In-situ tuning of Sn doped In$_2$O$_3$ (ITO) films properties by controlling deposition Argon/Oxygen flow

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**ABSTRACT**

In this work, we report that the properties of Sn-doped In$_2$O$_3$ (ITO) can be properly tuned by varying Argon/Oxygen (Ar/O$_2$) percentage during the sputtering process from 7% O$_2$ to 93% O$_2$. The characteristics of the ITO grown in oxygen deficient to the oxygen-rich condition are properly studied. It is found that there is a strong correlation between the concentration incorporation of oxygen with the properties of ITO films. ITO films were grown in oxygen deficient condition (7% O$_2$) resulted in a rougher surface, wider band gap, and lower resistivity compared to the other films grown with 33%, 67%, and 93%. Blue shifts in absorbance edge and band gap widening indicate that the number of carrier concentration was also changed linearly with the presence of oxygen in the film. These findings provide a simple way to effectively tune the properties of ITO films for ITO to be applied in optoelectronics, power device as well as sensor applications.

1. Introduction

Tin-doped Indium Oxide (ITO) is often chosen as the Transparent Conductive Oxide (TCO) for optoelectronics based applications owing to the material’s optical and electrical properties. ITO can be fabricated by various methods such as electron beam evaporation [1], thermal evaporation [2], sol-gel [3], spray pyrolysis [4], pulse laser deposition (PLD) [5] as well as by Direct Current (DC) and Radio Frequency (RF) magnetron sputtering [6,7]. Among all available methods, magnetron sputtering has the advantages to produce good quality thin films owing to a low contamination and controllable deposition parameters. However, Kurdesau et.al demonstrated that RF sputtered ITO produced a crystalline structure whilst via DC method amorphous with nano-scale grain was obtained [8]. Hence, in this work, RF sputtering method was chosen. Via RF technique, the properties of this material especially the electrical properties are reported can be easily tuned either during the process or post-processing method [9]. Other than via Sn doping into In$_2$O$_3$ to improve the electrical conductivity, the oxygen concentrations is also demonstrated to strongly influence the electrical behavior of ITO [10–12]. The presence of oxygen vacancies is demonstrated to play a crucial role to the ITO properties [13,14]. The oxygen concentration in ITO can be controlled either by working gas flow rate [13] gas pressure [15], substrate heating during deposition [16], sputtering power [17] or post annealing treatment [18].

In this study, ITO films were grown via RF sputtering by in-situ varying the oxygen flow during the deposition process. Microstructural, morphology, optical as well as electrical of grown ITO films were holistically investigated. We aim to correlate the oxygen concentration with all the characteristics that can be observed in the as-grown ITO films.

2. Methodology

Tin (Sn) doped Indium oxide (In$_2$O$_3$) (ITO) was deposited on top of glass and silicon substrate via Radio Frequency (RF) magnetron sputtering. The substrates were cleaned with acetone, propanol and deionized water subsequently for 5 min prior the sputtering process. The deposition process were carried out with the ITO target consisted of 90% In$_2$O$_3$ and 10% tin oxide (SnO$_2$) in a chamber with base pressure of $1 \times 10^{-6}$Torr for 10 min. The substrate temperature of 200 °C, sputtering pressure of 5 mTorr and sputtering power of 200 Watt were kept at constant for all samples. On the other hand, a mixture of working gas; Argon/Oxygen (Ar/O$_2$) was varied at 14:1 (7% O$_2$), 10:5 (33% O$_2$), 5:10 (76% O$_2$) and 1:14 (93% O$_2$).

The as-grown ITO films were then investigated using X-ray diffraction (XRD) Siemens D5000 with Cu Kα radiation source and $\lambda = 0.154$ nm. The transmittance spectra and was obtained using UV–visible spectroscopy (UV–vis) using Perkin Elmer Lambda 750 UV/
3. Results and discussion

3.1. Microstructural properties

The influence of oxygen flow percentage to ITO films microstructure is shown by XRD pattern in Fig. 1. The trend in the patterns implies that the crystal growth of ITO films is dependent on the oxygen flow percentage during deposition process. It can be seen that the peak intensity of (4 0 0) and (2 0 0) plane changed linearly with the oxygen flow percentage, which indicate the oxygen deficient and oxygen efficient conditions in the grown ITO film [20]. At high Ar percentage, a prominent peak of (4 0 0) plane orientation is clearly observed which is in agreement with the literature [21]. As the deposition process to grow ITO film used two different gases; Argon (Ar) and Oxygen (O2), there could be interplay between these two gases that leads to the variation of the ITO crystallinity. It has been reported that the film deposited with pure Ar is heavily oxygen deficient [22]. With the presence of the O2 during the deposition, re-sputtering of the film can occur via high-energy oxygen atoms (negative oxygen ions, O2−) [23], hence decreasing the number of oxygen deficient in the structure. The negative oxygen ions will also result in the growth rate and grain size of ITO films, which will be discussed in latter section. When the oxygen flow percentage was increased, the intensity of (4 0 0) peak was observed to reduce and (2 0 0) peak increased simultaneously. At higher oxygen percentage, peak (2 2 2) appears higher than that of (4 0 0) peak, implying the co-existence of (1 0 0) and (1 1 1) orientation [17,24]. Fig. 4(b) depicts the ratio of (2 2 2) plane intensity to (4 0 0) plane. It is shows that the intensity ratio increases as the oxygen percentage increases. High oxygen induce a formation of In-O bonding thus trigger the growth at the (2 2 2) plane [20]. This result is in agreement with the literature reported on the sputtering process with mixing gas of Argon and Oxygen [15,21,25].

As discussed previously, the presence of the negative oxygen ion will affect the grain size of the grown film. In this work, the grain size of the preferred orientation of ITO films was calculated from the diffraction peaks using the Debye-Scherer’s formula and plotted in Fig. 2. The grain size value calculated decreased from ~247 nm to ~187 nm when the oxygen percentage was increased from 7% to 93%, which is consistent with the reported literature [19].

Fig. 3 shows FESEM micrographs of ITO grown in this work. A substantial change with apparent nanocolumnar structure is observed to occur for all ITO grown. At low oxygen flow, obvious nanocolumn ITO structure with large grain size is observed. A number of void fractions in the structure can also be observed due to the presence of high oxygen deficiency [26,27]. This is consistent with the aforementioned XRD pattern, where (4 0 0) plane is desirable for oxygen deficient film while (2 2 2) plane is for well-stabilized structure. As the oxygen percentage was increased, the nanocolumn ITO film became dense and the grains size became smaller. It is also observed from FESEM that the ITO film thickness decreased from to ~471 nm (7%) to ~174 nm (93%) as the environment changed from oxygen deficient to oxygen rich condition. Samples deposited at the highest oxygen percentage of 93% in Fig. 3(d) yielded the minimum nanocolumnar thickness in the range of 174–179 nm. This is due to decrease of growth rate and lower degree of perpendicular orientation of the nanocolumnar compared to other samples.

The as-grown ITO surfaces were further investigated via AFM shown in Fig. 4 and the average roughness of each sample is tabulated in Table 1. It was measured that the sample grown at the lowest oxygen percentage (7%) exhibits the roughest surface of 3.305 nm, whilst the sample with the highest oxygen percentage shows the least rough
surface of 1.139 nm. This observation is found to have a strong agreement with the FESEM results as well as the grain size presented beforehand. Thus far, the behavior of ITO microstructure grown can be explained by correlating with the presence of oxygen vacancy in the sample. The formation of oxygen vacancy in the samples is further verified with room temperature photoluminescence (RT-PL) spectra shown in Fig. 5.

While stoichiometric In$_2$O$_3$ is reported to exhibit no PL emission [28], all ITO films grown in this work show PL emissions at 429 nm, 490 nm, 539 nm and a strong PL peak at 675 nm. Blue emission at 429 nm reported is due to the deep level emission of oxygen defects in nano-structure ITO [29], while PL peak at 490 nm is reported to be due to the formation of singly ionized oxygen (Ov) defects [30]. It is interesting to see that there is a prominent orange emission for all samples. To author’s best knowledge, not many literature reported on the orange emission of ITO film. Na et al is reported to observe an enhancement of orange emission (near 626 nm) as they doped metal into In$_2$O$_3$-ITO nanocomposites, and they correlate this to the oxygen-deciency based defects [31]. This result shows a strong correlation between the oxygen defects and the percentage of oxygen flow during the sputtering. Higher oxygen vacancies allows more electrons to occupy the defect state and recombine with photogenerated holes, producing high PL emission [32].

Fig. 6(a) shows transmission spectra of ITO films grown in this work. It can be clearly observed that the number of fringe was higher for the ITO film grown at lower oxygen percentage (7%). As the oxygen percentage was improved, the number of fringe reduced. It is reported that the oscillation frequency of the film is dependent on the film thickness as well as the film refractive index [33]. The rough surface allows more light scattering, thus results in low transmittance [19]. As the oxygen flow increased, the transmittance at the visible range is improved. Less scattering for the samples grown in higher oxygen percentage flow implies that the films may consider as homogenous surface without any anisotropy [34]. It is also shown that absorbance edge of oxygen deficient sample (7%) lies at higher wavelength compared to other samples. As the oxygen percentage flow was increased to 33%, the absorbance peak shifts to lower wavelength. Blue shift of absorbance edge as well as band gap were clearly observed as the oxygen percentage was increased. This is in agreement with the literature reported thus far, which can be explained using Burstein-Moss effect [4,35]. The band gap calculated via Tauc plot as shown in Fig. 6(b). The ITO film grown at 7%, 33%, 67% and 93% exhibits 3.85 eV, 3.80 eV, 3.73 eV and 3.68 eV respectively. This band gap widening as the oxygen was reduced is reported due to the increasing of carrier concentration in the film, which is in consistent with PL results presented hitherto.

The electrical resistivity of ITO is reported to be dependent on the and the oxidation state flow during deposition [25]. As shown in Fig. 7, the resistivity of the films is found to decrease linearly with the oxygen percentage. The lowest resistivity value of 3.58 × 10$^{-5}$ Ω cm was calculated for the sample prepared at the 7% oxygen flow. While the sample grown with 33%, 67% and 93% exhibit resistivity of 5.14 × 10$^{-5}$ Ω cm, 5.87 × 10$^{-5}$ Ω cm, 6.49 × 10$^{-5}$ Ω cm.
The reduction of oxygen vacancies as shown in PL spectra before resulted in higher resistivity of the ITO film grown. This observation is also in agreement with the reported literature\[25,37\]. According to Wu and Chiou, the increasing in resistivity is attributed to the combined effect of changes in carrier concentration and Hall mobility as shown in Table 2 [13]. It is measured that as the resistivity increased, the carrier concentration as well as the mobility decreased, which is consistent with the reported literature [4].

4. Conclusion

By varying the mixture of working gas; Argon and Oxygen during the deposition process, the properties of Sn doped In$_2$O$_3$ (ITO) grown can be properly tuned. Our findings show that there is a strong correlation between the concentrations of oxygen incorporation with the properties in ITO films. ITO films grown with 7% oxygen flow resulted in a rougher surface, wider band gap and lower resistivity compared to the other films grown with 33%, 67% and 93%. ITO grown via RF sputtering and by merely in-situ tuned the oxygen flow adding more options for ITO to be applied in optoelectronics, power device as well as sensor applications.

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References


