The negative influences of excessive oxygen gas on the electrical properties of ITO films deposited by magnetron sputtering

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Abstract

Indium tin oxide (ITO) films deposited on glass substrate can be used as the transparent electrode for thin film photovoltaics, such as CdTe-based thin film solar cells. The most widely used fabrication technique for ITO films is the magnetron sputtering directly from ITO targets. While the preparation of ITO films is known for decade, there is still lacking of consensus whether adding oxygen to the sputtering ambient of Ar is beneficial to the electrical properties of ITO films. Herein, we present a systematic experimental study comparing the properties of ITO films deposited under pure Ar ambient *versus* under mixing Ar-O_2 ambient with increasing O_2 partial pressure. Our results of Hall measurements show that adding *excessive* oxygen in the sputtering gas actually has negative influences on electrical conductivity of ITO films. The origin of these negative effects are discussed based on the measured carrier concentration and the results of grain size analysis. The ITO film microstructure was characterized using XRD, STEM and high-magnification SEM analysis. The ITO film oxygen vacancy concentration was characterized using XPS analysis.

1. Introduction

In the last five years, the world record of CdTe thin film solar cell conversion efficiency has been increased from 16.5% to 21.5% [1]. Through the spectral quantum efficiency measurement and data analysis, it was estimated that the most noticeable efficiency improvements have been originated from the development of better superstrate - including a transparent conducting oxide (TCO) layer, a high resistant transparent (HRT) layer and a wide band gap buffer layer. For the TCO layer that is used as the transparent electrode for solar cells, a higher electrical conductivity presumes a thinner film is needed. This in turn could reduce the absorption of light, and thus enhance the conversion efficiency of thin film solar cells.

Among the large list of different TCO materials, indium tin oxide (ITO) is the most widely used one because of its relatively high conductivity and transparency in the visible range. One of the common methods to deposit ITO films is magnetron sputtering directly from ITO targets. The electrical properties of ITO films depend on the sputtering condition, especially on the oxygen partial pressure. Choi et al. showed that the increase of oxygen partial pressure results in a reduction of both carrier mobility and concentration, leading to an increase of resistivity in ITO thin films [2]. Another study by Kim et al. [3] on the other hand showed that carrier mobility increases with higher oxygen partial pressure, leading to a decrease of resistivity in ITO thin films. A more recent study by Zhu et al. [4] also visited such issues showing that at higher oxygen partial pressure the carrier concentration increases but the carrier mobility decreases. Apparently, despite having been subject to extensive research, there is still lacking of consensus whether adding oxygen to the sputtering ambient of Ar is beneficial to the electrical properties of ITO films. We believe more work can be useful to clarify such point, maybe supporting one argument over another.

Herein, we intend to address the aforementioned issue by presenting an experimental study comparing the properties of ITO films deposited under pure Ar ambient *versus* under mixing Ar-O_2 ambient with increasing O_2 partial pressure. The comparisons were performed systematically - using identical sputtering condition (except oxygen flow rates), a simple sputtering process at 250 °C without additional annealing, and identical film thickness. We employed Hall effect measurement to evaluate the carrier mobility and concentration, and the film resistivity. We employed X-ray diffraction (XRD), high-magnification scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM) analysis to characterize the film microstructure, obtaining information such as grain size distribution. We employed X-ray photoelectron spectroscopy (XPS) analysis to estimate the oxygen vacancy concentration. The results of these analysis will be used to discuss the observed effects of excessive oxygen gas on the electrical properties of sputtered ITO films.

2. Experimental

All ITO thin films were deposited on glass substrates by dc magnetron sputtering using a sputtering power of 80W. The substrate temperature was maintained at 250 °C for all depositions. The sputtering targets were purchased containing 97 wt.% of In_2O_3 and 3 wt.% of SnO_2. The Glass substrates were consistently cleaned before placing into the deposition chamber. Argon and oxygen gases with purity of 99.999% was used at a working pressure of 0.4 Pa, with a maximum base pressure of 8×10^{-4} Par. While Ar flow rate was kept constant at 80 sccm, various oxygen flow rates, i.e. 0, 2, 3, 4, 5 and 6 sccm were used for different sputtering gas mixtures, corresponding to O_2 addition ratios $[O_2/(Ar+O_2)$ %] of 0, 2.44, 3.61, 4.76, 5.88 and 6.98%, respectively. The thicknesses of all ITO films were fixed at 100 nm, unless otherwise stated.

