

## Ion-Assisted Deposition of E-gun Evaporated ITO Films at Low Substrate Temperatures

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### ABSTRACT

ITO films have traditionally been deposited by sputtering on low temperature substrates and by evaporation on substrates heated to high temperatures. Recent work in our Application Laboratory using ion assisted deposition (IAD) at low substrate temperatures with a broad beam cold cathode ion source has resulted in ITO film properties comparable to non-IAD high temperature evaporation. This work reports the electrical and optical properties for ITO films deposited over a broad parameter space.

### INTRODUCTION

Considerable data has been generated and reported on the use of ion sources [1] for both substrate pre-cleaning and assisting in the deposition and growth processes of thin films (IAD) over the last 15 years. [2,3,4] There is now a plethora of ion sources available for commercial use as well as many "improvements" on the older designs. It has been well established that ion assisted deposition (IAD) modifies many of the optical and physical characteristics of thin films used for interference coatings. We have reported previously on deposition parameters and film characteristics for a variety of materials using the broad beam cold cathode ion sources [5,6,7]. It is a natural extension of this previous work to consider the viability of IAD on InSnO (ITO) films.

Optically transparent conductive films are useful in a variety of devices such as liquid crystal displays, electro-luminescent back-lighting, transparent touch panels and low emissivity coating in the automotive industry. Fundamentally there is a conflict between visible transmission and electrical conductivity. However, ITO is one of the better film materials available for these applications. As a stoichiometric material, ITO has dielectric properties. However, as an oxygen deficient material it behaves like a metal, becoming conductive, optically absorbing and highly reflective in the infrared.

ITO has been prepared by many methods including reactive evaporation [8,9] and by sputtering; DC magnetron reactive [8,10], C-MAG<sup>®</sup> rotatable targets [11] and rf sputtering

[12]. All of these processes involve a reactive background of oxygen. The oxygen level during process being a critical component in controlling quality of the films. Traditionally the better films (i.e. low resistivity high transmission) are deposited at elevated temperatures [8,9]. Honda, et al [13] studied the oxygen content of films deposited at a range of substrate temperatures from ambient room temperature to 400 °C. In some cases, films that are deposited at low temperatures can then be annealed at higher temperatures to achieve lower resistivities [9,12]. Typically plastic substrates cannot be heated above 100 °C (and must be kept as low as 70-80 °C in some cases). Therefore, neither the advantage of high substrate temperature nor high annealing temperatures can be used. This limitation can be moderated by employing an energetic process to incorporate oxygen into the films. For evaporation this means using oxygen ions. Using a broad beam cold cathode ion source to do this is ideal since it will run in pure oxygen. A further advantage of this technique is there is no requirement for argon (which is needed for sputtering and for some hot filament ionization sources). Thus the process can be run in the low 10<sup>-4</sup> Torr range. Previous work has been reported [14] for using a broad beam cold cathode ion source. However, the newer ion sources can produce higher ion current densities and result in faster deposition rates for similar film properties.

This effort was directed in part by Customer requirements to adapt existing high temperature process for glass optics to plastic substrates. The initial goal was applications requiring as high a transmission through the visible as possible and resistivities of 50 Ω/ and 140 Ω/ . An additional requirement came in for a 250 Ω/ coating with high transmission in the 600 nm to 900 nm spectral range. ITO has a refractive index with a real part of about 2.05 [8,11,12,14] in the visible range and decreasing out into the near IR and then increasing towards the higher wavelengths. The extinction coefficient is bowl shaped with a minimum centered in the visible and increasing towards shorter and longer wavelengths [8,11,12,14]. All applications allowed for a low index quarter-wave outer layer to increase the transmission. The higher resistivity application had no limitations on the thin film structure. Therefore, the ITO could be incorporated into an MLAR (multi-layer anti-reflection) structure. Because of this it was desirable to fully characterize the optical properties of the films.

