

# ITO coating by reactive magnetron sputtering—comparison of properties from DC and MF processing

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## Abstract

The aim of ITO process technology development is to obtain stable film properties with exceptionally low resistivity and high transmittance within the visible spectrum range. The challenge for this development is to upgrade such ITO technology for large area coating in production. Therefore, a comparison of processing with oxide or metallic targets for both DC and MF mode was performed. The comparisons with regard to ITO film properties are related to InSn alloy targets vs. ceramic ITO targets, single or dual magnetrons, process control mode, dynamic deposition rate and substrate temperature. Plasma Emission Monitor control works as an useful tool to deposit optimized ITO films having both low resistivity and high transmittance. Best results are obtained in dual DC mode with resistivities of less than  $1.6 \times 10^{-4} \Omega \text{ cm}$  at dynamic deposition rates of  $110 \text{ nm} \times \text{m/min}$ . © 1999 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

Coatings on glass with highly transparent conductive oxide films (TCO) are performed mostly by using indium tin oxide layers (ITO) [1–3]. This oxide material is very common for applications where both high electrical conductivity and optical transmittance are essential. ITO films are reactively sputtered with single magnetron sputter sources of different sizes. The aim of ITO process technology development is to obtain stable film properties for large area coating with exceptionally low resistivity and high transmittance within the visible spectrum range.

There are two different techniques for sputtering of ITO films. One is using reactive sputtering of relatively cheap metallic indium tin alloy targets. The other is using more expensive ceramic oxide target for pseudo reactive sputtering. The prerequisite for production with the first technique is a special feedback control for keeping the film stoichiometry constant provided by plasma emission monitoring PEM<sup>®</sup> [1,4,5]. The properties of ITO films sputtered with the ceramic oxide target result in lower resistivities and the sputter technology is less complicated.

To test the advantages of mid frequency (MF) sputtering (e.g. [6–8]) vs. DC sputtering a comparison of this techniques was performed. Surprisingly lowest film resistivities

for moving substrates in single pass mode are reached in DC mode.

## 2. Experimental

The ITO films were deposited in a horizontal in-line sputter system equipped with a pair of rectangular magnetrons and DC and MF power supplies (Advanced Energy: Pinnacle  $2 \times 6 \text{ kW}$  and PEII  $10 \text{ kW}$ ). Metallic targets of InSn90/10 alloy and ceramic ITO targets of  $\text{In}_2\text{O}_3\text{SnO}_2$ 90/10 have been used. The size of the targets was  $160 \times 610 \text{ mm}^2$ , respectively. The glass substrates fixed in a carrier were moved in multiple pass mode between the sputter section and a heating chamber with a speed of  $4.25 \text{ m/min}$ . The target to substrate distance was always  $48 \text{ mm}$ .

The following experimental arrangements have been investigated (cf. Fig. 1):

1. Single magnetron powered in DC mode (metallic InSn target or ceramic ITO target);
2. dual magnetron, both magnetrons powered in DC (ceramic ITO target);
3. dual magnetron powered by mid frequency ( $40 \text{ kHz}$ , ceramic ITO target).

The set up of the plasma emission monitor PEM<sup>®</sup> used for reactive sputtering from the metallic InSn target is shown in Fig. 1a) too. Further details are given in [5].

