

Sol-gel deposition and plasma treatment of intrinsic, aluminum-doped and gallium-doped zinc oxide thin films as transparent conductive electrodes

Zhaozhao Zhu*[†], Trent Mankowski*[†], Kaushik Balakrishnan[†], Ali Sehpar Shikoh[‡], Farid Touati[‡],

Mohieddine A. Benammar[‡], Masud Mansuripur[†], and Charles M. Falco[†]

[†]College of Optical Sciences, The University of Arizona, Tucson, Arizona, USA

[‡]Department of Electrical Engineering, Qatar University, Doha, Qatar

Abstract

Zinc oxide and aluminum/gallium-doped zinc oxide thin films were deposited via sol-gel spin-coating technique. Employing plasma treatment as alternative to post thermal annealing, we found that the morphologies of these thin films have changed and the sheet resistances have been significantly enhanced. These plasma-treated thin films also show very good optical properties, with transmittance above 90% averaged over the visible wavelength range. Our best aluminum/gallium-doped zinc oxide thin films exhibit sheet resistances (R_s) of $\sim 200 \Omega/\text{sq}$ and $\sim 150 \Omega/\text{sq}$, respectively.

Introduction

Transparent conductive electrodes (TCEs) are essential components for today's opto-electronic devices such as smartphones and solar cells. The TCE market has been dominated by Indium Tin Oxide (ITO), owing to its superior optical and electrical properties¹⁻³. Besides the excellent performance of ITO (when integrated into opto-electronic devices), the maturity of its manufacturing methods and also being amenable to etching contribute to its favorable use⁴. However, due to a global short supply of indium, finding replacements for ITO is crucial for the future market of TCEs.

Zinc Oxide (ZnO) is an intrinsically n-type doped semiconductor that has many intriguing properties suitable for TCE applications. Due to its wide bandgap, it is transparent in the visible wavelength range, and due to its semiconducting nature, doping with boron group elements (Boron, Aluminum, Gallium) has proven beneficial to improve its electrical conductivity. Sputtering Al- or Ga-doped zinc oxide on glass substrates yields good sheet resistance under $20 \Omega/\text{sq}$ with optical transmittance $\sim 85\%$ ^{5,6}. However, sol-gel deposition has also been widely investigated due to its low cost and scalability, while exhibiting sheet resistances in $\text{k}\Omega/\text{sq}$ range even for doped zinc oxide⁷⁻¹⁰. Typically, sol-gel deposition of ZnO or doped ZnO thin films requires a high-temperature ($550 \text{ }^\circ\text{C} - 750 \text{ }^\circ\text{C}$) annealing step in a special gas environment (N_2 or reducing atmosphere). Here we report the observation of enhanced electrical conductivity in ZnO, aluminum-doped zinc oxide (AZO), and gallium-doped zinc oxide (GZO) obtained with plasma treatment as a post-annealing treatment technique (instead of the usual high-temperature thermal annealing). Our sol-gel deposited and plasma-treated thin films show good electrical conductivity and high optical transmittance in the visible range.

Methods

Zinc Acetate is dissolved in 2-Methoxyethanol at a concentration of 0.5 mol/L, while Diethanolamine (DEA), a stabilizing agent, is added at 1:1 molar ratio to zinc precursor. This mixture is then stirred at $60 \text{ }^\circ\text{C}$ for an hour to achieve a homogeneous and clear solution, and aged in air for 18 – 24 hours. Before coating, $\text{Al}(\text{NO}_3)_3$ or $\text{Ga}(\text{NO}_3)_3$ is added to the solution at 0, 1 and 2 atomic percent (at.%) to Zn^{2+} (e.g. $[\text{Al}]/[\text{Al} + \text{Zn}]$ or $[\text{Ga}]/[\text{Ga} + \text{Zn}]$), and the solution is stirred again and made available for spin-coating on glass substrates. One spin-coating cycle consists of spinning at 1000 rpm for 30 s followed by spinning at 4000 rpm for 10 s. Upon finishing each spin-coating cycle, the thin films are heated at $400 \text{ }^\circ\text{C}$ on a hot-plate for 10 minutes and gradually cooled down to room temperature. (This step is hereby referred to as pre-annealing.) By repeating the spin-coating and pre-annealing steps, any desired film thicknesses can be achieved. After all layers are deposited, the resulting thin film stack is exposed to low-pressure (< 5 torr) air plasma generated by a plasma-cleaner (PLASMA-PREEN-II-862) for various durations. Control groups are prepared by post-anneal at $600 \text{ }^\circ\text{C}$ in air for 1 hour to observe the differences in film morphologies.

