Transparent conducting thin films by co-sputtering of ZnO-ITO targets

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Transparent and conductive ZnO-ITO (ZITO) amorphous thin films have been deposited by the rf magnetron co-sputtering of ITO (In$_2$O$_3$ with 10wt % SnO$_2$) and ZnO targets at room temperature. A constant rf power of 50W was used for the ITO target, whereas the rf power to ZnO target was varied from 25W to 150W. The Zn content ratio in the films was varied from 17 to 67% when the rf power to the ZnO was changed from 25W to 150W. The lowest resistivity of 6.6×10$^{-4}$ Ωcm, was achieved for the films with Zn content ratio 17%. A highest mobility of 4 cm$^2$ V$^{-1}$ s$^{-1}$ was observed at lower zinc concentrations in the film. The carrier concentration decreased with increasing Zn content from 5.0×10$^{19}$ cm$^{-3}$ for pure ITO to 6.7×10$^{19}$ cm$^{-3}$ for the films deposited at 150W for ZnO. The films showed an average transmittance over 80% in the visible wavelength range and due to the decreased free carrier density, the transparency in the near infra red region increased with increase in Zn content of the film.

The band gap of the samples varied from 3.64 for the ITO to 3.28eV for the ZITO films with zinc content ratio 67%. The ZITO films deposited at room temperature with lower Zn content ratio showed better optical transmission and electrical properties compared to ITO film.

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**2 Experimental** ZITO layers were deposited by rf magnetron co-sputtering of ZnO and ITO in pure argon gas atmosphere. The targets were 3 inch in diameter and with purities of 99.995% for ZnO and 99.99% in the case of ITO (In2O3 with 10 wt % SnO2). A constant rf power of 50 W was used for the ITO target, whereas the rf power to ZnO target was varied from 25 W to 150 W in steps of 25 W (see Table 1, for sample identification). The target to substrate distance was kept at 12 cm and a substrate rotation of 10 rpm was used to achieve uniform composition in the films during co-sputtering. There films were deposited onto 5 × 5 cm² Corning glasses (1737F) at a pressure of 2.6 mTorr without any intentional heating of the substrate. The deposition time was controlled to achieve a thickness around 215 nm for all the films.

| Table 1 The deposition powers of the ZITO samples with the cation content estimated from XPS |
| Sample | ITO (W) | ZnO (W) | In (%) | Zn(%) | Sn(%) |
|---------|---------|---------|--------|-------|-------|
| ITO     | 50      | 0       | 89.3   | 0     | 10.7  |
| ZITO25  | 50      | 25      | 75.5   | 17.1  | 7.5   |
| ZITO50  | 50      | 50      | 57.6   | 36.6  | 5.8   |
| ZITO75  | 50      | 75      | 46.7   | 48.5  | 4.8   |
| ZITO100 | 50      | 100     | 41.8   | 53.8  | 4.4   |
| ZITO125 | 50      | 125     | 34.5   | 62.8  | 2.7   |
| ZITO150 | 50      | 150     | 30.2   | 67.3  | 2.6   |

The thickness of the film was measured by using a Dektak 3030 profilometer. The structure of the films was analysed using powder X-ray diffractometry (PANalytical X’Pert PRO MPD Alpha1 powder system) using copper Kα radiation (λ = 1.5406 Å) as the source. The film composition was analysed using X-ray Photoelectron Spectroscopy (XPS) with a PHI 5500 Multitechnique System from Physical Electronics. The optical transmission (T) and reflection (R) spectra were recorded by using a UV-vis-NIR spectrophotometer (Perkin Elmer Lambda 19). The sheet resistance was measured by using a four point probe system (Jandell RM3). Mobility (μ) and carrier concentration (n) were determined from the Hall effect measurements by using standard Van der Pauw method in a magnetic field of 0.3T.

**3 Results and discussion** All the films showed good adhesion to the substrate and were physically stable. As the power of ZnO increased, the deposition rate increased linearly till it reached 6.2 nm/min at 150 W of ZnO and 50 W of ITO. It has to be considered that ITO has a deposition rate of 2.2 nm/min while ZnO shows a deposition rate of 1.2 nm/min at the same power (50 W). This means that as we sputtered both the ITO content was almost twice for the same power. As we increased the ZnO RF power, the Zn content increased till it overcame the In content due to the increased sputtering rate of ZnO target. In our case this happened at 75 W as can be seen in Table 1.

