Lowering the resistivity of aluminum doped zinc oxide thin films by controlling the self-bias during RF magnetron sputtering

Stamate, Eugen

Published in:
Surface and Coatings Technology

Link to article, DOI:
10.1016/j.surfcoat.2020.126306

Publication date:
2020

Document Version
Peer reviewed version

Citation (APA):
Lowering the resistivity of aluminum doped zinc oxide thin films by controlling the self-bias during RF magnetron sputtering

Eugen Stamate

PII: S0257-8972(20)30975-0
DOI: https://doi.org/10.1016/j.surfcoat.2020.126306
Reference: SCT 126306

To appear in: Surface & Coatings Technology

Received date: 23 June 2020
Revised date: 10 July 2020
Accepted date: 14 August 2020

Please cite this article as: E. Stamate, Lowering the resistivity of aluminum doped zinc oxide thin films by controlling the self-bias during RF magnetron sputtering, Surface & Coatings Technology (2020), https://doi.org/10.1016/j.surfcoat.2020.126306

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier.
Lowering the resistivity of aluminum doped zinc oxide thin films by controlling the self-bias during RF magnetron sputtering

Eugen Stamate\textsuperscript{1,2}

\textsuperscript{1}DTU Nanolab, National Centre for Nano Fabrication and Characterization, Technical University of Denmark, Ørsted Plads, Kgs. Lyngby – 2800, Denmark

\textsuperscript{2}Email: eust@dtu.dk

Keywords: transparent conducting oxides, RF magnetron sputtering, aluminum-doped zinc oxide.

Abstract:
Transparent conducting thin films based on aluminum-doped zinc oxide are regarded as a viable alternative for low-cost and large-area applications such as solar cells and smart windows. Despite of intensive research, the thin film growth mechanism by magnetron sputtering is under debate concerning the role of energetic oxygen negative ions and the spatial distribution of atomic oxygen during the deposition. As the negative ions energy is directly related to the self-bias during RF driven magnetron sputtering, this work demonstrates a method to lower the thin film resistivity with a factor above 2 by including a tuning electrode between the target and the substrate. The electrode increases the RF coupling, reduces the dc self-bias and improves the electronic properties uniformity over the substrate. Consequently, resistivity below $3 \times 10^{-3} \ \Omega \text{cm}$ is obtained over a substrate area comparable with the target surface for an averaged transmittance above 90\% without intentional substrate heating.
1. Introduction

Transparent conducting oxides (TCO) are essential in several key technologies including touch panels, solar cells, smart windows and organic light-emitting diodes [1]. While high end portable electronics can yet afford indium tin oxide (ITO) as TCO, other large-area and big-market applications, including smart windows and solar cells, need a cost effective solution based on abundant materials, with aluminum doped zinc oxide (AZO) deposited by magnetron sputtering as one of the best choices [2-5]. However, intensive research on AZO revealed significant uniformity problems for optoelectronic properties with respect to the erosion tracks with record resistivity values (below 5x10^{-4} \ \Omega \text{cm}) only for areas much smaller than the magnetron’s cathode area [4, 6]. So far, the spatial distributions of oxygen negative ions and the atomic oxygen assisting the film growth are regarded as the two main reasons for poor AZO performance when implemented for large area processes [3-5]. The oxygen negative ions energy was recently reported to be higher in DC than in RF sputtering, with an evident correlation in spatial distribution with the erosion tracks [7-9]. Moreover, AZO sputtering shows a very narrow process window, with resistance values exhibiting two orders of magnitude change within 10 mm shift on the substrate surface for a magnetron cathode of 2 inch in diameter [10]. Since most of the energetic negative ions are produced by attachment of low energy electrons (secondary emission at the target surface) followed by acceleration in the DC sheath, it is expected to have a direct correlation between negative ion energy and the self-bias. In this context, a possible solution is to improve the AZO resistivity by reducing the oxygen negative ion energy. In this work, we are reporting the possibility to improve the AZO resistivity by controlling the DC self-bias during RF deposition using a tuning electrode. The method is easy to implement and has
direct impact on low-cost and large-area applications using TCO such as solar cells, smart windows and touch panels.