Sheet resistances are measured by a 4-probe method using a Keithley 2400 Source Measurement Unit. The optical transmittance is measured with Cary-3000 spectrophotometer and corrected for the bare glass substrate. X-ray diffraction (XRD) measurements are made using a PANalytical X'pert Instrument equipped with a programmable incident beam slit with the slit fixed at 1° , and an X'Celerator Detector. The XRD measurements were made in the bisecting geometry, and the x-ray radiation used was $\text{Cu K}\alpha$, $\lambda = 1.5418 \text{ \AA}$. Scanning Electron Microscopy (SEM) images were acquired with a Hitachi S-4800 Type-II SEM.

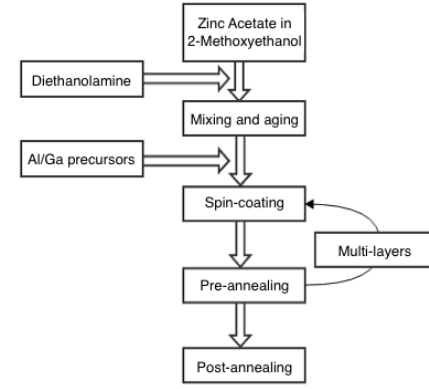


Figure 1. Sol-gel deposition and annealing processes for ZnO, AZO, and GZO thin film transparent conductive electrodes.

Results

To examine the effectiveness of plasma treatment on ZnO, AZO and GZO thin films, controlled cycles of 5 to 15 minute plasma treatment were applied to the sol-gel deposited (and pre-annealed) thin films. The measured sheet resistances of all the samples thus prepared are plotted versus the number of layers in figures 2a, 2b and 2c, corresponding to plasma exposure times of 5, 10, and 15 minutes, respectively. From figures 2a – 2c, it is seen that the sheet resistance monotonically decreases as a function of the increasing number of deposited layers (from 3 layers to 7 layers). Before plasma treatment, all samples had such poor electrical conductivity that their sheet resistances did not even register on our probe (200 M Ω range). However, after being plasma treated for 5 minutes, the R_s of all the samples reduced into the k Ω range, with AZO and GZO (both 1 at.% and 2 at.%) having lower resistances than our un-doped ZnO. After a second round of 5-minute plasma treatment, the sheet resistances further declined, with 2 at.% doped AZO having $R_s \approx 200 \Omega/\text{sq}$, and 1 at.% doped GZO having $R_s \approx 150 \Omega/\text{sq}$. Interestingly, after another 5 minutes of plasma treatment (total of 15 minutes), there is a slight increase in sheet resistances, as can be seen in figure 2d.

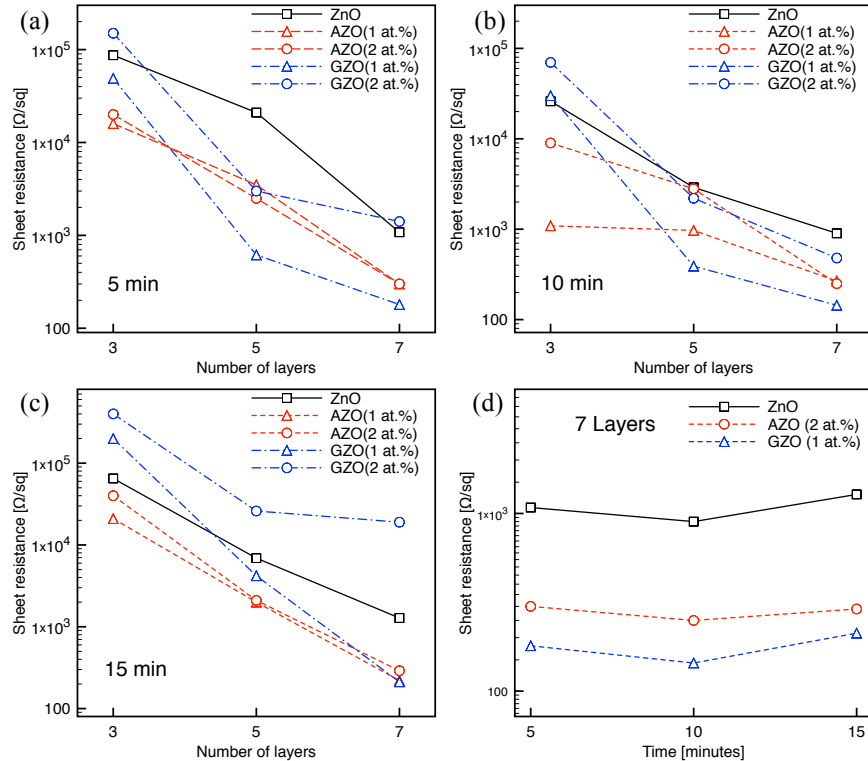


Figure 2. (a-c) Measured sheet resistances versus number of layers after plasma treatment of sol-gel deposited thin films of ZnO, AZO, and GZO, treated for 5, 10, and 15 minutes. d) Sheet resistances of 7-layer thin-film stacks of ZnO, AZO (2 at.%) and GZO (1 at.%), plotted as functions of their plasma treatment time.

