

Magnetron Sputtered Molybdenum Oxide for Application in Polymers Solar Cells

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Abstract. Thin films of molybdenum oxide were deposited by radio frequency (RF) magnetron sputtering in Ar from a MoO₃ target at different deposition power on glass and silicon substrates. The thickness of the films was determined by profilometer measurements and by ellipsometry. The films were annealed in air at temperatures between 200 and 400°C in air. The optical transmission and reflection spectra were measured. The conductivity of the as deposited and annealed films was determined. The crystal structure was probed by Raman spectroscopy. The oxidation state of the surface was studied by X-ray photoelectron spectroscopy (XPS) spectroscopy. The deposition technique described above was used to experiment with MoOx as a hole transport layer (HTL) in polymer solar cells with bulk heterojunction active layer, deposited by spin coating. The performance of these layers was compared with poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), which is the standard material used in this role. The measured current-voltage characteristics of solar cells with the structure glass/ITO/HTL/Poly(3-hexyl)thiophene (P3HT):[6,6]-phenyl-C61-butyric acid methyl ester (PCBM)/Al demonstrate that the studied MoOx layer is a good HTL and leads to comparable characteristics to those with PEDOT:PSS. On the other hand the deposition by magnetron sputtering guarantees reliable and repeatable HTLs.

1. Introduction

Organic polymer solar cells are the subject of intense research activity with the aim of increasing their efficiency and stability. The most widely used kind of polymer solar cells is that based on the so called bulk heterojunction where the donor and the acceptor are intermixed in a single layer. The functioning of such devices depends on the use of selective layers – hole transport (HTL) and electron transport layers, which facilitate the extraction of one type of charge carrier and present a barrier to the other. The typical HTL is PEDOT:PSS. Because of some problems that the use of PEDOT:PSS presents connected with the stability of the cells there has been a search for alternatives. A number of inorganic oxides have been experimented and one of them is molybdenum oxide. It has been successfully applied in both normal and inverted polymer solar cells [1,2] on glass as well as on flexible substrates [3,4]. Molybdenum oxide is found to have a high work function, which is close in value to the highest occupied molecular orbital (HOMO) of a lot of the donor materials in bulk heterojunction polymer solar cells like P3HT, Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-



benzothiadiazole)] (PCDTBT), etc. [5,6]. This fact makes it a good hole transport material while the barrier for electrons in the lowest unoccupied molecular orbital (LUMO) of the acceptor is high. The oxide layer is quite thin, on the order of 5 -10 nm.

The most often used method for the deposition of molybdenum oxide as HTL is thermal evaporation [7]. There are a few studies of sputtered films for this purpose [8,9]. In all cases however the sputtering is done from a metal target in reactive O_2+Ar atmosphere. In this contribution molybdenum oxide layers obtained by magnetron sputtering of a MoO_3 target in pure Ar are presented and it is shown that they can be successfully employed as hole transport layers.

2. Experimental

Thin films were deposited by magnetron sputtering of a MoO_3 target (76.2 mm dia. x 3.18 mm thick, purity 99.99%) purchased from Testbourne Ltd. It was water cooled during the deposition. The sputtering was performed in Ar atmosphere for 10 min and the RF power was varied between 100 W and 250 W. The substrates were glass (76x26 mm) and 2" Si wafers. The target and substrate holder are situated vertically at a distance of 8 cm from each other. The substrate holder is rotated at a rate of 80 rpm/min during the deposition which leads to greater homogeneity of the films. The deposition rate was between 35 and 90 Å/min depending on the RF power. Some of the films on glass were annealed for 1 hour in air at 200 °C, 300 °C and 400 °C.

The thickness of the films was measured by a Talystep profilometer. The optical transmission and reflection of the films was measured with a Shimadzu UV-3600 spectrophotometer. The Raman spectra were measured on glass substrates with a Horiba Jobin Yvon LabRAM HR800 spectrometer using the 600 l/mm grating and HeNe laser for excitation. The samples were placed under the 100X achromatic objective of a BX41 microscope and measured in back scattering configuration. The sheet resistance was measured using the four point method. The XPS spectra were recorded with an AXIS Supra spectrometer of Kratos Analytical Ltd. and fitted using CasaXPS software package. The background intensity for scans was calculated using a Shirley background substitution.

