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

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It is certified that the work contained in the thesis titled "**Role of defects in improving electrical and optical properties of solution-processed transparent conducting Al-doped ZnO thin films**" by **ANURAG KUMAR** has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive examination, Candidacy and SOTA for the award of Ph.D. Degree.

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DECLARATION BY THE CANDIDATE

I, **Anurag Kumar**, certify that the work embodied in this thesis is my own bona fide work and carried out by me under the supervision of **Dr. Mohammad Imteyaz Ahmad, Assistant Professor** for a period of 5 years and 2 months from **July, 2017** to **October, 2022**, at the **Department of Ceramic Engineering**, Indian Institute of Technology (BHU), Varanasi. The matter embodied in this Ph.D thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, theses, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

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Anurag Kumar

TABLE OF CONTENTS

List of Figure

List of Table

Abstract

Good electrical conductivity, high chemical stability in harsh environments, and transparency in the visible range make transparent conductive oxides (TCOs) suitable for numerous applications in optoelectronic devices. Indium-tin oxide (ITO) is the most widely used TCO due to its high transmittance in the visible region and low resistivity. However, the shortage of indium resources, toxicity, and cost are a cause of concern for the fast-growing optoelectronic device industry. Owing to the increasing demand, higher cost, and limited availability of In, alternatives for the ITO with comparable properties and low cost are being sought. Over the last decade, ZnO-based TCOs have emerged as a possible earth-abundant, non-toxic replacement for ITO for many optoelectronic applications. ZnO films have high chemical and thermal stability and a higher bandgap (~3.3-3.6 eV), ensuring transparency in the visible regime. Out of the available choice of dopants, Al is earth-abundant and has ionic radii close to that of Zn, making it the dopant of choice. Although various methods can be utilized to deposit ZnO films, low resistivity (~10^{-4} Ω-cm) and high transparency (>85%) have traditionally been achieved by sputtering/PLD mainly because of good crystallinity and orientation, which enhances carrier mobility. However, the installation and processing cost of sputtering or PLD is high and not easily scalable. On the other hand, solution-based processing techniques are much cheaper and simpler and at the same time, easily scalable. However, AZO films processed through the solution route generally result in lower resistivity values. A straightforward way to increase the electrical conductivity while maintaining the optical transparency is to increase the carrier

concentration, passivate the defect and grain boundaries and enhance mobility. However, carrier concentration can be helpful up to a certain extent. A high concentration (generally $>10^{20}$ cm^{-3}) in ZnO-based TCOs results in greater scattering and reduced mobility. The main objective of this work is to improve the performance of solution-processed ZnO-based TCO at par with that of sputtered films.

Initially, Al-doped ZnO films were deposited on glass substrates by the sol-gel spin coating route. The formation of the wurtzite structure was confirmed by the x-ray diffraction (XRD) pattern; however, the films were not oriented. Transparency of about 85% was obtained in visible and near IR regimes as examined by UV-Vis spectroscopy. The bandgap increased from 3.14 to 3.19 eV on increasing Al concentration from 0 to 3 at.%. The obtained resistivity was in the order of 10^{-2} Ω-cm while charge concentration and mobility were ~10^{19} cm^{-3} and ~15 cm^2/Vs, respectively. Photoluminescence of Al-doped zinc oxide thin film indicated the presence of Zn interstitials. The carrier concentration increased up to 2 at% Al doping while greater doping resulted in a reduction in carrier concentration, which was attributed to the formation of greater amounts of Al_2O_3 at the grain boundaries. Both scanning Kelvin probe microscopy and photoluminescence confirmed the presence of defects localization at grain boundaries.

To improve film orientation, increase carrier concentration and achieve a better surface finish, spray pyrolysis was utilized for deposition. The deposited films were vacuum annealed for twenty minutes. Electrical, optical, morphological, and surface-specific properties of zinc oxide and aluminum doped zinc oxide thin film

was investigated. The effect of oxygen vacancies on the Fermi level and conductivity of the films were analyzed. The Fermi level was at 3.21 and 3.31 eV for the pure and 1 at% Al-doped films (1AZO), which on vacuum annealing, increased to 3.27 and 3.4 eV, respectively. The work function of the as-deposited zinc oxide and 1AZO films were 5.65 and 4.38 eV, which on vacuum annealing decreased to 4.05 eV and 4.04 eV, respectively. A carrier concentration as high as ~$1.77x10^{20}$ cm^{-3} with mobility of ~50 cm^2/Vs and resistivity close to ~$2x10^{-3}$ Ω-cm was achieved for 1 at. % Al-doped ZnO (1AZO) film. Transparency greater than ~82% and a figure of merit 1.14 was achieved, which is one of the best-reported values for solution-processed AZO films. Although the film met the critical requirement, transparency of the film was on the lower side. At the same, it involved vacuum annealing for defect generation, which had concerns about stability.

In order to enhance the performance and stability and reduce the thermal budget, the spray-deposited films were radiatively annealed (10 s at 480 °C) in a 5%H_2 + Ar atmosphere. Fast radiative annealing improved the mobility while increasing the carrier concentration by as much as 10 times when compared with as-deposited films. Resistivity as low as ~$2x10^{-3}$ Ω-cm with ~94% transparency at 550 nm wavelength for 2% Al-doped ZnO (2AZO) films was achieved. PL and Raman spectroscopy revealed that the hydrogen passivated the defects (Zn_i and V_O) and grain boundaries resulting in improved mobility and transparency. XPS and UV visible spectroscopy revealed activation of greater amounts of Al dopants at the same time, passivating V_O by partial H^+ substitution, increased carrier concentration, and wider optical bandgaps.

To further minimize the resistivity of radiative annealed 2AZO film, thallium (Tl) was introduced as a co-dopant. Scanning electron microscopy images showed columnar grain growth in Tl-Al co-doped ZnO. The transparency of the film further improved after co-doping to ~92%, while the resistivity of the film was ~9 x 10^{-4} Ω-cm. Charge concentration increased to ~2.4 x 10^{20} cm^{-3} while the mobility was ~56 cm^2/Vs. High mobility was attributed to the lower electron effective mass in the presence of thallium due to greater s orbital overlap, while the presence of Tl also increased the carrier concentration.