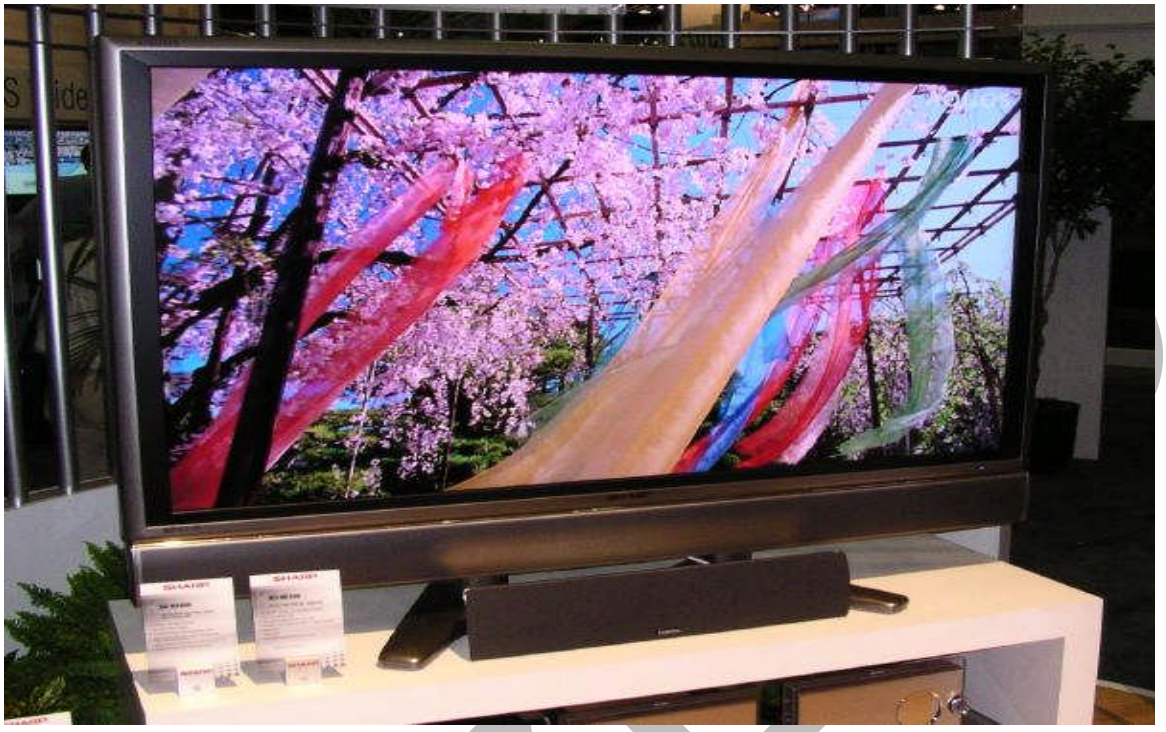
Indium Tin Oxide Technology (ITO)



ITO in Display Manufacture: TVs and

Abstract

This review is a valuable introduction to the specialist field of transparent conductive oxide technology. Particular emphasis is given to the application of thin films of Indium Tin Oxide (ITO) by various sputtering technologies. A review of indium supply provides current insight into drivers and enablers for ITO target production and an overview of this technology is given. An analysis of sputtering techniques is given containing important processing parameters, valuable for those wishing to experiment or indeed trouble-shoot production problems in the light of academic research. BizEsp provides turnkey packages for manufacture of large TFT-LCD grade ITO targets as well as all associated sputter processing technologies and know-how.

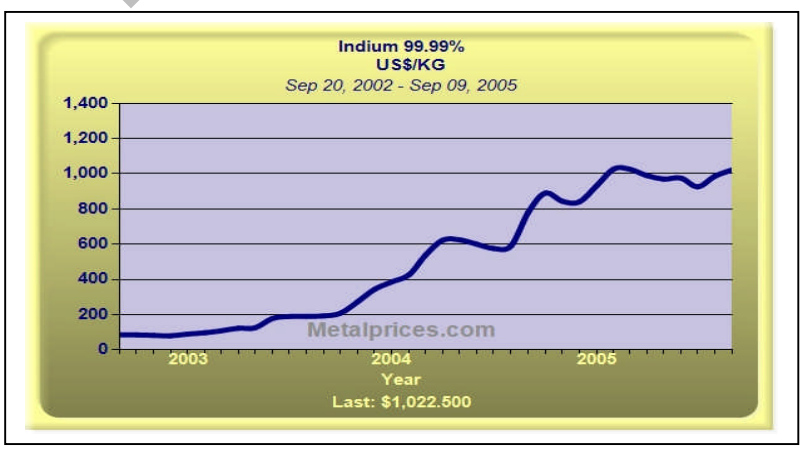
Key words: ITO, indium, target, sputtering, nodules, density, substrate-temperature, sputtering-voltage, evaporation, film-properties

Contents

INTRODUCTION

The science of thin film deposition is now a set of well established technologies playing critical roles in many segments of industry. In the electronics industry, thin film deposition is used for producing resistors, capacitors, memory devices, and is an essential component in the fabrication of integrated circuits. Methods employed are dictated by throughput, materials technology and end application, and include: vacuum evaporation by e-beam, or resistive heating, sputtering, various chemical vapor deposition routes, chemical methods (electro- and electroless plating, ion plating, anodization, gaseous anodization, thermal growth). The advantages and disadvantages of the various methods are summarized in Table 1. Evaporation and sputtering technologies are perhaps the most commonly used because of their wider applicability (Table 2).

Among thin film coatings, transparent conductive oxides (TCO) receive much attention because of their many important applications, e.g. window electrodes of solar cells, transparent electrodes in display devices (liquid crystal display, electro-luminescent display, and electrochromic displays), conductive windscreens for aircraft, and EMI shielding. There are also several applications of TCO coatings for architectural use (e.g. IR reflective coatings - heat mirrors). The market for transparent conductors is growing despite a fluctuating world economy. This continued upward trend in TCO usage is driven by popularity of lap-top computers, the introduction of flat screen monitors for desk-top PC's and a growing market for LCD-TV's, all of which require TCO on screens. Typical TCO coatings use an In90:Sn10 composition and so the price and availability of indium metal impacts indium-tin-oxide (ITO) sputtering target pricing.



Methods of applying thin films (M=Metals, S=Semiconductors, I=Insulators)

Method	Order of rate of deposition, Å S^{-1}	Rate control	Type	Advantages	Disadvantages
Electroplating	Up to 10^4 normally 10^2 –	Current density	M	Simple apparatus	Metallic substrate -
Chemical reduction	10^3	Solution temp	M	Simple apparatus. Can put metals on insulators	Limited number of materials with suitable reactions
Vapor phase	10	Pressure, temp	M, S, I	Single crystal, clean films are possible	Substrate temp may have to be high (>1000°C). Low-pressure gas systems may be required
Anodization	1-10^3	Current density	I	Simple Apparatus. Amorphous films, continuous at low thickness can be obtained	Metallic substrate. Only limited number of metals can be anodized. Total thickness limited.
Thermal	10	Pressure, temp.	I	Simple Apparatus	Limited number of materials give coherent films
Evaporation	1 - 10^3	Source temp.	M, S, I	Large range of materials and substrates possible	Vacuum apparatus required. Some materials decompose on heating
Sputtering	10	Current density. Target potential	M, S, I	High Adhesion. Using RF techniques, very wide range of materials possible	Suitable target required. Vacuum apparatus required

Table 2. Applicability of Thin Film Deposition Methods in Microelectronics

	Electroplating	Chemical Reduction	Vapor Phase	Anodising	Thermal	Evaporation	Sputtering
Conductors, Resistors, etc							
Insulators, capacitors							
Active devices							
Magnetic Materials							
Superconductors							

Single hatching indicates the component can be prepared by the method and cross-hatching indicates the method is widely used.

INDIUM MARKET

Indium occurs as an impurity in zinc and, occasionally is also found in tin, lead and copper. Indium has a similar abundance to silver, however, its extraction for industrial usage has only developed over the last ~30 years and demand has grown sharply over the last decade being almost exponential growth since 1997. As a result the relatively insubstantial supply base and previously low demand of indium has contributed to significant price instability. This instability coupled with (until recently) a relatively small worldwide consumption of indium is the reason why few zinc producers bother to extract indium.

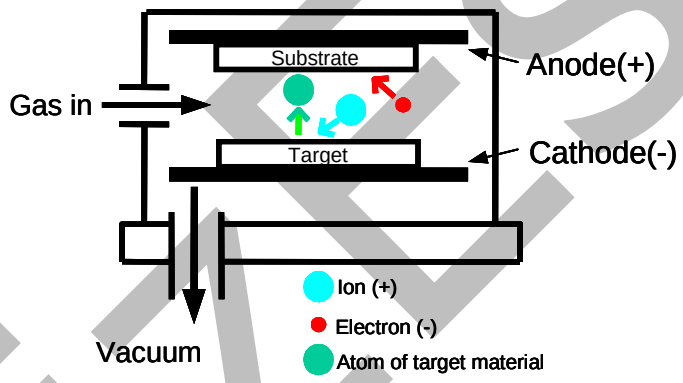
The massive recent demand for indium and the lack of supply, exacerbated by closure of zinc refineries (probably driven by reduction in zinc usage) led to increase in indium prices from ~ US$60.00/kg to prices exceeding US$600.00/Kg and in early 2005 prices as high as US$1100/Kg. Zinc refineries in China and elsewhere may re-open to address this

shortage and the economic drivers are there for this to happen, though the price of zinc may fall as a result. However technology will not be thwarted for long by lack of materials and cheaper alternatives based on Zn-Al couples and various tin binaries are being investigated as alternative TCO's, but are not in mass usage for displays due to insufficient and reliable conductivity and transmittance.

SPUTTERING

Sputtering is a process in which material is removed from a target (the cathode) by ion bombardment, carried by a plasma and deposited on a substrate (the anode) Figure 1.

Figure 1



Theoretical aspects of sputtering have been dealt with in several text books and review articles and are beyond the scope of this report. The interested reader is referred to references 1,3, & 4. Many types of thin films for various applications have been produced by sputter deposition (Table 3). The method is versatile with regard to the range of materials which can be deposited. Several types of sputter deposition systems have been used. These systems are classified according to the different discharges by which the plasmas are generated, in addition to the arrangement of target and substrate. The types of discharge currently most widely used are the diode types (operated by DC or RF) and the magnetron types (either RF or DC).

A cross-sectional view of an electrode used in diode-type equipment operated by DC or

RF is shown in Figure 2. The target is water cooled from the back to prevent an increase in temperature and is surrounded by shields (which are normally grounded~. The shields serve to avoid any occurrences of discharge at undesirable regions of the electrode surface and to localize the sputtering to only the target surface.

