Tin doped indium oxide thin films: Electrical properties

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Tin doped indium oxide (ITO) films are highly transparent in the visible region, exhibiting high reflectance in the infrared region, and having nearly metallic conductivity. Owing to this unusual combination of electrical and optical properties, this material is widely applied in optoelectronic devices. The association of these properties in a single material explains the vast domain of its applicability and the diverse production methods which have emerged. Although the different properties of tin doped indium oxide in the film form are interdependent, this article mainly focuses on the electrical aspects. Detailed description of the conduction mechanism and the main parameters that control the conductivity is presented. On account of the large varieties and differences in the fabrication techniques, the electrical properties of ITO films are discussed and compared within each technique. © *1998 American Institute of Physics.* [S0021-8979(98)02705-4]

I. INTRODUCTION

Ever since the first report of transparent conducting CdO films prepared by Bädeker[1] in 1907, there have been remarkable developments in optoelectronics technology, with progress in ceramic materials paralleling electronics developments. Because of the increasing interest in the interactions of light with electricity and electronically active materials, transparent electrically conducting films are particularly attractive. Many new materials and manufacturing techniques have been developed to satisfy stringent technological requirements. The required quality of the films increases with increasing sophistication of the applications. These materials find applications in wide areas such as liquid crystal displays, transparent electrodes of solar cells, and photodetectors. The simultaneous occurrence of high optical transparency (~90%) in the visible region together with electronic conductivity require the creation of electron degeneracy in wide-gap oxides (≥3 eV) by suitably introducing nonstoichiometry and/or appropriate dopants. These conditions can be fulfilled in various oxides of cadmium, tin, zinc, indium, and their corresponding alloys in film form. In view of their practical importance, a great deal of basic research and development have been carried out on the electrical and optical properties of indium oxide based ceramics. Rupprecht[2] carried out one of the first investigations on an In_2O_3 semiconductor. Since then, various manufacturing techniques have been attempted to meet both economic and technological demands. dc and rf sputtering, spray pyrolysis, chemical vapor deposition, and vacuum evaporation are some of the preparation methods currently used. In recent years, solution processes including the sol–gel reaction have arisen as promising techniques for the preparation of materials of technological interest. In particular, considerable attention has been devoted to the study of tin doped indium oxide (ITO) films with the intention of their utilization in technology.

There is also fundamental interest in the conduction mechanism. The association of physical properties with details of the microstructure has been the objective of many solid-state science studies carried out on these films. Such a quantitative correlation requires knowledge of the crystallite size and orientation, as well as of the density of planar, linear, and point defects.[3] Achievement of the lowest possible resistivity is of practical significance in the respect that it provides some flexibility in selecting the film thickness in order to achieve high optical transmission while still retaining low sheet resistance. However, transparency in the visible region is strongly affected by the electrical properties of the film as well. The mechanisms of electrical conduction and optical transmission are very much interdependent.[4] Good electrical properties can be achieved but often at the expense of transmission.

The properties of ITO films are strongly dependent on the preparation method. There is a wide diversity in the reported band gap values as well as the optimized dopant concentration among other properties and parameters. Attempts aimed at understanding the limiting physical phenomena in oxide semiconductors are hampered by the variety of preparation methods. A marked scattering of results is found. Vossen,[4] Jarzebski,[5] Manifacier,[6] Dawar and Joshi,[7] and Chopra *et al.*[8] have reviewed the methods of preparation and the properties of transparent conductors and their importance in thin film technology. They covered the work up to 1983 without being restricted to just ITO films. Hamberg and Grangvist[9] summarized the basic optical properties of oxide semiconductors and discussed their applicability to coatings for obtaining the energy efficiency of windows. This article aims at providing an up to date picture of the work done on the electrical properties of ITO films and identifying important areas for further research. First, general aspects of the electrical properties of ITO including the electrical conduction mechanism and the important factors that determine the carrier concentration and mobility are introduced and discussed. Then, the film properties with respect to the impor-

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tant methods currently used in their preparation are summarized and discussed.

II. ELECTRICAL PROPERTIES: GENERAL ASPECTS

A. Conduction mechanism

Electrical conductivity (σ) depends on the concentration (N) and mobility (μ) of relevant free carrier as follows:

$$\sigma = N\mu e,$$

where e is the electron charge. In order to obtain films with high conductivity, high carrier concentration and mobility should be simultaneously realized.