The conditions of different sputtering techniques are

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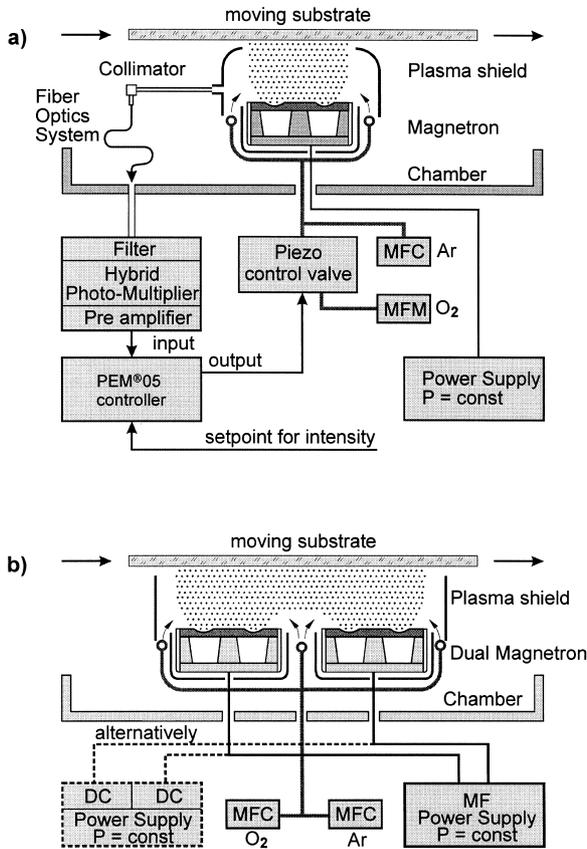


Fig. 1. Arrangement for reactive sputtering of ITO. (a) Single magnetron in DC mode with InSn-target PEM<sup>®</sup> controlled. (b) Dual magnetron in MF mode or DC mode with ITO target.

summarized in Table 1. Essential differences are in substrate temperatures during ITO film deposition. Whereas samples from metallic target were deposited in vacuum at room temperature and annealed after that in air, the samples from ceramic targets were deposited at temperatures between room temperature and 300°C in vacuum without any subsequent treatment.

In single magnetron arrangement a plasma shield with an aperture of 130 mm was used, whereas in the dual arrange-

Table 1  
Conditions and results of different sputtering techniques

Magnetron	Single	Single	Dual	Dual
Power supply mode	DC	DC	DC/DC	MF
Target	Metallic	Ceramic	Ceramic	Ceramic
Substrate temperature (°C)	RT <sup>a</sup>	155	255	255
Power (kW)	1.3	3.0	2 × 3.0	8.0
Power density (W/cm <sup>2</sup> )	1.3	3.0	3.0	4.0
Plasma shield	With	With	Without	Without
Resistivity (10 <sup>-4</sup> Ωcm)	2.5	2.0	1.6	2.3
Transmittance (%)	89	89	89	89
Dynamic deposition rate (nm × m/min)	31	35	110	110

<sup>a</sup> Annealing at 320°C in air after deposition.

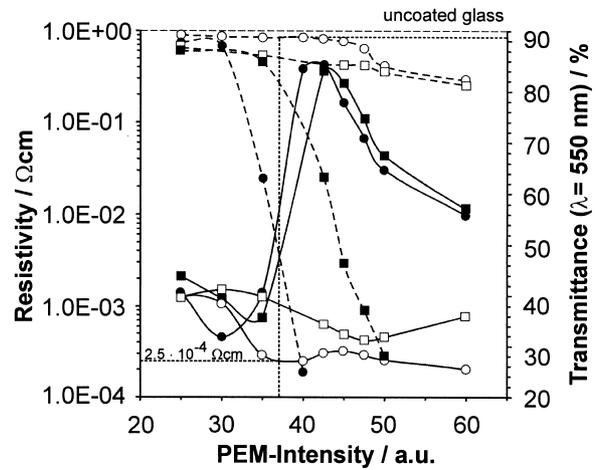


Fig. 2. Resistivity (solid lines) and transmittance (dashed lines) of reactively DC-sputtered ITO films with PEM<sup>®</sup> control in single magnetron arrangement for different film thicknesses on glass (circles, 200 nm films; squares, 20–40 nm thick films; full, as-deposited; empty, annealed).

ment no such shielding existed. The total opening width in the second case was 400 mm.

