



# Microstructure influenced variation in the local surface electrical heterogeneity in thickening Al-doped ZnO films: Evidence using both scanning tunnelling spectroscopy and conductive atomic force microscope



Tvarit A. Patel<sup>1</sup>, Chetan C. Singh<sup>1</sup>, Emila Panda\*

Department of Materials Science and Engineering, Indian Institute of Technology Gandhinagar, Palaj 382355, Gujarat, India

## ARTICLE INFO

### Keywords:

Conductive AFM  
STS  
Al-doped ZnO  
Microstructure  
Nanoscale surface electrical properties  
Surface chemical heterogeneity

## ABSTRACT

In this study, variation in the local surface electrical heterogeneity within and also for a thickening Al-doped ZnO film is studied using both the Conductive atomic force microscope/Spectroscopy (C-AFM/C-AFS) and Scanning Tunnelling Microscope/Spectroscopy (STM/STS) techniques. To this end, these films were deposited by varying the deposition time from 15 to 120 min by RF magnetron sputtering. The local surface electrical heterogeneity was found to be strongly dependent on the overall microstructure of the film grown at a particular deposition time. X-ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscope-Energy Dispersive Spectroscopy (TEM-EDS) were used to discern the distribution of the chemical constituents over these film surfaces. This study correlates the presence of a large amount of chemisorbed oxygen and/or segregated  $Al_xO_y$  at the grain boundaries associated with relatively non-uniform and/or rough films to the overall lower surface current values. Subsequently, a uniformly thick AZO film with a homogenous microstructure grown at an optimum deposition time is found to have the least amount of chemisorbed oxygen along with an effective distribution of Al doping on the film surface, leading to an increase in the overall surface current. This higher surface current is then found to increase the surface electrical heterogeneity of the film due to increased difference between a defect and defect-free region, contrary for a non-uniform and/or rough film.

## 1. Introduction

Electrical properties of a transparent conductor are extremely important to comprehend for better design of the devices in several applications, like, thin film solar cells, liquid crystal displays, light emitting diodes, electrochromic devices, etc, as these films are used as charge injection layers, hence playing a major role on the device performance [1–6]. Moreover, with the constant efforts to shrink the device dimensions, these properties have become even more crucial to understand at the local level, i.e., it is more desirable to have an electrically homogeneous layer at the nanoscale. This is because, performance and stability of the devices depend strongly on the homogeneity in the local electrical properties, like, electrical conductivity, carrier concentration and carrier mobility, and any heterogeneity in these properties may cause local hot spots, resulting in to significantly higher leakage current. Moreover, it is very important to understand the electrical properties (and its heterogeneity) of these film surfaces at the nano level as these films are usually present in a stack, thus influencing the electrical properties of the next layers and thus the entire device.

Al-doped ZnO (AZO) is one of the promising n-type wide band gap semiconductor because of its higher optical transmittance (of above 85% in the visible range), lower electrical resistivity ( $\rho$ ) (in the order of  $10^{-4} \Omega\text{-cm}$ ), low cost and earth abundant, low toxicity, easy fabrication and higher plasma stability [7–9]. These have led significant research in the literature to optimize the optoelectronic properties of these films [10–18]. However, most of these works have been emphasized on their bulk optoelectronic properties, with only a few stressing on their local electrical properties [19–23]. Likovich et al. investigated the local density of states of the sputtered AZO films in the vicinity of the grains and the grain boundaries using scanning tunnelling microscope/spectroscopy (STM/STS) and found pronounced differences in their tunnelling conductivity [19]. Wu et al. demonstrated the surface electrical activation in different ZnO orientations with the help of conductive atomic force microscope/spectroscopy (C-AFM/C-AFS) [20]. Kumar et al. studied the local electrical transport properties of the AZO thin films to understand the effect of UV-exposure on the photoconductivity using C-AFM/C-AFS and Kelvin probe force microscope (KPFM) [21]. In another study Kumar et al. investigated the role of defects and

\* Corresponding author.

E-mail address: [emila@iitgn.ac.in](mailto:emila@iitgn.ac.in) (E. Panda).