The electrical properties of the oxides depend critically upon the oxidation state of the metal component (stoichiometry of the oxide) and on the nature and quantity of impurities incorporated in the films, either intentionally or inadvertently. Perfectly stoichiometric oxides are either insulator or ionic conductors. The latter is of no interest as a transparent conductor due to the high activation energy required for ionic conductivity.[4] Effective doping can be achieved provided that the dopant is of the same size as or smaller than the host ion it replaces and that no compounds of the dopant oxide with host oxide are formed.

In_2O_3 has the cubic bixbyite structure in which O^{2-} ions occupy, in an ordered manner, three-fourths of the tetrahedral interstices of a face-centered-cubic In^{3+}-ion array.[10] Indium oxide should have a filled $O^{2-}:2p$ valence band that is primarily oxygen $2p$ in character.[11] The $In:3d$ (Ref. 10) core lies below the valence-band edge Ev. The conduction band is the metal-$5s$ band with an edge Ec about 3.5 eV above Ev.[12,13] The next higher band is the metal-$5p$ band. As prepared, indium oxide generally lacks stoichiometry due to oxygen-array vacancies V_O. At high V_O concentration, a V_O impurity band forms and overlaps Ec at the bottom of the conduction band producing a degenerate semiconductor. The oxygen vacancies act as doubly ionized donors and contribute at a maximum two electrons to the electrical conductivity as shown in the following equation:

$$O_O^X \rightarrow V_O + 2e^- + \tfrac{1}{2}\,O_2(g).$$
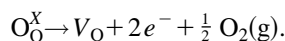
The material composition can be represented as In_2O_{3-x}. In addition to providing conduction electrons, the oxygen vacancies also allow for O^{2-} ion mobility. Therefore, In_2O_{3-x} should be a mixed conductor, having both electronic and O^{2-} ion conduction,[11] although the latter is negligible when compared to the electronic conduction. The electron carrier can be generated by doping it with elements of the valence electron equal to or higher than four. Although there are few reports on the use of Ge,[14–16] Cu,[17] Te,[18] S,[19] Zn,[20–24] Pb,[25] Er,[26,27] and F (Refs. 28–35) (on anion sites), much work has been done on tin-doped indium oxide (In_2O_3:Sn, ITO). Tin acts as a cationic dopant in the In_2O_3 lattice and substitutes the indium. In In_2O_3, since indium has a valence of three, the tin doping results in n doping of the lattice by providing an electron to the conduction band. Therefore, the overall charge neutrality is preserved. Hence, the theoretical maximum carrier density due to only Sn doping is 3.0×10^{20}

$\times C_{Sn}$ (at. %), where C_{Sn} is the tin concentration. However, practically, the carrier concentration does not increase as expected.

B. Carrier concentration

We now want to address the question of the basic conduction mechanism in the ITO films when the density of free carriers is large enough for the assumption of degeneracy to be justified. Most of the efforts made to improve the conductivity of the material have been focused on increasing the effective number of free carriers (N) via doping. Although this method had some success, it is self-limiting. As the dopant atoms occupy random sites in the host lattice, the process of doping certainly impairs the mobility while increasing N. Hence, obtaining the lowest possible resistivity is a trade-off between carrier concentration and electron mobility. The following relation deduced by Johnson and Lark-Horovitz[36] for a complete degeneracy, $\mu = (4\,e/h)(\pi/3)^{1/3}N^{-2/3} = 9.816 \times 10^{14}N^{-2/3}$ (cm^2 V^{-1} s^{-1}), shows that the mobility (μ) and carrier concentration (N) are no longer independent but are governed by a rule $\mu = \propto N^{-2/3}$. This results in an optimum conductivity of the order of 5000 S cm^{-1}. Furthermore, at high dopant concentrations, the observed carrier concentration of ITO films is lower than that expected assuming that every soluble tin atom contributes one free electron. This implies that a portion of the tin remains electrically inactive. Assuming that the higher the tin content the more probable the tin ions occupy the nearest-neighboring anion sites compensating their donor is how Köstlin, Jost, and Lems[37] have explained their experimental results. To elucidate the annihilation effect of two Sn cations, they presented two arguments as follows.

(1) The additional Sn anion changes its valency from $4+$ to $2+$, forming a neutral complex $Sn^{2+}-Sn^{4+}$ with respect to the normal matrix.
(2) The tin pair substituting two neighboring indium atoms strongly binds an additional oxygen, forming a neutral complex which consists of the two Sn^{4+} and the additional oxygen, that is, Sn_2O_4.

Based on Mössbauer spectra which did not confirm the existence of divalent Sn anions at any tin concentration, the second possibility seems to be the more probable. Meng *et al.*[38] supported this view by performing an x-ray photoelectron spectroscopy (XPS) measurements. They showed that the increase in carrier concentration after high temperature annealing is not ascribed to the transition of SnO to SnO_2.