### 3. Results

Resistivity and transmittance for films with both thin and thick ITO films sputtered from a metallic InSn target in DC mode vs. PEM<sup>®</sup> setpoint are shown in Fig. 2. To deposit the thin films six passes of the substrate carrier were performed over the source. Therefore, the film thickness lies between 20 and 40 nm depending on the changed deposition rate due to the changed PEM<sup>®</sup> setpoint level. For the thick films with 200 nm thickness the product of intensity and deposition time was kept constant for each working point, to reach a constant film thickness with  $\Delta d/d < 2\%$ . The resistivity curves are slightly shifted for different film thicknesses. Same film properties are obtained at increased thickness at lower intensities. The minimum resistivity for as-deposited films at room temperature were measured at  $4.5 \times 10^{-4} \Omega \text{ cm}$  for 200 nm films and  $8 \times 10^{-4} \Omega \text{ cm}$  for 25 nm films. By a following annealing of the films the differences for the resistivities can be reduced. Nevertheless the resistivity of the as-deposited film is decisive for the value obtainable after annealing. The minimum resistivities for the as-deposited films with high transmittance are obtained in a very narrow range of the PEM<sup>®</sup> intensity (30–35%) only. These optimized range for ITO films with minimum resistivity is limited to the ‘metallic side’ by a critical increase of the resistivity at nearly constant high transmittance after annealing. By shifting the working point to 35–40% films are obtained with lowest resistivity of  $2.5 \times 10^{-4} \Omega \text{ cm}$  and high transmittance after annealing.

Furthermore, Fig. 2 shows that the starting point for the increased film absorption is identical with the minimum

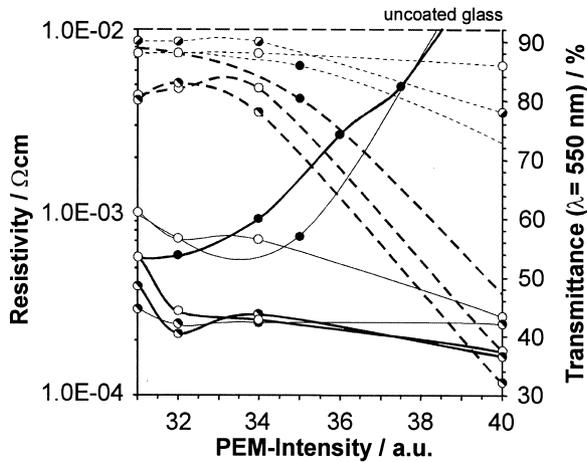


Fig. 3. Influence of annealing processes for resistivity (solid lines) and transmittance (dashed lines) of reactively DC sputtered ITO films (single magnetron arrangement with metallic InSn-target and PEM<sup>®</sup> control) for different film thicknesses on glass (thin lines, 30 nm films; thick lines, 90 nm films; full, as-deposited; empty, annealed in vacuum, half full, annealed in air, see text).

resistivity. Due to the tuning of a defined impact rate between reactive gas and metal particles for reactive sputtering by means of PEM<sup>®</sup> control the spectral line intensity works as a highly sensitive parameter for the properties of such compound films.

The following annealing procedure is necessary due to the insufficient conductivity and transmittance and the high chemical reactivity making the as-deposited films unstable. They are amorphous or microcrystalline. It is known from X-ray diffraction experiments [4] that the change of the film properties is connected with crystallization of the as-deposited films during annealing. Decisive for the resistivity is the density of electron donors directly depending on the density of oxygen vacancies. This density is variable depending on annealing parameters too. Fig. 3 compares the properties for the as-deposited and the air or vacuum annealed films for different working points. All annealing experiments are carried out at a temperature of 300°C for 30 min. For thin films the properties were improved in the whole intensity range. Obviously the annealing in vacuum leads to better values for the resistivity as the annealing in air. The as-deposited films probably have the highest density of oxygen vacancies. This density is decreased at the annealing in air due to the chemisorption of oxygen from the gas phase which leads to an increase in the resistivity. During the annealing in vacuum more and more oxygen vacancies are produced and therefore the resistivity is decreased. But the films are not completely stable during additional annealing in air for temperatures higher than 350°C.