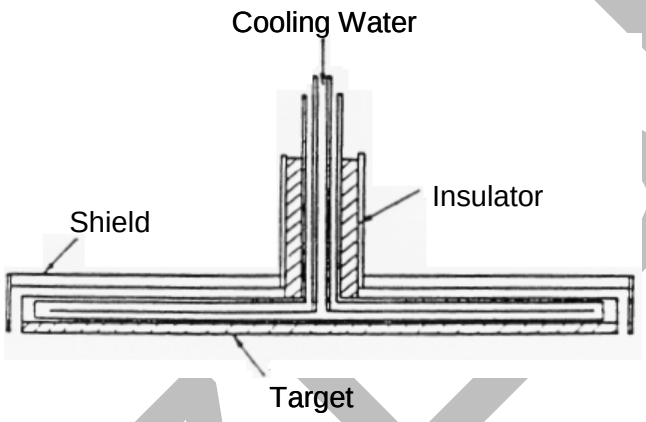


Figure 2 Cross Section of cathode used in diode type equipment

If a magnetic field is applied perpendicular to an electric field, electrons are trapped near the surface of the target (cathode) and trace cycloidal orbits. Such devices using crossed electric and magnetic fields are called magnetrons. They can be cylindrical, circular, or planar and can be operated by either DC or RF. A cross-sectional view of a planar magnetron electrode is shown in Figure 3.

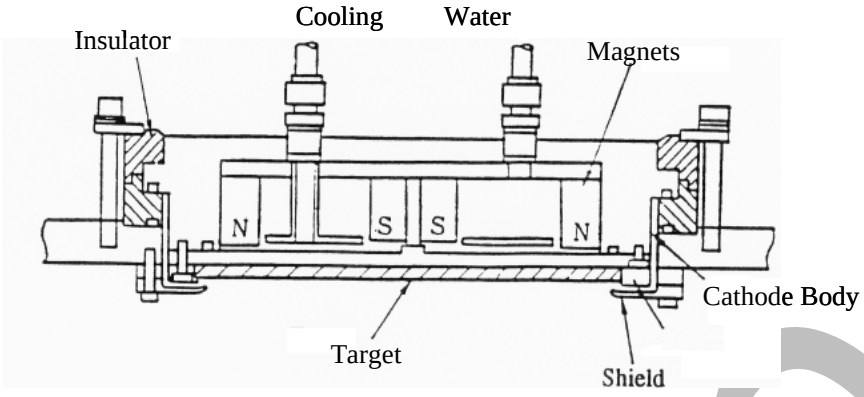


Figure 3. Planar Magnetron Electrode

Permanent magnets are arranged to form a toroidal-type magnetic tunnel in which electrons are trapped and follow cycloidal motions (Figure 4). The plasma density increases in this magnetically confined region, which causes a decrease in discharge impedance.

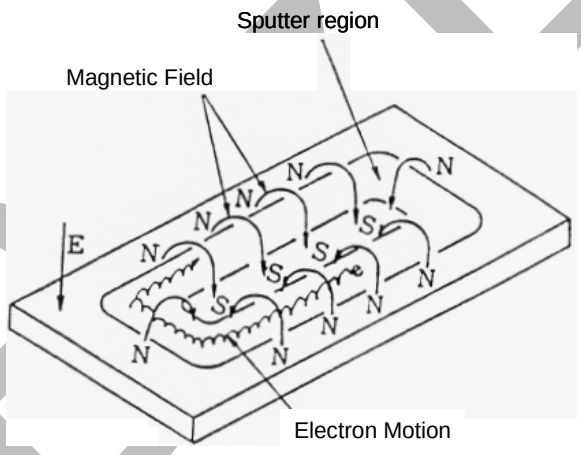


Figure 4. Electric & Magnetic Fields and electron motion in a planar magnetron electrode

Therefore, by using magnetrons, a higher ion current density can be obtained. This enables an increase in the deposition rate of films. Consequently, the deposition rate per unit power density, at the target, also increases and results in more efficient utilization of energy.

The typical current voltage characteristics of DC or RF planar magnetrons, DC- and RF-diodes are shown in Figure *5.* Another advantage of magnetrons is that since high-energy

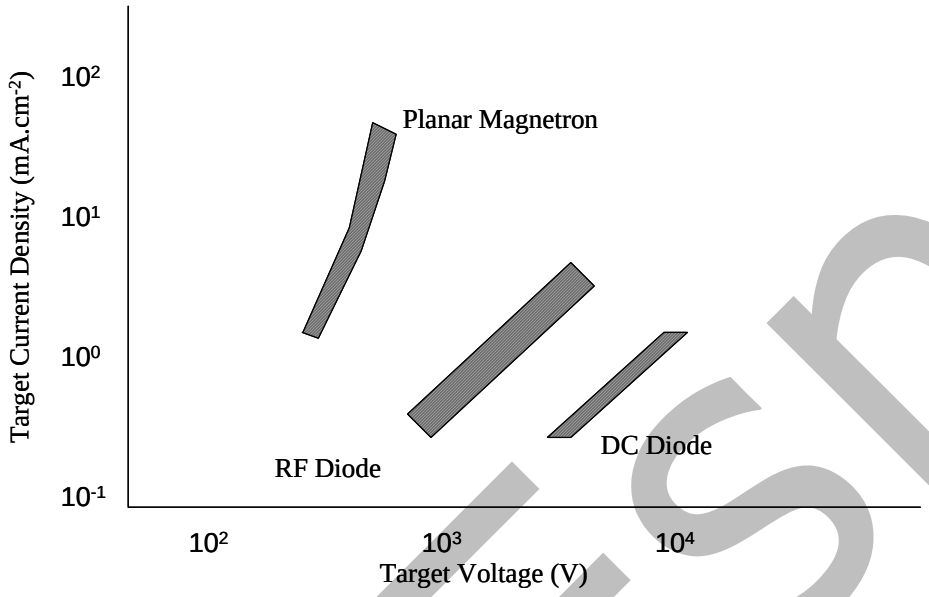


Figure 5 Current – Voltage characteristics of three types of sputtering systems

electrons are kept in the vicinity of the target, electron bombardment of the substrate is suppressed. As a result, temperature rise of the substrate and damage to ITO thin film (by impinging electrons) are restrained.

A typical sputter deposition apparatus is depicted in Figure 6. The pressure in the reaction chamber is controlled by adjusting the argon flow rate using a variable leak valve or a mass flow controller. An oil diffusion pump is commonly used for evacuating the reaction chamber. Recently, turbo-molecular pumps or cryo-pumps have also been used. The electrode configuration in which the substrate is placed in the face-up manner is commonly employed.

ITO thin films can be deposited by reactive sputtering using an indium tin alloy target and plasma containing oxygen as tile reactive gas, or by essentially non-reactive sputtering with a ceramic ITO target of tile same stoichiometry as the thin film[26]. The

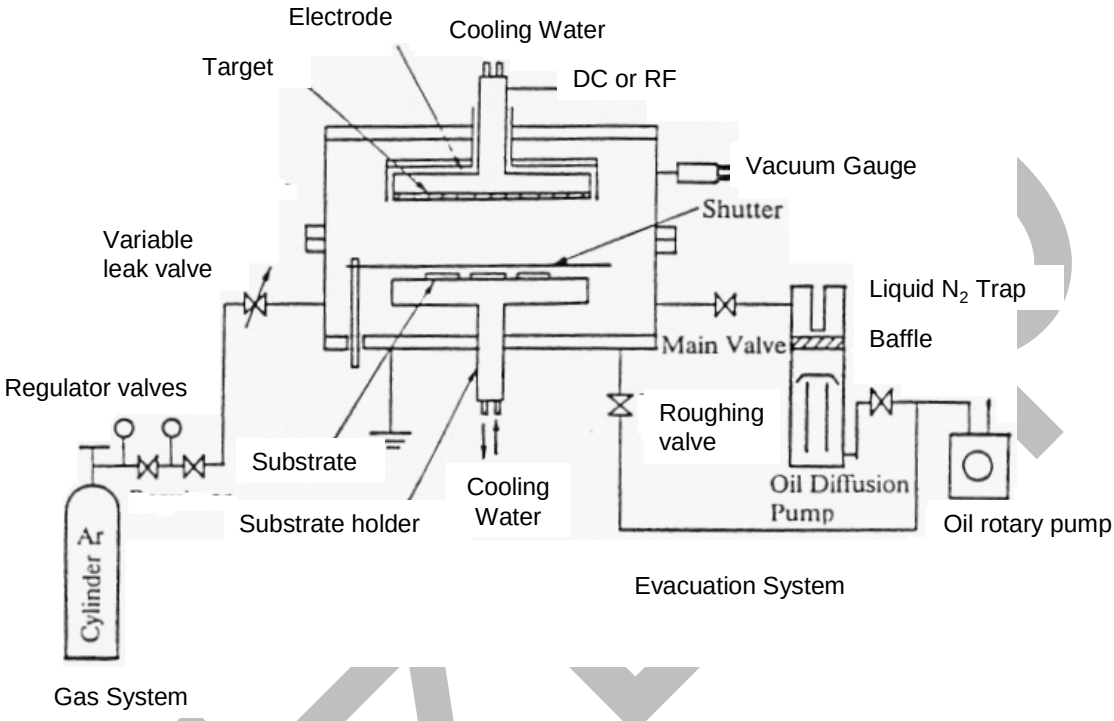


Figure 6. Typical Magnetron Sputtering system

advantage of reactive sputtering is that it is not limited by availability of suitable target material and can be used to prepare a range of thin films. The disadvantages are poor controllability of deposition process, poor reproducibility of results, and extreme sensitivity to changes in operating parameters (e.g. 0_2 flow rate). In contrast, sputtering using a ceramic oxide target is a more robust process and is now the main method for ITO thin film preparation.

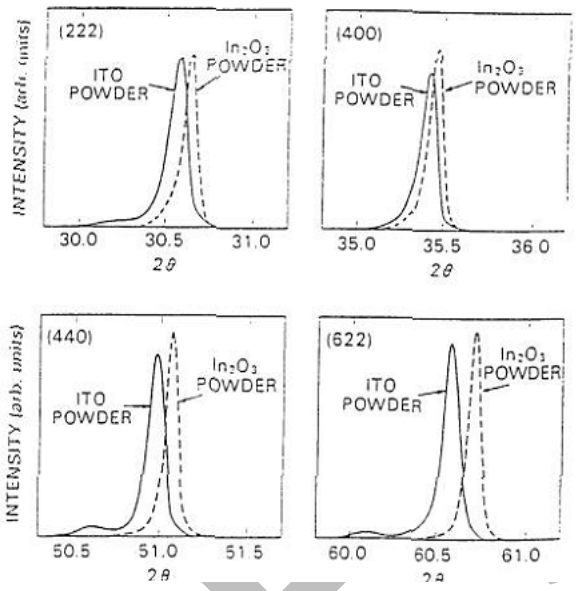
INDIUM TIN OXIDE TARGET MANUFACTURE

To prepare ITO targets. an intimate mixture of oxide powders is prepared and then hot pressed, hot isostatically pressed or slip cast and sintered. A common composition is In_2O_3

(90%) : SnO_2 (10%). Sputtering using a In90:Sn10 target leads to ITO thin films with carrier density 10^{21} cm3. It can be shown that such a carrier density requires a dopant concentration of only 3.5%. However sputtering using an ITO target with SnO_2 3.5 wt. % leads to films of carrier density $<10^{21}$ cm3. This implies that most of the dopant is trapped in crystalline defects and is electrically inactive. A 10wt.% $Sn0_2$ content gives optimum electrical properties. Dopant levels significantly greater than 10 wt.% have an adverse effect on electrical characteristics. By optimizing target properties (particularly density), enhancement of sputtering rate is obtained. Other important target performance parameters are: porosity, thermal conductivity, resistivity, resistance to cracking, target life-time, stoichiometry, purity, sputtering rate, and degree of oxide reduction. Typical target performance parameter values are shown in Appendix 1 for a TOSOH target. TOSOH have now started to market what they claim is an enhanced profile ITO target[7]. These targets feature additional ITO material in the erosion track of the target, providing a target material utilization of up to 50% to 60%. TOSOH claim that traditional planar ITO targets experience material utilization of 20-30%. TOSOH offer one piece targets of 5" x 2" or larger sizes as multipiece constructions.

