curves are quite similar. The transmittance is measured to be higher than 80\% on a wide spectral band that can be tailored by the thickness of the upper dielectric material. The optical window $\Delta \lambda$, for $T > 80\%$, can be tuned in the 400–800 nm spectral band, according to the thickness of TiO\textsubscript{x} in the 25–50 nm range. This variation allows us to adapt our electrode to organic materials in order to optimize the performance of organic solar cells. The sheet resistance obtained is around to $7 \Omega$/sq, which gives our electrodes the transparent and conductive character simultaneously. A typical parameter to compare the electrodes is the merit figure, which questions the average optical transmission $T_{av}$ in the visible range and the sheet resistance $R_{sq}$. By applying this figure to many manufactured electrodes, the obtained optimal structure of our TCEs is demonstrated to be ZnS (40 nm)/Ag (10 nm)/TiO\textsubscript{x} (30 nm).

Keywords: Multilayer / thin film / dielectric / metal / oxide / in-free transparent and conductive electrodes / organic solar cells / TMM numerical calculation

1 Introduction

The excessive use of fossil fuels causes the release of large amounts of CO\textsubscript{2}, leading to global warming of our planet. In order to limit the emission of greenhouse gases, fossil energy sources are being replaced by renewable sources such as sun, wind, etc. As a result, wind, hydraulic and solar energy are to be preferentially employed.

Solar energy based on the photovoltaic effect can be an efficient alternative. It is a well-adapted answer for the clean, inexhaustible production of electricity, and is a relatively well-distributed resource in the world, even if the average power received annually at the surface of the globe varies according to the regions. Furthermore, the size of photovoltaic systems can be adjusted and adapted to many applications.

The photovoltaic sector can be classified into three major categories: inorganic, organic and hybrid cells. The organic cells [1,2] are essentially composed of an active layer sandwiched between two electrodes (cathode and anode). The photosensitive layer differs according to the nature of the organic material used, one of the two electrodes being metallic (Al, Ag,...) [3,4] while the other

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must be both transparent (allowing the passage of light in the heart of the cell) and conductive (to collect the electrical charges). The photovoltaic effect is based on the light conversion into electrical energy. This conversion involves a set of physical processes namely the absorption of the incident photons, exciton generation, exciton diffusion and dissociation, transport and collection of charges carriers.

Nowadays, ITO [5] remains the most widely used transparent conductive electrode (TCE) because of its excellent optical and electrical properties compared to other TCEs. The current objective is then to keep these performances without employing indium, which becomes increasingly rare in nature. In addition, ITO cannot be used as flexible electrode given because of these poor mechanical properties. Among various alternatives, the three-layer dielectric/metal/dielectric structure [6,7] can be seriously envisaged. Knowing that these structures are considered as a parallel connection of three resistors, and that the resistivity of the dielectric is much greater than that of the metal, so the total resistance of the entire stack is equivalent to that of the metal. From where we can admit that such tri-layers gain their character conductive of the presence of the metal.

ZnS has been used for many multilayer structures [8], associated with other dielectrics namely MoO₃ [9,10], WO₃ [11],... or alternating multilayers with Ag (ZnS/Ag/ZnS/Ag) [12]. The ZnS/Ag/TiO₂ three-layer was developed by Peres et al. [13] in 2016. He presented a study according to the thickness of Ag with a thickness of TiOₓ around 45 and 50 nm. Our first objective consists in optimizing such multilayer with minimal thickness of TiO₂ while keeping the performance of ITO. A second, rather important objective is to have the possibility of controlling the bandwidth (for transmission greater than 80%) and its spectral position with respect to the absorption band of the organic material likely to be used in as an active layer in an organic solar cell.