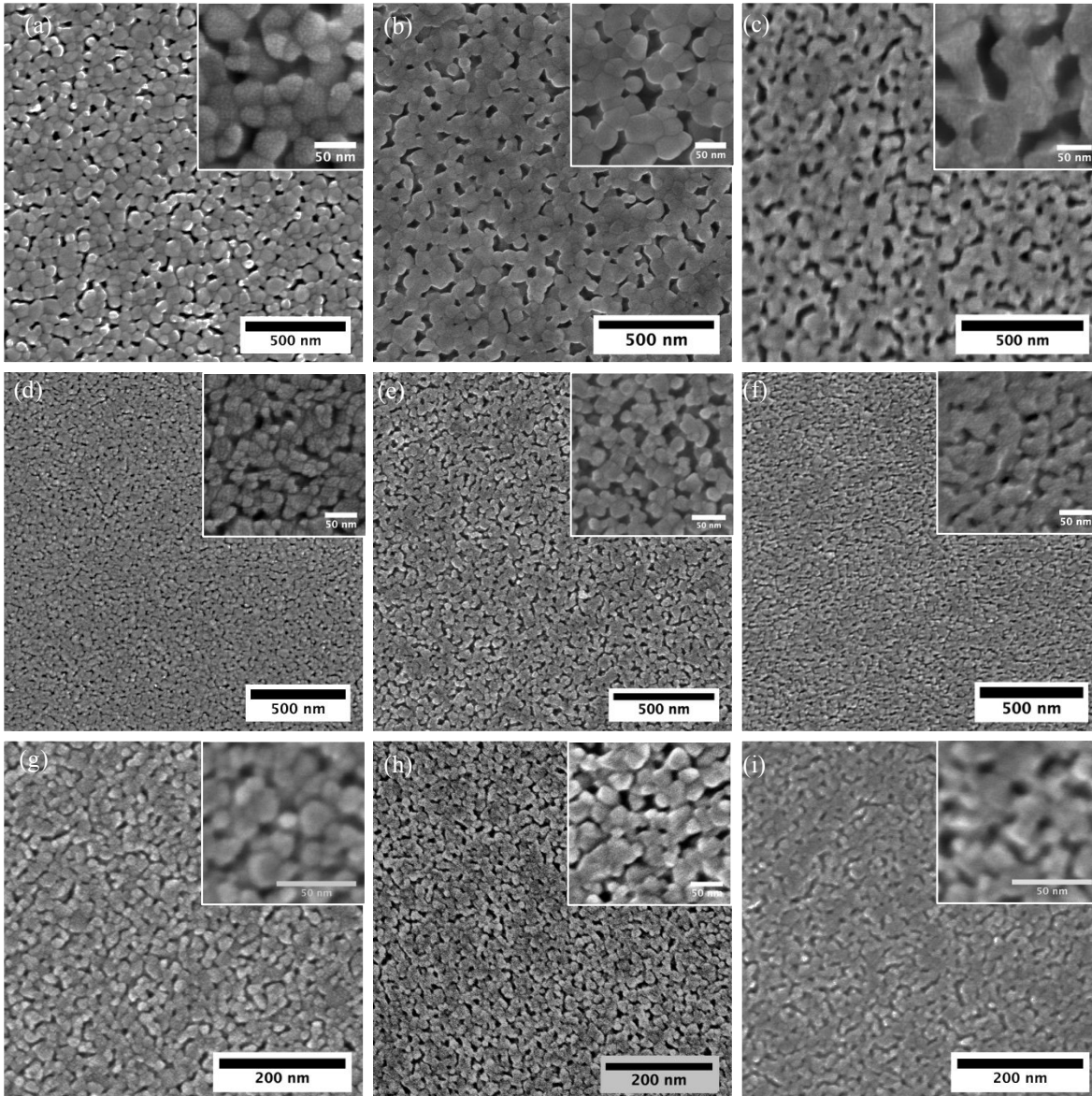


Figure 3. SEM images of our 7-layer thin film stacks: ZnO after (a) pre-annealing, (b) annealed at 600 °C in air environment and (c) plasma treatment; AZO (2 at.%) after (d) pre-annealing, (e) annealed at 600 °C in air, (f) plasma treatment; and GZO (1 at.%) after (g) pre-annealing, (h) annealed at 600 °C in air and (i) plasma treatment. The insets show higher magnification SEM images for each sample.