ITO powder for manufacture of targets used in literature studies is prepared by heating an intimate oxide mixture of In90:Sn10 at a temperature of around 1500 °C for many hours. This powder is completely soluble in 6N HCI, whereas $Sn0_2$ powder is insoluble. It has been shown by conversion electron and transmission Mossbauer spectrometry that all the Sn atoms in the powder are in the Sn(IV) state and incorporated in the $1n_20_3$ lattice.[8] There are no Sn atoms which are in the segregated Sn(IV) state (like Sn atoms in $Sn0_2$) or in the Sn(II) state. XRD peaks of the ITO powder and pure $1n_20_3$ powder heat-treated at 1500 °C are shown in Figure 7 for (222), (400), (440), and (622) planes. All the peaks have been assigned to the cubic bixbyite structure of In_2O_3. The presence of SnO_2 peaks was not observed. The lattice parameter of the ITO powder was higher by 0.18% than the lattice constant of pure In_2O_3 powder. This result has been used to infer that since the ionic radius of In(III) and Sn(IV) are 0.81 and 0.71 A. a large amount of Sn(IV) must exist as interstitial atoms in the In_2O_3 lattice.

Figure 7 XRD peaks of ITO 90:10 and In_2O_3



SPUTTERING PROCESS PARAMETERS

Sputtering

Tile process parameters are:

Substrate temperature **T_s**

Total system pressure **p_s**

Oxygen partial pressure **p_0**

Argon flow rate **FR_{Ar}**

Sputtering power **P_s**

Rate of deposition **R_d**

Typical conditions for the growth of ITO films by RF sputtering are: target composition In_2O_3 : SnO_2 (90:10) ; p_s $l0^{-2}$ torr; p_0 (3-4) x 10^{-5} torr; FR_{Ar} 20 cm^3/min.; P_s (RF) 550W: T_s 450°C. The R_d obtained was in the range 100 - 200 Å/min. The method is essentially non-reactive. The oxygen is used because it results in significant improvement in crystallinity, mobility, visible transmittance, and IR reflectance. RF reactive deposition of ITO films has

also been reported. Typical process parameters are: target composition In:Sn (90:10 wt.%); plasma composition 80%Ar / 20% 0_2 vol %: P_s density (RF) 1.9 W/cm^2 (13.56 MHz frequency); T_s 350°C. Power densities as high as 190-260 W/cm^2 have been reportedly used in RF reactive sputtering. Typical DC magnetron sputtering parameters reported for ITO films are: T_s 300°C; p_s 7.3 x 10^{-3} torr; p_0 (0 - 8) x 10^{-5} torr; P_s (DC) 1.40 W/cm^2 (power densities of up to 11 W/cm^2 have been reported): R_d 2 nm/s using In_2O_3:$Sn0_2$ (90: 10 Wt. %) hot pressed 429 cm^2 target. ITO films have been deposited also by DC magnetron reactive sputtering using In:Sn (90:10 wt.%) targets (12.7 x 33.6 cm^2). Typical process parameters are: T_s 300 °C; p_s 7.5 x $l0^{-4}$ torr; p_0 4.9 x $l0^{-4}$ torr; P_s density (DC) 90-100 W/cm^2: R_d 0.1 nm/s.

In the above processes, it is normal practice to pre-sputter the target for 0-15 minutes before deposition on to the actual substrate. Film deposited onto unheated substrate tends to be amorphous and increasing the substrate temperature or annealing improves the crystallinity and grain size and decreases the density of structural defects, leading to higher mobility and carrier concentration. The optimum values of the substrate and annealing temperature obtained by various workers vary over a wide range from 150 to 600 °C.

VACUUM EVAPORATION

Various vacuum evaporation methods have been used to prepare transparent conducting films. Advantages of vacuum evaporation are its simplicity, economy, and efficiency (higher deposition rate than by sputtering). In contrast to sputtering, the amount of literature on ITO thin films deposited by vacuum evaporation is relatively low. This is a reflection of the popularity of sputtering. Important control parameters are evaporation rate, substrate temperature, source-to-substrate distance, and oxygen partial pressure, high vacuum ($l0^{-5}$ torr). The entire vacuum chamber and substrate are baked at 400 °C to remove adsorbed material such as water that would prevent good adhesion of the film [1,2].

DIRECT EVAPORATION

Thin films of IO, ITO, and zinc oxide have been deposited by thermal or electron beam evaporation of oxides. Owing to its high melting point TO is deposited by electron beam or flash evaporation methods. When pure or mixed oxides are evaporated they reduce and form opaque films of lower oxides. To obtain transparent conducting oxides, introduction of oxygen during evaporation, or post-deposition oxidation of the lower oxides film is necessary.

ITO material for evaporation is prepared by mixing SnO_2 and In_2O_3 (7.5 - 10 % wt. SnO_2) and then pressing into small pellets. Most of the recent studies reported in the literature employ electron bombardment for supplying heat required for evaporation[9a]. This is termed electron beam deposition. Typically, T_s 25-400 °C; p_s $l0^{-4}$ –10^{-6} torr (Ar and 0-50% O_2, at. volume ratio); R_d upto 6.7nm/s. Hjortsberg et al. (Chalmers University of Technology, Gothenberg, Sweden) have reported on ITO thin films deposited by reactive electron beam evaporation[9b]. They used In_2O_3 9mol% SnO_2 (obtained from Kyodo International, Japan, 99.99% purity), 8 kW electron gun. Corning 7059 glass substrate, electron gun/substrate distance of 50cm, T_s 25 - 400°C, R_d, 0.2 nm/s. The atmosphere during evaporation was controlled by continuous inlet of O_2, through a precision valve at full pump capacity.

Mizuhashi (Ashi Glass Co., Japan) has reported on ITO thin films deposited by thermal evaporation and studied the effect of varying In_2O_3:SnO_2 ratio on film properties[9c]. Mizuhashi used beryllia crucibles, P_{02} 10^{-4} torr, P_s 10^{-5} torr, substrate to crucible distance of 30 cm, and soda-lime glass substrate. A tantalum foil heater was used to avoid contamination of ITO films because tantalum oxide has a fairly low vapour pressure compared with tungsten oxide or molybdenum oxide. Mizuhashi has also reported on ITO thin films obtained by evaporation of sub-oxides followed by oxidation in air. These films, however, have relatively high resistivity (2 x $l0^{-3}$ ohm cm).

WHY SPUTTER

In sputtering, atoms ejected from the target strike the substrate surface with energies between ten and several hundred electron volts. Some of the sputtered atoms develop sufficient energy to penetrate several atomic layers of substrate surface, resulting in anchoring and films of excellent adhesion. The high energy of the depositing atoms also leads to highly compact, dense films with the highest degree of optical transmission and the lowest resistivity.

ELECTRO-OPTICAL FILMS AND STRUCTURAL PROPERTIES OF SPUTTERED FILMS

ITO THIN FILM PARAMETERS

ITO thin film parameters are:

- Film thickness
- Resistivity
- Optical Transmittance
- Carrier Concentration
- Hall Mobility

The resistivity, carrier concentration and Hall mobility are determined by the four-point probe method and Hall effect measurements. The relationship between ITO thin film parameters and film structure have been extensively studied[1,2,4,6,8-13]. The effect of target and process parameters on thin film properties/structure has also been examined.

EFFECT OF SUBSTRATE TEMPERATURE AND ANNEALING

Latz et al. (Leybold AG, Germany) using DC magnetron sputtering with ITO ceramic targets have reported ITO film resistivity rapidly decreases and optical transmittance increases as T_s increases above 84°C[10]. This has been attributed to growing of the crystalline phases of ITO films. At room temperature and at 84 °C there is only a weak indication for a (222)-orientated crystalline phase. At 109°C, the (222)-orientation shows a

high increase. As T_s increases over 200 °C, the (400)-orientation becomes intense. At T_s = 300°C, the (400)-orientation exceeds the (222)-orientation. SEM analysis has shown that grain size grows with increasing T_s. At T_s = 300°C. 1µm long grains with a predominant (400)-orientation can be detected. Such large grains cause less scattering of carriers because there are less grain boundaries. Additionally, a high T_s leads to a more uniform distribution of tin and oxygen atoms. Latz has reported a resistivity of 1.4 x $l0^6$ ohm/cm (film thickness 100 nm) at T_s 300°C.

Similar phenomena have been reported by Oyama et al. (Ashi Glass Co., Japan) on ITO thin films deposited at T_s 50, 125, 180 °C using EB evaporation[9]. The film deposited at 50 °C showed an amorphous phase, whereas the film deposited at T_s 180 °C was polycrystalline. The film deposited at T_s 125 °C showed the coexistence of amorphous and crystalline phases, clearly demonstrated by the halo pattern around the (222) peak of In_2O_3 in the XRD pattern (Figure 8).

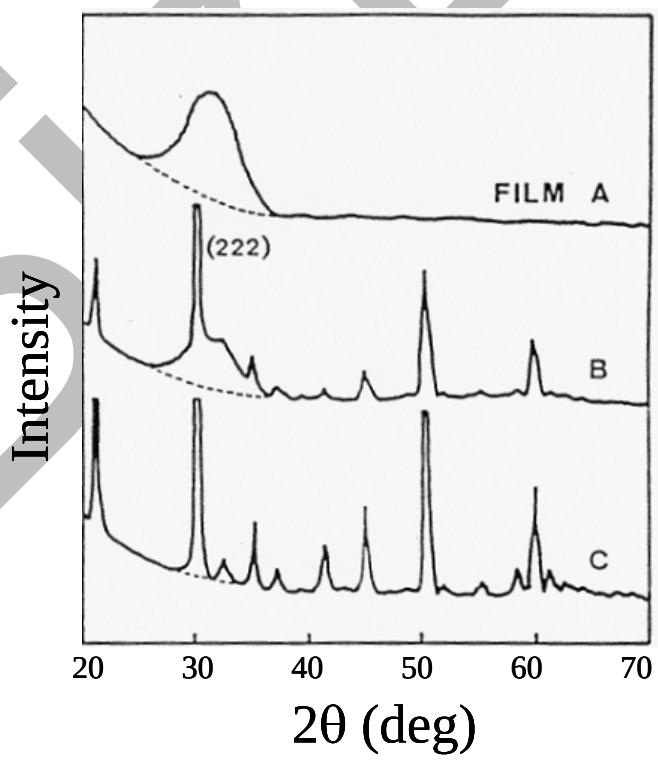


Figure 8. XRD patterns of ITO films deposited at different T_s: Film A 50°C Film B 125°C and Film C 180°C

The co-existence of crystalline and amorphous phases has been explained as follows. In the initial stage of the deposition, the substrate temperature (approx. 125 °C) is just below the crystallization temperature of ITO and, as a result, the film begins to grow in the amorphous phase. In the successive deposition process, the substrate temperature gradually increases because of the high radiation from the evaporation sources. When T_s = crystallization temperature, the arriving atoms and molecules form the crystalline ITO film on top of the amorphous film. At almost the same time, the underlying amorphous layer begins to re-crystallize. In the process of re-crystallization, the volume of the film decreases because of the difference in density of the two phases. Oyama has reported an ITO film surface deposited at 100°C**,** showing the onset of re-crystallization. Several small crystalline parts indicating the gathering of small grains are observed in the amorphous structure with smooth surface. The density difference leads to dimples at the crystalline parts.

