Thin Solid Films xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Numerical and experimental investigation of transparent and conductive $TiO_x/Ag/TiO_x$ electrode

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ARTICLE INFO

Article history:
Received 16 July 2015
Received in revised form 18 December 2015
Accepted 19 December 2015
Available online xxxx

Keywords:
Multilayer
Oxide/metal/oxide
Transparent conductive electrode
Thin film
Silver
Spectroscopic ellipsometry
Titanium dioxide
Numerical optimization
Organic solar cells

ABSTRACT

Indium Tin Oxide (ITO) is the most commonly used transparent and conductive electrode (TCE) for organic solar cells and other optoelectronic components. One possible alternative to ITO is to use an Oxide|Metal|Oxide multilayer TCE. A numerical and experimental study resulting in an optically and electrically optimized $TiO_x|Ag|TiO_x$ (TAT) TCE is presented. Single Ag and TiO_x layers as well as $Ag|TiO_x$ and $TiO_x|Ag$ bilayers are first investigated. Both oxide thicknesses are then adjusted to give to the TAT trilayer electrode its best transparency in the considered absorption spectral band. The metal layer thickness controls both electrical and optical (mainly in the near-infrared spectral range) properties of the electrode. Electrodes with such TiO_x (37 nm)|Ag (13 nm)|TiO_x (42 nm) design have been produced, which present excellent balance between transparency — 91% of solar energy in the target spectral band that passes through the multilayer – and sheet resistance – average value around 4.7 Ω/□.

1. Introduction

Indium Tin Oxide (ITO) presents a high transparency around 90% in the visible spectrum, a high optical bandgap, a low resistivity around 1-2 × 10^{-4} Ω.cm and a high work function. These advantages have made ITO an intensively used Transparent and Conductive Electrode (TCE). Nevertheless, the Indium used in ITO layers could become rare and expensive. Moreover, the ITO deposition methods can damage the organic materials (such as a flexible substrate made of poly(ethylene terephthalate)) due to the high temperature and the plasma created during the sputtering process. The ITO ceramic structure also restricts its application in flexible devices. Consequently, the search of ITO-free TCE is a substantial scientific investigation field for the international community [1].

One of them consists in using a thin metal layer integrated between two other layers (TCOs, oxides or dielectrics) that are typically called Oxide|Metal|Oxide or OMO electrodes. This idea comes from an early work published by Gillham et al. in 1955 [2] that presented a $Bi_2O_3|Au|Bi_2O_3$ transparent and conductive trilayer for cockpit plane defrosting. A maximum transparency, higher than 80%, and a low sheet resistance, less than 5 Ω/□, were already reached. This trilayer structure was further studied as heat or IR reflector for windows application [3–9]. Then, the concept of trilayer was introduced as TCE in organic solar cells. The first objective was to limit the thickness of the ITO layer, and many publications described ITO|metal|ITO [10–14] multilayers. Then, a large range of materials has been used to replace ITO such as: PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) [15], ZnO [16–20], SnO_2 [21–24], ZnS [25–29], MoO_3 [26,29–34], V_2O_5 [35], WO_3 [36–38], Ga-doped ZnO [39], Al-doped ZnO [39,40], TiInZnO [41], Nb_2O_5 [42], ZrON [43]… Several metals have also been studied such as Ag [27,36], Cu [44,45], Au [11], Mo [40,46], and Al [30,47,48].

Some publications of Fan et al. [49,50] about $TiO_2|Ag|TiO_2$ based on several patents [51,52] around 1975 are earliest works about trilayer using TiO_2 as oxide layers. They present a Glass|TiO_2 (18 nm)|Ag (18 nm)|TiO_2 (18 nm) design for transparent heat-mirrors with a higher than 83% maximum transparency and a very low sheet resistance. Other more recent studies on $TiO_2|Metal|TiO_2$ [53–62] with mainly Ag as metal layer have been led. Lately works [61,62] from Kim et al. present a TiO_2 (40 nm)|Ag (18.8 nm)|TiO_2 (40 nm) multilayer. A high transparency level of 97% – when normalized by transmission of the glass substrate – around the wavelength of 550 nm, associated with a low sheet resistance around 4 Ω/□, are reported. A publication from Lansåker et al. [56] also reveals an interesting numerical and experimental study on $TiO_2|Au|TiO_2$.

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http://dx.doi.org/10.1016/j.tsf.2015.12.041
0040-6090/

The experimental optimization of such trilayer electrodes is often done by maximizing the figure of merit which takes into account the transmittance T and the sheet resistance R_S of the electrode. Such figure of merit Φ_T, proposed by G. Haacke [63], for transparent conductors is given by:

$$\phi_T = \frac{T^{10}}{R_s}$$

The conductivity of the OMO multilayer is mainly controlled by the thickness of the thin metal film. From the equivalent electrical circuit presented in Fig. 1, the resistance R_{OMO} of the trilayer electrode can be deduced by:

$$\frac{1}{R_{OMO}} = \frac{1}{R_{Ox1}} + \frac{1}{R_{Metal}} + \frac{1}{R_{Ox2}}$$

As the oxide layers (R_{OX1}, R_{OX2}) are much more resistive than the metal layer (R_{metal}), the equivalent resistance of the trilayer corresponds to that of the metallic film. Above a critical value of metal thickness which generally ranges in literature between 5 and 15 nm, the resistivity of the trilayer drops down drastically [22,40]. This limit value depends on the metal nature, but also on the underlying oxide, on the employed deposition method, and on the deposition speed [64]. The thickness of each layer in the OMO electrode can be optimized to reach the highest transmittance in the desired spectrum [18,65]. For example, in the case of an organic solar cell, the considered spectral band will depend on the active layer's absorption spectral range. The metal layer morphology is also a key point [66] to successfully embed an OMO transparent electrode in an organic solar cell. A non-uniform, island-like morphology can increase R_{OMO} due to the lack of connectivity between metal islands. Such morphology can also induce optical scattering and Surface Plasmon Resonance (SPR) that lead to increased photon absorption in the electrode [27,66–69].

