# Atmospheric pressure dielectric barrier discharge (DBD) for post-annealing of aluminum doped zinc oxide (AZO) films

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## ARTICLE INFO

## ABSTRACT

Aluminum-doped zinc oxide (AZO) is a material that can have high electrical conductivity while being highly transparent at the same time. It has been used in many applications such as displays, mobile devices and solar cells. Currently AZO films are considered as attractive alternatives to materials such as indium–tin oxide (ITO) due to its much cheaper cost and comparable high electrical conductivity. A process of depositing AZO film by dual DC magnetron and RF enhancement system has been developed. Film thicknesses were measured to be at about 200 nm by a stylus contact profilometer and transparency of greater than 90% in the visible range was measured with spectrophotometry methods. Film conductivities were on the order of $10^{-3}$ Ω-cm using the four-point probe method. By using a dielectric barrier discharge operating at atmospheric pressure, the conductivity of film can be further lowered. A 300 mm × 60 mm line source operating at a nitrogen flow of ~250 L/min was used and ~0.4 L/min hydrogen gas was also introduced into the discharge system to create hydrogen radicals for surface modification. A 10%–15% decrease in electrical resistance was observed with no changes in the optical properties of the AZO films.

## 1. Introduction

Transparent conducting oxides (TCOs) are an important class of metal oxide semiconductor materials that is used in photovoltaic, display and LED technologies [1]. In order to help in decreasing the cost associated with mass production of thin film and enable a flexible roll to roll production for these applications, low cost materials, such as plastic substrates, are needed [13]. The use of polymeric substrates, however, limits deposition temperature as well as post-deposition annealing temperatures that have been shown to significantly improve the quality of TCOs, such as aluminum–zinc oxide (AZO) thin films [2–5]. For example, polyethylene terephthalate (PET) is a common polymer substrate material that is suitable for these applications. However, it has a glass transition temperature of 100 °C which markedly limits the process temperature window.

Metal oxide semiconductors such as zinc oxide (ZnO) can replace the existing indium-based TCOs, as the supply of indium in the world market is depleting [7]. Thin ZnO films can be deposited via sputtering techniques with high optical transmission and low resistivity. Doped ZnO is used as a TCO window layer and has been identified to achieve high efficiency in thin film solar cells using copper–indium–gallium selenide (CIGS) as an absorber layer [6]. In laboratory trials, sputtering processes (DC or RF) have been identified as the best deposition methods to fabricate impurity-doped ZnO thin films such as AZO [7]. Thus, there is a need to further investigate sputtering processes that can produce high-quality ZnO films that are scalable to large-area substrates at low temperatures [7–10]. Also, since the as-deposited film will have a certain amount of structural defects, these microstructure defects will have an effect on the physical and electrical properties of the film. Currently, these properties could be improved by post-annealing. The process will improve the stoichiometry or the crystallinity of the film [12]. However, this process is normally done at around 300–400 °C and not suitable for many flexible substrates and they would melt and deform under these conditions. A cold plasma, such as a dielectric barrier discharge (DBD) plasma, could operate in conditions close to room temperature. This would avoid the heating issue and thus be ideal for annealing films on flexible substrates after deposition.

In this paper, the effects of supplemental RF power created plasma on AZO film properties were investigated to evaluate the viability of plasma enhancement for improved low-temperature TCO thin film processing. In addition, improvement with atmospheric pressure DBD plasma post-annealing on electrical properties of the ITO and AZO film was also investigated. Both the deposition experiments and the post-annealing experiments will be discussed. In the AZO deposition part, the effect of RF plasma enhancement on the magnetron plasma will be shown, then followed by the effect of oxygen and thickness variation of the deposited AZO samples; in the post-annealing part, ITO samples would first be treated as a demonstration of the effect of hydrogen-containing atmospheric plasma on TCOs, then the deposited AZO samples will be treated to see the effect of the annealing plasma on the AZO films deposited in the SHADE experiment.