2 Numerical and experimental methods

To model our structures, we use an algorithm based on the Transfer Matrix Method (TMM) [14,15], which assumes that the layers deposited are flat, massive and homogeneous; it also estimates that the light comes from a semi-infinite substrate in normal incidence and that the stack is surrounded by air [16]. This method [17,18] makes it possible to calculate the reflectance (R), the transmittance (T) and the absorbance (A) of our structures after entering the complex optical constants (see Eq. (1)) of the materials used and the thicknesses of each layer as input data in the spectral [350,1500] based.

\[ \tilde{n} = n + ik. \]  

The electrodes are deposited on VWR® microscope slides 1 mm-thick cut and cleaned. These substrates are placed in an Oerlikon Leybold Vacuum Univex 300 electron beam evaporator at normal incidence and 20 cm away from the crucibles containing the materials to be evaporated. The Ag thin film is deposited from 99.99% pure Ag at an average speed of 1 nm/s and a vacuum around 4.10⁻⁵ mbar. The TiOₓ layer is deposited from a 99.995% TiO₂ pure material at a rate of 0.2 nm/s and a vacuum around 9.10⁻⁵ mbar. No oxygen is added during the deposition process, involving a non-stoichiometry TiOₓ. That of ZnS is deposited from a 99.999% pure powder of Zinc Sulphide at a speed close to 0.5 nm/s and a vacuum around 5.10⁻⁵ mbar. The thicknesses are controlled via a quartz crystal oscillator monitor placed near the substrate during deposition and confirmed posteriori by a mechanical profilometer. Quartz does not give an exact value of the thickness, which makes the repetition caused by a thickness measurement error of the order of ±5 nm for the oxides and ±1 nm for the metals. The samples are optically characterized by spectrophotometry, including an integrating sphere. The absorption spectra (A = 1 - R - T) are deduced from the R and T measurements.

The electrical measurements are carried out by the 4-point method which consists of applying a current intensity I and of measuring the voltage difference ∆V. The sheet resistance can be then calculated according to the following equation (2):

\[ R_{eq} = 4.53 \times \frac{\Delta V}{I}. \]  

3 Results and discussion

To determine the input parameters of our modelling algorithm, i.e. the complex optical constants of each material, we use data previously obtained by ellipsometry spectroscopy on monolayers of ZnS and TiOₓ. From a Tauc-Lorentz model, it was possible to adjust the measured ellipsometric values tan(ϕ) and cos(Δ) of ZnS and TiOₓ [14]. Optical constants of bulk Ag are coming from the literature [19].

The simulation of the transmission as a function of the thicknesses of the three layers for the Glass/ZnS/Ag/TiOₓ structure is investigated. For optimum conductivity, a thickness of 10 nm Ag was previously set [20,21]. In the thickness ranges 20–50 nm for ZnS and 0–50 nm for TiOₓ, mapping of the calculated transmission can be drawn and reported in Figure 1.

For a transmission greater than 80%, it can be predicted from Figure 1 that the optimal thicknesses of ZnS and TiOₓ are ranging in 20–50 nm. The transmittance is also able to exceed 85% in the range 27–48 nm for TiOₓ and 22–50 nm for ZnS. The optimal thicknesses of the two peripheral layers of our structure can be centered around 40 nm for ZnS and 35 nm for TiOₓ; in this configuration, the calculated transmittance, reflectance and absorbance curves can be plotted versus wavelength in the 400–1500 nm spectral band for the ZnS (40 nm)/Ag (10 nm)/TiOₓ (35 nm) electrode (see dashed lines in Fig. 2). It is then clearly observed a wide transmittance bandwidth (for while T is > 80%) in the 400–800 nm
After manufacturing of the electrodes around the optimal thicknesses values, we are able to compare the experimental optical properties measurements (transmission, reflection and absorption) to those obtained by simulation (Fig. 2). The measured curves are in full line, while the simulated curves are in dashed lines. Results are globally in good agreement for Glass/ZnS (40 nm)/Ag (10 nm)/TiOx (35 nm) electrode. However a slight difference can be observed towards the UV spectral part, probably due to the morphology of Ag, which is probably not totally homogeneous but can present some nano-islands for the very thin thickness of 10 nm. This can result in enhanced absorption due to plasmonic resonances, involving a decreased transmittance for the experimental electrodes compared to the theoretical ones (heterogeneities in Ag morphology are not taken into consideration by simulation).

The experimental optical and electrical results obtained from various fabricated electrodes are summarized in Table 1. The thickness of silver is fixed to 10 nm, while the ZnS thickness is equal to 35 nm and TiOx varies between 25 and 50 nm (with a step of 5 nm). This latter value is varied in order to have benefit of the ability of the upper layer to tune the transmittance frequency band (due to the interferential effect occurring in the whole multilayer). All electrodes have a low sheet resistance (less than 8 Ω/sq) which values varying between 7.4 and 7.8 Ω/sq. The ZnS (35 nm)/Ag (10 nm)/TiOx (30 nm) electrode appears to the most conductive one (7.43 Ω/sq).