In order to test the applicability of the sputtered MoO_x films as HTL in polymer bulk heterojunction (BHJ) solar cells the following devices were prepared. On structured ITO covered glass substrates from Ossila Ltd. was deposited either PEDOT:PSS by spin-coating or MoO_x by RF magnetron sputtering at 150 W for 3 min. to get a 15 nm thick layer. On top the P3HT:PCBM BHJ was spin-coated. Al back contacts were evaporated. The devices were annealed after encapsulation at 110 °C for 10 min. on a hot plate. Their current-voltage characteristics were measured using a halogen lamp and computer controlled equipment. The illumination used was not standard so the measured characteristics cannot be directly compared to those in the literature. However all solar cells were measured under identical illumination conditions and can be compared between themselves.

3. Results and Discussion

3.1. Optical Properties

The optical transmission of the as deposited films is shown in figure 1. All films have a greyish colour. The difference in the transmission between the films sputtered at 100 and 150 W is connected to the difference in thickness. The film sputtered at 250 W is darker.

Figure 2 presents the Tauc plots for assessing the optical band gap of the as deposited films. It is not possible to determine very accurately the optical gap of these disordered not fully stoichiometric films but the values are within the range cited in the literature for MoO_x layers [7,10].

Annealing in air improves the transparency of the layers as demonstrated by the data in figure 3 for a film deposited at 150W. The best results are achieved after annealing at 300 °C. This annealing temperature is too high if the layers are to be deposited on top of the polymer active layer but could be used in the case when the HTL layer is deposited before the organic one.

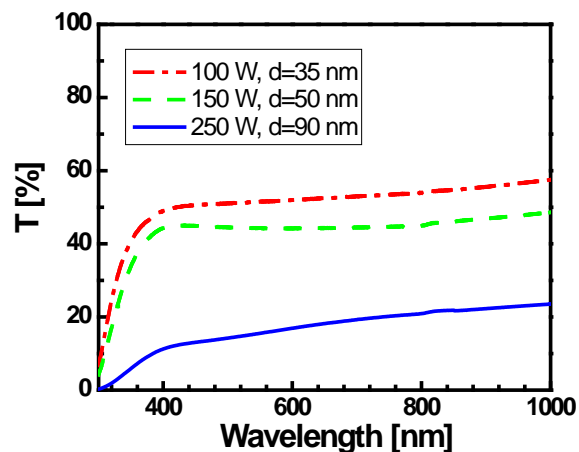


Figure 1. Optical transmission of MoOx films deposited by magnetron sputtering at different power. The thickness of the films is indicated in the figure.

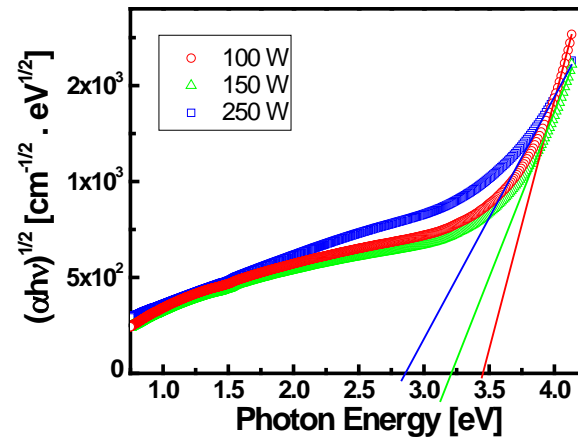


Figure 2. Optical band gap determination of the same films as in the previous figure.

3.2. Raman Spectra

Raman spectra (figure 4) show that the as deposited films are amorphous. Annealing above 300 °C leads to the appearance in the Raman spectra of a number of sharp lines. After annealing at 400 °C in most cases the majority of the lines in the Raman spectrum can be assigned to the orthorhombic α -MoO₃ crystalline phase [11,12] (figure 4).

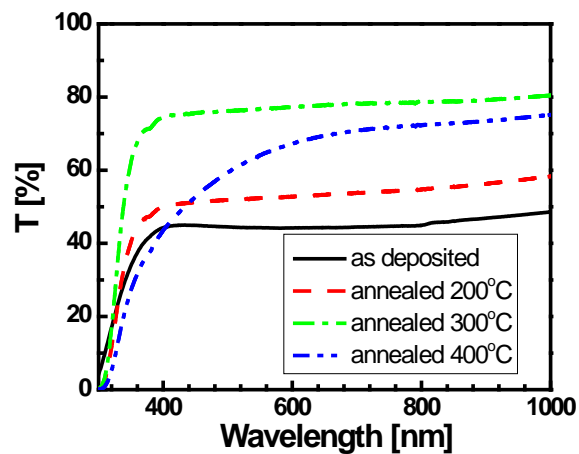


Figure 3. Optical transmission of the film deposited at 150 W as a function of annealing temperature as indicated in the figure.