Deposition of ITO films with optimized properties from metallic InSn targets is not possible using a mass flow controlled process. Fig. 4a shows that the interesting working range can not be stabilized due to the changed monotony

of the curve in this region. Process stabilization is possible by PEM<sup>®</sup> control only since the crucial measure 'oxygen flow to intensity' increases monotonously (Fig. 4c) with decreasing intensity. With decreasing intensity the impact rate of oxygen species is relatively increased resulting in target poisoning and more oxidized film stoichiometry. As shown in Fig. 4b the ITO deposition by sputtering from ceramic target is less complicated compared to deposition from metal target due to the monotonous dependency of plasma intensity vs. oxygen flow.

For DC sputtering from ceramic target fixed at a single magnetron best results were obtained at 300°C substrate temperature and 3 kW for 200 to 300 nm thick films (Fig. 5). A resistivity of  $2 \times 10^{-4} \Omega \text{ cm}$  with 89% transmittance for 550 nm was realized with a dynamic deposition rate of  $35 \text{ nm} \times \text{m/min}$ .

In the case of the dual magnetron arrangement powered by two DC supplies the dynamic deposition rate increases dramatically. The obtained rate of  $110 \text{ nm} \times \text{m/min}$  was 60% higher than the rate of the single arrangement related to the size of one magnetron and the same power density. This may be due to the omitted separation wall between both magnetron cathodes. No additional loss of ITO material by condensation on this wall took place. Therefore, the utilization of sputtered material will be improved by this dual arrangement. Even at a substrate temperature of

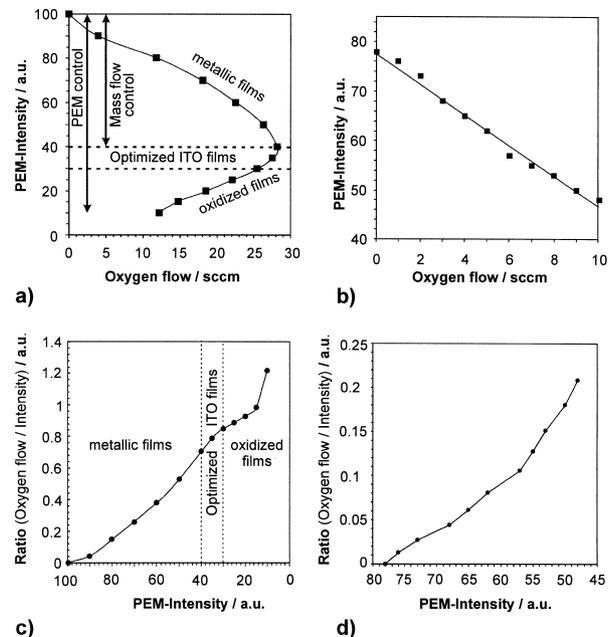


Fig. 4. Spectral intensity of an indium emission line as a tool for process control. (a) Possibilities for process stabilization with PEM<sup>®</sup> control in comparison to MFC for reactive DC sputtering of ITO using a metallic InSn-target. (b) Intensity of the indium line vs. oxygen flow for DC sputtering of ITO using a ceramic ITO-target. (c) Ratio of oxygen flow to intensity vs. PEM<sup>®</sup> controlled intensity as a measure for the stoichiometry of ITO films using a metallic InSn-target (cf. (a)). (d) Ratio of oxygen flow to intensity vs. intensity as a measure for the stoichiometry of ITO films using a ceramic ITO-target (cf. (b)).