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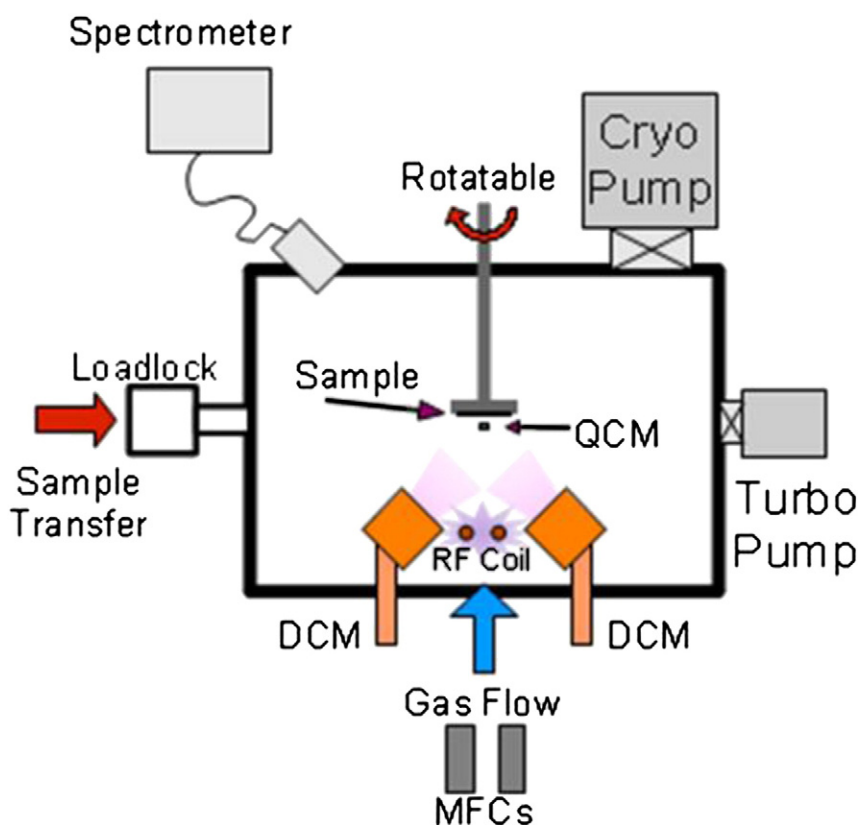E-mail address: wu139@illinois.edu (Y.L. Wu).

**Fig. 1.** Schematic of the SHADE vacuum chamber used to produce AZO films, showing the locations of the sample load lock, vacuum pumps, dual magnetrons and RF antenna.

## 2. Experimental

Samples were made in the Sputtering High-purity Atomic Deposition Experiment (SHADE) (Fig. 1). It has a dual magnetron setup for depositing thin films under an ultra-high vacuum (UHV) environment. A secondary RF antenna is also used in order to tailor the properties of the deposited films. The RF antenna is placed in between the two magnetrons with opposite polarity and the plasma is formed in between (Fig. 2). By using an unbalanced dual magnetron configuration, closed field lines can be generated that trap plasma over a large volume, thus allowing more ionizations to take place in the plasma. Base

pressure of the vacuum system was $5 \times 10^{-7}$ Torr. Standard microscope glass substrates were used in all the samples deposited and annealed in SHADE except for the purchased ITO samples (Sigma Aldrich, surface resistivity 300 $\Omega$/sq, 749796) where the substrates were made with polyethylene terephthalate (PET). The purchased film has a 100 nm ITO sputter coated on top of the PET making the total thickness of the film as 5 mil (0.127 mm). The AZO targets used in the dual magnetron setup were sputtering ceramic targets (98 wt.% ZnO + 2 wt.% $Al_2O_3$) and the processing gas was Ar/$O_2$. Oxygen flow varied from 0 to 0.6% of argon flow and the total pressure was kept at 5 mTorr during deposition. The magnetrons were operated in constant current (DC)
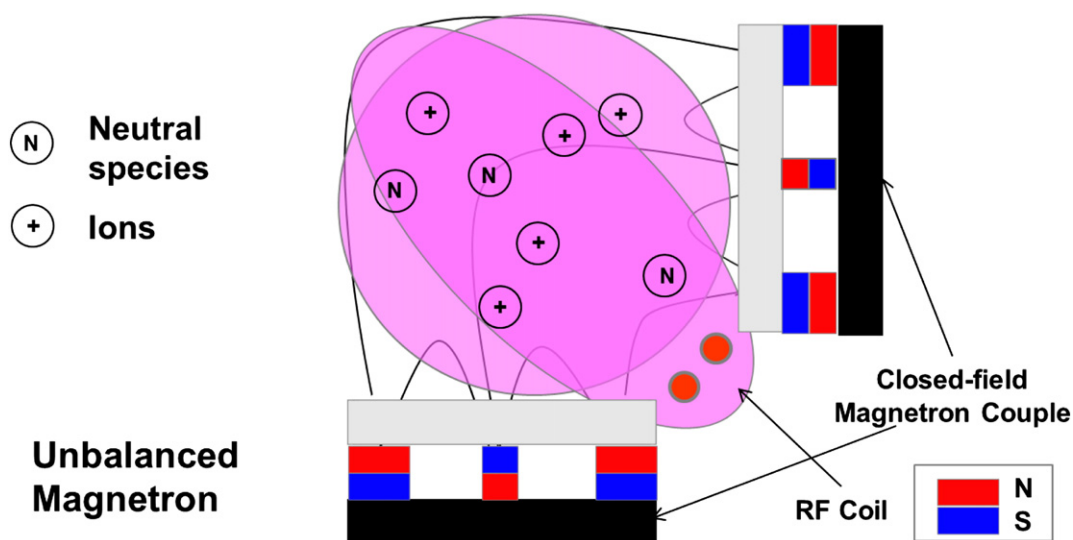