Two more models are considered in literature[39,40] for the compensation of tin donor:

(1) Anion interstitial model: Completely filled cation sublattice with an excess of $\delta/2$ oxygen (O_i) on a quasianion sublattice neutralizing the δ ionized tin donors, formally, $In_{2-\delta}Sn_\delta(O_i)_{\delta/2}O_3$.
(2) Cation vacancy model: Creation of $\delta/3$ cation vacancies (V_{In}) to preserve electrical neutrality, formally, $In_{2-4\delta/3}(V_{In})_{\delta/3}Sn_\delta O_3$.

Frank and Köstlin[41] rejected the second model because they did not notice any increase in film thickness during oxidation as expected. On the basis on the first model they proposed the formation of the following neutral defects.

(1) $(Sn_2^{\cdot}O_i'')$: Two Sn^{4+} ions which are not on nearest-neighbor positions loosely bound to an interstitial oxygen anion. This interstitial defect dissociates on annealing under reducing conditions: $Sn_2^{\cdot}O_i'' \rightleftharpoons 2Sn^{\cdot} + 2e^- + 1/2O_2^{(g)}$.

(2) $(Sn_2O_4)^x$: Two nearest-neighbor Sn^{4+} ions bound to three nearest neighbors on regular anion sites and an additional interstitial oxygen ion on nearest quasianion site. This neutral defect was previously discussed.[37]

(3) $(Sn_2^{\cdot}O_i'')(Sn_2O_4)^x$: Associate of the two above mentioned defects.

Other macroscopic factors to control the doping efficiency were postulated. According to Mizuhashi[42] the high impurity level results in the distorted crystal lattice so that it can no longer be effective either in generating Sn^{4+} ions on substitutional sites or in generating oxygen vacancies. Excessive disorder in the form of an intergranular amorphous phase is also observed.[43,44] Na *et al.*[45] studied the way in which excessive tin oxide affects the properties of ITO films. They observed continuous SnO_2 precipitates along the grain boundaries. Ryabova *et al.*[46] deposited ITO films by the pyrolysis method. The film homogeneity has increased by annealing as a result of the diffusion of tin atoms in the In_2O_3 matrix. As a consequence, the lattice disorder has decreased and hence the mobility in the annealed films increased. Recently, Haynes and Shigesato[47] showed that In^+ implantation into ITO films prepared by conventional electron beam evaporation increases the carrier concentration by simultaneously generating excess vacancies (displacement of atoms from lattice sites during collisions) and stabilizing the excess oxygen vacancies (introduction of cations). However, this process partially deactivates the Sn donors by crystal disorder and a post-implant annealing is thus required. It was also reported[48] that the implantation of H^+ up to 4×10^{16} cm^{-2} improved the resistivity of sputtered ITO films from 0.5 to 9×10^{-4} Ω cm due to the creation of oxygen vacancies. In contrast, a similar study by Shigesato and Paine[49] has shown that the electrical properties of ITO films deteriorates with H^+ implantation. In the former study, the effect of implantation might be in the improvement of the crystallinity rather than in the creation of oxygen vacancies. However, for the latter investigation the films were well crystallized and the implantation may have created some defects. In addition, the implanted ion and the atom to be displaced should be of comparable mass in order to create oxygen vacancies. This is not the case when H^+ is used and the implantation effect seems to be just thermal. Implantation of arsenic and boron[50] was also tried but no significant improvement in conductivity was observed.

Postannealing is known to be very effective in increasing the carrier concentration. The annealing effect can be quite reasonably explained by Frank–Köstlin model. Reports on annealing experiments[51] have used different combinations of temperature and various choices of ambient gas and partial pressure such that a maximum conductivity and visible transmission be obtained. Consequently, the annealing effect and interpretation of the results differ. Bárdos and Libra[52] deposited their films in order to study the effect of vacuum annealing on the electrical and optical properties. The improvement in the electrical properties was attributed to the outdiffusion of excess oxygen atoms from interstitial positions since the decrease in sheet resistance was slower in thicker films.