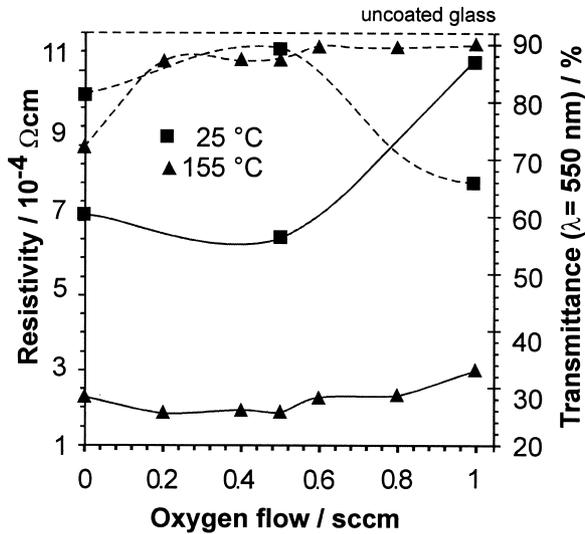


Fig. 5. Resistivity (solid lines) and transmittance (dashed lines) of DC sputtered ITO films (single magnetron arrangement with ceramic ITO-target) on glass as function of oxygen flow for different substrate temperatures (film thickness 200–300 nm).

255°C a resistivity of  $1.6 \times 10^{-4} \Omega \text{cm}$  and a transmittance of 89% was obtained (Fig. 6). The oxygen flow needed in sputtering from the ceramic target in dual arrangement had to increase by a factor of 4 compared to the single magnetron.

As shown in Fig. 7 such good resistivities were not achieved by MF sputtering surprisingly. At the same parameters like those in the dual DC process the resistivity was only  $2.3 \times 10^{-4} \Omega \text{cm}$ . To obtain the same rate it was necessary to increase the total power in MF mode by a factor of 1.3 compared to the dual DC process.

Table 1 summarizes the results obtained by the different

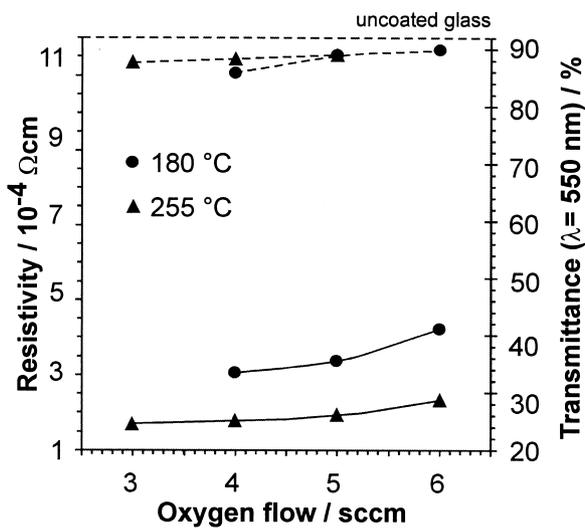


Fig. 6. Resistivity (solid lines) and transmittance (dashed lines) of DC sputtered ITO films (dual magnetron arrangement with ceramic ITO-target) on glass as function of oxygen flow for different substrate temperatures (film thickness 200–300 nm).

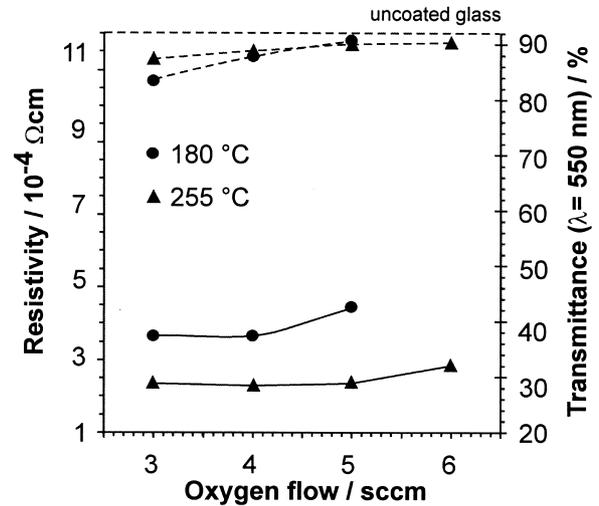


Fig. 7. Resistivity (solid lines) and transmittance (dashed lines) of MF sputtered ITO films (dual magnetron arrangement with ceramic ITO-target) on glass for different substrate temperatures.