3. Results and discussions

Figure 1 shows the results of Hall effect measurements on 100 nm thick ITO films. The conductivity and carrier concentration of ITO films are decreasing with increasing oxygen partial pressure. There may be an overall trend of increasing Hall mobility with oxygen addition, though the measured data show certain degrees of fluctuation. Clearly, our results demonstrate that adding excessive oxygen in the sputtering ambient actually has negative influences on electrical conductivity of ITO films.

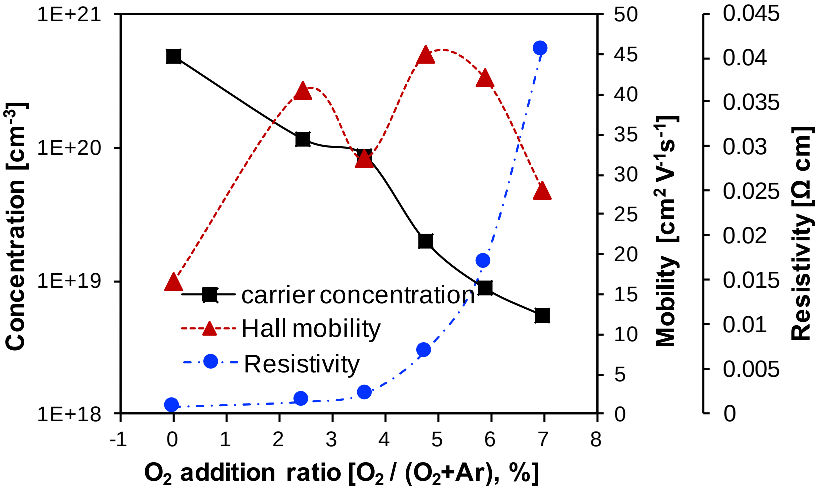

Figure 1: The measured carrier concentration, Hall mobility and resistivity of ITO films as a function of increasing oxygen addition in Ar-O_2 sputteirng gas mixture.

Figure 2 summarizes the results of microstructural characterizations. Figure 2(a) shows the STEM micrographs for the cross-section of a typical ITO thin film deposited on glass substrate. For the purpose of STEM analysis, the thickness of this ITO film was selected to be 25 nm. The deposited film is polycrystalline with no or low evidence of amophous phases. As shown by the high resolution STEM micrograph (see bottom inserted micrograph), each ITO crystallite may acutally occupy the entire film thickness. Based on this observation, we gestimated the columnar grain structure from the faceted top surface, as sketched in the inserted micrgrpah near the top. We acknowledge that the columnar grain structure observed for 25 nm thick film may not represent the microstructure of thicker films. The grain probability of survival diminishes with increasing film thickness, as described in a typical competitive van der Drift type crystallite growth that occurs during film deposition. Figure 2(b) shows the results of XRD analysis on several 100 nm thick ITO films as a function of increasing O_2/Ar ratio in the sputtering gas mixture. All ITO films are polycrystalline single-phase SnO_2-doped In_2O_3 solid solution with a body-centered cubic (bcc) crystal structure (Ia-3 (206)). As oxygen partial pressure increases, the resulted ITO films become slightly more textured with [222] preferred growth orientation. In addition, close inspection of the XRD patterns reveal that there is diffrantion peak broadening for films deposited at higher oxygen partial pressure. Therefore, we performed grain size analysis using Scherrer equation to estimate the average grain size of each film. For XRD grain size analysis, the instrumental broadening was carefully determined by using LaB_6 standard material and subtracted from the measured line broadening. Figure 2(c) shows the average grain size of ITO films as a function of increasing O_2/Ar ratio in the sputtering gas mixture. The average grain size of ITO film becomes gradually smaller with oxygen addition. This trend of decreasing grain size can also be directly observed from the high-magnification SEM micrographs of the six ITO films, as shown in Figure 2(d).

