Conference Paper

Possibility to Use Low Temperature Pulsed RF Sputtered Indium Tin Oxide for the Fabrication of Organic Solar Cell

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In this work we have used pulsed RF sputtering method to deposit indium tin oxide (ITO) for the fabrication of P3HT:PCBM based bulk heterojunction polymer solar cell. We have deposited ITO at low substrate temperature (100°C) and for different pulse modes. Oxygen was used as an admixture to the sputtering gas argon, and the percentage was varied from 0 to 6%. During deposition, plasma was studied by optical emission spectroscopy (OES) method. For our present range of deposition conditions lowest resistivity of ITO is around $2 \times 10^{-4} \Omega\text{-cm}$, and it is deposited in High-Low mode with 1% of oxygen added to argon. The effect of oxygen admixture on electrical and optical properties of ITO thin films has been studied for different pulse modes. ITO films have been optimised by measuring their resistivity, transparency, and X-ray diffraction. Finally we have applied the ITO film for the fabrication of P3HT:PCBM based solar cell.

1. Introduction

Many parameters of ITO thin film such as electrical conductivity, optical transparency, and depth of film to minimize sheet resistance must be considered in solar cell fabrication. The electrical and optical properties of this wide bandgap oxide semiconductor can be controlled by adjusting the deposition conditions. Various techniques, such as electron beam evaporation [1], ion beam assisted deposition [2], pulsed laser ablation [3], ion implantation [4], and DC/RF magnetron sputtering [5], are used for the growth of ITO thin films. Pulsed RF sputtering technique is a promising technique which can modify and improve the properties of sputtered films via control of energy of ions impinging on substrates. But pulsed RF sputtering is still not well tested for the deposition of thin ITO film at low temperature. In this work we have developed ITO by pulsed RF sputtering technique and applied that film for the fabrication of P3HT:PCBM based solar cell. We have also compared the cell performance with the cell deposited on commercially available ITO.

2. Experimental

Thin film of ITO was deposited using a pulsed RF (13.56 MHz) sputtering system (ANELVA). An indium tin alloy (95:5) of 99.99% purity was used as target. Initially, the chamber was evacuated to 1×10^{-6} Torr (base pressure), and the required sputtering pressure inside the chamber was achieved by introducing argon gas through mass flow controller. Once the pressure was achieved, the deposition was carried out in argon and oxygen atmosphere. Oxygen was used as admixture to the sputtering gas, and the percentage was varied from 0 to 6%. The target was presputtered in argon atmosphere for 10 min with a shutter on the substrate, in order to remove the surface oxide layer formed on the In-Sn target during air exposure. The oxygen was introduced again after presputtering, and shutter was removed for the deposition of the film on the substrate. Depositions have been carried out in two pulse modes: (i) ON-OFF (like Figure 1(a)) and (ii) High-Low (like Figure 1(b)).

FIGURE 1: Two types of pulse modes used in this study.

We have fabricated bulk heterojunction (BHJ) polymer solar cell on ITO coated glass substrates modified by poly(3,4-ethylenedioxythiophene): polystyrene-sulfonic acid (PEDOT:PSS). Aluminium electrodes have been deposited by vacuum evaporation method. The final structure of BHJ solar cell is ITO/PEDOT:PSS/P3HT:PCBM/Al. Thickness was measured by an Ellipsometer (Five lab MARY-102), and sheet resistance was measured by four-point probe method. Sheet resistances were converted to resistivity using the measured thickness value. Optical transmission was recorded by Hitachi U-4000 UV/VIS spectrophotometer. The solar cells have been characterized by current density-voltage (J - V) measurement in dark and under white light. An optical emission spectroscopy system is installed on the multisource sputtering chamber. The optical emission system consists of a 0.25 m spectrograph coupled with a 1024-element photodiode array, a detector, and fiber optics. Light for OES analysis is collected from the plasma by fiber optics. Three vacuum-compatible fiber optic cables are located inside the deposition chamber. Scanning and data acquisitions were carried out by a PC. Each spectrum was obtained by averaging 25 exposures of 15 s each.

3. Results and Discussion

The effect of oxygen admixture on electrical and optical properties of ITO thin films has been studied for different pulse modes. Here oxygen was used as the admixture to the sputtering gas argon and was varied from 0 to 6 percent. For all the depositions working gas pressure is 5 mTorr and substrate temperature is 100°C. Two types of pulses are used for ON-OFF and High-Low mode. For ON-OFF mode pulse on time duration (t_{ON}) is 800 μ s, 1200 μ s and off time is 200 μ s, 300 μ s, respectively. All the depositions in this mode have been carried out at 100 W power. For High-Low mode two types of pulses with 100 W-80 W and 100 W-100 W are used.