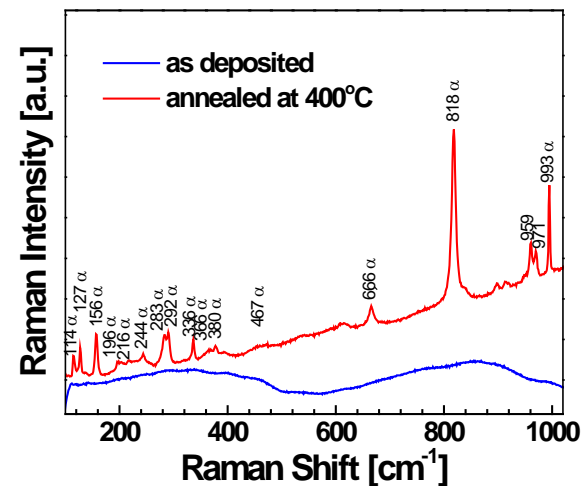


Figure 4. Raman spectra of an as deposited MoOx layer and one annealed at 400°C (upper curve). The lines marked by α are assigned to orthorhombic α -MoO₃.

3.3. Conductivity Measurements

The measured sheet resistance of the as deposited and annealed films is shown in table 1. The conductivity has a metal character, the type of majority carrier could not be determined.

Table 1. Values of the sheet resistance of MoOx films before and after annealing (Ω/\square).

Annealing	Deposition power (W)		
	100 W	150 W	250 W
as deposited	540 Ω/\square	680 Ω/\square	680 Ω/\square
200°C	540 Ω/\square	680 Ω/\square	680 Ω/\square
300°C	250 Ω/\square	-	260 Ω/\square
400°C	260 Ω/\square	260 Ω/\square	260 Ω/\square

3.4. XPS Spectra

The XPS spectra of the surface of the films deposited on silicon were measured. They do not vary much with the deposition power and those of the sample deposited at 150W are shown in figure 5 for Mo3d electrons and in figure 6 for O1s electrons. The information extracted from the spectra after fitting is given in table 2 and table 3 respectively. The content of the different oxidation states of molybdenum is derived from the relative area of the corresponding XPS Mo3d doublet peaks obtained from the fitting. A similar procedure is used for the bonds of oxygen in the O1s XPS spectrum. The fits using the CasaXPS software are very accurate and the content can be evaluated to a precision better than 0.1 at. %. On the basis of the content of the different oxidation states of molybdenum the O:Mo ratio in the molybdenum oxide is calculated presuming that all molybdenum ions in the sampled region are accounted for by the Mo3d XPS spectra.

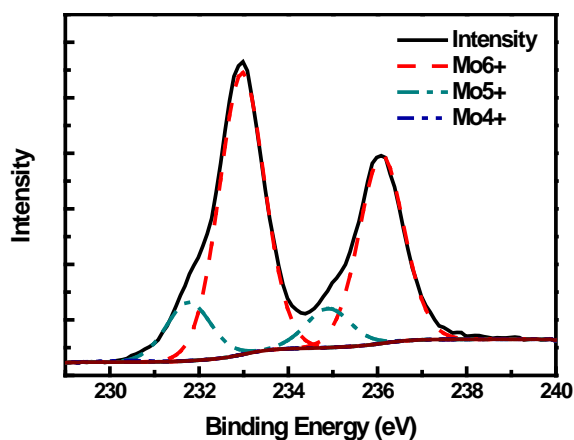


Figure 5. Mo3d XPS spectrum of the sample sputtered at 150W.

