Role of defects in improving electrical and optical properties of solution-processed transparent conducting Al-doped ZnO thin films

Thesis submitted in partial fulfillment
for the Award of Degree

Doctor of Philosophy

by

Anurag Kumar

DEPARTMENT OF CERAMIC ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI – 221005
INDIA

Roll No. 17031003 2022

Chapter 8

Conclusions and Scope of Future Research

In this chapter, the important findings of this thesis are summarized. The primary conclusion drawn from the work is specified, and the scope of future work in this area has been suggested indicating possible refinement and modifications.

8.1 Brief Summary and Conclusions

The thesis discussed the deposition/processing of aluminum-doped zinc oxide thin films TCOs on a glass substrate. The effort is geared towards devising strategies to achieve the electrical and optical properties of solution-processed TCOs at par with that of vapor-based techniques.

Chapter 1 briefly introduces TCOs, their properties, and their classification. Zinc oxide-based TCOs, and the role of intrinsic and extrinsic impurities in improving the electrical and optical properties were also discussed.

Chapter 2 presents a survey of deposition techniques and post-deposition annealing strategies for AZO is presented. Both vapor-based and solution-based deposition technique has been discussed in brief. The chapter outlines important processing parameters and their effect on the performance of the AZO is also outlined with greater emphasis on solution-based processing, mainly spin coating and spray pyrolysis. The role of post-deposition annealing and the effect of annealing environments on performance is also discussed.

Chapter 3 details the processing and characterization techniques utilized in this work. Materials preparation, deposition of the films, and post-deposition annealing strategy used in this thesis, along with processing parameters, are presented in this chapter. The chapter also details the structural, electrical, and optical characterization techniques and the analysis method.

Chapter 4 presents the results obtained for the spin-coated pure zinc oxide and 1-3 at % Al-doped films on a glass substrate. The deposited AZO films were ~150 nm thick. The lowest resistivity value of 10^{-2} Ω-cm along with transparency ~ 85% was obtained. Bandgap increased with doping level, which was in line with the earlier observed trend. The XRD showed that the films lacked orientation, while SKPM and PL showed the localization of defects and oxidation of aluminum.

To achieve the preferred orientation along (002), spray pyrolysis was utilized for the deposition of AZO films. **Chapter 5** describes the preparation and characterization of AZO films deposited using spray pyrolysis. The carrier concentration and mobility were enhanced by post-deposition annealing in a vacuum. The AZO films with columnar morphology were oriented in [002] direction. On vacuum annealing, an increase in the concentration of defects such Zn_i and V_O was observed, which resulted in enhanced carrier concentration. The increase in the carrier concentration also manifested in increased bandgap due to the BM shifting, which resulted in the Fermi level moving into the CB. With this strategy, electrical resistivity as low as ~ 2 x 10^{-3} Ω-cm, along with ~82% transparency, was achieved. The figure of merit was 1.44, which is probably a record for any solution processed AZO.

In Chapter 6, radiative annealing in the 5%H_2+Ar atmosphere was utilized, further reducing the resistivity and improving the transparency of the spray-deposited ZnO and Al-doped ZnO-based TCOs. A quick 10 s radiative annealing can improve the optical and electrical properties. Transparency was as high as ~94%, with resistivity as low as ~2×10^{-3} Ω-cm achieved for 2AZO films. Radiative annealing for 10 sec improved the crystallinity and passivated the defects resulting in improved mobility (up to ~58.14 cm^2/Vs in pure ZnO films). At the same time, radiative annealing in 5%H_2 also activated the dopant and acted as a source for additional carriers resulting in a carrier concentration as high as ~2.29×10^{20} cm^{-3} for 2AZO films.

In chapter 7, a new co-dopant (Tl) was explored to further enhance the performance of the solution spray-deposited AZO films. With the addition of Tl as a co-dopant, transparency could be improved to ~92% in the visible range, while the charge carrier concentration and mobility of the radiatively annealed films were ~2.4×10^{20} cm^{-3} and ~56 $cm^2V^{-1}s^{-1}$ respectively. The enhanced carrier concentration and mobility resulted in a lower resistivity of ~9.92×10^{-4} Ω-cm, which is in the same order as reported for vapor-based techniques.

Therefore, with a suitable co-dopant and post-deposition annealing, it is possible to improve the performance of the solution-processed TCOs at par with that processed through costly vapor-based technologies.

8.2 Suggestions for future work

The thesis provides an understanding and possible ways to improve the conductivity and transparency of the solution-processed ZnO-based TCOs. The main target of improving the conductivity of the solution-processed films at par with the vapor-based deposition methods has largely been achieved. The Author feels that solution-based TCOs can further be improved. Based on the insight from this work, a few suggestions for future efforts in this area are as follows:

1. Solution-based deposition of ZnO-based TCOs generally requires annealing at temperatures ≥500°C. However, optoelectronics technologies are moving towards flexible electronics using substrates such as polyimide and polyethylene terephthalate (PET). These substrates usually deform at 200°C. Therefore, solvents that can be decomposed at a lower temperature can be explored to fulfill the requirements of flexible devices precursor. Solvents like diluted sodium hydroxide and ammonia solution and precursors such as zinc nitrate hexahydrate can be explored.
2. The higher conductivity and transparency were achieved using post-deposition radiative annealing was utilized. However, its stability, in the long run, remains unchecked. Therefore, the reliability of film in ambient and in harsh environments should be examined.
3. Radiative annealing can be assembled with the spray deposition for exploring continuous roll-to-roll processing.
4. Thallium doping is beneficial in improving the charge concentration while at the same time, mobility. Tl can be further explored to optimize the Tl co-doping levels.
5. AZO film prepared by the solution-processed method has more roughness than vapor-based processing routes and has more grain boundaries;

therefore, the film deposited by the solution-processed route can be explored for sensor-based application.