**Fig. 2.** Schematic of the dual magnetron setup and the RF plasma inside the SHADE vacuum chamber. The unbalanced field lines originate from one magnetron and terminates at the other, and the RF coil is placed in the middle between the two magnetrons to generate a secondary plasma in the region between.

mode and the films were deposited at low temperature (<100 °C) by reactive magnetron sputtering with argon and oxygen. Substrates in SHADE were affixed to a sample holder and were moved from the load lock using a transfer arm and secured to a pedestal in the center of the chamber.

During deposition, the entire holder/pedestal assembly rotated continuously in order to improve film uniformity resulting from the geometric issues with circular magnetron targets. The distance between the samples to the RF coil was about 70 mm. The AZO samples prepared were typically about 200 nm thick. Surface electrical properties (sheet resistance) were measured with typical four point probe methods.

The post-annealing process employs a non-thermal plasma working in atmospheric pressure. It is a dielectric barrier discharge (DBD) with a discharge area of 300 mm × 60 mm (model: NPT-304) (Fig. 3). The system allows independent control of voltage and frequency of the applied power, and also flow rate of the gasses by mass flow controllers. It has a remote plasma design which the outer electrode was grounded, and thus only neutrals and radicals generated from the plasma were allowed to reach the substrate. This prevents the highly energetic ions from reaching and subsequently heating the substrate surfaces, thus allowing a cold plasma annealing process. Processing gas used for the system was nitrogen, at a flow rate of 250 Lpm. The system has three independent flow controllers. Addition of other processing gas such as oxygen, hydrogen, helium and argon was also possible. It also has a translational stage with a 1 mm/s accuracy for sample uniformity and annealing time control. The temperature of the substrate could be kept below 40 °C while operating at a power of about 2 kW and a frequency of 30 kHz. The sheet resistances in the annealed ITO and AZO samples were also measured with the four point probe method.

## 3. Results and discussions

The transmittance and sheet resistance showed an opposite trend as the amount of RF power applied increases, as shown in Fig. 4. However, these two curves neither monotonically increases nor decreases, and deposited films having both high transmission and low resistivity were possible. When no RF power is used, the average optical transparency was slightly over 50%, but it was reduced to 30% at 100 W RF power. At 125 W and above, the average transparency of the film increased to over 80%. From the four point probe measurements, however, the sheet resistance decreases as the RF power was increased. The sheet resistance reaches a minimum of 50 Ω/sq at 60 W RF power, and above this power the sheet resistance increased, especially sharp at above 125 W. At around 125 W RF power, an AZO film with high transparency and low sheet resistance could be obtained, and that was the optimum condition of RF power in producing the AZO films.

The effect of oxygen in the processing gas was then investigated. It was found that at a current greater than 1.5 Amps and fixed voltage, a sheet resistance minimum was observed at around 0.3% $O_2$, while the
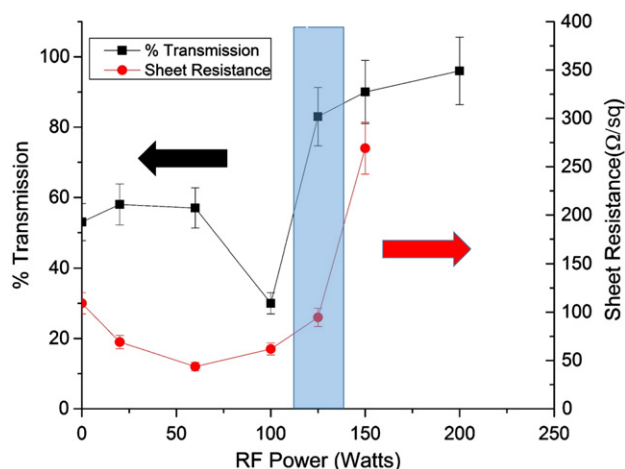


**Fig. 4.** Variation of percentage transmittance and sheath resistance of the sample versus input RF power. Optimum balance of the two was found around 125 W of RF power. Area of optimum balance between transmittance and sheath resistance is highlighted.

transparency generally increases as the percentage of oxygen added (Fig. 5a and b). Next was the effect of RF power. By using 0.3% $O_2$ as the optimal argon–oxygen processing gas mixture and varying the RF power at different cathode currents, it was found that a further small improvement in the sheet resistance could be observed at around 100 W RF power and 2.1 Amp cathode current on the magnetrons (Fig. 6). Temperature on the samples remained low throughout deposition; maximum peak temperature recorded was 82 °C with 500 W RF power and magnetrons were running at 2.1 Amps.

The effect of AZO layer thickness on sheet resistance was also investigated (Fig. 7). A series of films with variable thickness were deposited at a 5 mTorr total pressure, 2.1 Amp cathode current, 100 W RF power and 0.3% oxygen. Film thickness was varied by changing the deposition time and the results were measured by spectroscopic ellipsometry. Similar trends in sheet resistance with film thickness have been reported in the literature [5]. Sheet resistance in Fig. 7 decreases from approximately 120 to 60 Ω/sq as film thickness increases from 180 to 220 nm, respectively, demonstrating that AZO layer thickness does make a significant contribution to trends observed previously as expected.

In order to find out the effect of processing gas on TCO post-deposition annealing, ITO coated PET films were annealed using helium plasma with hydrogen, oxygen and argon added in atmospheric pressure (Fig. 8). The sheet resistance of the AZO film before and after annealing was measured with the standard four point probe method and it was observed that the sheet resistance for the hydrogen containing plasma had decreased by about 50% on average, while the sheet resistance for the oxygen and argon containing plasma increased by about 170% and 80% respectively. The difference arises due to the oxide suppressing ability of hydrogen radicals in the plasma [11]. As there are
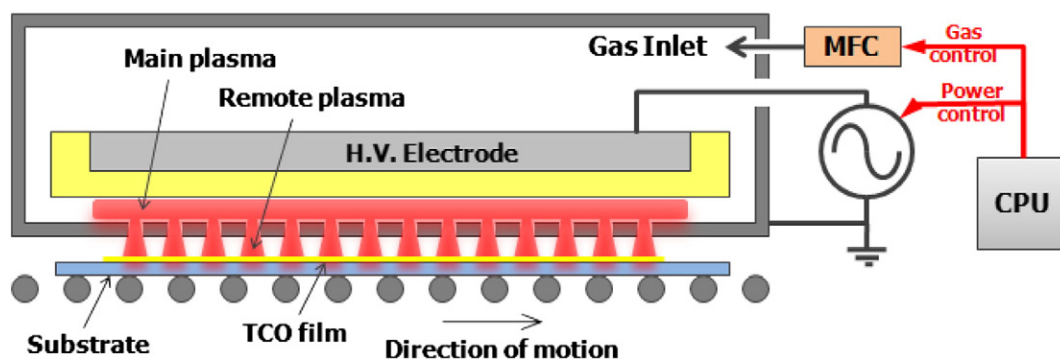


**Fig. 3.** (Top) Picture showing outside of the DBD machine (model no. NPT-304), capable of both manual and automatic controls along with automatic ventilation systems. (Bottom) Picture showing the electrode head inside the DBD machine, along with the moving stage for samples and overhead cooling utilities above the head.
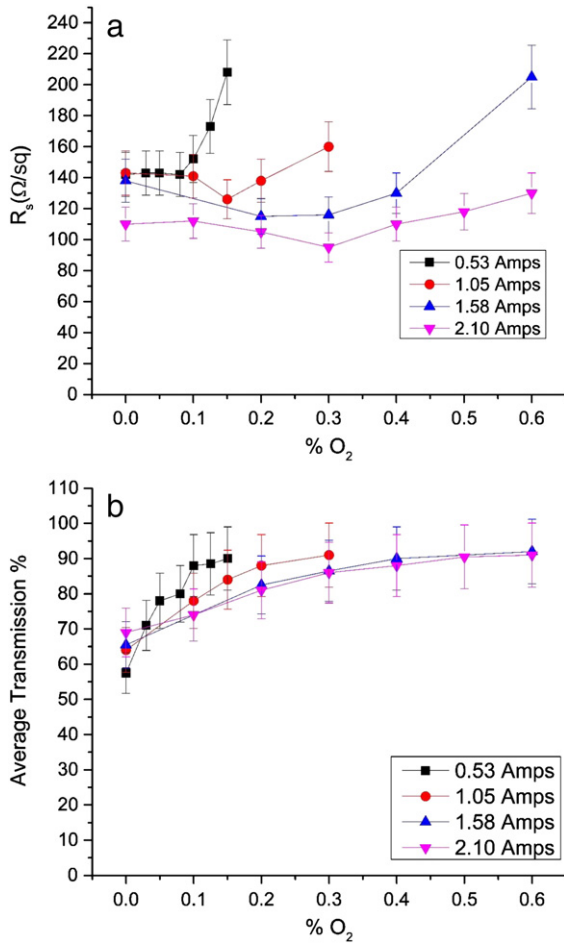
**Fig. 7.** Variation of sheath resistance in the AZO samples versus deposited layer thickness.

**Fig. 5.** AZO (a) sheet resistance & (b) average % T vs. % $O_2$ at 0.53, 1.05, 1.58 and 2.1 Amp cathode current levels. Sheath resistance has a minimum of around 0.3% additional oxygen for current level above 1.5, and the average transmission increases as the amount of additional oxygen increases, regardless of the magnetron current during deposition.

always some weakly bonded atoms on the film substrates after sputter deposition, the use of hydrogen-containing atmospheric plasma could etch and re-deposit the top part of the TCO film during the annealing process. The hydrogen radicals in the plasma improves the electrical properties of these TCO films by removing the carbon or natural oxides generated on the film surface after the samples were removed from the
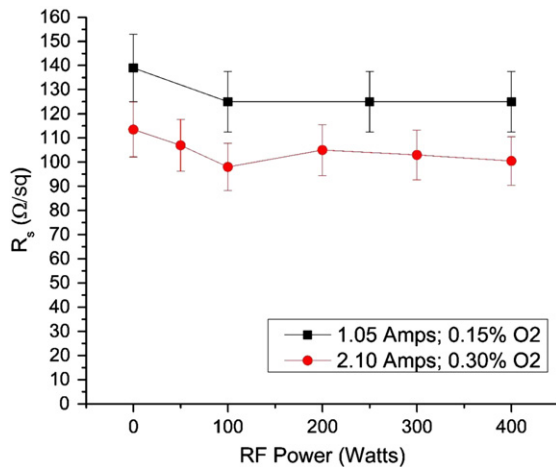
chamber, while at the same time helps the rearrangement of the bulk of TCO film and passivate the film surface as well. The result is that films would have a thinner natural oxide layer after annealing, and showed lower electrical resistance on average. Similar results have also been observed [11]. Fig. 9a and b showed the cross-sectional SEM images for the ITO films on glass substrate before and after the atmospheric annealing process. It can be observed that the annealed sample had fewer amorphous voids on average compared with the pre-annealed sample. This etching and re-deposition process of the film by the atmospheric pressure plasma may have caused the film material to form into larger clusters and have a lower sheet resistance value on average.

Like the hydrogen plasma annealing with the ITO samples, the AZO films deposited in SHADE were also post-deposition annealed in atmospheric pressure DBD plasma. Nitrogen is chosen as atmospheric nitrogen plasma could generate reactive radical and ions, which then could react with the surface native oxide and loosely bonded atoms at the film surface. It is also much more readily available and could provide a huge economic benefit over helium. Pure nitrogen gas was used in one experiment, and 0.4 Lpm of hydrogen gas was added into the nitrogen plasma in the other (Fig. 10). A 15% reduction in the surface resistivity was observed in the nitrogen and hydrogen plasma, whereas there was about a 10% reduction in resistivity in the pure nitrogen plasma case. In all the samples treated the optical transmission percentages



**Fig. 6.** Change of sheath resistance versus input RF power in different magnetron currents and oxygen gas additions. A small improvement could be seen at around 100 W RF power for the 2.1 amp deposition current with 0.3% additional oxygen.
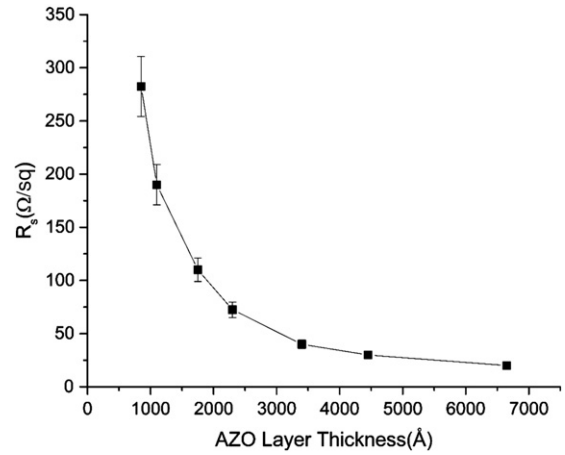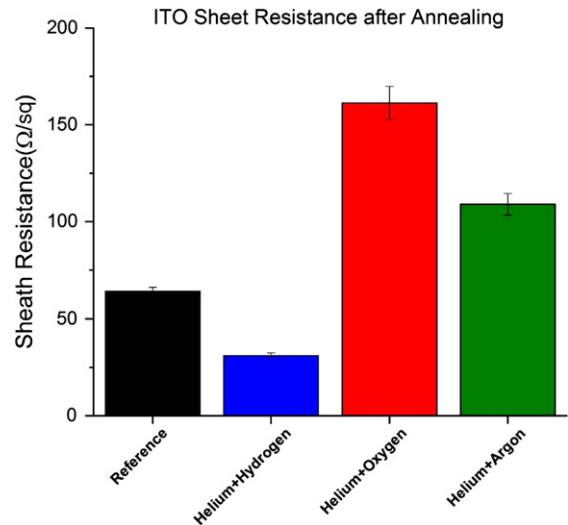


**Fig. 8.** Change of sheath resistance in post-annealing with different processing gas conditions. Hydrogen containing atmospheric plasma had reduced the sheath resistance while other gasses such as oxygen and argon had an opposite effect and sheath resistance was increased after annealing.
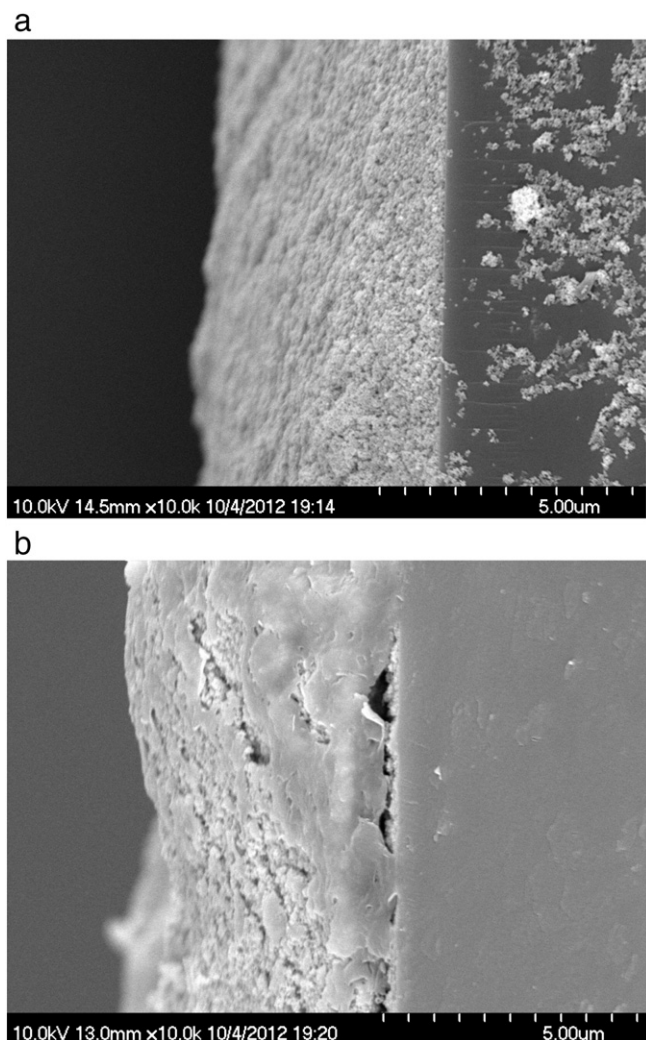
a



10.0kV 14.5mm ×10.0k 10/4/2012 19:14    5.00um

b



10.0kV 13.0mm ×10.0k 10/4/2012 19:20    5.00um

**Fig. 9.** SEM images showing surfaces of the ITO sample (a) before and (b) after annealing treatment. Change of amorphous void areas was observed after annealing treatment.



**Fig. 10.** Comparison in changes in sheath resistance of the AZO samples after annealing and between atmospheric nitrogen and nitrogen/hydrogen plasma annealing. All three as-deposited samples were carried out at 5 mTorr Ar, 100 W RF supplemental power and all around 180 nm in thickness. Two samples were then subsequently annealed with nitrogen plasma, and the third was annealed with nitrogen/hydrogen plasma.

were not affected by the post-annealing process. This result was in agreement with the previous experiment that the addition of hydrogen and its radicals helped in reducing the surface resistivity of the TCO films [11]. The atmospheric nitrogen/hydrogen plasma annealing provided more improvement in resistance value reduction over pure nitrogen, but the differences were about 5% and thus comparable, and pure nitrogen annealing may be more economical when used in practice. This showed that DBD remote plasma annealing after deposition could improve the electrical properties of the film, and the process could be done under atmospheric pressure and without heating the substrate, allowing films on the flexible substrate to be annealed without damaging the substrate itself.

## 4. Conclusion

AZO samples were deposited using the SHADE setup. The sheet resistance and optical transmittance were measured with a four point probe and a visible spectrometer respectively. The RF power during deposition should be controlled to be between 100 W and 125 W in order to obtain low sheet resistance and high optical transmittance simultaneously. Oxygen flow levels in the processing gas and the thickness of the deposited film had significant effects on the film resistance values. The resistance value approaches minimum when the right amount of oxygen is added in the processing gas, but the value changes rapidly around the minimum point and slight changes in oxygen level
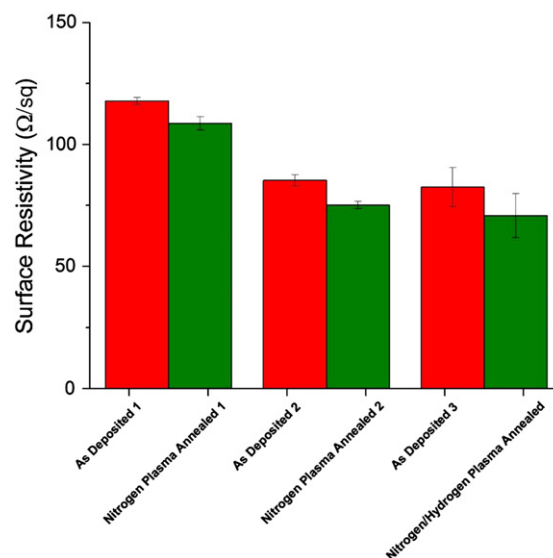
can cause a rapid increase in the resistance value. This change was more rapid at lower deposition current levels. Electrical properties of both ITO and AZO film samples could be improved by using an atmospheric pressure annealing process after film deposition, and hydrogen was shown to have a positive effect in reducing sheet resistance in both ITO and AZO film samples. While the atmospheric nitrogen/hydrogen plasma annealing provided the most improvement in resistance value reduction, the effect of atmospheric nitrogen plasma annealing process yielded comparable improvement and may be more economical when used.

## Conflict of interest

No conflict of interest.

## Acknowledgment

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