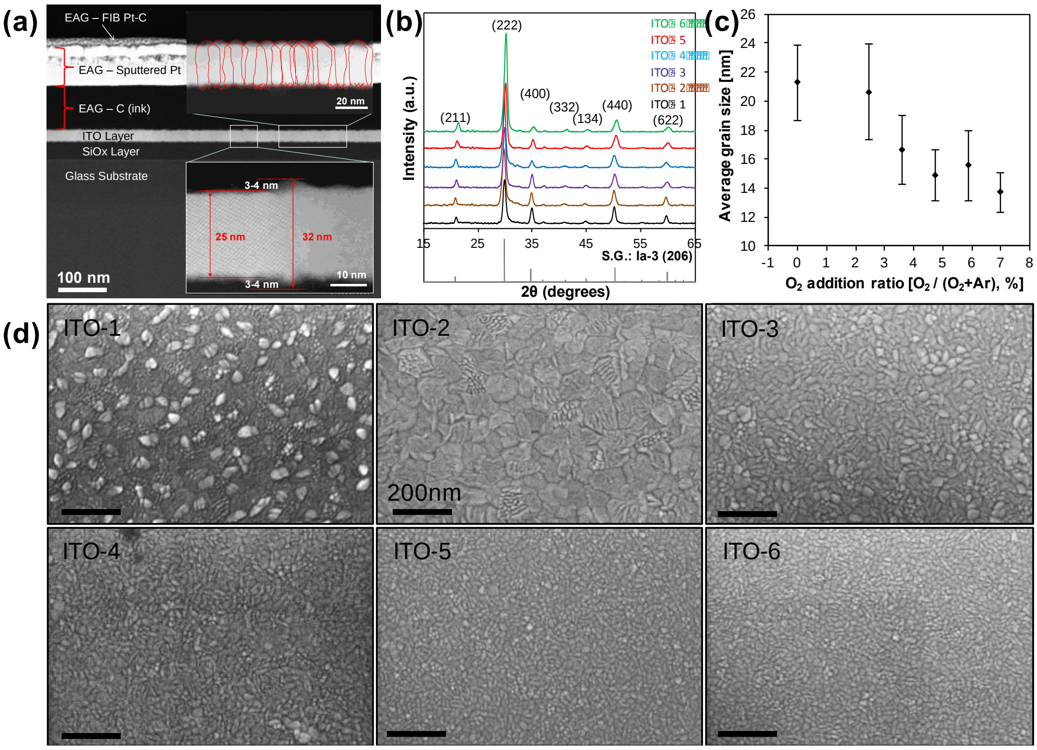

Figure 2: (a) STEM micrographs for the cross-section of a typical ITO thin film deposited on glass substrate. (b) XRD analysis on ITO films as a function of increasing oxygen addition in Ar-O_2 sputteirng gas mixture. (c) The results of grain size analysis. The error bars show the deviation from the mean. (d) High-magnification SEM micrographs of ITO films. ITO-1 to 6 represent films deposited with O_2 addition ratios $O_2/(Ar+O_2)$ % of 0, 2.44, 3.61, 4.76, 5.88 and 6.98%, respectively.

Consideirng the carrier mobility in polycrystalline materials is limited by scattering mechanisms such as ionized impurity, phonon and boundary scattering. A decrease in grain size should in principle result in higher probabilities of boundary scattering, leading us to expect a decrease in carrier mobility as the oxygen partial pressure increases in the sputtering gas. However, as shown in Figure 1, the measured Hall moblity does not follow such expectation. This suggests that for the ITO films investigated here the change in grain size is not a predominant factor, or plays only a secondary role behind the observed trend of electrical properties.

