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$Mo(S_xO_y)$ thin films deposited by electrochemistry for application in organic photovoltaic cells

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HIGHLIGHTS

- Electrochemical deposition of $Mo(S_xO_y)$ Thin films.
- $Mo(S_xO_y)$ annealing in room air provides powerful hybrid MoS_x:MoO_3 thin film.
- Anode buffer layer deposited by wet technique, optimized by soft annealing.
- MoS_x:MoO_3 hybrid anode buffer layer improves organic photovoltaic cells efficiency.

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ABSTRACT

In this study, $Mo(S_xO_y)$ thin films were deposited onto fluorine doped tin oxide (FTO) using pulsed electrochemical deposition method. It is shown by scanning electron microscopy, energy-dispersive spectroscopy and X-ray photoelectron spectroscopy that after water cleaning the deposited $Mo(S_xO_y)$ film corresponds to a hybrid layer MoS_x:MoO_3. This hybrid is used as anode buffer layer (ABL) in planar organic photovoltaic cells (OPVCs) based on the couple copper-phthalocyanine/fullerene. It is shown that it is necessary to proceed to a soft annealing-5 min at 150 °C- of the anode FTO/$Mo(S_xO_y)$ to clean the ABL surface in order to obtain efficient contact with the organic material. The OPVC with the optimum $Mo(S_xO_y)$ thickness, 12 nm, showed a power conversion efficiency, PCE = 1.41% under an illumination of AM1.5, which is 12% higher than that achieved with a simple MoO_3 ABL. This improvement is attributed to the fact that using a hybrid MoS_2:MoO_3 ABL allows to combine the advantages of its both constituents. The MoS_x blocks the electrons, while the high work function of MoO_3 induces a high hole extraction efficiency at the interface electron donor/anode.

1. Introduction

In recent years, renewed interest appeared on two dimensional (2D) materials such as transition metal dichalcogenides (TMDs) due to their suitability for future optoelectronic device applications [1]. In particular, molybdenum disulfide (MoS_2) [2], has been identified as a possible anode buffer layer (ABL) in Dye Sensitized Solar Cells [3] and organic photovoltaic cells (OPVCs) based on bulk-heterojunctions [4–6]. MoS_2 is a material which crystallizes in a layered structure. In such material, strongly bonded two dimensional S—Mo—S sandwiches are loosely coupled to each other by weak van der Waals bonds. These van der Waals planes are inert chemically without dangling bonds. There are a lot of useful properties of MoS_2 such as chemically inert, lubricant, catalyst. All that makes that it was used as lubricant [7], in transistors [8], batteries [9] and catalysts [10]. MoS_2 exhibits an indirect band gap of 1.30 eV and a direct band gap of 1.85 eV and quite high carrier mobility of 200 $cm^2\ V^{-1}\ cm^{-1}$ in monolayer [11].

Due to its versatile properties MoS_2 was introduced in different devices. However, some years ago it was unsuccessfully

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studied as absorbent in inorganic photovoltaic thin film cells [12,13]. Twenty years later it is back in the photovoltaic field, but as anode buffer layer in OPVCs [4–6]. As a matter of fact, organic photovoltaic cells are, nowadays, extensively studied because of their specific properties such as lightness, flexibility, large area processing low cost. The hearth of these cells is based on a heterojunction electron donor/electron acceptor (ED/EA). Two organic solar cell families are encountered, that using a polymer as electron donor and that using small molecules. The polymeric systems, allows achieving good power conversion efficiency (PCE) through the optimization of the morphology of the materials mixed in bulk heterojunction (BHJ) configuration [14]. The second family based on planar heterojunctions (PHJ) uses small molecules often deposited by vacuum deposition technique. Due to the easiness to control the thickness and morphology of the organic materials this technique allows obtaining reproducible results and was used in the present work. These OPVCs are classically based on an organic bilayer sandwiched between two electrodes. One of these electrodes must be transparent and the other must be highly reflexive. The bilayer corresponds to the heterojunction ED/EA. Here, CuPc is used as ED and C_{60} as EA. About the electrodes, while aluminum is often used as reflexive cathode, the transparent conductive anode is usually the indium tin oxide (ITO). To increase the PCE of the OPVCs it is necessary to improve the properties of the active organic materials (ED and EA), however, this is not enough, and we must also ensure the quality of the contacts electrodes/organic materials. To achieve efficient charge transport at the interfaces it is necessary to introduce an interlayer. In particular, it is necessary to introduce an anode buffer layer (ABL) between the anode and the electron donor [15]. Among the known ABL, MoO_3 is one of the most often used, due to its high efficiency. MoO_3 thin films deposited by sublimation under vacuum are oxygen deficient, which makes that they are n-type, with work function W_F of 6.86 eV under ultra-high vacuum [16] and at least 5.9 eV if exposed to ambient air [17], while its electron affinity is 6.70 eV and its ionization energy is 9.68 eV. This last value makes impossible for the hole to transit from the ED to the anode through the MoO_3 valence band. More probably, hole injection from ITO to the organic (in the case Organic Light Emitting Diodes) results from electron extraction from the HOMO of the organic through the MoO_3 conduction band and then into ITO, while hole collection (in the case OPVCs) corresponds to electron transfer from the BC of MoO_3 towards the HOMO of the organic material [18]. Moreover, it was shown that creation of oxygen vacancies increases Jsc, due to the fact that these vacancies open a second path for electron transfer via gap states induced by these vacancies [19,20]. Nevertheless, the HOMO of ED matches the BC of MoO_3, which makes that electron transfer between the 2 layers are probable. It can be concluded that, If MoO_3 is very effective as holes collecting layer, it is probably not as electron blocking layer [18]. Moreover, even if it is semiconductor due to oxygen deficiency, its stays quite highly resistive $10^5\ \Omega^{-1}cm^{-1}$ [21]. All that makes, that OPVCs should exhibit higher efficiency if an electron blocking layer with good conductivity could be associated with MoO_3.

