RF-Sputtered High-Mobility Indium Molybdenum Thin Films for Organic Solar Cell Applications

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1. Introduction

Due to the issue of global warming, renewable energies are the most important components of the global new energy strategy in the 21st century. Among them, solar energy appears as one of the most promising candidates. Nowadays, about 90% of the worldwide solar cell production is silicon-based. However, organic solar cells (OSCs) have the potential as an alternative. OSCs are attractive because of the advantages of low-cost, mechanical flexibility, ease of processing and large scale production.

One of the main reasons for the reduced OSC efficiency is the optical loss in the OSC device. The optical loss comes from the absorption by the front contact and various inactive window layers. Therefore, it is necessary to develop new transparent conductive oxide (TCO) with better properties applied to the top contact. The top contact TCO requires the following characteristics: high optical transmittance, low electrical resistivity, high carrier mobility, and low free carrier absorption. As predicted by the Drude model, decreasing the resistivity without compromising the transmittance can only be obtained by increasing the mobility without raising concentration. This results in greater valence difference between the dopant and the substituted ion. In this connection, Meng et al. firstly reported molybdenum-doped indium oxide (IMO), with a valence difference of 3, in 2001 [1], and thereby attracted much attention.

In this paper, we propose the use of IMO films as front contact of P3HT/PCBM based OSCs. High quality IMO films are prepared by sputtering, and the effect of post-annealing is investigated. The IMO films have an optimum efficiency of 3.77%, indicating that IMO films will be the alluring candidate as transparent contact and window layer for OSCs.

2. Experimental

IMO films were deposited on Corning glasses, and deposition was carried out by radio frequency (RF) sputtering, whereas In₂O₃ and Mo targets were employed as sputtering sources. The working pressure was kept at 0.67 Pa under the ambient of pure argon. The deposition temperature was room temperature. The relative weight ratios of Mo in IMO films were ranging from 1.91 to 3.08 wt%, depending on the RF power supplied to the In₂O₃ target. After deposition, IMO films were post-annealed at 300°C for 140 sec. Then, a blend solution made of P3HT and PCBM was spin-coated on these IMO films to form the active layer of our OSC devices. Afterwards, Ca and Al layers were evaporated sequentially on the active layer.

The thickness of the IMO films was measured by a surface profiler. The relative weight ratios of Mo in IMO films were determined by electron probe microanalyzer (EPMA). The electrical characteristics were measured by Hall measurement. Optical transmittance spectra were measured by spectrophotometer. The current-voltage characteristics were measured under 100 mW/cm² (AM 1.5) irradiation from a solar simulator.

3. Results and Discussion

Table I lists the electrical characteristics of as-deposited and post-annealed IMO films with 2.36 wt% Mo. By co-sputtering the In₂O₃ and Mo targets, Mo atoms (1.45 Å) substitute In atoms (1.55 Å) in the In₂O₃ lattice without significantly affecting the lattice constant. However, when the concentration of Mo is increased, they may not occupy proper lattice sites in the In₂O₃ because of the solubility limit of Mo atoms in In₂O₃. Since the atomic radius of Mo is smaller than that of In, the excess Mo atoms may occupy the interstitial positions and result in lattice deformation. Thus, scattering by the defects in the crystal and grain boundaries increases with the increasing Mo concentration. In this paper, the optimum content of Mo of 2.36 wt% is observed.

After post-annealed at 300°C, the resistivity of IMO films (with Mo content of 2.36 wt%) decreases from 2.02 × 10⁻⁸ to 3.55 × 10⁻⁸ Ω-cm, while the carrier concentration and mobility increase from 2.44 × 10²⁰ to 4.23 × 10²⁰ cm⁻³ and 12.68 to 41.56 cm²/Vs, respectively. Since the resistivity is inversely proportional to the carrier concentration and mobility, the reduced resistivity can be explained as following. First, it was reported that to activate the Mo dopant, the threshold temperature is between 300 to 400°C [2]. It can be clearly observed from table I that the carrier concentration is raised after thermal annealing, meaning that more free carriers releasing from Mo, and starting to contribute to the conductivity. Second, a significant improvement in
mobility is also observed, which is believed to be a result of better film crystallinity after post annealing.

Table I  Effects of post annealing on electrical properties of IMO thin films.

<table>
<thead>
<tr>
<th></th>
<th>Resistivity (Ω·cm)</th>
<th>Concentration (cm⁻³)</th>
<th>Mobility (cm²/V·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>2.02 × 10⁻³</td>
<td>2.44 × 10²⁰</td>
<td>12.68</td>
</tr>
<tr>
<td>After annealing</td>
<td>3.55 × 10⁻⁴</td>
<td>4.23 × 10²⁰</td>
<td>41.56</td>
</tr>
</tbody>
</table>

Figure 1 depicts the effect of post annealing on optical transmittance of IMO films with Mo content of 2.36 wt%. The spectra were measured in the wavelength range of 300-800 nm. The average transmittance of IMO films with post annealing in the visible region is around 80%. Another noticeable phenomenon observed is that the optical transmittance at 550 nm exceeds 80%. It is evident that the increment in optical transmittance is very significant after post annealing. The increase in optical transmittance is due to the improvement in crystallinity of the IMO films. After post annealing, larger grain size and lower defect density result in less scattering loss. Moreover, the optical transmittance increases apparently in the near UV region after post annealing, suggesting the widening of the energy band gap. Compared with Table I, the widening of the band gap correlates well with the increase of carrier concentration, which is related to the Burstein-Moss effect [3]. Burstein reported that the raise of the Fermi level in the conduction band leads to the band gap widening. The band gap widening is related to the concentration as below,

\[ \Delta E_g = \frac{\hbar^2}{8m^*} \left( \frac{3}{\pi} \right)^{2/3} n^{2/3} \]

where \( h \) is the Planck’s constant and \( m^* \) is the electron effective mass.

\[ J_{sc} = \frac{A \varphi_0}{2} \left( \frac{3}{\pi} \right)^{2/3} n^{2/3} \]

where \( A \) is the area, \( \varphi_0 \) is the built-in voltage, and \( n \) is the carrier concentration.

Figure 2 reveals the comparison of I-V characteristics of OSCs with IMO or ITO electrodes measured under 100 mW/cm² irradiation. The OSC with IMO electrode shows an open-circuit voltage of 603 mV, a short-circuit current of 9.48 mA/cm², and a conversion efficiency of 3.77%. In contrast with the efficiency of OSC with ITO electrode, which is 3.51%, the OSC with IMO electrode offers a higher efficiency. The higher efficiency of OSC with IMO electrode is mainly due to the high-mobility IMO films. IMO films with a high mobility would reduce the series resistance of OSCs, and hence result in a superior efficiency. This result indicates that the IMO is the promising candidate that can be used on OSCs in the future.

3. Conclusions

In this paper, we have discussed the characterization of IMO films grown by rf sputtering. The relationship between post annealing and electrical and optical properties of IMO films is examined. After post annealing, the lowest value of electrical resistivity is 3.55 × 10⁻⁴ Ω·cm, and meanwhile, the optical transmittance at 550 nm reaches 80%. Moreover, the efficiency of OSC with IMO electrode is 3.77%, which is higher than that with ITO electrode. Thus, the IMO films are believed to be alluring candidate as transparent electrode for OSCs.

References