<sup>1</sup> Authors contributed equally to this work.

polarization on the local band bending of AZO thin films at the grain boundaries [22]. Chen et al. described the effect of substrate temperature on the local conductivity and work function of the AZO thin films with the help of C-AFM and scanning surface potential microscope (SSPM), where they observed positive correlation between the concentration of  $O^{2-}$  and  $Al^{3+}$  ions on these AZO film surfaces with the local surface conductivity and work function [23]. Moreover, none of these reported work established a correlation between the heterogeneity in the surface electrical properties of these AZO films with their chemical heterogeneity, induced from their microstructure. Hence, through this work attempts have been made to understand the local surface electrical properties at a nanoscale dimension and then correlated with their microstructure. To this end, AZO films were deposited onto the soda lime glass substrates by varying the deposition time ( $t$ ) from 15 to 120 min at 623 K substrate temperature ( $T_s$ ) in RF magnetron sputtering. RF magnetron sputtering is used here as films grown using this technique are found to have an overall good quality in addition to good adherence to the substrate [24,25]. Then the detailed local surface electrical properties and their heterogeneities were measured using both the C-AFM/C-AFS and STM/STS techniques. In C-AFM, the tip is placed in direct contact with the sample surface by means of an applied controlled force and captures simultaneously the variations in surface morphology and local conductivity, hence giving insight on the morphology dependent nanoscale surface conductivity of these films [20–23,26–35]. In STM, the tip is not kept in physical contact with the sample surface and depending on the polarity of the applied bias voltage, tunnelling current starts to flow from the tip to the sample or vice versa, thus mapping the local surface electronic states of the surface of a sample on either side of the Fermi energy [36]. Further, using C-AFS and STS, local  $I$ - $V$  profiles can be obtained which give additional information about the nature of these local points (i.e., whether, locally the film surface is conducting, semi-conducting and/or non-conducting) [37–48]. Then the local surface electrical heterogeneity was compared with the overall microstructure of these film surfaces using X-ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscope-Energy Dispersive Spectroscopy (TEM-EDS). While XPS gives the overall surface constitution of these films, TEM-EDS discerns the distribution of the chemical constituents over these film surfaces. In the end, the influence of the deposition time towards developing a particular film surface is discussed.

## 2. Experimental details

Series of Al-doped ZnO (AZO) films with average thicknesses varying from 115 to 348 nm were deposited on ultrasonically cleaned (1 cm × 1 cm) soda lime glass (SLG) substrates using RF Magnetron Sputtering and by varying the deposition time ( $t$ ) from 15 to 120 min

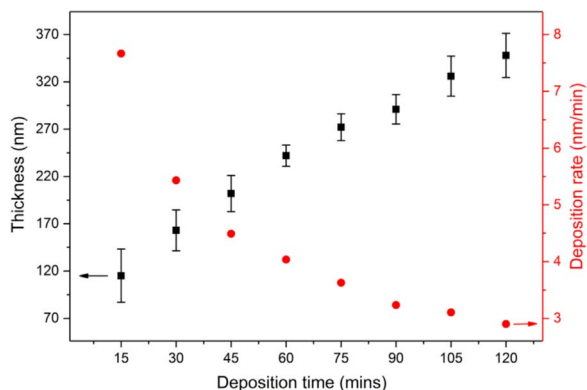


Fig. 1. Variation in film thickness and deposition rate of Al-doped ZnO films deposited on soda lime glass substrates by RF magnetron sputtering at  $t$  varying in the range of 15–120 min.

(see Fig. 1). AZO ceramic target (of 99.99% purity with composition of 98 wt% ZnO and 2 wt%  $Al_2O_3$ ) was used to deposit these films at the deposition condition optimized in a separate study [49]. These are, 623 K substrate temperature ( $T_s$ ), 50 W RF power to the target,  $7.0 \times 10^{-3}$  mbar chamber pressure ( $P_{chamber}$ ), 40 SCCM Argon (of purity 99.99%) to the chamber, 15 RPM substrate rotation and 7.0 cm substrate to target distance.