The composition of the films were analysed using XPS and the percentage of cations in the films with the sample identity are shown in Table 1. The Sn/In composition ratios were nearly constant (~0.10) in all the films, because both Sn and In came from the same ITO target. The plot of Zn content ratio in the film [Zn]/[(In]+[Sn]+[Zn]) with the ZnO power is shown in Figure 1. The Zn content ratio varies from 17% for ZITO25 to 67.3% for ZITO150. The Zn content in the film is found to proportional to the rf power applied to the ZnO target, therefore we will consider the rf power of ZnO to discuss the film properties.

The XRD profiles of the films are shown in Figure 2. All the films appeared to be amorphous in nature. The broad peak that appeared at around 25º corresponds to the Corning glass. Another halo peak is superposed with this and its maximum varies between 31.7 º for ITO to 33.7 º for ZITO150. This peak shift suggests the presence of a few grains changing its orientation from the ITO byxbyte cubic (111) to the wurtzite ZnO (001). However, we can-

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**Figura 1:** The growth rate and the Zn content ratio of the ZITO films deposited with different ZnO powers.

**Figura 2:** The XRD profiles of the ZITO films deposited with different ZnO powers.
The ITO film showed a resistivity of 7.58×10^{-4} \Omega \text{cm}. Resistivity of the as-deposited ZITO samples slightly decreased as we started introducing ZnO (ZITO25) reaching the minimum value of 6.6×10^{-2} \Omega \text{cm} for ZnO power of 25 W corresponding to a Zn content ratio of 17%. Such low resistive ZnO-ITO films have been reported earlier for Zn content fraction of about 0.2 to 0.4. The low resistivity of the films deposited at room temperature with a lower Zn content fraction is attributed to the formation of an amorphous-like ternary compound of Zn_{2}In_{2}O_{5} [10]. The conductivity of ITO is due to the free carriers generated by the oxygen vacancies and from the substitutional doping of In^{3+} by the Sn^{4+} ions. When ZnO is added to ITO in relatively low concentrations, the Zn^{2+} ions may substitute Sn^{4+}, possibly due to the fact that the ionic radius of Sn^{4+} (0.71 Å) is very close to that of Zn^{2+} (0.74 Å), whereas the ionic radius of In^{3+} is 0.8 Å. This may favour the formation of this ternary amorphous phase (Zn_{2}In_{2}O_{5}). At higher ZnO concentrations, may either fill the oxygen vacancies or the

not confirm any kind of crystallinity because the peak intensity is too low. Further studies should be done to confirm a possible hypothesis of nano grains.


twO films is shown in three cases. The transmittance in the near infrared region with the increase in Zn content in the film. This increase in transmission is caused by the reduction in free carriers. The absorption coefficient (\alpha) was determined from the transmittance and reflectance value by means of Eq. (3) [12].

\begin{equation}
T = (1-R)^2 e^{-\alpha d}
\end{equation}

where d is the layer thickness, R is the reflectance and T is the transmittance.

For direct transitions, the absorption coefficient is given by Eq. 2 [11].
α(hν) = A* (hν - Eg)\(^{1/2}\)  \quad (2)

where hν is the incident photon energy, Eg is the bandgap energy and A* is a constant.

The optical band gap energies of the films were deduced from the (αhν)\(^2\) against hν plots. The ITO film showed a band gap of 3.64 eV and the band gap energy of ZITO films were found to decrease with the ZnO power (Figure 6). A lowest valued of 3.28 eV was obtained for ZITO150 film with a Zn content ratio of 67.3%. This band gap shrinkage can be understood in terms of the Moss-Burstein effect, where the decrease of the band gap is correlated with the decrease in carrier concentration.

4 Conclusions Amorphous transparent conducting, zinc indium tin oxide (ZITO) thin films have been developed by the rf magnetron co-sputtering of ITO and ZnO targets at room temperature. The film composition was varied by adjusting the power to the sputtering targets. The ZITO films with less Zn content showed better transmission and electrical conductivity than the ITO film. A lowest resistivity of 6.6x10\(^{-4}\) Ωcm was achieved for the ZITO films with less Zn content ratio of 17%. A highest mobility of 9.4 cm\(^2\) V\(^{-1}\) s\(^{-1}\) was observed for the films with 37% zinc content ratio. The carrier concentration and optical band gap was found to decrease with the increase in Zn content in the film. The ZITO films deposited at room temperature with better properties than ITO will find many applications in thin film solar cells, and also in transparent electronics where low temperature deposition is needed.

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