2. Results and discussion

The RF magnetron sputtering discharge is based on a direct electromagnetic coupling between the biased cathode and the grounded anode. Consequently, changes in the anode properties (area, proximity, conductivity) are expected to influence to a greater extent the plasma properties when depositing at short cathode to substrate distances on dielectric substrates than at larger distances. In order to investigate this possibility, we introduced a coupling electrode between the cathode and substrate as presented in Figure 1(a). The vacuum chamber was large enough (50 cm in diameter and 30 cm in height) to accommodate 8 samples placed on a rotatable substrate holder. The two-inch TORUS ® cathode (Kurt Lesker) was placed off axis with respect to a large rotatable disk plate (see Figure 1 (b)) that have three circular openings of 100 mm in diameter that could be each vertically aligned with the cathode by rotation. Location $L_1$, was used to act as shutter during pre-sputtering and $L_2$ for conventional sputtering ($\phi =100$ mm). By filling the 100 mm in diameter space with a ring-like tuning electrode (made of aluminum) of 95 mm in external diameter and an inner opening of $\phi =50$ mm for $L_3$ and $\phi =60$ mm for $L_4$ it was possible to deposit the 8 sample (indicated with $S_1$ to $S_8$) under different conditions without turning off the discharge, a fact that allows monitoring of thin film properties changes for small variations in process parameters. The shutter plate supporting the tuning electrode could be translated vertically in the space between magnetron cathode and substrate (defined by distance $D_1$) and be positioned at different locations defined by $D_2$. The tuning electrode was electrically insulated from the shutter plate and could be DC biased at potential $V_T$. The target material was ZnO/Al$_2$O$_3$, with a percentage by weight of 98/2 provided by Kurt Lesker.
The AZO deposition process optimization revealed a narrow range of parameters that could produce the lowest resistivity values, summarized as following: RF discharge power, $P_{\text{RF}}$, 15 to 40 W, $D_1 < 40$ mm, discharge pressure $0.26 < p < 0.53$ Pa [8]. These parameters are in concordance with previous reports on AZO [11-31]. If the energy of the oxygen negative ions is correlated with AZO resistivity then is should be manifested by a lower DC self-bias in the range of optimized parameters when deposition is performed using the location $L_2$ ($\Phi = 100$ mm). The DC self-bias as a function of pressure for 30 and 60 W and different $\phi$ is presented in Figure 2 for $D_1 = 35$ mm, $D_2 = 10$ mm and $V_T = 0$ V. The increase in power from 30 to 60 W led an increase of more than 70 V in DC self-bias with minimum values at 0.4 Pa for 30 W and 0.35 Pa at 60 W. The tuning electrode had a significant effect for self-bias reduction at pressures below 0.67 Pa and presented a mild effect above 0.67 Pa. While only a shallow minimum is present for $\phi = 100$ mm, instead, $\phi = 50$ and 60 mm produced an almost 50 V reduction for 30 W at 0.4 Pa and more than 50 V for 60 W at 0.33 Pa. Fine tuning of $D_2$ affected the self-bias as well. Since no significant difference was observed for $15 < D_2 < 5$ mm, it was keep constant at 10 mm for all reported results presented in here.

The self-bias dependence of $D_1$ for different $\phi$ and $V_T = 0$ V is presented in Figure 3 for 30 and 60 W, at pressures exhibiting the lowers values (see Figure 2), 0.33 and 0.4 Pa, respectively. It reveals a steeper self-bias increase for $D_2 < 40$ mm followed by a certain saturation for larger distances. Noticeable, 30W, 0.4 Pa and $\phi = 100$ mm (equivalent with no tuning electrode configuration) produced a self-bias below 100 V for $D_1 < 30$ mm, which correlates very well with the optimized parameters mentioned at the beginning of this paragraph. Over all, the tuning electrode with $\phi = 50$ and 60 mm was able to reduce the self-bias with more than 25 V at 30 W and more than 50 V at 60 W for $30 < D_1 < 40$ mm.
Most TCOs are deposited on glass substrates and following the results above it is expected that the electrical properties of the area facing the cathode can also contribute to the RF matching and consequently influence the self-bias. To test this assumption, the self-bias as function of pressure was measured for $\phi=50$ mm, $D_1=40$ mm, $D_2=10$ mm, $V_T=0$ V and $P_{RF}=30$ W when the cathode was facing the metallic substrate holder having placed at the center: i) no sample; ii) 1×5 cm$^2$ lime glass; iii) 5 cm in diameter lime glass; iv) 10×10 cm$^2$ lime glass (all glass samples were of 0.5 mm in thickness) and the results are presented in Figure 4. While the sharp decrease with a minimum value at 0.27 Pa is present for all configurations, the self-bias for a cathode facing a conducting and grounded surface was with 20 V lower than when facing an insulating surface. This proves the importance of the sample size and nature of the substrate holder as well as the sensitivity of the RF coupling with respect to changes in conductivity of nearby cathode and anode surface.

Another way to influence the coupling, with a more direct impact on plasma, is to bias the tuning electrode. A negative bias with respect to plasma potential is commonly used to accelerate positive ions in many plasma processes such as sputtering, etching and ion implantation and is known of having limited impact on plasma properties [32]. However, a positive bias draws a large electron current and can elevate plasma potential when above the ionization threshold. A particular situation relates to electronegative discharges where the reduced electron density allows one to apply even hundreds of volts above plasma potential without affecting the plasma potential or igniting an anodic glow [33]. Our context relates to a small tuning of $V_T$ around plasma potential. The self-bias as a function of pressure for different $V_T$ is presented in Figure 5 for $P_{RF}=30$ W, $D_1=35$ mm, $D_2=10$ mm and $\phi=50$ mm. While $V_T=15$ V almost translated up the pressure dependence with 25 V, $V_T=15$ V translated it down with 20
A more positive $V_T$ (=30 V) was able to further reduce the self-bias for $p<0.4$ Pa, followed by a distorted pressure dependence above this value.

The effectiveness of the tuning electrode to improve the AZO resistivity by lowering the DC self-bias was tested by consecutive deposition (60 min) of three samples of glass (1×5 cm$^2$, 0.5 mm in thickness) after one hour pre-sputtering for $D_1=35$ mm, $D_2=10$ mm, $P_{RF}=30$ W, $p=0.4$ Pa for $\phi=50$, 60 and 100 mm and $V_T=0$ V (grounded). The sample geometry has the advantage to provide the spatial distribution of electronic properties measured as sheet resistance and thickness with a resolution of 1 mm. The sheath resistance, thickness and resistivity are presented in Figure 6 (a), (b) and (c), respectively. The sheath resistance was below 170 $\Omega$/sq for all $\phi$ and $r$ and shows direct correlation with the erosion track as previously reported for AZO [6]. The $\phi=60$ mm tuning electrode shows lower sheath values than $\phi=100$ mm for all $r$, except for three points at the edge ($r\geq20$ mm) that exhibited the lowest value of 24 $\Omega$/sq. The film thickness was about twice for $\phi=100$ mm than 50 and 60 mm, suggesting a RF coupling mode of lower plasma density. The calculated resistivity shows lower values, with a factor of 2, for $\phi=50$ and 60 mm, except for three points at the sample edge, where the minimum value gives $5.7\times10^{-4}$ $\Omega$cm. This value is important to notice when looking for a record-low resistivity, without taking into account the area exhibiting that very value with respect to magnetron cathode surface. However, for practical applications one should assess the whole area mirrored by the cathode on the substrate. In this regard, we can state that the tuning electrode produced resistivity values below $3.5\times10^{-3}$ $\Omega$cm for $-23\leq r \leq 23$ mm. Small changes in pressure, $D_1$ and discharge power resulted in higher resistivity values and fluctuations over one order of magnitude within 5 mm as reported very recently [10].