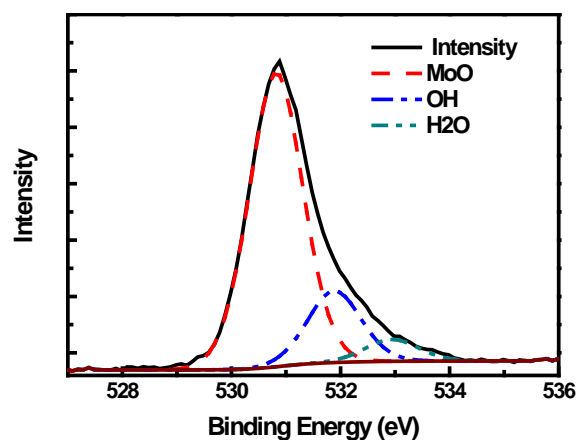


Figure 6. O1s XPS spectrum of the sample sputtered at 150W.

Table 2. Data derived from the Mo3d XPS spectra of the 150W sample.

Mo3d	Mo ⁶⁺	Mo ⁵⁺	Mo ⁴⁺
3d ^{5/2} position (eV)	236.1	234.9	233.6
3d ^{3/2} position (eV)	233.0	231.8	230.4
content	82.5%	17.1%	0.4%
O:Mo	2.91		

The presented XPS data show that the as deposited material is just a little bit substoichiometric molybdenum oxide MoOx with $x=2.91$ and predominantly 6+ and some 5+ oxidation states of Mo, traces of 4+ and no lower oxidation states. There is some water and –OH groups on the surface which

is normal for layers kept in ambient atmosphere. These values for the oxidation state of molybdenum in the as deposited amorphous films correspond to data in the literature for good HTL molybdenum oxide layers [7].

Table 3. Data derived from the O1s XPS spectra of the 150W sample.

O1s			
	Mo-O	OH ⁺	H ₂ O
position (eV)	530.8	531.9	532.9
content	75.8%	18.5%	5.7%

3.5. Results for Application in Solar Cells

The measured current voltage characteristics under identical illumination of the two types of solar cells with the structure glass/ITO/HTL/P3HT:PCBM/Al, differing only in the HTL layer – either MoO_x sputtered at 150 W, or PEDOT:PSS deposited by spin-coating, are presented in figure 7. The MoO_x layer has not been optimized for this device in any way. In spite of this, the results for the solar cell with the oxide HTL are comparable to those with PEDOT:PSS. This is a positive result showing that the films sputtered from a MoO₃ target only in argon can be employed instead of evaporated or reactively sputtered films but further optimization of the thickness and of the deposition and treatment conditions are needed.

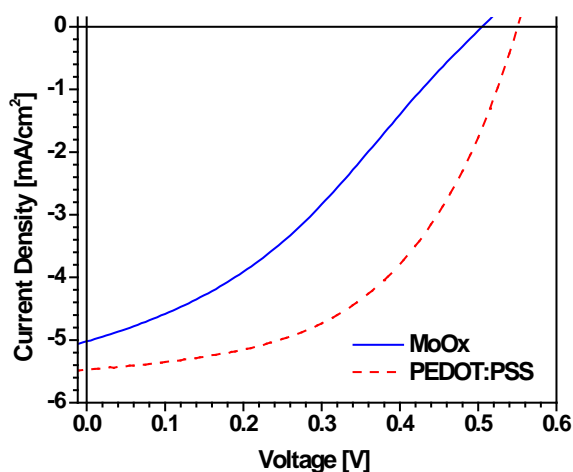


Figure 7. Current-voltage characteristics of solar cells with two different hole transport layers – PEDOT:PSS and MoO_x.

4. Conclusion

The results from this study demonstrate that samples deposited by RF magnetron sputtering in pure Ar from a MoO₃ are amorphous. Their transparency in the visible is not very good but good enough for films of about 10 nm thickness to be used as HTL in polymer solar cells. The optical gap estimated from the optical transmission and reflection spectra is around 3 eV and corresponds to values found for amorphous molybdenum oxide in previous studies. According to XPS measurements the as deposited samples are suboxide MoO_x with $x=2.91$. Oxidation states lower than 5+ are found only as traces on the surface. The samples exhibit high planar conductivity.

Polymer solar cells with not optimized sputtered MoO_x hole transport layer demonstrate comparable J-V parameters to those of similar cells with PEDOT:PSS HTL. Further optimization of the oxide hole transport layer is needed. However this study demonstrates that magnetron sputtering in

pure Ar from an MoO₃ target can be used instead of reactive sputtering or thermal evaporation to obtain MoOx layers for application in solar cells.

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