sputtering techniques. To understand the differences in deposition by dual DC and MF processing ITO films were deposited stationary at the same deposition rate without substrate movement. The cross-section shapes of resistivity vs. target width (this corresponds to the direction of substrate movement) was measured. This W-shaped curves for the resistivity vs. target width is plotted in Fig. 8. The minimum of resistivity with  $1.14 \times 10^{-4} \Omega \text{cm}$  exists near the race track position for the dual arrangement in DC mode. The measured sheet resistances for the MF sputtered sample was always slightly higher in the regions of the race track. Between the two cathodes a lower sheet resistance was obtained in MF mode due to the higher plasma density in this region for this kind of discharge. At the edges of race track positions where an increased resistivity was measured the films were slightly absorbent.

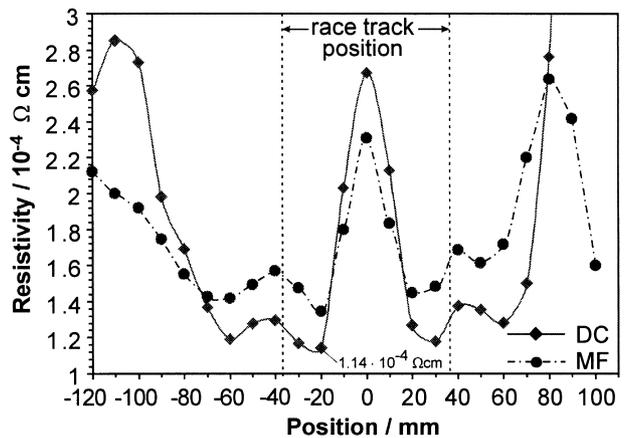


Fig. 8. Resistivity vs. magnetron width for stationary coated ITO films (thickness 250–300 nm) in comparison between DC and MF mode (0 mm is center line of one magnetron of the dual arrangement, the mirror plane between both magnetrons lies at -110 mm).

#### 4. Conclusions

Different techniques for reactive sputtering were investigated for deposition of low ohm ITO films on moving glass panes.

The prerequisite for production by reactive sputtering from a metallic alloy target is a special feedback control for keeping the film stoichiometry constant. Additional efforts are essential for providing a controlled gas inlet system with the capability of precisely distributing the flow of oxygen over the width of the substrate panes. This flow must be exactly dosed in accordance to the indium metallic sputter rate measured in situ by PEM<sup>®</sup> to ensure both the long term stability and uniformity of the said properties. Resistivities of  $4 \times 10^{-4} \Omega \text{ cm}$  are common for ITO deposition at room temperature with film thickness of more than 100 nm. The lowest resistivities with highly transparent films are obtained at  $1.9 \times 10^{-4} \Omega \text{ cm}$  after annealing at 350°C in vacuum.

The application of ITO ceramic targets results in low ohm ITO films with less complicated processing

Precisely mass flow controlled O<sub>2</sub> gas inlet provides a good film uniformity. Dual magnetron arrangements in DC mode with high dynamic deposition rate of 110 nm × m/min can be used advantageously related to single magnetrons. Low resistivities of  $1.6 \times 10^{-4} \Omega \text{ cm}$  averaged vs. film

thickness were obtained in DC dual arrangement. Minimum values of  $1.14 \times 10^{-4} \Omega \text{ cm}$  can be measured at stationary deposited ITO films. Substrate temperatures of 250°C in vacuum are necessary during the deposition of lowest ohm ITO films. The application of dual magnetron arrangements combines both high dynamic deposition rates and outstanding properties of ITO films at reasonable utilization of sputtered target material.

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