The surface morphologies of the films were examined with a Scanning Electron Microscope (SEM) and the images thus obtained are shown in figure 3. Figures 3a, 3d and 3g are SEM images of ZnO, AZO (2 at.%), and GZO (1 at.%) films immediately after pre-annealing (without any post-annealing). The grains in these images are readily distinguishable, and their boundaries are clearly identifiable. The crystalline grains of the ZnO film are seen to be larger than those of AZO and GZO films. Figures 3b, 3e and 3h show the SEM images of the ZnO, AZO (2 at.%), and GZO (1 at.%) annealed at 600 °C for 1 hour for comparison purposes. The grain sizes are similar to those before any post-annealing, and the grain boundaries are still identifiable in higher magnification images. Figures 3c, 3f and 3i show the SEM images of ZnO, AZO (2 at.%), and GZO (1 at.%) films after 15 minutes of plasma treatment. In all three cases, the average grain size does not appear to have changed in consequence of plasma treatment, although the higher magnification SEM images (shown as insets) indicate that the originally separated grains are sintered. This sintering caused by the post-annealing plasma treatment of our sol-gel deposited thin-film stacks is apparently responsible for the significant enhancement of the electrical conductivity of the samples.

X-ray diffraction analysis was conducted on 7-layer ZnO, AZO (2 at.%), and GZO (1 at.%) samples both before and after plasma treatment. The measurements were carried out under identical conditions, and the results are shown in figure 4a. Characteristic peaks such as (100) (002) and (101) are observed for wurtzite zinc oxide crystalline structure. It is also seen that there is no significant change in the XRD patterns before and after plasma treatment. This indicates that the improvement in conductivity of the samples is caused by sintering during plasma treatment rather than by a change of the crystal structure.

Finally, the optical transmittance of the thin-film samples was measured with a UV-vis spectrometer; the results are plotted versus the wavelength in figure 4b. The transmittance of all the samples is seen to be greater than 90% across the entire visible wavelength range. Specifically, the average optical transmittances (in the range 400 – 800 nm) for 7-layer ZnO, AZO, and GZO thin-film stacks are above 90%. This property, of course, is particularly beneficial for TCE applications. For ZnO thin films with different thicknesses, since the absorption in the visible range is negligible, no significant loss is observed for thicker films. Instead, interference patterns of transmittance become significant as the film thickness increases; this phenomenon is explained elsewhere¹¹. The potential thus exists for further reductions of the films' sheet resistance R_s by depositing more layers without sacrificing the (average) optical transmittance.

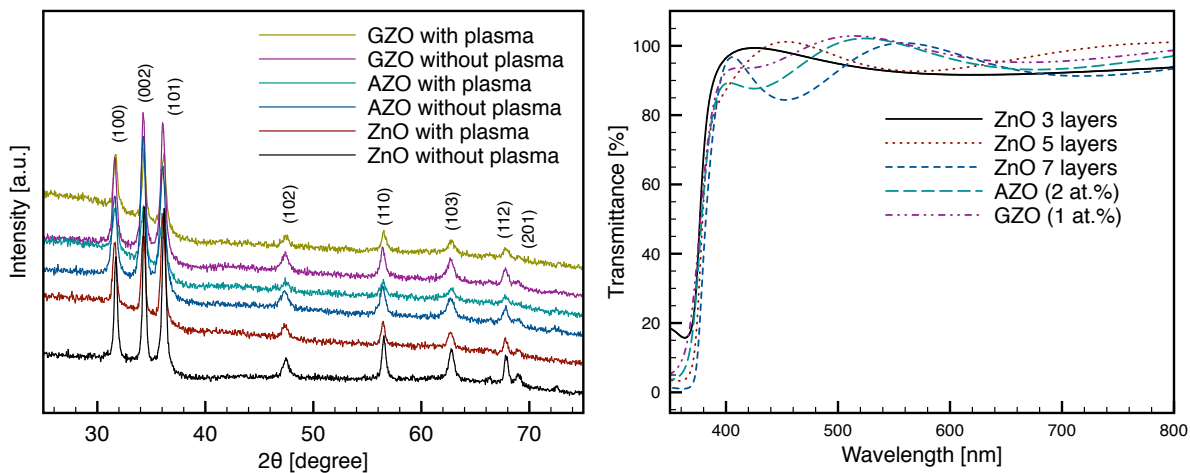


Figure 4. a) XRD patterns of 7-layer ZnO, AZO (2 at.%), and GZO (1 at.%) samples, both before and after plasma treatment. b) Measured optical transmittance of various ZnO, AZO, and GZO samples as functions of the wavelength.