Ishibashi (Institute for Super Materials, ULVAC Japan) has reported data on ITO film resistivity as a function of T_s at various DC sputtering voltages (Figure 9)[11]. Again, film resistivity shows a decrease with increasing T_s.

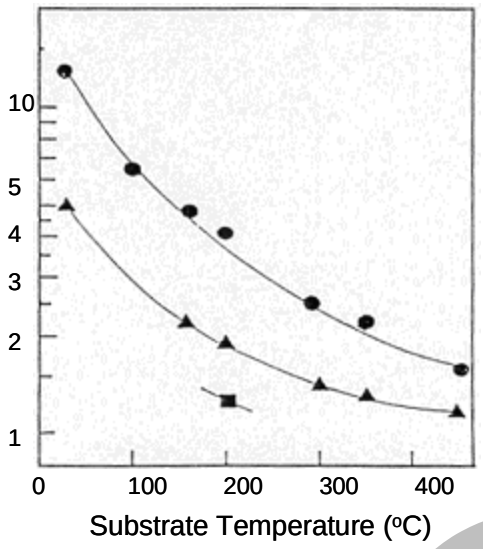


Figure 9. Dependence of ITO resistivity on T_s at different V_{sp}: -400 ● , -250 ▲ , 80 ■

Results of a study on effect of post-deposition vacuum annealing on properties of ITO layers have indicated the dependence of sheet resistance R_s after a constant annealing time of 70 min, on annealing temperature (T_a) as shown in Figures 10, 10a[12]. Again the importance of substrate temperature (T_s) on ITO film resistivity can be seen. It is also clear that resistivity falls rapidly with annealing temperature down to a roughly constant annealed value. X-ray analysis of ITO layers showed that vacuum annealing causes an increase in film crystallinity. The annealed layer exhibits a characteristic strong X-ray reflection in the (222) plane in contrast to the un-annealed layer. The latter shows only a weak reflection in the (222) plane. Optical transmittance of annealed and un-annealed layers does not show significant differences.

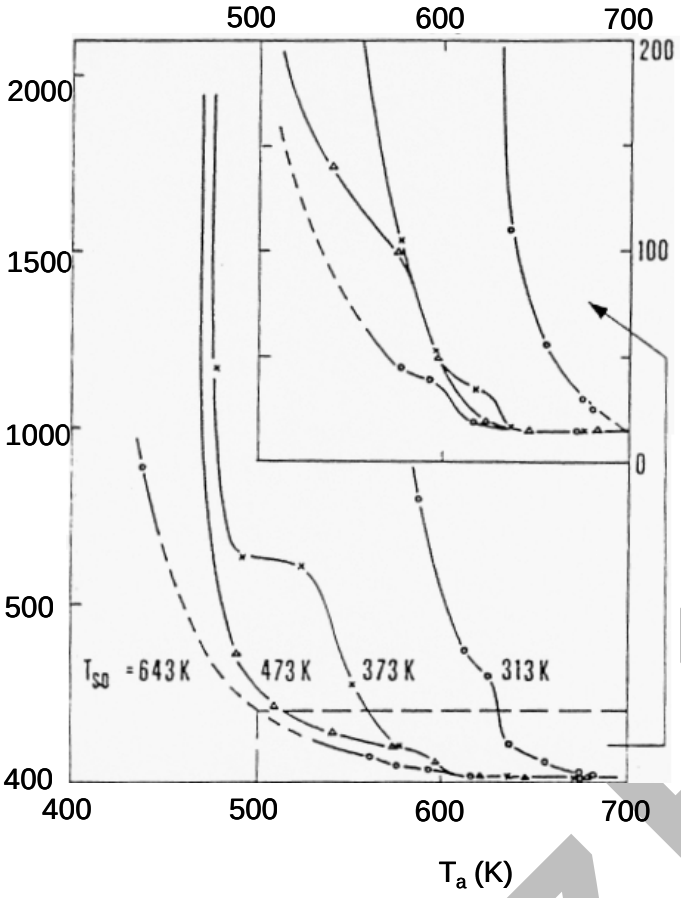


Figure 10. Dependence of ITO Sheet resistance (after 760mins post-deposition anneal) onaneealing temperature (T_a) for films deposited at various T_s

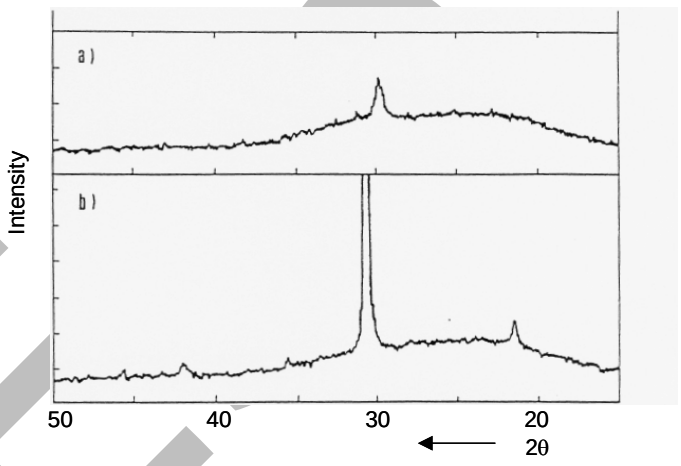


Figure 10a. XRD pattern of ITO layer deposited onto glass substrate (T_s = 420K) before (a) and after (b) annealing (t_a = 90min T_a=640K)

EFFECT OF SPUTTERING VOLTAGE (V)

Ishiibashi has reported on low resistivity and high transmittance ITO film deposited on glass by DC magnetron sputtering[11]. The set-up used is depicted in Figure 11. The results obtained at a VS_{sp} of -370 V at T_s 22, 200, and 350°C are shown in Figure 12.

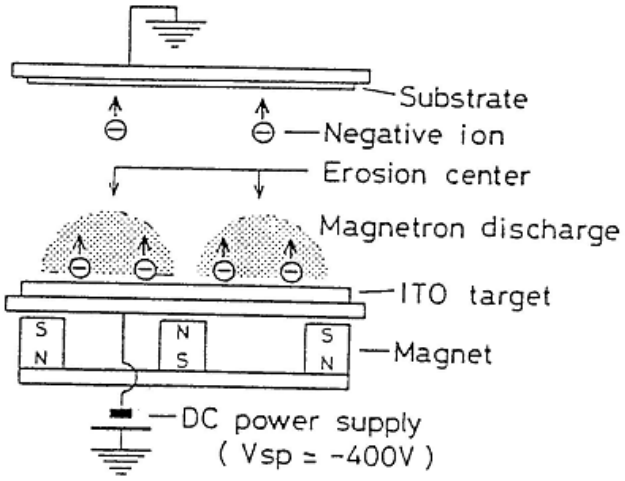


Figure 11. DC magnetron sputtering. A model of resistivity increase caused by negative ions

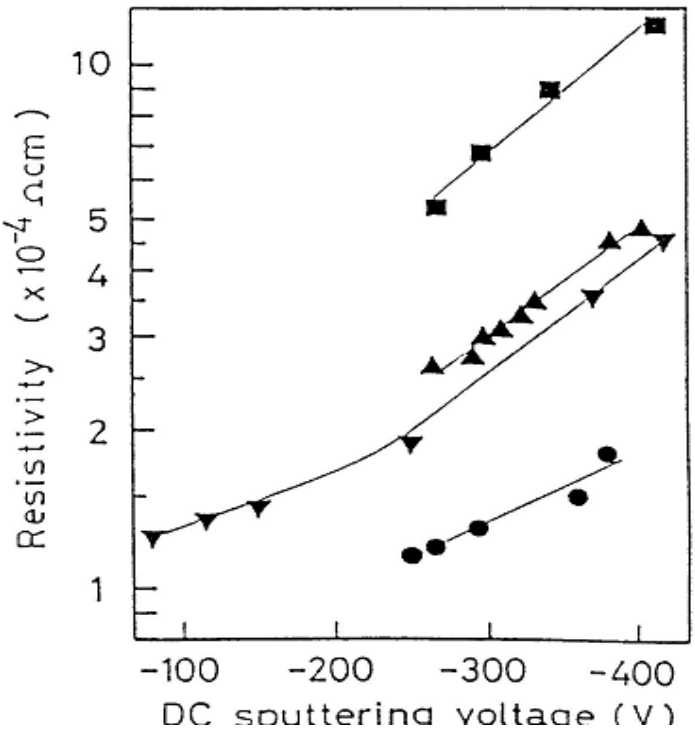
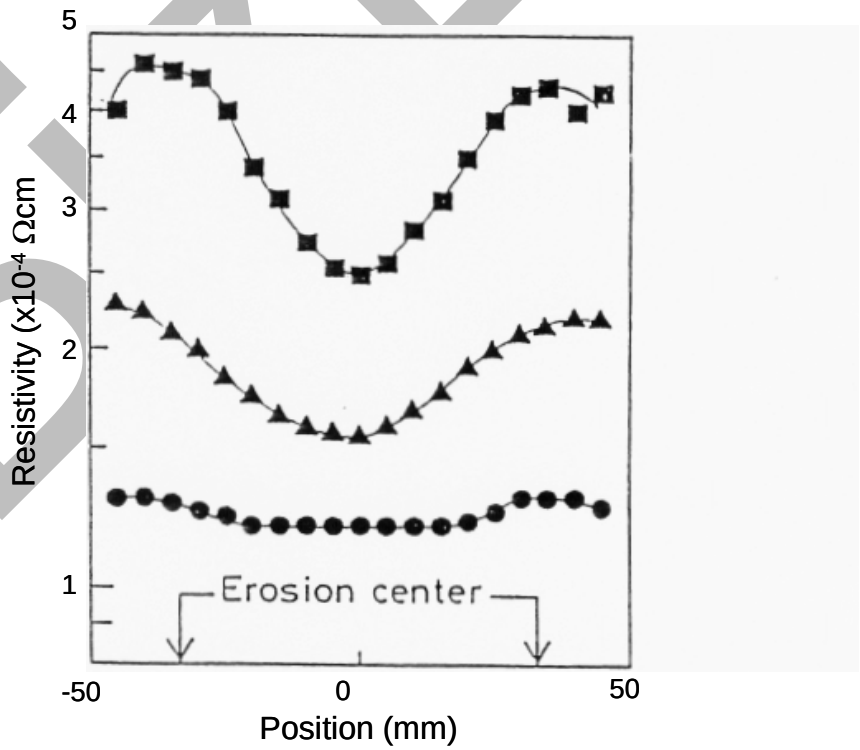


Figure 12. Dependence of ITO films resistivity on V_{sp} At T_s 22 ■ , 160 ▲ , 200 ▼ , and 460 ●

As discussed earlier, the effect of T_s on resistivity can be ascribed to improved crystallinity of films. Another point to note is that at each T_s, the thin film directly above the erosion area shows higher resistivity than the film at other positrons. Ishibashi has attributed the increase of resistivity to ITO film damage caused by impinging negative ions (Figure 11). Negative ions. e.g. oxygen ions, generated in target surface are accelerated by the negative potential in almost direct angle from the target, and collide with the substrate to cause ITO film damage. The negatively charged oxygen ion density is high on the erosion areas because, in magnetron discharge, the plasma is concentrated on the erosion area. Therefore, film damage by negative ions is larger above the erosion area and so is the resistivity. Above the centre of the target, however, there are less negative ions colliding with the film and resistivity is lower. It follows, therefore, that a lower collision energy of negative ions could reduce the resistivity of ITO film. Ishibashi has reported on ITO films deposited at a lower voltage of -110 V (Figure 13).