The effect of different $V_T$ on thin film properties: (a) sheath resistance, (b) thickness and (c) resistivity, is presented in Fig. 7 for $p=0.4$ Pa, $P_{RF}=30$ W, $D_1=35$ mm, $D_2=10$
mm, $\phi=50$ mm and 30 minutes deposition time. While the sheath resistance was lower for $V_T=15$ and 30 V than at $V_T=0$ V, a larger film thickness at 30 V resulted in best resistivity values for $V_T=15$ V. A direct estimation of plasma potential, $V_{pl}$, is difficult to perform due to probe contamination [34]. However, Fig. 5 indicates a certain plasma disturbance for $V_T=30$ V, which is expected to occur for voltages exceeding $V_{pl}$ with the ionization energy (15.7 eV for Ar). This gives a hint of $V_{pl} \sim 15$ V, a value that also correlates with $V_T$ giving the lowest and most uniform resistivity.

The radial distribution of the transmittance spectra for data presented in Fig. 7 at $V_T=15$ V are presented in Fig. 8 (a) and the corresponding averaged transmittance (400 to 700 nm) in Fig. 8 (b) where the measurements for $\phi=100$ mm were also included. The averaged transmittance was above 90% for all experimental points, with slightly higher values for $\phi=50$ mm. One can also notice a shallow correlation with the erosion track as a few percent higher values while a stronger correlation was reported for the energy band gap [10]. As shown in Figures 2 to 4, the deposition parameters window for a self-bias below 100 V is very narrow. The pressure should be around 0.4 Pa, $D_1$ below 45 mm and power below 35 W. Lowering $D_1$ brings the cathode to close to the substrate, disturbing the ability of the magnetic field to sustain the magnetron discharge. Power increase is also not an option for this short cathode to substrate distances. For example, discharge powers above 35 W led to resputtering at the sample center with significant drop in film thickness.

3. Conclusions

The resistivity of AZO is very sensitive to the deposition process parameters and strongly correlated with the erosion track on the cathode (target) surface. While a race for very low
resistivity values is still ongoing, practical applications such as solar cells, smart windows and touch panels, require from moderate to excellent optoelectronic properties (depending on specific application) obtained over an area comparable with the magnetron cathode surface. Several attempts have been made to avoid the negative ions during AZO deposition, including facing target sputtering [34], cathode tilt [35], off axis deposition [36] or magnetic field deflection when operating the discharge in high power impulse magnetron mode [37]. Despite of not knowing the exact mechanism of AZO thin film growth, this work demonstrates that lowering the DC self-bias below 100 V can improve the resistivity with a factor larger than 2 not only for certain locations on the substrate but over an area almost equal with that of the magnetron cathode. Since the negative ion energy correlates directly with the self-bias, it supports the argument that negative oxygen ions are one of the key factors to be further investigated in direct correlation with plasma and thin film properties. The method is easy to implement in existing conventional sputtering systems and has the advantage of causing a very limited reduction of the flux of sputtered material, as the tuning electrode opening is of the same dimension with magnetron cathode.

4. Acknowledgments

This work was supported by the SmartCoating project: 6151-00011B, financed by Innovation Fund Denmark.
5. References


https://doi.org/10.1088/0022-3727/33/4/201.

https://doi.org/10.1063/1.4811647.

https://doi.org/10.1002/vipr.201300518


Figures captions

**Fig. 1** (a) Schematic of the sputtering system, (b) details of the rotatable plate including the tuning electrodes with openings of 50, 60 and 100 mm. $D_1$ is the cathode to substrate distance, $D_2$ the tuning electrode to substrate distance and $\phi$ the opening diameter of the tuning electrode.

**Fig. 2** The DC self-bias as a function of pressure for 30 and 60 W and different $\phi$ for $D_1=35$ mm, $D_2=10$ mm and $V_T=0$ V.

**Fig. 3** The self-bias dependence of $D_1$ for different $\phi$ and $V_T=0$ V for 30 and 60 W, at pressures exhibiting the lowers values (see Figure 2), 0.33 and 0.4 Pa, respectively.

**Fig. 4** The self-bias as function of pressure measured for $\phi=50$ mm, $D_1=40$ mm, $D_2=10$ mm, $V_T=0$ V and $P_{RF}=30$ W when the cathode was facing the metallic substrate holder having placed at the center: no sample, $1 \times 5$ cm$^2$ lime glass, 5 cm in diameter lime glass or $10 \times 10$ cm$^2$ lime glass.