Therefore, in the present manuscript, in order to improve the efficiency of the ABL, we use an original hybrid buffer layer composed of MoO_3, which collects the holes and of MoS_x, which blocks the electrons. Different techniques can be used to grow MoS_2 thin films such as, solid state reaction [22], reactive sputtering [23], sulfurization of a molybdenum layer [24,25], chemical vapor deposition [11,26,27], hydrothermal method [28] and electrochemistry [3]. Here the films are deposited by electrochemistry onto fluorine doped tin oxide (FTO) coated glass substrates.

2. Experimental

2.1. Realisation and characterization of $Mo(S_xO_y)$ thin films

FTO electrodes were supplied by SOLEMS, France. The standard substrate dimensions were 10 mm by 20 mm. Since FTO covered the whole glass substrates, some FTO must be removed to obtain the under electrode. After masking a broad band of 10 mm by 10 mm, the FTO was etched by using Zn powder + HCl as etchant. The substrates were cleaned in an ultrasonic bath using successively acetone, deionized water (DI), and ethanol. The substrates were dried with an air flow and then loaded into the electrochemical cell. Then, the FTO was perturbed by a pulsed electrochemical deposition (ECD) in a cell containing an N_2-saturated aqueous precursor solution: $2\cdot10^{-3}$ mol L^{-1} solution of $(NH_4)_2(MoS_4)$ in 0.1 mol L^{-1} KCl in DI water for obtaining molybdenum sulphide films. The pulsed ECD was performed using a potentiostat CHI 750 in a conventional three-electrode cell at a controlled temperature of 30 °C, under N_2 atmosphere. A Pt coil of large surface and an Ag|AgCl were used as the counter and reference electrodes, respectively. In each perturbation cycle, voltages of −0.15 V and −0.9 V vs. Ag|AgCl were applied during 1.5 s and 2.5 s, respectively. Samples were obtained by 500, 300, 150, 125, 100, 75, 60 and 30 cycles.

Then the films were characterized by Scanning Electron Microscopy (SEM), X-Ray Diffraction, Optical absorption and X-ray photoelectron spectroscopy (XPS).

The morphology of the deposited layers was observed through scanning electron microscopy (SEM) with a JEOL 7600F. The SEM operating voltage was 5 kV. Images were done using secondary electron detector and backscattered electron detector. The composition of the films has been studied by energy dispersive spectrometry (EDS) with a BRUKER Quantax silicon drift detector (SDD) mounted to the SEM.

The thin films structures were analyzed by X ray diffraction (XRD) by a Siemens D5000 diffractometer using Kα radiation from Cu ($\lambda_K\alpha = 0.15406$ nm). Optical transmission spectra were recorded on a Carry spectrophotometer.

XPS measurements were carried out at room temperature. An Axis Nova instrument from Kratos Analytical spectrometer with Al Kα line (1486.6 eV) as excitation source has been used. The core level spectra were acquired with an energy step of 0.1 eV and using a constant pass energy mode of 20 eV, to obtain data in a reasonable experimental time (energy resolution of 0.48 eV). Concerning the calibration, binding energy for the C1s hydrocarbon peak was set at 284.8 eV. The pressure in the analysis chamber was maintained lower than 10^{-7} Pa. The background spectra are considered as Shirley type.

2.2. Realisation and characterization of the OPVCs

The OPVCs were deposited onto FTO coated glass substrates covered, or not with $Mo(S_xO_y)$. The bare FTO substrates being use to grow OPVC of reference. The substrates were loaded into a vacuum chamber (10^{-4} Pa). The planar heterojunctions were based on the couple CuPc/C_{60} sandwiched between two electrodes, the FTO coated glass substrate as anode and an Al film as cathode. Between the Al cathode and the fullerene layer the exciton blocking layer (EBL) was Alq_3 [20]. CuPc, C_{60}, Alq_3 were successively sublimated under vacuum and finally the aluminium anode was evaporated on the top of the device. Deposition rate and film thickness were measured in situ by quartz monitor, after calibration for each material. The top electrode was deposited through a mask with 2 × 8 mm^2 active area. All the film thicknesses were optimized in previous publication [14,20].