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Deposition temperature effect of RF magnetron sputtered molybdenum oxide films on the power conversion efficiency of bulk-heterojunction solar cells

Xi Fan, Guojia Fang, Pingli Qin, Nanhai Sun, Nishuang Liu, Qiao Zheng, Fei Cheng, Longyan Yuan and Xingzhong Zhao

Key Laboratory of Artificial Micro- and Nano-structures of Ministry of Education, Department of Electronic Science and Technology, School of Physics and Technology, Wuhan University, Wuhan, 430072, People’s Republic of China

E-mail: gjfang@whu.edu.cn

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Abstract

We have reported efficient bulk-heterojunction (regioregular poly(3-hexylthiophene) : (6,6)-phenyl C61 butyric acid methyl ester (P3HT : PCBM)) solar cells with MoO3 as a hole-selective layer deposited at different substrate temperatures from 100 °C to 400 °C by radio-frequency magnetron sputtering. The structure, morphology, optical and electrical properties of the MoO3 films deposited at different substrate temperatures are also investigated. MoO3 thin films deposited at 200 °C and below are amorphous in nature. However, the films deposited at 300 °C and 400 °C exhibit the presence of monoclinic Mo9O26 and orthorhombic MoO3, respectively. The electrical resistivity values of the MoO3 thin films are close to each other from 100 to 300 °C and decrease from 2.7 × 106 to 2.6 × 105 Ω cm with increasing substrate temperature from 300 to 400 °C. X-ray photoelectron spectroscopy core level analysis reveals the presence of Mo6+ oxidation state only in the films. We found that the optical band gap of MoO3 has reduced from 3.82 to 3.67 eV with decreasing substrate temperature from 400 to 100 °C. This decrease in band gap reduces the potential barrier between FTO and P3HT : PCBM, leading to an increase in the short circuit photocurrent density from 8.51 mA cm−2 to 9.50 mA cm−2 and an increase in efficiency of ∼20.7%.

1. Introduction

Molybdenum oxide (MoO3) has been widely used in recent years in bulk-heterojunction (BHJ) solar cells as an electron-blocking and hole-selective layer to replace poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT : PSS) [1–3]. Recently, the electronic structure of MoO3 thin film has been investigated [4, 5]. However, in the fabrication process of electronic and optoelectronic oxide semiconductor devices, it is necessary to know the roles played by MoO3 in the device as well as the physics and chemistry at the anode/MoO3/BHJ interfaces/cathode devices. In our study, it is seen that MoO3 has a band structure well suited for poly (3-hexylthiophene) : (6,6)-phenyl C61 butyric acid methyl ester (P3HT : PCBM) BHJ solar cells and provides an ohmic contact to P3HT. In recent years, many methods have been employed to deposit molybdenum oxide films such as thermal evaporation [1], radio-frequency (RF) magnetron sputtering [6], pulsed-laser deposition (PLD) [7], sol–gel deposition [8, 9] and chemical vapour deposition [10]. Among them, thermal evaporation has been used most widely to prepare MoO3 films for BHJ solar cells. We select magnetron sputtering instead of thermal evaporation because the film properties can be optimized through various deposition process parameters such as O2 partial pressure in the mixture gas, total pressure, substrate temperature and sputtering power...
[6, 11–13]. To the best of our knowledge, MoO3 films deposited by RF magnetron sputtering have been rarely reported for BHJ solar cells. In our work, we report the strong effect of MoO3 deposition temperature on the current-voltage (J–V) characteristics of BHJ solar cells, and show that with decreasing deposition temperature from 400 to 100 °C, the short circuit current density (JSC) of the BHJ solar cells increases from 8.51 to 9.50 mA cm−2, and the power conversion efficiency (PCE) increases from 2.71% to 3.27%. To understand the effect of the MoO3 thin films at different substrate temperatures on the PCE, the structure, morphology, and chemical states of the MoO3 films were necessarily investigated. Mo oxidation states in the films were given by x-ray photoelectron spectroscopy (XPS). Fluorinated tin oxide (FTO)/MoO3/P3HT : PCBM/Al structure device was fabricated to confirm its potential device applications.

2. Experimental details

Molybdenum oxide thin films were deposited on fused silica substrates at different substrate temperatures ranging from 100 to 400 °C by RF magnetron sputtering from a Mo metal target. The thin films were deposited at a relative oxygen partial pressure O2/(Ar + O2) of 50% without post-deposition annealing. The base pressure of the deposition chamber was below 10−6 Pa. All the films were deposited at a total pressure of 0.5 Pa and a RF power of 130 W. Before deposition, the target was pre-sputtered for 10 min to remove some possible contaminants. The MoO3 thin films were deposited on fused silica substrates for 20 min. After one day, the compositions and chemical states of the molybdenum oxide films were examined by XPS (XSAM800).