**Fig. 5** The self-bias as a function of pressure for different $V_T$ for $P_{RF}=30$ W, $D_1=35$ mm, $D_2=10$ mm and $\phi=50$ mm.

**Fig. 6** (a) The sheath resistance, (b) thickness and (c) resistivity of AZO thin films deposited for 60 min after one hour pre-sputtering for $D_1=35$ mm, $D_2=10$ mm, $P_{RF}=30$ W, $P=0.4$ Pa for $\phi=50$, 60 and 100 mm and $V_T=0$ V (grounded).

**Fig. 7** The effect of different $V_T$ on thin film properties: (a) sheath resistance, (b) thickness and (c) resistivity, for $P=0.4$ Pa, $P_{RF}=30$ W, $D_1=35$ mm, $D_2=10$ mm, $\phi=50$ mm and 30 minutes deposition time.
Fig. 8 (a) Radial distribution of transmittance spectra for $V_T=15$ V, $p=0.4$ Pa, $P_{RF}=30$ W, $D_1=35$mm, $D_2=10$ mm, $\phi=50$ mm and 30 minutes deposition time and (b) averaged transmittance (400 to 700 nm) for $V_T=15$ V, $p=0.4$ Pa, $P_{RF}=30$ W, $D_1=35$mm, $D_2=10$ mm, 30 minutes deposition time and $\phi=50$ mm and $\phi=100$ mm.
Fig. 1

![Diagram of experimental setup](image)

**Graph:**

- **DC Self bias [V] vs. Pressure [Pa]**
- **30 W:**
  - $\phi=50$ mm: Red dots
  - $\phi=60$ mm: Black squares
  - $\phi=100$ mm: Blue triangles
- **60 W:**
  - $\phi=50$ mm: Red dots
  - $\phi=60$ mm: Black squares
  - $\phi=100$ mm: Blue triangles
Fig. 2
Fig. 3

![Graph showing the relationship between DC self-bias and pressure for different sample conditions, including 'no sample', '1x5 cm² glass', '5 cm diam. glass disk', and '10x10 cm² glass'.]
Fig. 4

![Graph Image]

- $V_T = -15$ V
- $V_T = 0$ V (GND)
- $V_T = 15$ V
- $V_T = 30$ V

$DC$ Self-bias [V] vs. Pressure [Pa]
Fig. 5
Fig. 6

(a) Sheet resistance $\Omega/\text{sq}$

(b) Thickness $t_{\text{th}}$ [nm]

(c) Resistivity [$\Omega\cdot\text{cm}$]
Fig. 7

![Graph showing transmittance vs. wavelength (nm).](image)

Fig. 8

![Graph showing averaged transmittance vs. radius (mm).](image)
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Eugen Stamate
Figure 2

- **DC Self bias [V]**
- **Pressure [Pa]**

### Lines and Symbols

- **60 W**
  - \( \phi = 50 \text{ mm} \) (Red Circle)
  - \( \phi = 60 \text{ mm} \) (Red Square)
  - \( \phi = 100 \text{ mm} \) (Blue Triangle)

- **30 W**
  - \( \phi = 50 \text{ mm} \) (Red Circle)
  - \( \phi = 60 \text{ mm} \) (Red Square)
  - \( \phi = 100 \text{ mm} \) (Blue Triangle)
Figure 3
Figure 4

DC self bias [V] vs. Pressure [Pa]

- Solid black line: no sample
- Red circle line: 1x5 cm² glass
- Blue triangle line: 5 cm diam. glass disk
- Purple triangle line: 10x10 cm² glass
Figure 5

The graph shows the relationship between DC Self bias [V] and Pressure [Pa] for different values of $V_T$:
- $V_T = -15$ V
- $V_T = \text{GND}$
- $V_T = 15$ V
- $V_T = 30$ V

The graph indicates a decrease in DC Self bias as the pressure increases for all values of $V_T$. The specific values and trends can be observed from the plotted points and lines.