Figure 3 shows the transmission of ZnS (35 nm)/Ag (10 nm)/TiOx (y nm) structures for different thicknesses y of TiOx. Our structure has a large optical transmittance window (for T>80%), and it approaches that of the ITO. The width of this optical window can also be controlled by the thickness of the y upper layer of our structure. This is confirmed by the inset curve inside Figure 3, which shows the variation of the width of the optical band as well as its spectral position. Indeed, the optical window widens by decreasing the thickness of TiOx, and turns towards the infrared for thicknesses greater than 45 nm. The spectral range is 375–695 nm for y = 25 nm; 395–720 nm for y = 30 nm; 400–786 nm for y = 35 nm; 595–830 nm for y = 45 nm; and 715–805 nm for y = 50 nm.

Figure 4 shows the displacement of λmax with the increase of TiOx thickness, from 575 nm for 25 nm-thick TiOx to 765 nm for 50 nm-thick TiOx. We can notice from the same figure that the value of Tmax also depends on the thickness of the upper layer of our structure. Indeed, for small thicknesses, Tmax increases up to 85.19% for 30 nm-thick TiOx, then decreases for thicknesses greater than 30 nm until reaching a value of 80.84% for 50 nm-thick TiOx.
The optical window ($\Delta \lambda_{T>80\%}$) for which the transmission exceeds 80% is also presented (Tab. 1). This transmission window can be tailored between 375 and 830 nm, and can therefore be adapted to the useful absorption band of the photoactive material employed in the organic solar cell (Fig. 5). The absorption band of an organic solar cell is mainly dependent on the electron donor material, and is generally included in this previous cited range.

As shown in Figure 5, different organic materials used as an active layer in organic solar cells are presented. Two
For photovoltaic applications, it is also essential to have a suitable work function of the considered electrodes. The commercial ITO has a work function varied from 4.4 to 4.8 eV [24]. We have previously studied and measured the work function of tri-layer electrodes made by electron beam deposition by means of Kelvin Probe Force Microscopy. By using Ag as metal and SnOx, TiOx or ZnS as dielectric in the multilayer electrodes, we obtained for example the work function values of 4.83, 4.75 and 4.48 eV for TiOx/Ag/TiOx, SnOx/Ag/SnOx and ZnS/Ag/ZnS respectively [25]. Because of similarities in the design of the TCE and in the materials properties, we can estimate that the values of the ZnS/Ag/TiOx will remain around these values, which are close to that of the ITO and allow keeping equivalent charge transfer properties.

The opto-electrical performances of our electrodes are at the-state-of-the-art of this ETC field [26]. With a fairly large merit figure comparable to literature values [23,27–29], such transparent, conductive three-layer electrodes are good candidates for use as indium-free electrode in organic solar cells.

4 Conclusion

Glass/ZnS/Ag/TiOx structures are optically and electrically optimized to obtain the best compromise between high transmittance and low sheet resistance. Such ETC are manufactured by e-beam evaporation. Their measured optical properties are in good agreement with the predictive optical simulation. A transmittance level higher than 80% is obtained on a wide spectral range while a sheet resistance of the order of 7.6 Ω/sq is measured. The optical transmittance bandwidth can be tuned by the thickness of the TiOx upper layer in the 400–800 nm absorption spectral band of the most electron donors involved in organic solar cells. An optimal ZnS (40 nm)/Ag (10 nm)/TiOx (30 nm) electrode, with a figure of merit of 23.10−4 Ω−1, is realized. Such ETCs are at the-state-of-the-art of the domain, and could be employed for producing Indium-free organic solar cells.

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Author contribution statement

As PhD student, M.A.C. did the numerical and experimental work, and wrote the first version of the paper. A.L. contributed to the experimental part. D.B. supervised the experiments and contributed to the interpretation of the results. As co-director of the thesis of M.A.C., S.T. approved the presented results. Ph.T. is the co-director of the thesis of M.A.C.; he supervised the work and the data analysis, contributed to the interpretation of the results, and coordinated the manuscript preparation and submission.
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