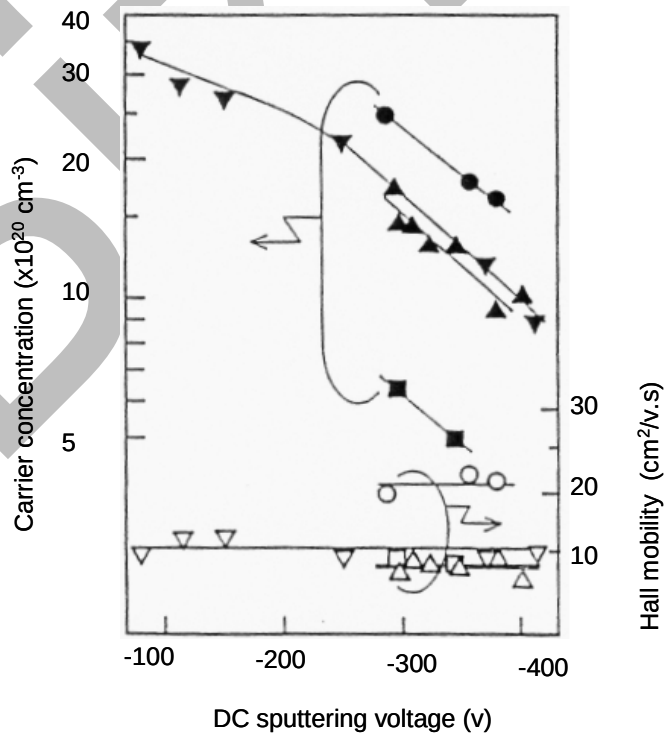
Figure 13. Resistivities of ITO films deposited on fixed 200C substrates
At each plasma position (see also Figure 11) when V_s were –370 ■ , -250▲ , and –110 ●



The results show a decrease in resistivity at each substrate temperature and no increase of resistivity directly above erosion area. Evidently, lowering V_{sp} leads to a decrease in ITO film damage caused by negative ions. Variation of resistivity with plasma positions at V_{sp} -370, -250. and -110 V (Figure 13) shows a reduction in resistivity, at all plasma positions, with lower V_{sp}. Furthermore, the degree of resistivity increase above the erosion area becomes smaller. Thus a lower V_{sp} is very effective in reducing ITO film resistivity.

Ishibashi has also reported on carrier concentration and Hall mobility of ITO pass-by coated films (investigated by Van der Pauw's Hall effect measurement method) as a function of V_{sp} (Figure 14). At each T_s a reduction in V_{sp} does not affect the mobility. The carrier concentration, however, shows a decrease with increasing V_{sp}. This has been attributed to a reduction of oxygen vacancies as donors and to increase of bivalent In or Sn as acceptors.

Figure 14 Dependence of carrier concentration and Hall mobility Of ITO films on V_{sp} at T_s 160 ■ , 220 ▲,460 ▼ , and 22°C ●



The ITO target, when bombarded by Ar ions, generates the black and highly resistive sub-oxide on the surface (Reaction I).

$$In_2O_3 \longrightarrow \textbf{ion collision} \longrightarrow \textbf{2InO + O}$$

(trivalent) (bivalent)

It has been reported that in the ITO film itself, a high V_{sp} can generate black higher resistivity sub-oxide (InO) by negative oxygen ion collision. This will lead to an increase in film resistivity. The black sub-oxide has an adverse effect also on ITO film transmittance (Figure 15). Higher transmittance of the low resistivity film formed at -250 V is explained by a reduced amount of black InO. Shigesato (Asahi Glass Co., presently at Brown University) has reported on the effect of V_{sp} on ITO film resistivity.[13] It is known that magnetic field strength at the cathode surface (MFS) dominates the current-voltage (I-V) characteristics and offsets threshold V_{sp} requirement in the DC planar magnetron. Shigesato lowered V_{sp} from 540-330 V, keeping sputtering current constant at 2.7A, by increasing MFS from 140 to 480 G.

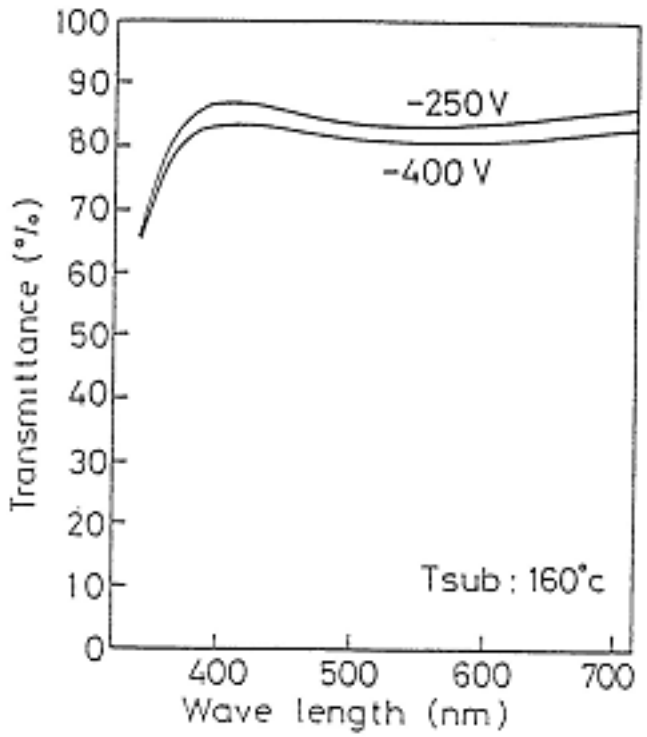


Figure 15 Transmittance of ITO films (T_s=160ºC) at different V_{sp}

Table 4 shows resistivity, mobility, and carrier concentration for films deposited at different $V_{sp.}$

Table 4 Electrical and structural properties of ITO films deposited at different V_{sp} (T_s=400°C)

Magnetic field: MFS (G)	Sputtering voltage: V_{sp} (V)	Sputtering current (A)	Thick-ness (Å)	Resistivity ($x10^{-4}$ Ω.cm)	Carrier Density x1020 cm^{-3}	Mobility (cm^2/Vs)
140	540	2.7	1140	1.92	7.48	43.0
350	380	2.7	1370	1.34	10.5	42.9
480	330	2.7	1240	1.35	10.3	43.1

Grain size[a] (Å) (222) (400)	Uniform Strain (%) (222)	(400)	Grain[b] orientation I(400) / I(222)
256 264	1.39	1.23	2.02
218 235	1.35	1.08	3.20
215 239	1.41	1.07	3.80

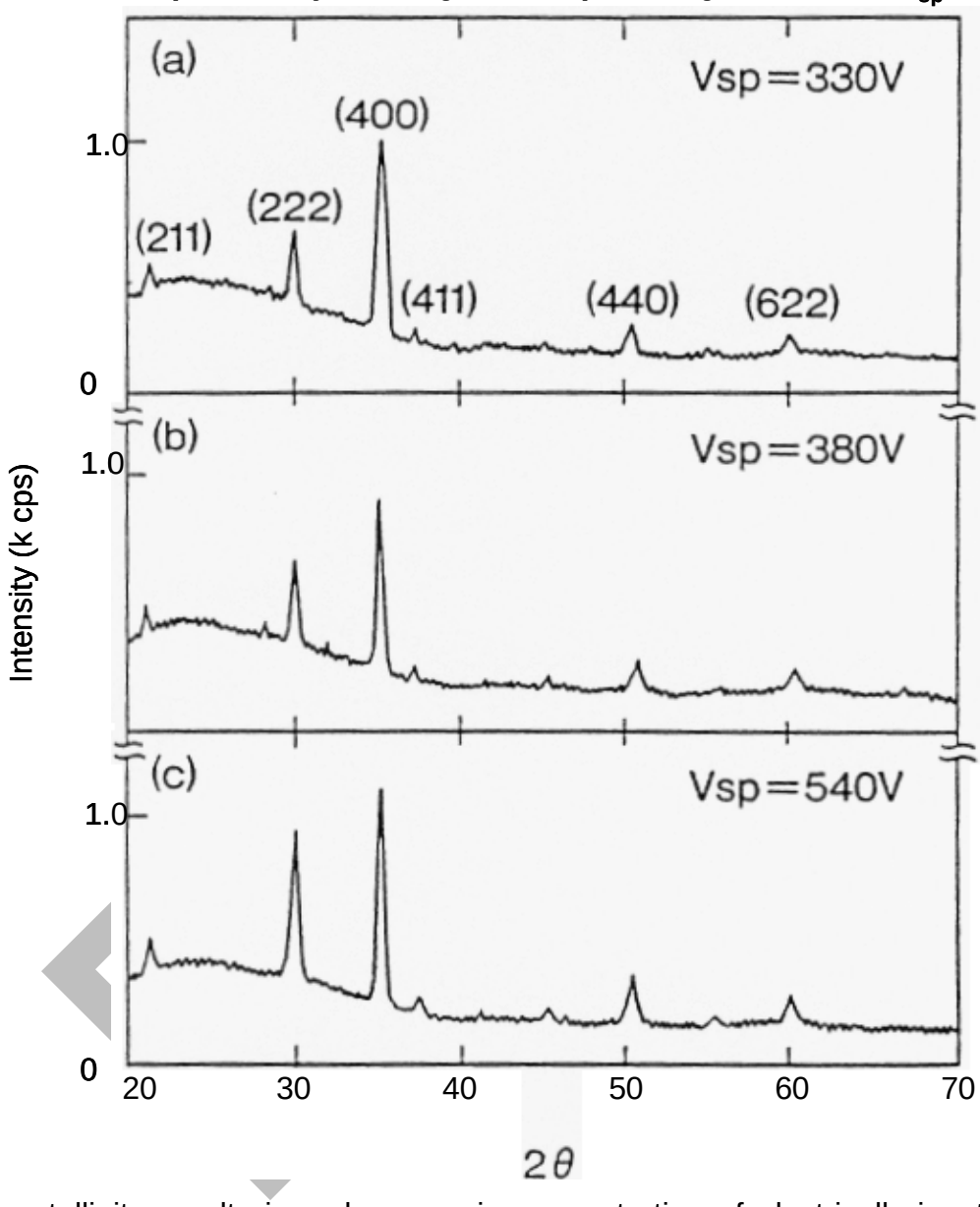
[a]These values were calculated by the Scherrer method using X-ray diffraction peak and were in the direction normal to the surface of the film.