In this work, the main objective is to present a numerical and experimental coupled study of $TiO_x|Ag|TiO_x$ multilayer. Optical and electrical properties at the state-of-the-art will be obtained on manufactured electrodes while a good agreement between the simulated and measured optical properties will be carried out. Other objectives are to optimize the multilayer by adapting each layer thickness to get the highest figure of merit and to understand the optical and electrical influence of each layer. For that, a simple numerical Transfer-Matrix Method (TMM) model previously described [70] is used and allows us to calculate the optical properties of single layers (Ag and TiO_x), bilayers (Glass|Ag|TiO_x and Glass|TiO_x|Ag) and trilayers.

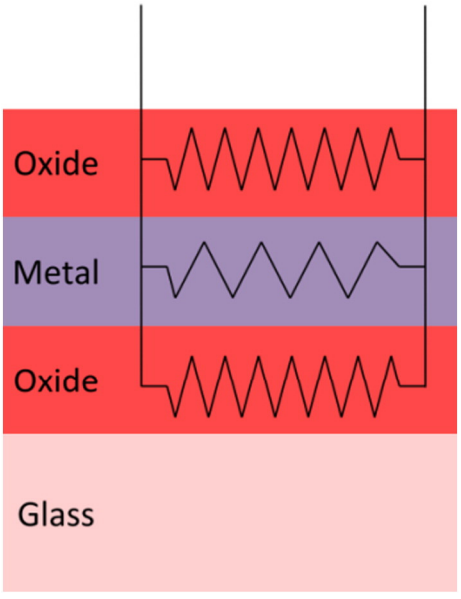

Fig. 1. Schematics of the electrical behavior of an Oxide|Metal|Oxide transparent and conductive electrode.

2. Experimental details

Layers are produced with an Oerlikon Leybold Vacuum Univex 300 E-beam evaporator at normal incidence and with a distance of 20 cm from the liner containing the material to be deposited. The substrates consist in cleaned plain glass slides with a 1 mm thickness. The Ag thin film is deposited from 99.99% pure Ag into a 4 cm^3 Graphite liner at an average rate of 2 $nm.s^{-1}$ under a pressure around 5×10^{-5} mbar. This Ag high deposition rate has been found to be crucial to get percolated Ag layers at the lowest thickness. The TiO_x layer is deposited from 99.99% pure TiO_2 into a 4 cm^3 Mo liner at an average rate of 0.05 $nm.s^{-1}$ under a pressure around 3×10^{-5} mbar. All depositions are done without intentional heating or gas supply. The oxide deposition process leads to an increase of the temperature inside the chamber that hasn't been monitored. This unintentional heat has an influence over the temperature of the substrate. If the silver deposition is realized just after the titanium oxide deposition, the temperature of the substrate is thus higher than ambient and absorption of the final trilayer will be much higher than in the case of a deposition on a substrate at ambient temperature. A waiting time is then systematically enforced between the first titanium oxide and silver depositions to avoid unintentionally heated substrate.

The thicknesses are controlled from a quartz crystal oscillator monitor placed near the substrate during the deposition then checked by a mechanical profilometer. Optical constants and further validation of thickness values have been measured from a SE-2000 spectroscopic ellipsometer of SEMILAB© using a fit model provided by SEA software. Samples are optically characterized by a LAMBDA 950 UV/Vis/NIR PerkinElmer Spectrophotometer with light entering the device via the glass substrate. Electrical measurements are performed at (0.1; 1; 10)*π/ln(2) mA with a CPS Resistivity Test Fixture from CASCADE© combined with a C4S 4-point Probe Head, which owns osmium probes with radii of μm and space between them of 1.55 mm.

3. Results & discussion

3.1. Single layers & optical constants

To determine input parameters of our calculation model, i.e. the optical constants of each material, we used the spectroscopic ellipsometric measurements at several angles – 55° to 75° with a step of 5° – of several single layers made of silver and titanium oxide. The fit of the ellipsometric values tan(Ψ) and cos(Δ) is based on a Tauc-Lorentz model for TiO_x and realized with bulk optical constants from literature [71] for Ag. Optical constants (n,k) for TiO_x and Ag are plotted on Fig. 2. The TiO_x layer used to determine these optical constants has a thickness of 32 nm and a RMS roughness of 1.14 nm. The optical constants of TiO_x and silver have been checked on several samples with different thicknesses.

These optical constants values allow us to validate the thicknesses of single layers, but also to deduce each thickness inside bilayer and trilayer structures from their ellipsometric measurements. The extinction coefficient k_{TiOx} curve demonstrates that the TiO_x has no inherent absorption for wavelengths ranging from 350 to 1500 nm.

From Fig. 3(A)–(a), a very good agreement between simulated and measured reflectance, transmittance and absorptance of the Glass|TiO_x (32 nm) single layer is observed. The transmission is also proved to be well simulated for several thicknesses as seen on Fig. 3(A)-(b). The low 1–3% absorption level of Glass|TiO_x from 600 nm to 1500 nm observed on Fig. 3(A) (a) is due to the glass substrate absorption. Several measurements of sheet resistances of

Please cite this article as: A. Bou, et al., Numerical and experimental investigation of transparent and conductive TiOx/Ag/TiOx electrode, Thin Solid Films (2015), http://dx.doi.org/10.1016/j.tsf.2015.12.041