As for the BHJ solar cell fabrication, first, a 10 ± 1 nm MoO3 layer was deposited on FTO substrates at different substrate temperatures from 100 to 400 °C. Then, the solution of P3HT : PCBM (20 mg : 20 mg) in chlorobenzene (1.0 ml) was deposited by spin coating at 1000 rpm on the MoO3 layer. Afterwards, Al electrodes (~100 nm) were deposited on the P3HT : PCBM layer (~150 nm) via thermal evaporation at a pressure of 10−4 Pa. The active area of device was 0.2 cm2. Finally, the devices were annealed at 150 °C for 8 min under argon atmosphere (<1 ppm O2 and <1 ppm H2O). The film thickness was measured by a surface profile meter (Talysurf Series II). The electrical resistivity (ρ) of the film was obtained using a Keithley 4200 semiconductor characterization system at room temperature. The crystal structure of the film was characterized by x-ray diffraction (XRD, Bruker Axs, D8Advance) using Cu Kα radiation at 40 kV and 40 mA. The spectral transmittances of the molybdenum oxide thin films were recorded using a UV–VIS–NIR spectrophotometer. The morphology of MoO3 deposited on the FTO substrates was characterized by atomic force microscopy (AFM, SPM-9500i3, Shimadzu, Japan). Photo-energy conversion characterization was recorded by a source meter (Model 2400, Keithley Instruments Inc., USA) under an illumination intensity of 100 mW cm−2 (Oriel 91192, AM 1.5, Global). From this, the performance parameters of the devices were calculated.

Figure 1 shows the light (top) and dark (bottom) J–V characteristics for the solar cell devices with MoO3 deposited at different substrate temperatures from 100 to 400 °C and the optimized PEDOT : PSS (~30 nm) by adjusting the speed of spin coating under simulated 100 mW cm−2 (AM 1.5G) solar irradiation. In this study, the devices show power conversion efficiencies of 3.27% and 3.12% at 100 °C and 200 °C, respectively, exhibiting a higher performance which is much higher than that of the devices with a PEDOT : PSS layer and an evaporated MoO3 layer. Hence, MoO3 prepared by RF magnetron sputtering is quite suitable for fabricating BHJ solar cells as an electron-blocking and hole-selective layer. Specially, it also shows that JSC increases from 8.51 to 9.50 mA cm−2 with decreasing substrate temperature from
400 to 100 °C. This trend is supported by the dark J−V curves in which the device exhibited a higher rectification ratio with decreasing deposition temperature, indicating the better hole injection and electron-blocking properties. For comparison, the performance parameters are shown in Table 1.

The XRD patterns of the MoO₃ films deposited on fused silica substrates at low temperatures. When the substrate temperature increases to 300 and 400 °C, the crystalline nature of the films is observed, owing to the perfect growth alignment of MoO₃. The thin films deposited at 300 and 400 °C show the presence of monoclinic Mo₉O₂₆ and orthorhombic MoO₃ with space groups P21/c (14) and Pbnm (62), respectively, which was also reported similarly in the literature by the same works [17, 18]. The direct band gap energy increases with an increase in substrate temperature, which might be attributed to the reduction of oxygen deficiency and the stoichiometric

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
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</thead>
<tbody>
<tr>
<td>Eₑ (eV)</td>
<td>3.67 ± 0.01</td>
<td>3.64 ± 0.01</td>
<td>3.72 ± 0.01</td>
<td>3.82 ± 0.01</td>
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<tr>
<td>ρ (Ω cm)</td>
<td>4.8 × 10⁶</td>
<td>8.1 × 10⁶</td>
<td>2.7 × 10⁶</td>
<td>2.6 × 10⁵</td>
</tr>
<tr>
<td>Growth rate (nm min⁻¹)</td>
<td>6.25</td>
<td>7.75</td>
<td>10</td>
<td>9.25</td>
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<tr>
<td>Jₑ (mA cm⁻²)</td>
<td>9.50</td>
<td>9.31</td>
<td>8.98</td>
<td>8.51</td>
</tr>
<tr>
<td>PCE (%)</td>
<td>3.27</td>
<td>3.12</td>
<td>2.95</td>
<td>2.71</td>
</tr>
</tbody>
</table>

Table 1. $E_e$, $\rho$ and growth rate of molybdenum oxide films deposited at various substrate temperatures and the corresponding bulk solar cell performances.
Figure 4. The dependence of \((a\nu)^2\) on \(\nu\) for molybdenum oxide thin films deposited at different temperatures.

Figure 5. XPS spectra of MoO3 deposited at 100 °C, 300 °C and 400 °C, respectively.

Figure 6. Core level spectra of MoO3 film showing the presence of Mo6+ oxidation state, only.

approach of film composition \([18]\). At a higher substrate temperature, the sputtering process may yield more active oxygen species due to the plasma decomposition of O2 than that at a lower temperature \([14]\). With the precise analysis of crystalline phase of XRD PDF cards, it is found that the thin films, annealed at 300 and 400 °C, exhibit the presence of monoclinic Mo9O26 and orthorhombic MoO3, respectively. The impurity energy state induced by oxygen deficiency might lead to a decrease in the band gap of MoO3.

We also reckon that there are some relationships between the band gap and the structures. Amorphous, monoclinic and orthorhombic molybdenum oxides have different atomic arrangements. The slight difference between the two band gaps (3.67 ± 0.01 eV, 3.64 ± 0.01 eV) is possibly due to the same amorphous phase.