Conclusion

Employing a well-established sol-gel deposition technique, we deposited ZnO, AZO, and GZO thin films on glass substrates. As an alternative post-annealing step, plasma treatment was applied instead of the conventional method of high-temperature thermal annealing. Our results indicate that plasma treatment produces a significant enhancement in the electrical conductivity of all ZnO, AZO, and GZO thin films without modifying the crystalline structure or adversely affecting the optical transmittance of the thin-film samples. Our best performing samples are 2 at.% doped AZO with R_s of $\sim 200 \Omega/\text{sq}$, and 1 at.% doped GZO having $R_s \sim 150 \Omega/\text{sq}$; both samples exhibit excellent optical transmittances of greater than 90% in the visible range. The combination of layer-by-layer sol-gel deposition, pre-annealing, and plasma post-treatment enables fast, large-area, cost-effective, and low-temperature ($< 400 \text{ }^\circ\text{C}$) fabrication of ZnO, AZO, and GZO transparent conductive electrodes for various opto-electronic applications.

Acknowledgement

This publication was made possible by the grant # 5-546-2-222 from the Qatar National Research Fund (a member of the Qatar Foundation). The authors also acknowledge partial support from the Arizona TRIF program. The authors thank Prof. Peyghambarian and Prof. Norwood for their access to facility and instrumentation for parts of the work shown here. The statements made herein are solely the responsibility of the authors.

Reference

- (1). Ginley, DS; Bright, C Transparent Conducting Oxides. *MRS Bulletin* **2000**.
- (2). Kim, H; Horwitz, JS; Kushto, G; Pique, A Effect of Film Thickness on the Properties of Indium Tin Oxide Thin Films. *Journal of Applied Physics* 88, no. 10 **2000**: 6021-6025.
- (3). Kim, H; Horwitz, JS; Kushto, GP; Kafafi, ZH Indium Tin Oxide Thin Films Grown on Flexible Plastic Substrates by Pulsed-Laser Deposition for Organic Light-Emitting Diodes. *Applied physics Letters* 79.3 **2001**: 284-286.

- (4). Huang, C. J., Yan-Kuin Su, and Shi-Lun Wu. The Effect of Solvent on the Etching of ITO Electrode. *Materials Chemistry and Physics* 84, no. 1 **2004**: 146-150.
- (5). Fang, Guojia, Dejie Li, and Bao-Lun Yao. Fabrication and Vacuum Annealing of Transparent Conductive AZO Thin Films Prepared by DC Magnetron Sputtering. *Vacuum* 68, no. 4 **2002**: 363-372.
- (6). You, Z. Z., and G. J. Hua. Electrical, optical and microstructural properties of transparent conducting GZO thin films deposited by magnetron sputtering. *Journal of Alloys and Compounds* 530 **2012**: 11-17.
- (7). Lee, Ka Eun, Mingsong Wang, Eui Jung Kim, and Sung Hong Hahn. Structural, electrical and optical properties of sol-gel AZO thin films. *Current Applied Physics* 9, no. 3 **2009**: 683-687.
- (8). Kim, Young-Sung, and Weon-Pil Tai. Electrical and optical properties of Al-doped ZnO thin films by sol-gel process. *Applied Surface Science* 253, no. 11 **2007**: 4911-4916.
- (9). Tsay, Chien-Yie, Kai-Shiung Fan, and Chien-Ming Lei. Synthesis and characterization of sol-gel derived gallium-doped zinc oxide thin films. *Journal of Alloys and Compounds* 512, no. 1 **2012**: 216-222.
- (10). Ng, Zi-Neng, Kah-Yoong Chan, and Thanaporn Tohsophon. Effects of annealing temperature on ZnO and AZO films prepared by sol-gel technique. *Applied Surface Science* 258, no. 24 **2012**: 9604-9609.
- (11). N. Bouchenak Khelladi, N. E. Chabane Sari. Simulation Study of Optical Transmission Properties of ZnO Thin Film Deposited on Different Substrates. *American Journal of Optics and Photonics* 1, No. 1, **2013**, 1-5.