To understand the local surface electrical properties of these in situ grown AZO thin films, conductive Atomic Force Microscope (C-AFM; a module in peak force tunnelling AFM (PF-TUNA) module of Scanning Probe Microscope (SPM)), Scanning Tunnelling Microscope/Spectroscopy (STM/STS) analyses under ambient condition were carried out (*Model: NanoScope Multimode 8.0, Supplier: Bruker Corporation*). To minimize the influence of moisture and atmospheric oxygen on conductivity of these AZO samples, all these samples were stored in a desiccator in a humidity controlled room maintained below 30% using dehumidifier and analyzed within 24 h of film deposition. In C-AFM, simultaneous variations in surface morphology and local conductivity were measured using conductive Platinum-Iridium (Pt-Ir) coated antimony doped silicon tip (SCM-PIT; *Supplier: Bruker corporation*) in contact mode (with a nominal radius of curvature of 20 nm and spring constant of 4 N/m). In addition to this, using Conductive Atomic Force Spectroscopy (C-AFS) mode, local  $I$ - $V$  characteristics pertaining to each of these captured  $1 \mu m \times 1 \mu m$  C-AFM images (and thus for those deposited AZO films) were acquired from 52 different locations including the vicinity of the grains and the grain boundaries. During these local  $I$ - $V$  measurements, the probe was held at a fixed position with constant peak force set point of 185 nN, while the applied sample bias was kept between  $-250$  mV to  $+250$  mV for all samples that are analyzed in this study. Similarly, STM images were acquired using Pt/Ir tip (*PT-10; Supplier: Bruker corporation*) of 0.25 mm diameter and 8 mm length. During the measurement, Pt/Ir tip was held at a fixed position with constant peak force set point and set current of 0.67 V and 1.5 nA respectively, while the applied sample bias was kept between  $-1.5$  V to  $+1.5$  V for all the samples. Then local STS  $I$ - $V$  characteristics from these AZO film surfaces were recorded from 52 different locations (including the grain and grain boundary regions) from each of the captured  $1 \mu m \times 1 \mu m$  STM images in the STS mode. To maintain electrical continuity while performing STM measurement, silver paint was used for grounding the bottom metal plate and top AZO thin films.

To understand the local chemical heterogeneity over the film surface, plan view samples for TEM were prepared by mechanical and ion-beam based standard techniques and TEM imaging and elemental quantitative analysis on these AZO films were performed using Energy Dispersive Spectroscopy (EDS, *Model: AZtec, Supplier: Oxford Instrument*) module of high resolution Transmission Electron Microscope (HRTEM; *Model: JEM – 2100, Supplier: JEOL Ltd.*) operated at 200 kV. The EDS spectra were recorded with a spot size of  $\sim 1$  nm. Additionally, X-ray Photoelectron Spectroscopy (XPS; *Model: PHI 5000 Versa Prob II, Supplier: ULVAC-PHI, Inc.*) with a spot size of  $10 \mu m$  was employed to investigate the surface chemical states of these films.

Moreover, overall structure and surface morphology of these AZO films were investigated using Grazing Incident X-ray Diffractometer (GIXRD; *Model: D8 Discover, Supplier: Bruker Corporation*) and Atomic Force Microscope (AFM; *Model: Nanoscope Multimode 8.0, supplier: Bruker Corporation*). Field Emission Scanning Electron Microscope ((FESEM; *Model: JSM 7600F, Supplier: JEOL Ltd.*) was used to determine the thicknesses of these films and their uniformity. Hall effect measurement system was used to know the sheet resistance, carrier concentration and carrier mobility of these samples.

## 3. Results and discussion

Fig. 1 shows the rate of deposition along with the thicknesses of the AZO films obtained with respect to the deposition time ( $t$ ). With increasing film thickness, the deposition rate was found to decrease from

متن کامل مقاله

دریافت فوری ←

**ISI**Articles

مرجع مقالات تخصصی ایران

- ✓ امکان دانلود نسخه تمام متن مقالات انگلیسی
- ✓ امکان دانلود نسخه ترجمه شده مقالات
- ✓ پذیرش سفارش ترجمه تخصصی
- ✓ امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله
- ✓ امکان دانلود رایگان ۲ صفحه اول هر مقاله
- ✓ امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب
- ✓ دانلود فوری مقاله پس از پرداخت آنلاین
- ✓ پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات