

## The Effect of Different Plasma Treatments on the Sheet Resistance of Sol-gel ITO and ATO Thin Films

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Single and multilayer transparent conductive ITO and ATO films were prepared by the sol-gel dip coating process. Each ITO and ATO thin film layer was fired at 550°C in a conventional furnace for half an hour. The thickness of the coatings was measured with a surface profiler. The sheet resistance of the ITO and ATO thin films decreased as the number of layers increased. The effects of different plasma treatments on sheet resistance of the ITO and ATO thin films were studied as a function of time. Changes in sheet resistance were measured by a linear four-point probe method. It was found that an Ar-plasma treatment increased the electrical conductivity of ITO thin films, but the other gas plasma treatment decreased the electrical conductivity of the ITO and ATO thin films.

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### I. Introduction

Today transparent electrically conducting coatings on glass are used in a wide range of optoelectronic applications [1, 2]. The materials which present the most interesting properties are the n-type semiconductors such as indium tin oxide (ITO) and antimony tin oxide (ATO). ITO and ATO thin films have a number of applications as transparent electrodes in liquid crystals, electrochromic and emissive displays, touch screens, solar cells and protective coatings fabricated by physical and chemical deposition methods [3]. Of these methods, the sol-gel techniques are particularly attractive due to their low equipment and fabrication costs and the ease of modifying the final material properties. However, the electrical conductivity properties of the tin dioxides produced by these techniques are not yet good enough to meet the requirements of display applications. The most typical way of increasing the electrical conductivity of tin dioxide is to dope the tin dioxide matrix with indium or antimony. This is relatively easy and effective, but the doping is limited by the saturation of the conductivity increase at a certain doping level, and also by a decrease in the optical transparency as the doping level increases [4, 5]. Another way of improving the conductivity is to remove the surface oxygen by means of various surface treatments [6].

The purpose of this work is to study the effects of plasma post-treatments on the conductivity of ITO and ATO thin films.

## II. Experimental

Single and multilayer sol-gel coatings were obtained by dip coating either on borosilicate glass or fused silica substrate at a withdrawal speed of 2 to 10 mm/s. The indium-doped tin oxide sols were prepared [7] by dissolving indium metal ingots in concentrated hydrochloric acid (12 N) to obtain indium chloride crystals. A measured amount of distilled water was then added to prepare the indium chloride stock solution. Sols corresponding to 6.0 wt.%  $\text{In}_2\text{O}_3$  were prepared. The desired amount of  $\text{InCl}_3$  solution was weighed out and acetic acid and acetylacetone were added as complexing agents. After 0.5 h of stirring, the desired volumes of isopropanol, 2-methoxyethanol and glycerol were added to prepare a 6.0 wt.%  $\text{SnCl}_4 \cdot 4\text{H}_2\text{O}$  required to maintain the In/Sn atomic ratios was then added. The final solution was stirred for another 0.5 h to achieve the dipping sol.

The antimony-doped tin dioxide sols were prepared [4] by weighing 2.01 g of  $\text{SnCl}_4 \cdot 4\text{H}_2\text{O}$  and 0.22 g of  $\text{SbCl}_3$  into a round-bottomed flask and adding 25 ml of pure ethanol as a solvent. The solution was stirred until the solid materials had dissolved. The resulting solution is appropriate for a dip, spin or spray coating in thin film processing. The thin film coatings were deposited on borosilicate glass substrates, which had been carefully cleaned in sequential ultrasonic baths of acetone, isopropanol and deionised water and then dried in an oven.

The obtained thin films of ITO and ATO were heated in a furnace at 550°C for a half-hour. The films were kept at 25°C and humidity of 40% RH; all measurements carried out on these films were be at the same conditions.

The film thickness,  $t$  was measured with a Tencor P10 Profilometer, and the sheet resistance,  $R$ , of the films was measured before plasma treatment ( $T < 0$ ) by the linear four-point method. The electrical resistivity,  $\rho$  was determined by the relation  $\rho = Rt$ . The effect of plasma treatment with different gases was investigated by using a Buck Plasma Electronic (Siemens). The ITO and ATO thin film samples were treated with plasma for two minutes under different gases such as,  $F_1$  : Ar-400 watt,  $F_2$  : Ar/O<sub>2</sub>-400 watt,  $F_3$  : O<sub>2</sub>-400 watt,  $F_4$  : O<sub>2</sub> and Ar-400 watt,  $F_5$  : Ar/O<sub>2</sub>-600 watt, and  $F_6$  : O<sub>2</sub>-600 watt. After the treatment, the substrates were allowed to cool in the plasma chamber to a constant room temperature of 25°C and the sheet resistances were measured again with a linear four-point probe.

## III. Results and Discussion

Fig. 1. Shows the variation in resistivity of ITO coatings of the same final thickness (110 nm) made by repeating the dip coating process several times (2-10 times). The resistivity is found to decrease with the number of layers. The resistivity of ATO coatings is also plotted versus the number of layers of the same final thickness (170 nm) made by repeating the dip coating process several times (2-10 times), as shown in Fig. 2.

Fig. 2. also shows that the resistivity of ATO thin films decreased as the number of layers increased. This was attributed to an increase in the fraction of denser material [8] in the film, resulting in a smaller resistivity. A decrease in the resistivity was also achieved when multilayers were deposited. For a constant thickness  $\rho \sim 1/n$ , where  $n$  is the number of layers.

The sheet resistance of ITO and ATO thin films was measured before and after plasma treatment under the same environmental indices. Fig. 3 shows the time dependence of the sheet resistance of ITO and ATO thin films before the plasma treatment. It is apparent from Fig. 3 that the sheet resistance of the films was nearly stable with time before the plasma treatment.

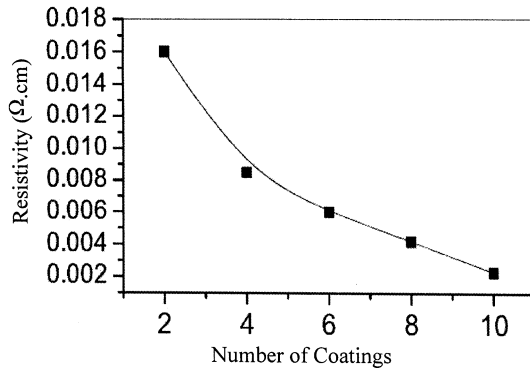


FIG. 1. Room temperature resistivity  $\rho$  versus the number of ITO layers deposited by dip coating (same final thickness of 110 nm).

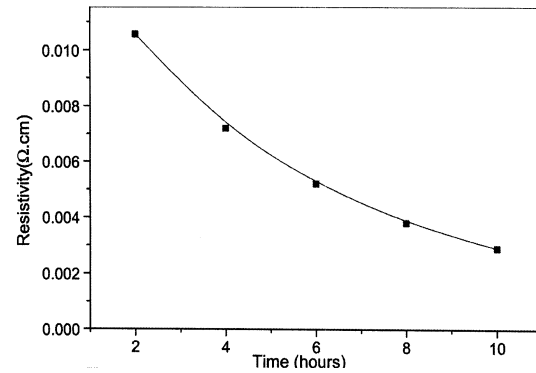


FIG. 2. Room temperature resistivity  $\rho$  versus the number of ATO layers deposited by dip coating (same final thickness of 170 nm).

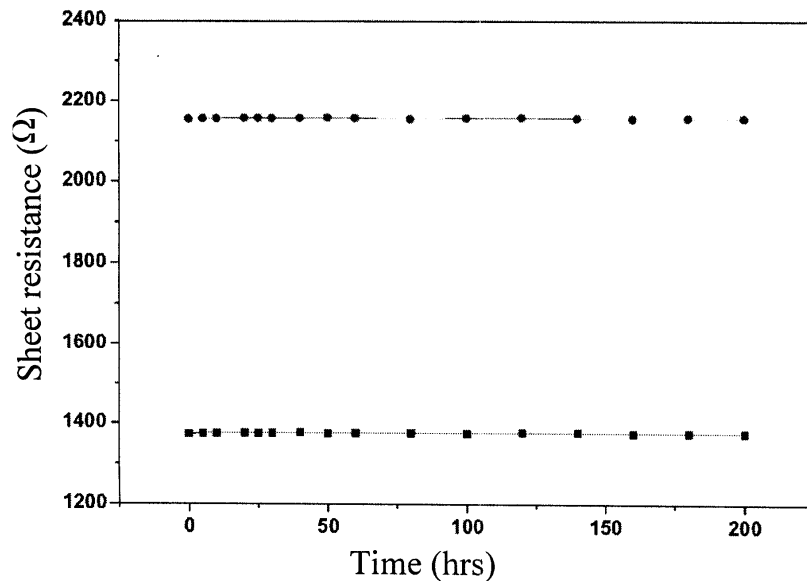


FIG. 3. Time dependence of the sheet resistance of ITO and ATO thin films before plasma treatment.

Fig. 4. Shows the time dependence of the sheet resistance of ITO thin films (110 nm) after treatment with plasma for two minutes under different gases (Ar-400 watt, Ar/O<sub>2</sub>-400 watt, O<sub>2</sub>-400 watt, O<sub>2</sub> and Ar-400 watt, Ar/O<sub>2</sub>-600 watt, and O<sub>2</sub>-600 watt). The resistance measurements clearly show that the Ar-plasma treatment decreases the sheet resistance (or increases the electrical conductivity) of the Indium – doped tin dioxide films. The sheet resistance of the Ar-plasma treated ITO films decreased from the value 1374 before the treatment ( $T = -10$  hr) to 600 after the plasma treatment ( $T = 0$ ) and then remains stable for a long time. The sheet resistance for the other gas plasma treatments of the ITO thin films increased suddenly at  $T = 0$ , and reached a

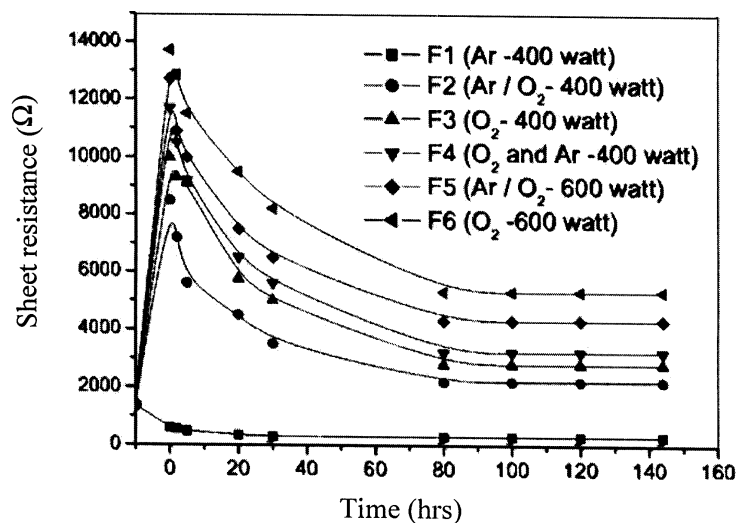


FIG. 4. The time dependence of the sheet resistance of ITO thin films (110 nm) after treatment with plasma for two minutes under different gases.

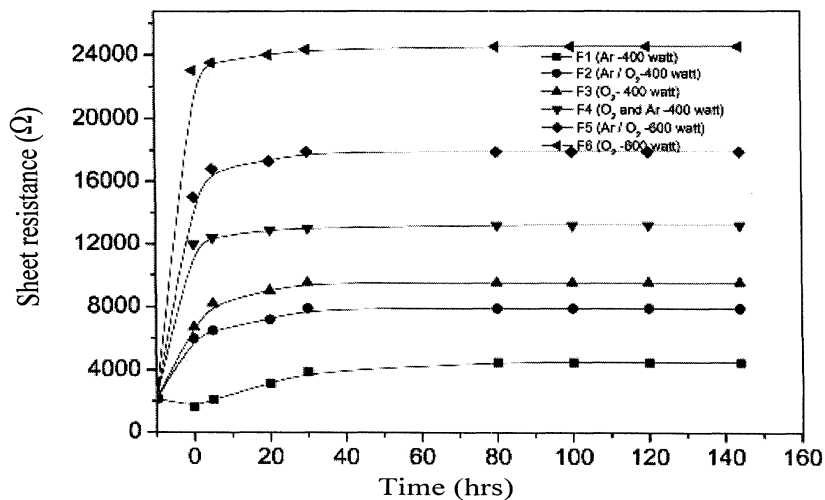


FIG. 5. The time dependence of the sheet resistance of ATO thin films (170 nm) after treatment with plasma for two minutes under different gases.

maximum value for the  $O_2$ -600 watt plasma. If these films were exposed to the same conditions as before the plasma treatment, their sheet resistance would decrease with time, until reaching a constant value in the time interval (80-140 hr). Thus, one can conclude that it is possible to improve the conductivity of ITO thin films by treating them with Ar-plasma. Thus, sol-gel fabricated indium-doped tin dioxide films may be said to be highly sensitive to argon plasma, and the improvement in conductivity may be attributed to the plasma treatment. The Ar-plasma treatment is effective enough to remove the depletion layers between the tin dioxide particles,

causing oxygen vacancies to form and migrate into the bulk, which leads to an increase in its electrical conductivity.

Fig. 5. shows the time dependence of the sheet resistance of ATO thin films (170 nm) after treatment with different gas plasmas. The sheet resistance of Ar-plasma treated ATO thin films, shows a small decrease from a value of 2155  $\Omega$  at  $T = -10$  hr to 1652  $\Omega$  at  $T = 0$ , and then increases to a value of 4500  $\Omega$  when the sample is exposed to the same conditions. The other curves, related to different gas plasma treatments, show a sudden increase of sheet resistance of ATO thin films at  $T = 0$ , and then become stable with time. The variation in values of sheet resistance of treated ATO thin films may be attributed to changes in the concentration of surface lattice oxygen that forms at the surface of the thin films, until it seems to stabilize with time, when the concentration of the oxidation layer becomes constant. Therefore it was impossible to improve the electrical conductivity of ATO thin films (170 nm) by Ar-plasma treatment for two minutes, because it was not possible to remove the oxidation layers from their surfaces.

The increase of electrical conductivity of the Ar-plasma ITO thin films was attributed to the removal of surface lattice oxygen by means of various surface treatments [6]. The resulting vacancies then migrated towards the bulk, where they were able to act as donors and increase the conductivity. Also, the removal of absorbed surface acceptors (e.g. oxygen), which form a positive space charged layer just below the surface of the tin dioxide and thereby decrease the electrical resistivity in thin films, leads to an increase in the electrical conductivity [9]. This means that all plasma treatments with oxygen gas or its mixture will decrease the electrical conductivity of ITO and ATO thin films due to the formation of a depletion layer [10] between the doped tin dioxide particles. It could also speculate that redox reactions between electrons released during oxygen vacancy formation and metal ions (Sn(IV), In(III) and Sb(V)) could be involved in the resistance change.

The present study indicates that further investigations of the time dependence of Ar-plasma treatment on the electrical conductivity of ITO and ATO thin films will be most important.

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