Furthermore, we performed XPS analysis to determine the oxygen vacancy concentration in the prepared ITO films, and hopefully being able to explain the observed trend of changing carrier concentration. Figure 3 shows the XPS O 1s spectra of the ITO films that were deposited at different oxygen partial pressures. The O 1s spectra can be fitted with two components at ~ 529.8 eV and ~ 531.3 eV, respectively. The former component, labeled as O_I, represents oxygen ions that have neighboring In atoms with their full complement of six nearest neighbor O^{2-} ions. The latter component, labeled as O_{II}, represent oxygen ions arising from the oxygen-deficient region [5], which in turn correlating to oxygen vacancies. As a result, comparing the integrated areas of O_I and O_{II} enables us to obtain a sensitive indicator of the level of oxygen vacancy concentration [5]. Our results demonstrate a decreasing oxygen vacancy concentration with oxygen addition to the Ar-O_2 sputteirng gas mixture. At present, it is believed by most researchers that oxygen vacancy is one of the fundamental sources acting as donors in ITO and some other TCOs [6]. By plotting the ratio of O_{II}/O_I together with our measured data of carrier concentration, not in a log scale (see Figure 3(b)), two sets of data actually have similar variation trends as a function of increasing O_2/Ar ratio. It is therefore safe for us to argue that the decreasing carrier concentration in ITO films, as shown in Figure 1, is due to the lower oxygen vacancy concentration, as supported by the results of our XPS analysis. Moreover, while oxygen vacancies are the donor, they also serve as scattering centers for carriers. As oxygen vacancy concentration decreases, the population of oxygen vacancy scattering centers also reduces accordingly. This might explain our observation that the carrier mobility increases with oxygen addition in Ar-O_2 sputteirng gas mixture. Finally, it should be noted that oxygen vacancies should only partially contribute to the measured carrier concentration. The carrier concentration is also provided by interstitial metal ion impurities.

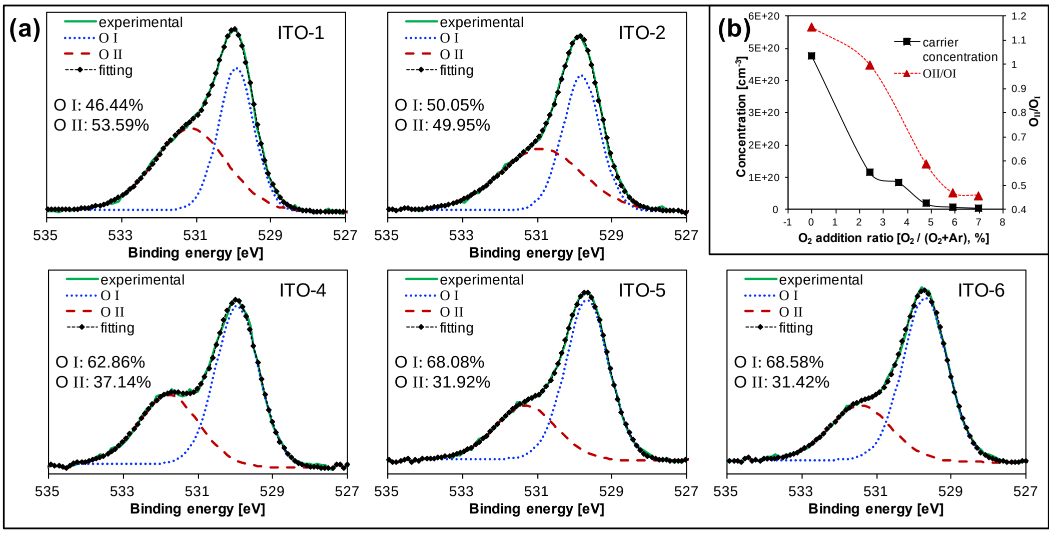

Figure 3: (a) XPS O 1s spectra of ITO films. ITO-1 to 6 represent films deposited with O_2 addition ratios $O_2/(Ar+O_2)$ % of 0, 2.44, 3.61, 4.76, 5.88 and 6.98%, respectively. (b) A comparison of O_{II}/O_I ratio with our measured data of carrier concentration shown in Figure 1.

4. Conclusion

We experimentally confirmed the influences of excessive oxygen gas on the electrical properties of ITO films deposited by magnetron sputtering. The conductivity and carrier concentration of ITO films are decreasing with increasing oxygen addition in Ar-O_2 sputteirng gas mixture. The negative influences of excessive oxygen gas on electrical properties are explained by the reducing oxygen vacancy concentration in the ITO films, as determined by XPS analysis. Our results are in accordance with the general understanding that oxygen vacancy is one of the fundamental sources of donors in ITO.

5. References

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