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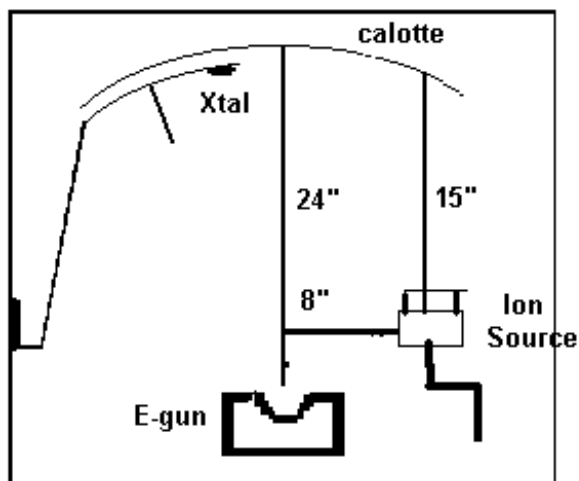


Figure 1. I-29 general equipment arrangement.

### DESCRIPTION OF EQUIPMENT

This study was conducted in an Integrity<sup>®</sup>-29 (I-29) fully automated ophthalmic Cryo-pumped coating chamber equipped with resistive sources, a 6-pocket E-gun, quartz crystal rate/thickness controller, 3 kW quartz lamp heater and a cryogenically cooled Meissner surface. Internal fixturing consists of a domed calotte, a curved uniformity mask below the calotte which has a quartz crystal mounted in it, an electron beam-gun with the deposition pocket centered in the chamber and cold cathode ion sources (Denton Vacuum CC-105) 8 inches off-center position, pointing straight up. The general equipment arrangement is shown in figure 1.

### EXPERIMENTAL TECHNIQUES

Although glass (microscope slides) and plastic samples were coated in many of the test runs, all of the characterization data reported herein comes from the glass samples. The coatings on the plastic samples were done to confirm that the electrical and optical properties were the same on both substrate types. The resistivities were measured on samples with parallel leads using an ohmmeter. Optical characterization was by a simple interference method reported previously [5,6] on the dielectric (lower k) samples and using a method by Knickerbocker [15] for the higher k regions. Several of the other references cited previously have also reported techniques for characterizing the more absorbing films [8,11,12].

The ion source was characterized by using the above equipment arrangement and putting Faraday probes into the tooling around the outer radius as shown in figure 2 (simulating the surface of the parts during deposition). For

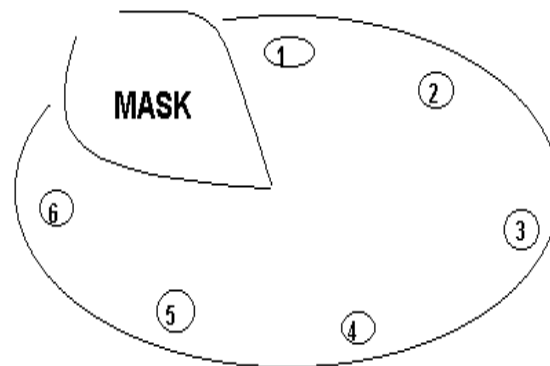


Figure 2. Faraday probes mounted in calotte. Position # 3 is directly above the ion source.

all runs the chamber was pumped to  $< 1 \times 10^{-5}$  Torr and was started at ambient substrate temperatures ( $\sim 25$  °C). Samples were prepared for various O<sub>2</sub> flow rates, deposition rates and ion current density levels. During the course of the deposition, the temperature would rise slightly due to thermal energy coming from the E-gun and the ion source. Typical temperature rise during deposition of a half wave at 560 nm was 5 °C – 10 °C. The highest temperature rise noted while depositing the thickest films was no more than 13°C. This is considerably less than the 120 °C temperature rises reported for some sputtering processes. In many of the sputtering processes, the substrate carriers (or drums in the case of roll coaters) for plastic substrates are water-cooled.

### RESULTS

Initial films were made to a half-wave optical thickness ( $\sim 1200$  Å) in the visible region with arbitrary control parameters chosen for the ion source, low deposition rates and oxygen flows yielding pressures in the  $2 \times 10^{-4}$  Torr range. The deposition rate and pressure were similar to what had been used for high temperature depositions. The first film was optically good (i.e. clear and non-absorbing) but was not a conductor. Increasing the deposition rate, reducing the oxygen flow and increasing the deposition rate resulted in a significant reduction in the resistivities while maintaining fairly good transparency in the visible. Although several parameters were varied, the resistivities were dropping significantly with the increasing deposition rate while the transmission at the half-wave optical thickness remained fairly high. The resistivity vs. deposition rate is plotted in figure 3.

The deposition parameters for the  $80 \Omega/\square$  sample represented a good starting point for the next step in developing a process. ITO is a material that exhibits the “Goldilocks Effect”. That is, as you vary the value of one

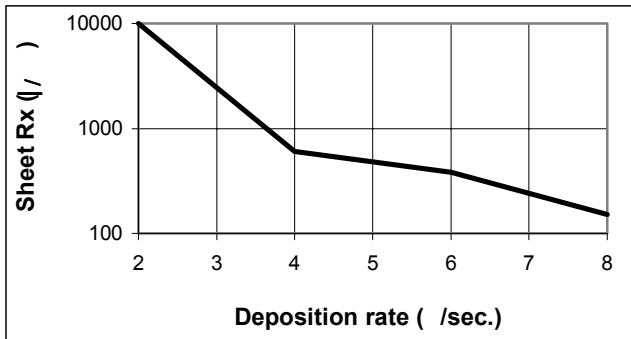


Figure 3. Sheet resistivity vs. deposition rate – preliminary data.

parameter while holding all the other constant, the term you are measuring will get better and then worse – too cold, just right and then too hot. Therefore, three test sets were run; where a) the rate was varied while holding the gas flow and the ion source drive current constant (figure 4), b) the gas flow was varied while holding the ion source drive current and the deposition rate constant (figure 5) and c) the ion source drive current was varied while holding the gas flow and deposition rate constant (figure 6). The lowest resistivity is obtained by using 8 Å/sec, 18 sccm O<sub>2</sub> flow and 2 A ion source drive current.

These parameters ( the oxygen flow was increased slightly to 20 sccm to make more transparent films) were then used to deposit three films of increasing thickness  $\lambda/2$ ,  $\lambda$  and  $3\lambda/2$  in the visible. The resulting films were 78 Ω/ , 40 Ω/ and 30 Ω/ and measured 1320 Å, 2500Å and 4200 Å thick respectively. Characterization by the interference method we had used previously resulted in refractive index values as shown in figure 7. The 1320 Å film is too thin to obtain dispersion data and is represented only by the index at the quarter-wave optical thickness. Only minimal absorption data could be extracted by this method since it required using spectral data from multiple half-wave thick wavelengths. Therefore, a method similar to that reported by Knickerbocker [15] was developed. This technique was to bring the spectral files (data taken every nm over the 350 nm to 2000 nm spectral range) into an Excel file to manipulate it to a form that was then available to a “solve” routine in a Mathcad worksheet. This work-sheet had n and k every nm as an output. The refractive index data was not as good as desired, obviously deviating from the real values near wavelengths where the film was  $3\lambda/8$ ,  $5\lambda/8$ ,  $7\lambda/8$ , etc thick. However, the extinction coefficient data looked good over most of the measured spectrum. If the obvious good data is selected from the output, then the index results for the three films are as shown in figure 8. Over the visible

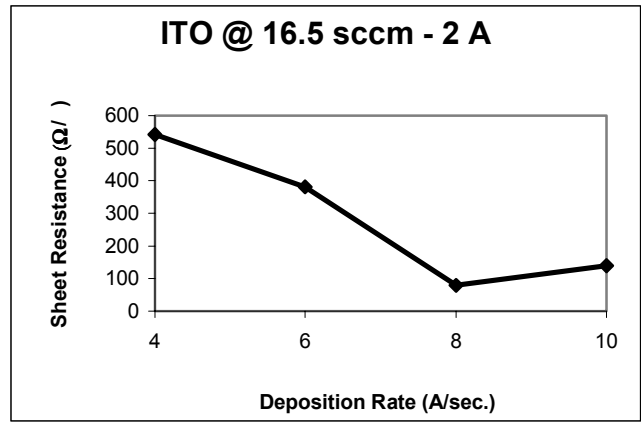


Figure 4. Resistivity vs. deposition rate with 2 A drive current and 16.5 sccm O<sub>2</sub> flow.

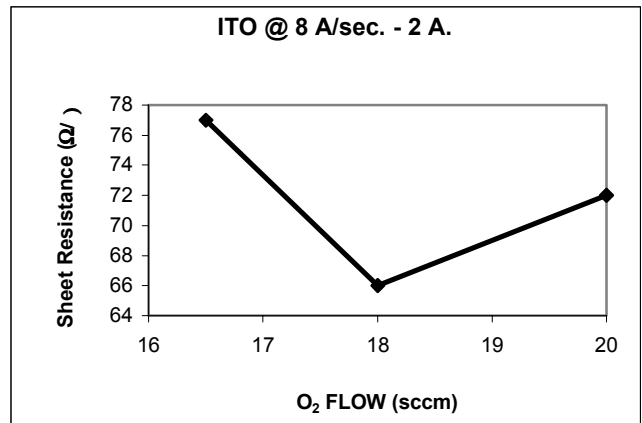


Figure 5. Resistivity vs. O<sub>2</sub> flow with 2 A drive current and 8 Å/sec deposition rate.

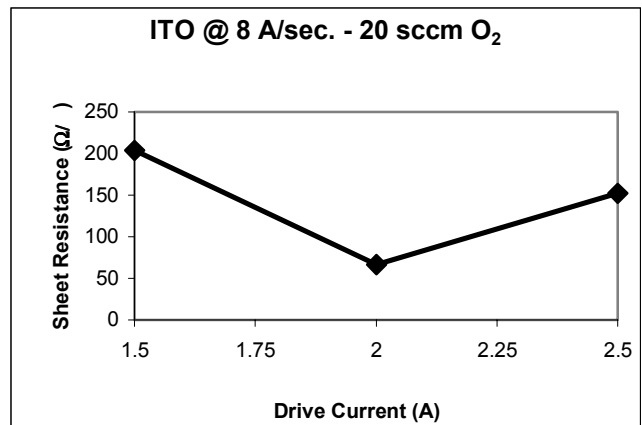


Figure 6. Resistivity vs. drive current with 20 sccm O<sub>2</sub> flow and 8 Å/sec deposition rate.

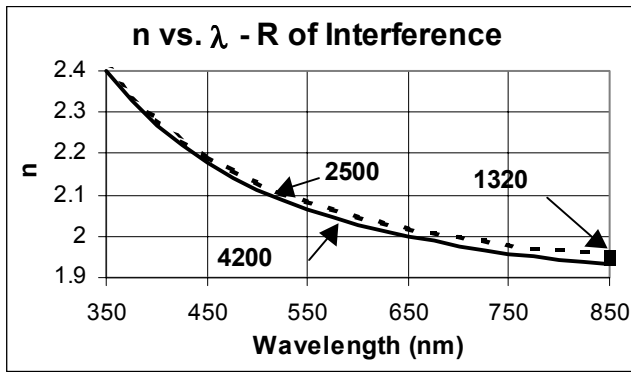


Figure 7. Refractive index of 3 different film thicknesses using an interference calculation.

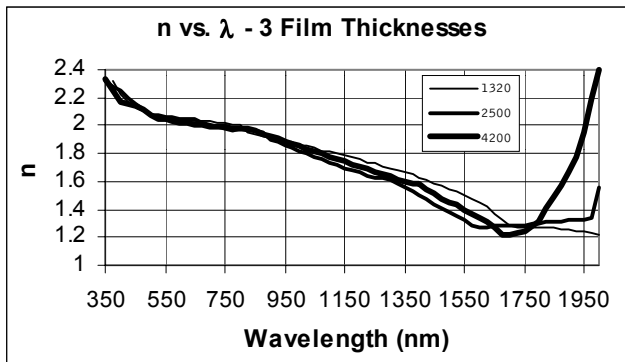


Figure 8. Refractive indexes of 3 different film thicknesses using method by Knickerblocker (see text).

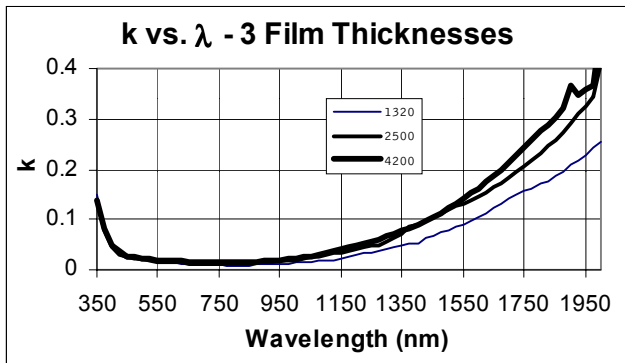


Figure 9. Extinction coefficient of 3 different film thicknesses using method by Knickerblocker (see text).

spectrum, these results are similar to what was obtained by simple interference method (see figure 7). The extinction coefficient data for the three films is shown in figure 9. The UV-visible extinction coefficients did not seem to vary much for the different thickness films. In the near IR the extinction coefficient seem to increase with increasing film thickness.

The transmission of the bare InSnO films has typical fluctuations based on the thicknesses and optical properties of the material. Over-coating the InSnO with a low index material (e.g. a QWOT of SiO<sub>2</sub>) will reduce the amplitude of the fluctuations and increase the transmission significantly. This overcoat also provides some protection to the conductive layer. Additional improvement in transmission can be achieved by inserting an impedance matching layer (such as a QWOT of Al<sub>2</sub>O<sub>3</sub>) between the substrate and the InSnO.

A series of 3 layer structures with different InSnO resistivities (50 Ω/ to 500 Ω/ ) were deposited and evaluated. These included impedance matching layers centered in the 500 nm spectral range and the 700 nm spectral range. The variations in the resistivities were achieved by increasing the O<sub>2</sub> flow levels while maintaining all the other deposition parameters the same (i.e. 8 Å/sec, 2 A drive current and 1300 Å thick). The higher O<sub>2</sub> flow levels resulted in films which were more oxidized and thus higher resistivities (see figure 10). One film was prepared with all the layers approximately 40% thicker to give the AR structure peaking at 700 nm.

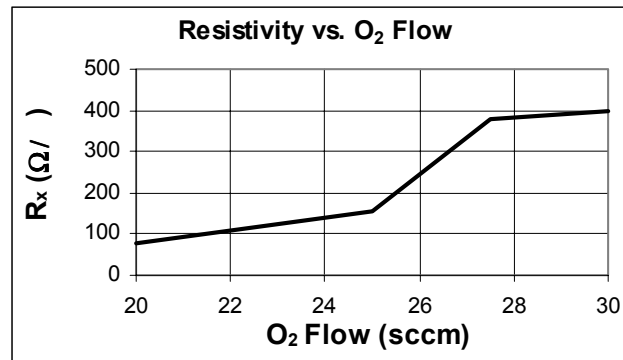


Figure 10. Resistivity of ITO films deposited at 8 Å/sec, 2 A drive current and various O<sub>2</sub> flow rates.

The transmissions of three of the films are shown in figure 11. In all examples the second surface is uncoated. The interesting feature of the many samples prepared, is that even though the thinner AR optical design may have been centered at 500 nm, the high transmission band extended out to 1000 nm. In fact, the longer wavelength AR did not even perform as well as the shorter wavelength ARs at the longer wavelengths. Thus, relatively high transmission could be achieved with one set of impedance matching thicknesses for the Al<sub>2</sub>O<sub>3</sub> and the SiO<sub>2</sub>.

The transmission of most of the samples averaged 92% or higher from 450 nm out to 900 nm. Below 450 nm the transmission would drop significantly due to the absorption in the conductive layer.

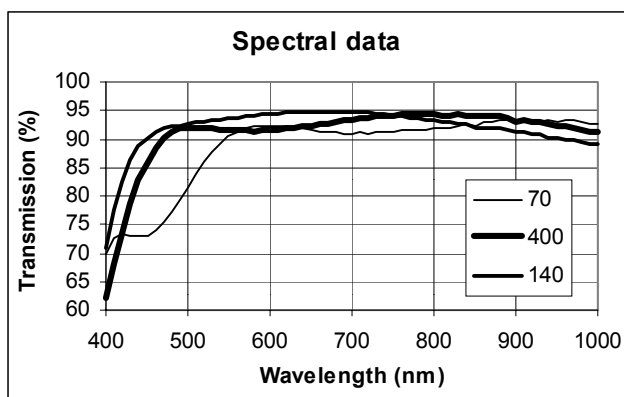


Figure 11. Transmission of several 3-layer (quarter-half-quarter wavelength structures). Parameter shown is the conductive layer resistivities in  $\Omega/$  .

## CONCLUSIONS

We have shown that IAD deposited InSnO films can be prepared at ambient substrate temperatures with resistivities in the 60  $\Omega/$  and higher range with transmissions greater than 90%. We have also determined that highly transparent film structures with higher resistivities can be prepared by introducing higher oxygen levels. Lower resistivity films require thicker conductive layers which will result in lower transmission levels.

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## REFERENCES

1. W. Essinger, "Ion sources for ion beam assisted thin-film deposition," *Rev. Sci. Instrum.*, (63) 11, 5217(1992).
2. James T. McNally, Report No. AFIT/CI/NR 86-77D (Dissertation at Univ. of New Mexico) (1986).
3. John R. McNeil, Alan C. Barron, S. R. Wilson and W. C. Herrmann Jr., "Ion-assisted deposition of optical films: low energy vs high energy bombardment" *Applied Optics*, (23) 4, 552 (1984).
4. John R. McNeil, G. A. Al-Jumaily, K. C. Jungling and A. C. Barron, "Applied Optics Properties of  $\text{TiO}_2$  and  $\text{SiO}_2$  thin films deposited using ion assisted deposition" *Applied Optics*, (24) 4, 486 (1985).
5. D. E. Morton, R. Danielsen, "Ion Assisted Deposition (IAD) of  $\text{TiO}_2$ ,  $\text{AlO}_2$ , and  $\text{MgF}_2$  Thin Films Using a High

Current/Low Energy Ion Source," 40<sup>th</sup> Annual Technical Conference Proceedings of the SVC, 203 (1997).

6. D. E. Morton, V. Fridman, "Measurement and Correlation of Ion Beam Current Density to Moisture Stability of Oxide Film Stacks Fabricated by Cold Cathode Ion Assisted Deposition," 41<sup>st</sup> Annual Technical Conference Proceedings of the SVC, 297 (1998).

7. D. E. Morton, V. Fridman, "Dense Moisture Stable Titania and Silica Ion Assisted Deposited Films Using a Compact Cold Cathode Ion Source," in *Optical Interference Coatings*, (9), OSA Technical Digest Series, OSA, 15 (1998).

8. C. Bright, "Optical Constants of Evaporated and Sputtered Transparent Conductive Oxides," 36<sup>th</sup> Annual Technical Conference Proceedings of the SVC, 63 (1993).

9. O. Marcovitch, Z. Klein, I. Lubezky, "Transparent Conductive Indium Oxide Film Deposited on Low Temperature Substrates by Activated Reactive Evaporation," *Applied Optics*, 28 (14), 2792 (1989).

10. L. R. Gilbert, S. P. Maki, D. J. McClure, "Comparison of ITO Sputtering Process from Ceramic Alloy Target onto Room Temperature PET Substrates," 36<sup>th</sup> Annual Technical Conference Proceedings of the SVC, 236 (1998).

11. K. P. Gibbons, C. K. Carniglia, R. E. Laird, R. Newcomb, J. D. Wolfe, S. W. T. Westra, "ITO Coatings for Display Applications," 40<sup>th</sup> Annual Technical Conference Proceedings of the SVC, 216 (1997).

12. W. W. Molzen, "Characterization of Transparent Conductive Thin Films of Indium Oxide," *J. Vac. Soc. Technol.*, 12 (1), 99 (1975).

13. S. Honda, A. Tsujimoto, . Watamori, K. Oura, "Oxygen Content of Indium Tin Oxide Films Fabricated by Reactive Sputtering," *J. Vac. Soc. Technol. A*, 13 (3), 1100 (1995).

14. J. A. Dobrowolski, F. C. Ho, D. Menagh, R. Simpson and A. Waldorf, "Transparent, Conducting Indium Tin Oxide Films Formed on Low or Medium Temperature Substrates by Ion-assisted Deposition," *Applied Optics*, 26 (24), 5204 (1987).

15. S. A. Knickerbocker, A. K. Kulkarni, "Evaluation and Verification of the Optical Properties of Indium Tin Oxide Based on the Energy Band Diagram," *J. Vac. Soc. Technol. A*, 14 (3), 757 (1996).