Table 1 also illustrates the growth rate of the molybdenum oxide films deposited at various substrate temperatures from 100 to 400 °C. The growth times of MoO3 films are all the same, about 40 min at different substrate temperatures. It is observed that the growth rate of the molybdenum oxide films almost increases linearly with increasing substrate temperature except at 300 °C. The electrical resistivity of the MoO3 films deposited at different substrate temperatures is also shown in table 1. It is obvious that the thin films exhibit a lower electrical resistivity at 400 °C, indicating the semiconducting nature of the films, and this may be also due to thermal excitation, impurities and lattice defects. The resistivity of the MoO3 films increases from 2.6 × 10^5 to 2.7 × 10^6 Ω cm with decreasing substrate temperature from 400 to 300 °C, which is much lower than the previous reports (>10^5 Ω cm) \([6, 19, 20]\). But the resistivity values are close to each other from 100 to 300 °C in our experiment, which indicates that the change in PCE has not resulted from the electrical resistivity of the MoO3 films.

The surface morphologies of the FTO substrate and MoO3 films deposited at different temperatures are compared in figure 7. The RMS of FTO is ∼15.55 nm. With decreasing deposition temperature from 400 to 100 °C, the RMS of the MoO3 film gradually decreases from ∼13.72 to ∼10.13 nm. The roughness of polycrystalline MoO3 films at higher deposition temperatures is higher than that of amorphous MoO3 films at lower deposition temperatures, mainly due to the formation of crystalline MoO3 particles. The slight difference in RMS results might have an effect on the performance parameters of solar cells but it is very limited. Further detailed
Figure 7. The morphologies of FTO substrate and MoO3 films deposited at different temperatures from 400 to 100 °C. (a) FTO: 15.55 nm; (b) MoO3 400 °C: 13.72 nm; (c) 300 °C: 12.65 nm; (d) 200 °C: 11.44 nm; (e) 100 °C: 10.13 nm. AFM height images of devices showing 1.00 µm × 1.00 µm surface areas.

Thus, J_{SC} and PCE seem to be roughly correlated with the optical band gap, although the effect of other characteristics of the MoO3 film on the BHJ morphology could account for such differences. In the FTO/MoO3/P3HT:PCBM/Al structure devices, the MoO3 layer is a hole-selective and electron-blocking layer as shown in figure 8. Due to the fact that the lowest unoccupied molecular orbital (LUMO) of P3HT is much lower than the energy level of the conduction band (CB) of MoO3, which significantly blocks the electron transfer to MoO3, the discrepancy of J_{SC} does not arise from the transfer and collection of electrons by the Al cathodes. Hole injection has an effect on J_{SC}. It can be assumed that the position of CB is invariable on changing the deposition temperature of MoO3. But since the optical band gap energy (E_g) of the MoO3 thin films decreases from 3.82 ± 0.01 to 3.64 ± 0.01 eV with decreasing deposition temperature, the valence band of the film rises gradually from −5.48 to −5.30 eV, therefore, the potential barrier between FTO and P3HT:PCBM decreases, leading to an increased efficiency with hole injection from P3HT to FTO in an easier way. Thus, the optimized devices have an efficiency of 3.27%, showing a significant improvement of 11.6% in J_{SC} and 20.7% in PCE. It also suggests a key design principle in BHJ solar cells: the buffer layer should have a suitable valence band between the highest occupied molecular orbital of P3HT and the Fermi level of the electrodes as well as a suitable CB, which is higher than the LUMO of P3HT.

4. Conclusion

P3HT:PCBM BHJ solar cells with MoO3 buffer layers deposited at different substrate temperatures by RF magnetron sputtering are studied. As a result, the PCE of FTO/MoO3/P3HT:PCBM/Al structure solar cells increases...
from 2.71% and 3.27% with decreasing substrate temperature from 400 to 100 °C. The structure, morphology, optical and electrical properties of the MoO3 thin films are investigated. As measured by XRD, the thin films deposited at 300 °C and 400 °C exhibit the presence of monoclinic Mo9O26 and orthorhombic MoO3 respectively. The optical band gap energy values of the MoO3 films increase from 3.67 to 3.82 eV with an increase in substrate temperature from 100 to 400 °C. The electrical resistivity values of the MoO3 thin films are close to each other from 100 to 300 °C and decrease from 2.7 × 106 to 2.6 × 105 Ω cm with increasing substrate temperature from 300 to 400 °C, due to a phase change from monoclinic Mo9O26 to orthorhombic MoO3. The XPS results show that it is difficult to observe Mo4+ and Mo5+ states at 100, 300 and 400 °C. Thus, the decrease in the optical band gap of the MoO3 might have resulted from the rise in the valance band, which decreases the potential barrier between FTO and P3HT : PCBM. Therefore, the efficiency of FTO/MoO3/P3HT : PCBM/Al structure solar cells is improved from 2.71% to 3.27%, with JSC increasing from 8.51 to 9.50 mA cm⁻².

Acknowledgments

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