At first we have measured the deposition rates at different conditions. Influence of oxygen admixture on different pulse modes has been shown in Figure 2. We see that for pure argon gas deposition rate is low, but it becomes high when little amount of oxygen is added to it. Interesting thing is that for all the cases deposition rate decreases with the increase in percentage of oxygen. Decrease in deposition rates with the increase in oxygen percentage was attributed to the oxidation of target surface [6], to the possibility of resputtering of the film by energetic particles in plasma, and to the compensation of deviated stoichiometry by the reacting gas [7]. To get

FIGURE 2: Variation of deposition rate with oxygen admixture for different modes.

FIGURE 3: Variation of spectral line intensities of indium 451 nm and argon 811.5 nm with oxygen admixture for different modes.

further insight we have studied emission lines of indium at 451 nm and argon at 811.5 nm. Figure 3 shows variation of integral peak intensity of Indium line (indium 451) and argon line (argon 811.5) with the change in oxygen percentage. From this figure we observe that with the introduction of oxygen,

FIGURE 4: Effect of oxygen admixture on resistivity for different modes.

indium 451 increases, and then it decreases with the increase of oxygen percentage. This behavior is same for both ON-OFF and High-Low modes. Now if we compare the variation of Indium 451 with deposition rate (Figure 2) we see that these two variations show similar trend. This demonstrates that the variation of deposition rate is proportional to the variation of indium 451. Intensity of argon 811.5 continuously decreases with the increase of oxygen admixture. This decrease of intensity is due to the decrease of argon partial pressure. We do not find any correlation between argon 811.5 line and material properties. Figure 4 shows the influence of oxygen admixture on the resistivity of the grown film at a fixed pressure and substrate temperature for different pulse modes. We see that the material deposited without oxygen does not give the lowest resistivity. But if we add little amount of oxygen to argon, resistivity decreases for all the cases. For our present range of deposition conditions lowest resistivity is around $2 \times 10^{-4} \Omega\text{-cm}$, and it is deposited in High-Low mode with 1% of oxygen added to argon. This value is very good in comparison to the ITO deposited by other methods. This is probably due to the fact that in time-modulated plasma properly selected pulse rate eliminates suspended macroscopic particles within the plasma. From Figure 3 we also observe that for all the cases minimum resistivity is found at the admixture of 1% or 2% of oxygen. Resistivity again increases with the increase of oxygen percentage. Minimum of the resistivity at a certain oxygen percentage is caused by the fact that an exact amount of reactive oxygen is needed in order to oxidize the metal atoms arriving at the substrate to a slightly substoichiometric film (oxygen-to-metal ratio approximately 1.5). Smaller amounts of oxygen lead to opaque films due to unoxidized metal clusters; larger amounts of oxygen cause fully oxidized films, which are highly resistive [8]. Also it is known that the variation in the resistivity of ITO thin film is related to the variation in carrier concentration of the film, which in turn is related to the variation of oxygen vacancies, a possibility of incorporation of oxygen atoms into the growing

FIGURE 5: XRD spectra of ITO film.

FIGURE 6: Transmittance spectra of films prepared at different oxygen percentages for High-Low mode.

ITO thin films [9]. Structural characterization has been done by XRD. The XRD spectra of the film deposited by 1% oxygen admixture have been shown in Figure 5, and the hkl planes have been identified which confirm ITO structure. We have also measured refractive indices of ITO films (data are not presented here) by spectroscopic ellipsometry. It is seen that for most of the samples refractive index lies within the range 2.075 and 2.095, but there is no general trend in the change with the variation of oxygen admixture. In Figure 6 we have shown the optical transmittances of two ITO films grown by High-Low (100 W-80 W) mode. The films deposited with 1% of oxygen show the highest transmittance and 0% of oxygen show the lowest transmission. Other films show intermediate transmission. Finally we have fabricated three P3HT:PCBM

FIGURE 7: Current density-voltage characteristic curves.

based bulk heterojunction solar cells on ITO deposited by pulsed RF sputtering method in High-Low (100 W-80 W) mode. Three sets of solar cells have been deposited on the ITO deposited by 1% oxygen admixture, on the ITO deposited by pure argon, and on commercially available ITO (10–15 ohm/sq. cm.). The current density-voltage characteristic curves of these three cells have been shown in Figure 7. From this figure we see that the performance of the solar cell deposited on 1% oxygen which diluted ITO is comparable with the cell deposited on commercial ITO. Open circuit voltage and short circuit currents are comparable for these two cells. Only series resistance is slightly higher for pulsed RF deposited ITO.

4. Conclusion

This study demonstrates that pulsed RF sputtering has the potential to prepare good quality ITO for solar cell application. Cell properties can further be improved by optimising the properties of pulsed RF deposited ITO.

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