[b]The value for the random orientation by ASTM is 0.33

Resistivity decreased from 1.92 to 1.34 x 10^{-4} ohm/cm with decrease in V_{sp} from 540 to 330 V due mostly to increase in *n* as a result of increase in crystallinity. SEM showed that all the films were similar to each other with a grain size of 200 - 300 Å. X-ray diffraction patterns of films deposited at various voltages are shown in Figure 16. The integrated intensity ratio of the (400) peak to the (222) peak [I(400)/I(222)] was 2.02 for films deposited at ~ 540 V and the value for random orientation by ASTM was 0.33. This is indicative of preferred orientation of grains in the <100> direction. With decreasing V_{sp} preference for the < 100> direction becomes stronger. This tendency is analogous to the effect of increasing T_s for sputtered ITO films. The uniform strain estimated by the (400) peak, which is diffracted by the grains in the preferred <100> orientation, showed steady decrease from 12.3 to 1.08% with the decrease in V_{sp} from 540 to 380 V. This reflects an

increase in crystallinity of ITO films. The higher

Figure 16. XRD patterns of ITO films (thickness 1200Å) deposited by DC magnetron sputtering at different V_{sp}

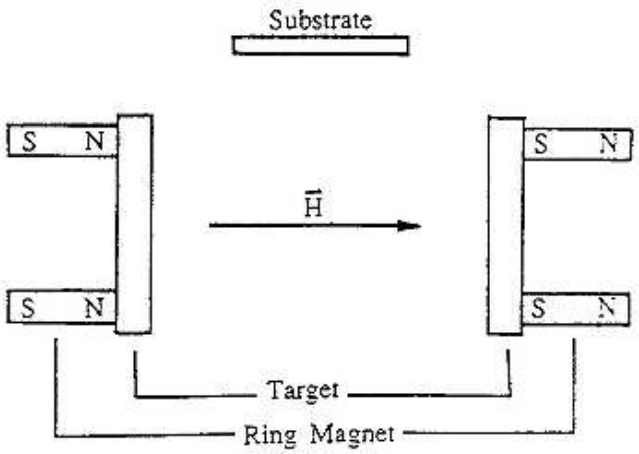


crystallinity results in a decrease in concentration of electrically inactive dopants (Sn or oxygen vacancy) trapped at crystalline defects (caused by bombardment of high energy negative oxygen ions during deposition) and hence increase electrically active species inside each grain. By using a stronger magnetic field, plasma impedance is decreased and low damaged films are deposited with a low resistivity of 1.34 x 10^{-4} ohm/cm.

a) Face Target Sputtering (FTS)

One point in common amongst the sputtering methods discussed earlier is that either the substrate has to be heated above 200 -400 °C during deposition or post-deposition annealing at > 300 °C in controlled atmospheres is necessary. However, for certain applications, the use of an elevated substrate or post-deposition annealing temperature is undesirable. Lee et al. (Mitsubishi Materials Corporation. Japan) have reported the deposition at low temperature (23°C) and pressure (0.1 - 10mTorr) of highly transparent and conductive ITO films by the face transfer sputtering (FTS) process in pure argon[14]. The FTS system used was FTS-C3 (Osaka Vacuum) with a 140mm distance between the targets (Figure 17) (125 mm diameter, In_2O_3 : SnO_2 90:10%Wt., 70% density made by Mitsubishi Materials Corporation, Japan). A RF discharge (13.56 MHz) of 200W was used and the targets were pre-sputtered for 15 mm before deposition. As the magnetic field of 150 Oe acts perpendicular to target planes, the plasma is confined between the two targets. Thus, bombardment damage of the substrate and growing ITO film by high energy particles such as electrons and negative ions is largely avoided.

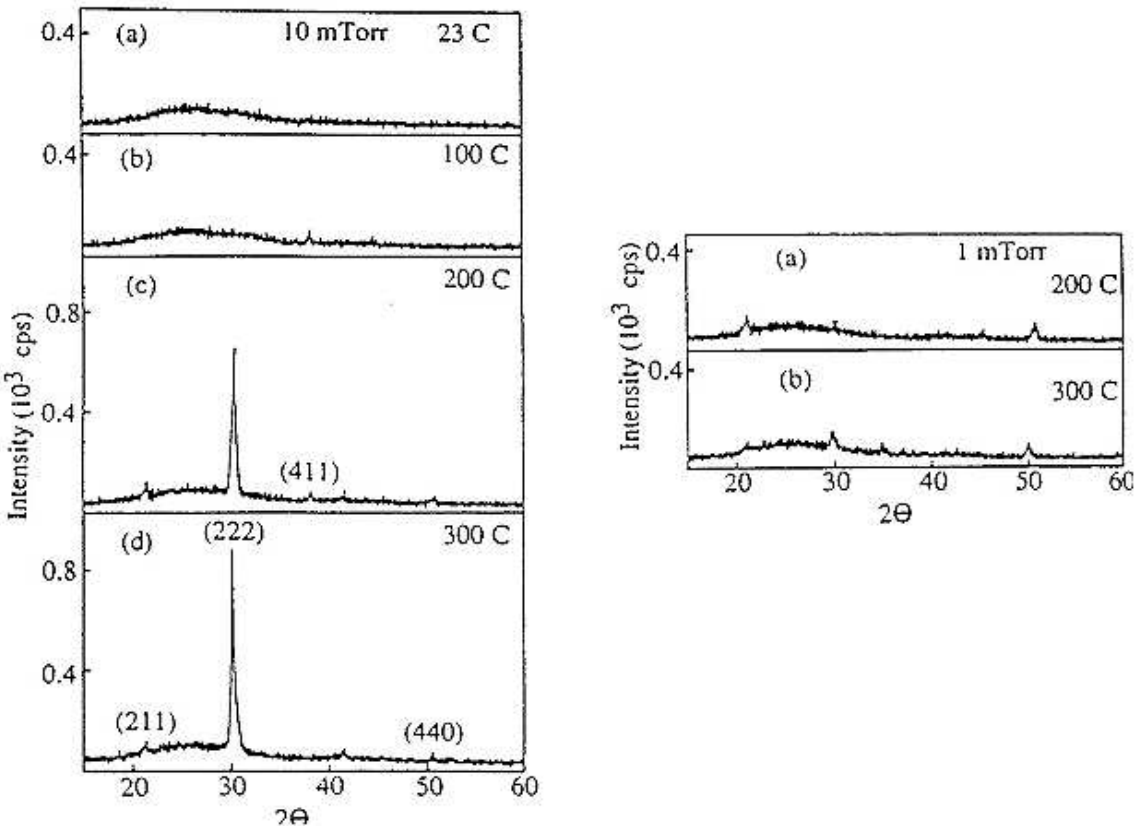
Figure 17 Schematic drawing of the face sputtering (FTS) system.



In the FTS system, the ITO thin film parameters are almost temperature independent.

Figure 18 shows XRD patterns of films deposited at various T_s and at pressures of 10 mTorr and 1 mTorr. At 10 mTorr, the usual trend of increasing crystallinity with T_s is observed. But the effect of T_s is completely eclipsed by a change in pressure and the films deposited at 1 mTorr are amorphous even at T_s 300°C. At 10 mTorr / T_s =200 & 300 °C, a grainy surface is obtained. At 1 mTorr / T_s = 200 & 300 °C, a plate-like structure is obtained and at T_s = 300 °C a grainy surface, with occasional spherical particles ranging from 0.2 to 0.3 mm, is observed at T, 200 °C. When the sputtering pressure is lowered to 0. 1 mTorr and T_s set at 300 °C, a rough grainy surface results. If T_s is lowered to 200 °C a surface with pin-holes results. Thus, low pressure facilitates formation of pin-holes. This effect of pressure has not been rationalised by Lee et al.

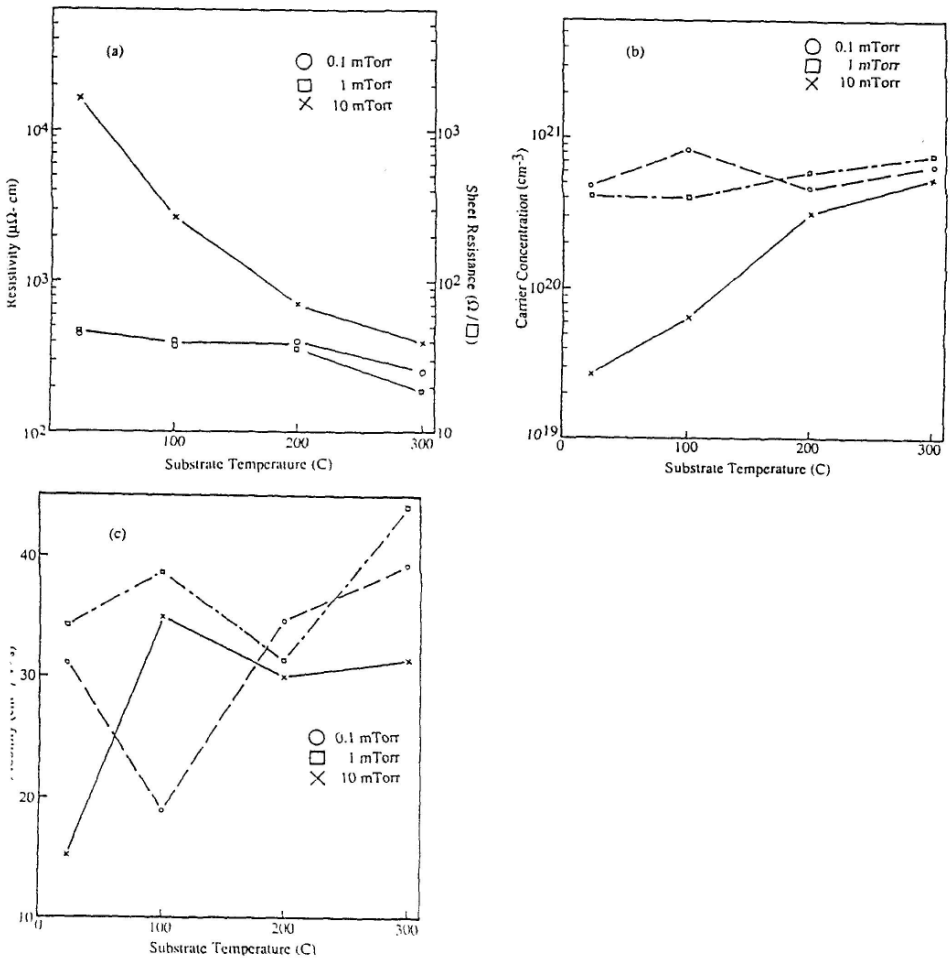
Figure 18 XRD patterns of ITO films deposited by the FTS method at various T_s and pressures.



The resistivity, carrier concentration and mobility of ITO films deposited at different T_s under various pressures are shown in Figure 19. At 0.1 mTorr and 1 mTorr there is no significant

change in resistivity and carrier concentration with T_s. All the films reported by Lee et al. have low carrier mobility and (u) varies from about 15 to 44 cm^2/Vs. In the FTS method of Lee et al., the transmittance of tile films between 400 - 900 nm does not vary significantly with either p_s or T_s. Since the films change from an amorphous to a textured crystalline phase at p_s 10 mTorr, it indicates that transmittance does not depend on the degree of crystallinity or orientation of films or surface morphology. Whether the film is covered with pin-holes or consists of fine grains, transmittance does not change significantly.

Figure 19 (a) resistivity and sheet resistance
(b) carrier concentration, and
(c) mobility of ITO films (deposited by the face sputtering method) as a function of T_s at various pressures.



As discussed earlier, it has been reported by various authors that ITO film properties are improved by adding a small amount of oxygen to the sputtering system during deposition. Lee et al. have reported, however, that the presence of oxygen in the FTS system is detrimental to the electrical properties of ITO thin films. Lee et al. have suggested that with increased oxygen partial pressure, the concentration of oxygen vacancies in the film is reduced. As the conductivity of ITO results from oxygen deficiency and a higher valent cation doping of In_2O_3, a decrease in charge carriers. Therefore, resistivity increases as oxygen is added during sputtering. The problem with this explanation is that if it was correct then a similar phenomenon should be observed in normal sputtering procedures. Why should it be limited to FTS? To conclude, the FTS system can be used to deposit films at low T_s which are comparable in their electrical properties to films deposited at higher T_s in normal sputtering procedures.

HIGH RATE INDIUM TIN OXIDE SPUTTERING

Most of the studies reported in the literature on high rate ITO sputtering have used DC planar magnetron reactive sputtering. As discussed earlier, reactive sputtering is difficult to control. In high rate large-scale deposition, the main problem is that as the reactive gas flow is increased, a transition occurs at the target surface from a metallic to a poisoned (oxide) target surface. Sputtering from a metallic target surface leads to high deposition rates. It is therefore desirable to operate the magnetron with a largely metallic target surface while having sufficient reactive gas pressure at the substrate to form the film.

For stable production of ITO film, it is necessary to have at the substrate surface:

a) a constant metal flux

b) a constant arrival rate of oxygen

c) a constant utilization of oxygen.

These parameters are inter-related in a way that can lead to instability. The metal flux depends on the state ~ the target which depends on the total reactive gas pressure (P_{o2})

The arrival rate of oxygen at the substrate also depends on (P_{o2}). It follows therefore that (P_{o2}) is a very important process parameter.

PRESSURE STABILITY IN DC REACTIVE MAGNETRON SPUTTERING

Spencer et al. (Loughborough university of Technology, UK) have reported on the effect of (P_{o2}) on target poisoning in reactive DC magnetron sputtering[15] At the target, the surface is constantly being poisoned (oxide build-up) and sputtered clean. When the poisoning rate exceeds the cleaning rate, a poisoned surface exists (leading to decrease in 0_2 consumption caused by a decrease in metal flux, and increase in (P_{o2}) and with increase in (P_{o2}) the proportion of poisoned surface increases. This cycle continues until the target is completely poisoned and then the metal flux remains roughly constant (Figure 21a).

Figure 20 Mechanism of instability in reactive DC magnetron

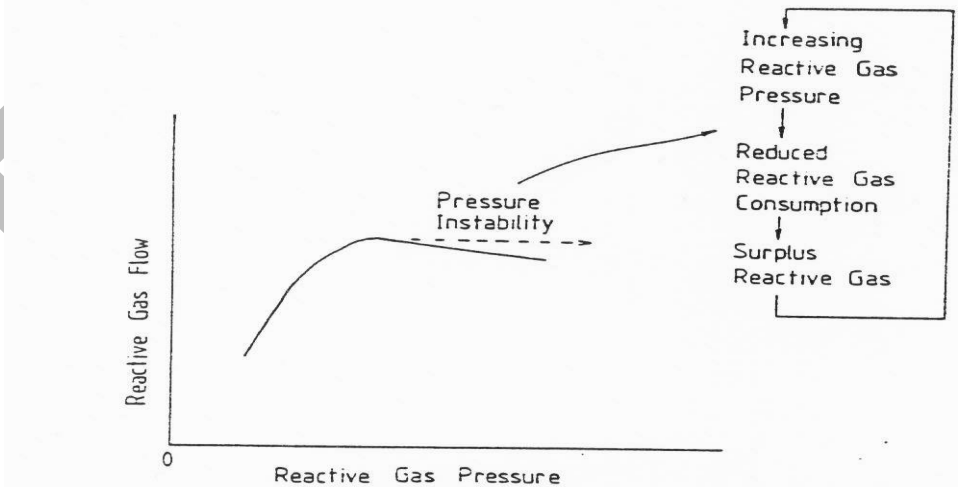
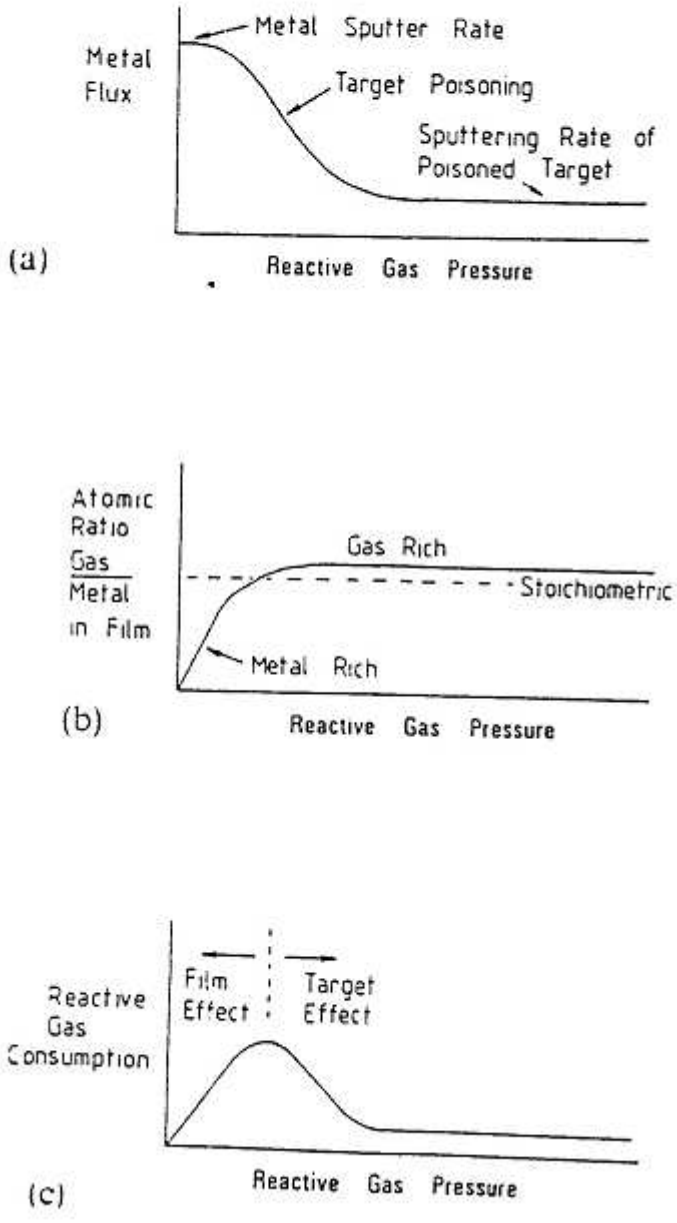


Figure 21. Reactive gas consumption:
(a) at the target, (b) at the substrate,
(c) the resulting gas composition.

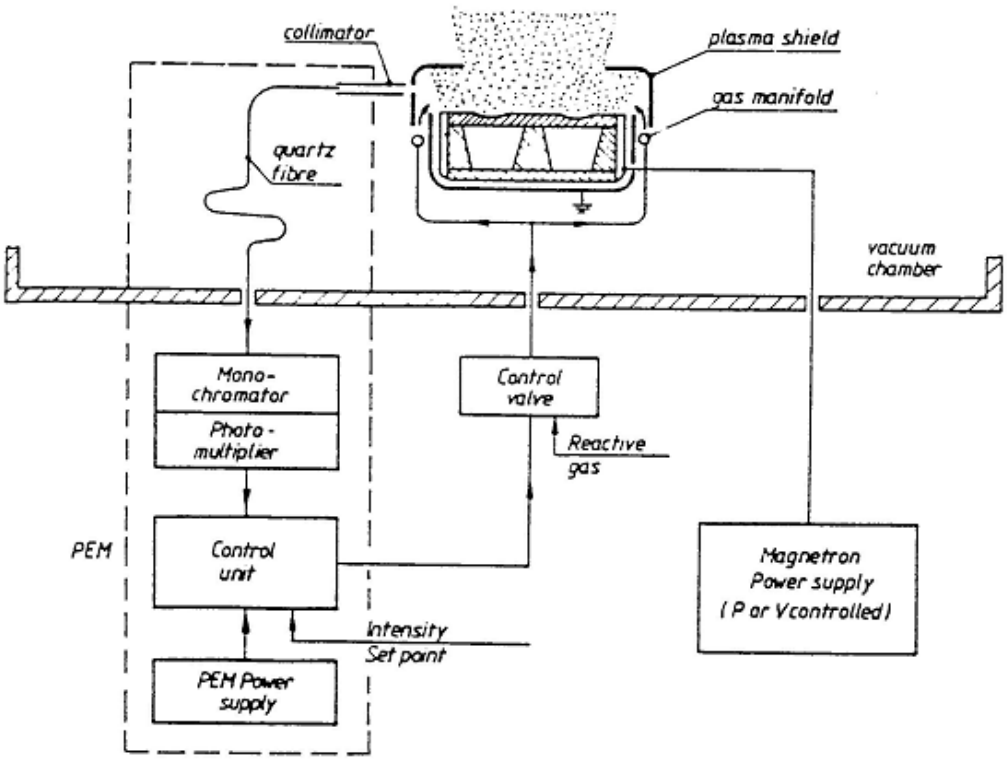


At the substrate, at low reactive gas (P_{o2}) the formation of ITO is limited by the arrival rate and utilization of the reactive gas and so a metal rich film is formed. As the reactive gas pressure is increased, the arrival rate of reactive gas increases and the film becomes less

metallic. This continues until the target is completely poisoned and the film is saturated with 0_2 (Figure 21b). The consumption of 0_2 is then limited by the metal arrival rate. The process at the target (Figure 21a) and substrate (Figure 21b) combine to give the gas consumption curve (Figure 21c). Schiller et al. have demonstrated an effective approach for controlling stability of reactive magnetron sputtering[16] . The approach involves control of the gas flow to keep constant the optical emission by metal in the plasma using a plasmaemission monitor (PEM).

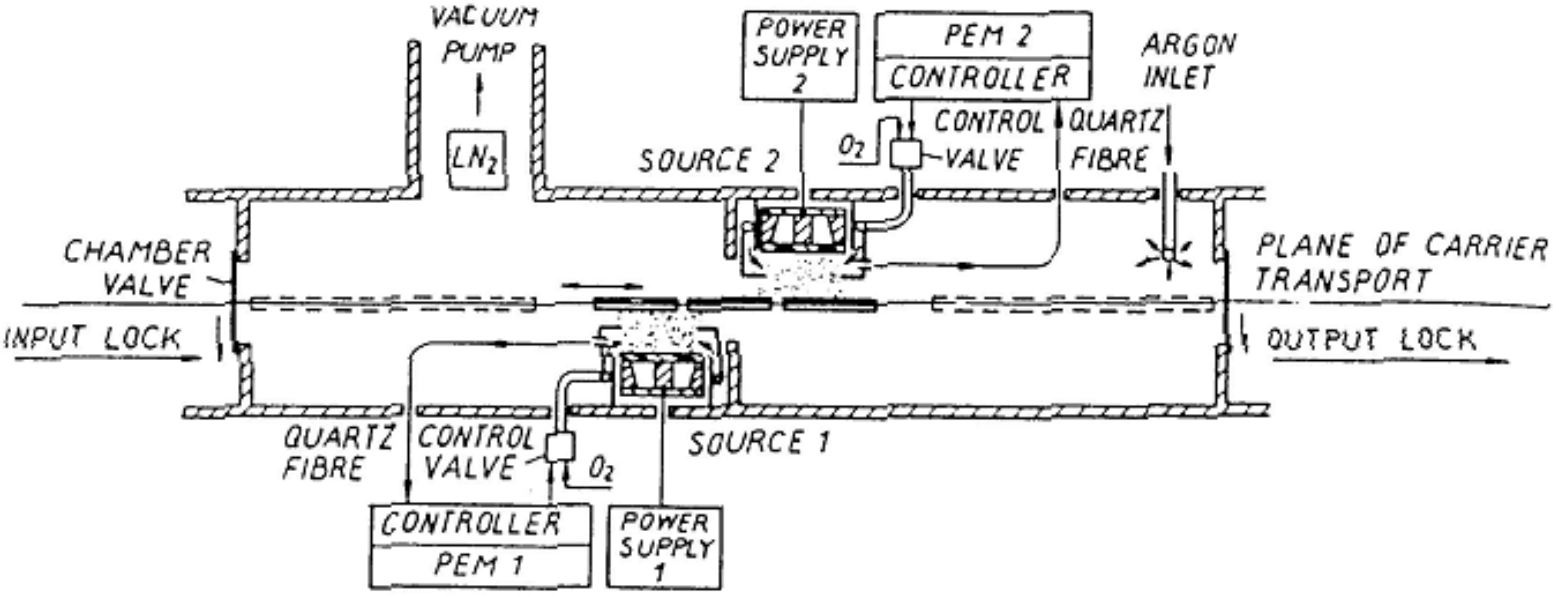
The use of optical plasma spectrometry has shown that the intensity ϕ of a spectral line of the plasma emission, being typical for the target material concerned, is an appropriate parameter for a control loop (Figure 22). Under practical sputter conditions the ϕ signal is a unique function of the metal sputter rate which indirectly includes the reactive gas flow because of its influence on the target coverage.

Figure 22 Arrangement of the plasma-emission monitor for control of a DC reactive sputtering process



As shown in Figure 23, after the plasma emission has been coupled out in the vicinity of the target with the aid of a suitable collimator, it is passed on via a fibre-optics system and a monochromator. The resultant intensity of a characteristic spectral line is converted into a ϕ signal by means of photomultiplier and applied to the PEM controller as the actual value. With the aid of a piezoelectric valve, the PEM controller then adjusts the reactive gas flow to keep the intensity constant. The system shown in Figure 29 has been used for ITO deposition. It is a HZ5-04 in-line sputter plant from VEB Electromat, Dresden (Germany) in which double sided coating is carried out to increase plant productivity. Two PPS-5 magnetron sources with a target size 610 x 160 mm are arranged below and above the substrate carrier of 500 x 500 mm designed to accommodate glass substrate. Each source is equipped with the power supply unit for the sputter source, the reactive gas inlet and manifold, the fibre-optics system and the **PEM** controller. The equipment can give deposition rates of up to 10 nm/s.

Figure 23. In-line sputtering plant for double-sided coating of glass substrates with reactive DC magnetron sputtering process controlled by PEM monitor at both sources.



Other less important problems encountered in large-scale reactive sputtering are:

Arcing

Gillery (PPG Industries Inc.. USA) has reported that in a large system, the whole power of 25 kW power supply can be diverted into an arc[17]. The arcs can adversely effect the equipment and also the cathode surface (localized melting due to a hot spot).

Nodule Formation

As explained earlier, ITO targets when sputtered by argon ions, generate black and high resistivity sub-oxide On the surface:

$$In_2O_3 \longrightarrow \textbf{ion collision} \longrightarrow \quad \textbf{2InO + O}$$

High resistivity oxide sputters at a lower rate and gives rise to nodules. High resistivity impurities in the target matrix can have a similar effect. Gehman et al. (Leybold Materials Inc.. USA) have suggested that there is a correlation between oxide target density and nodule population[18] . Their results indicate that dense targets have lower tendency for nodule formation. The reasons for this are not understood. Formation of nodules has also been observed by Czukor et al. (Courtaulds Performance Films. CA, USA) in DC magnetron sputter roll coater reactive sputtering using a metallic alloy target.[19] One of the targets studied by Czukor developed a layer of black, glassy nodules on the periphery of the magnetron racetrack. Czukor et al. report that the nodules have a much lower sputtering yield than the unmodified metallic target material. It is likely that nodules observed by Czukor are composed of the lower oxide of indium.

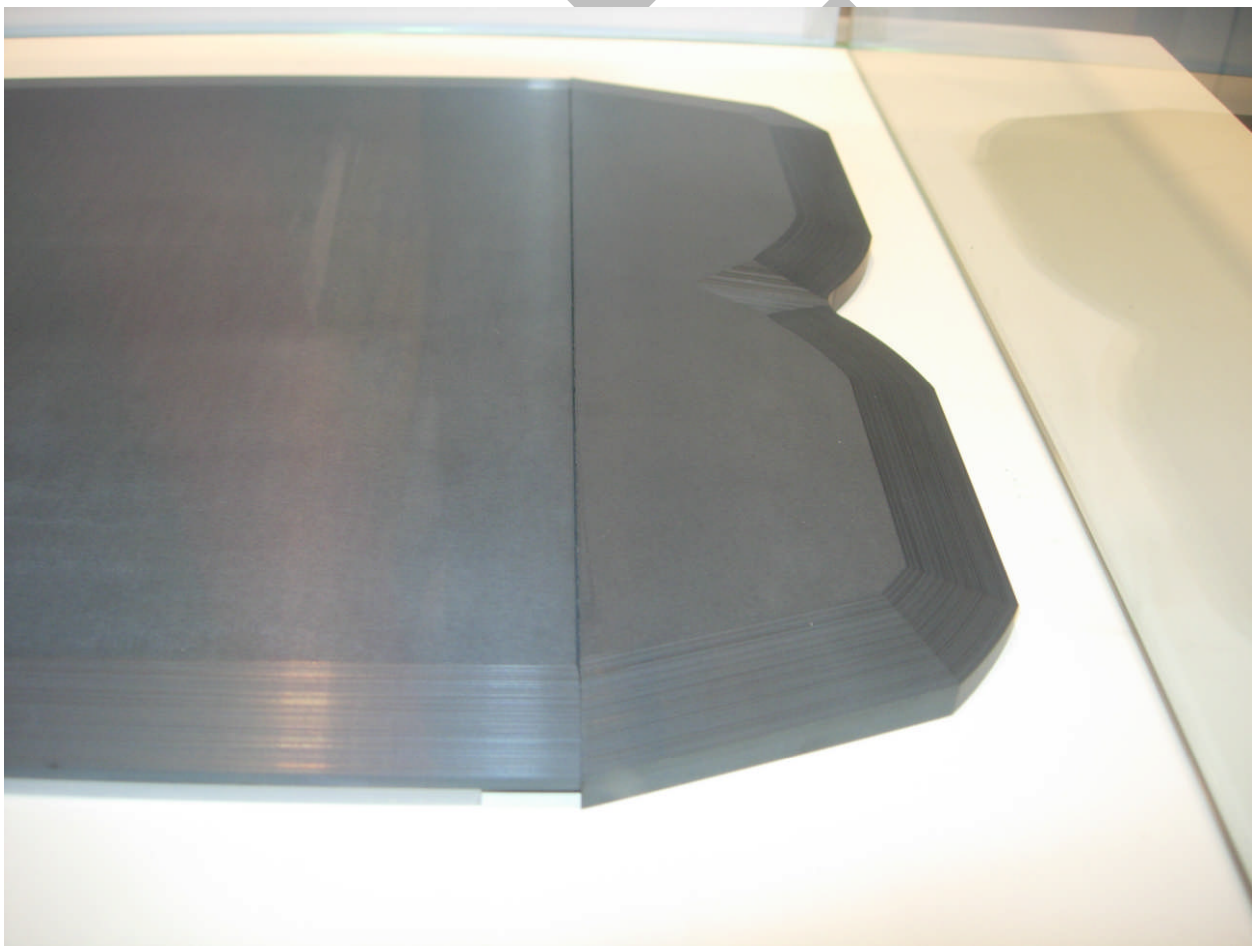
CONCLUSIONS

The market for products utilizing ITO thin films is continuing to grow, despite an often ambivalent world economy, due to increasing demand for LCDs. This trend is likely to continue, for example with the growing popularity of lap-top computers, flat screen desk-top monitors, hand-held gadgets and flat-screen TV's, and the future for ITO manufacturers looks rosy. The only future threat to ITO thin film market may come from

cheaper TCO materials such as doped zinc oxide films, provided that stability of electro--optical properties in zinc oxide films can be attained.

Currently, sputtering is the main method for ITO thin film production. Reactive sputtering using In:Sn alloy target has been a popular method as shown by the plethora of publications on the subject. This is attributed to the unavailability and expense of high quality oxide targets combined with the difficulty of bonding oxide targets to metal backing plates. The process of reactive sputtering is, however, very difficult to control. This method therefore has declined in popularity with increasing availability of high quality ITO targets. Non-reactive sputtering using ITO targets is now the most popular method for ITO thin film deposition due to excellent progress on: (1) optimizing target performance parameters, (2) solving difficulties encountered in non-reactive sputtering, for example, nodule formation. and (3) developing suitable target bonding materials.

TFT LCD Grade ITO



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Appendix 1

Indium Tin Oxide Thin Film Materials

Material Data Sheets

Typical Target Properties	
Composition —SnO_2	10 WT %, 5WT%
Actual Density	6.43g/cm^3 +
Theoretical Density	7.14g/cm^3
Actual % Density	90%+
Bulk Resistivity:	0.22 mOHM-cm
Thermal Conductivity	19.55 mcal/cm-sec- °C
Tensile Strength	12.8 kg/mm^2
Bonding Material	In, In/Sn, In/Bi
Bond Void Ratio	<2.0%

Typical ITO Film Properties	
Thickness	1500-3500 Angstroms
Sheet Resistivity	<20 OHMS/square
Optical Transmission	>85%

Purity Data		
Element	AVG ppmw	Standard Deviation
Si	37	14.8
Zn	24	10.7
Fe	8	3.2
Ca	15	6.6
Mg	5	3.2
Al	4	2.3
Cu	4	1.9
Zr	3	4.2

Total Metallics = 100.5 ppm
Purity = 4N*
All other metallic impurities reported as <1ppm. Data based on averages of 18 production lots.
* Production certification for individual lot is based on 4N ASTM specification.

Typical Process Conditions

Power Density	3.0-7.0 W/cm^2
Operating Pressure	3-5mTorr
Process Gas Flow	30-100 SCCM
O_2 Partial pressure %	0-2%
Target/Substrate Dist.	1.5-4.0"
Substrate Temperature	20°C-350°C
Note: These typical process conditions are meant only as a guide to the use of these materials and are not indicative of the optimum process conditions you can achieve with your system	