C. Carrier mobility

The highest reported room-temperature Hall mobilities of $\mu_H \sim 160$ and 170 cm^2/V s were reported by Weiher[53] for In_2O_3 single crystal and by Groth[54] for Zr doped samples, respectively. The electrical properties, namely, the mobility of the ITO films, are strongly influenced by disorder due to the particular structure of In_2O_3,[13,55] and also due to modification of the network[56] as a result of tin doping. As a consequence, there is a strong scattering effect on free carriers. Thereby the mobility is considerably lowered. There are many sources of electron scattering which may influence the electrical and optical properties of the ITO films. Scattering by grain boundaries and acoustical phonons[57] apparently play a subordinate role since in the majority of the cases the mean free path length of electrons is smaller than the crystallite size[58] and because no remarkable temperature dependence was observed between 100 and 500 °C, respectively. Nevertheless, grain boundary scattering[59–63] is sometimes, postulated in ITO films with small crystallite size as an important factor that contributes to the decrease in the mobility. The availability of a wide range of grain sizes[64] and a high electron mean free path are necessary conditions to explain the scattering effect of grain boundaries. In some cases, domain (coalescences of ordered grains) boundaries[65,66] are assumed to affect the mobility rather than the grain boundaries. Domain boundaries of an ITO film might act as a barrier height[67–69] which obstructs the motion of conductive electrons in the conduction band. Therefore, an increase in the Hall mobility might be expected in ITO films with larger domains. In ITO films with good crystallinity electron scattering by dislocations and precipitation[45] is expected to be of little importance. Moreover, the mobility of the free carrier is not affected by surface scattering[70] unless the mean free path is comparable to the film thickness. However, scattering by neutral and ionized impurities as well as the interaction (for closed pair of impurities) of the scattering centers[71] cannot be neglected in degenerate semiconductors with high carrier concentrations.

1. Neutral and ionized impurity scattering

The electrical properties of ITO films prepared by different methods could not be entirely explained in terms of lattice and/or grain boundary scattering as described above. The temperature behavior of the mobility, especially at low temperatures, indicates the existence of other important sources of resistivity. It was pointed out that scattering of the conduction electrons by neutral and ionized impurity centers can drastically affect the conductivity of semiconductors. Using the results of Massey and Moiseiwitch's work,[72] Erginsoy[73] evaluated the resistivity due to neutral impurities which
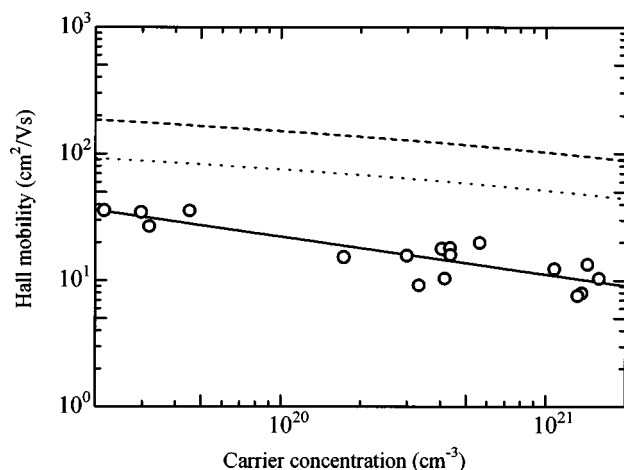
FIG. 1. Hall mobility vs carrier concentration: experimental data (–O–) and calculated mobilities based on scattering by ionized impurities and assuming that all the carriers are due to singly charged tin donor (- - -) or to doubly charged oxygen vacancies (....).

FIG. 2. XRD (θ–2θ) patterns for ITO films grown on a glass substrate (a) and grown on a single crystalline YSZ(001) substrate (b).

should be taken into account particularly in semiconductors with small degrees of ionization. The contribution to the resistivity by ionized impurities was calculated by Conwell and Weisskopf.[74] This theory was later reconsidered by Dingle[75] in order to derive a more refined description of the scattering effect. On the basis of the above mentioned theories, the following relations have been used by several authors[41,49,76–80] to describe the effect of neutral and charged scattering centers on the mobility of degenerate semiconductors:

$$\mu_N = (m^* e^3)/(20\epsilon_0\epsilon_r h^3 N_N), \tag{1}$$

$$\mu_I = [24\pi^3(\epsilon_0\epsilon_r)^2 h^3 n]/[e^3 m^{*2} g(x) z^2 N_I]. \tag{2}$$

The screening function $g(x)$ is given by

$$g(x) = \ln(1 + 4/x) - (1 + x/4)^{-1},$$

where

$$x = (4e^2 m^*)/[4\pi\epsilon_0\epsilon_r h^2 (3\pi^5)^{1/3} n^{1/3}],$$

where n is the carrier concentration, Z is the charge of the ionized centers, ϵ_0 is the permittivity of free space, m^* is the effective mass of the free electrons, and ϵ_r is the low-frequency relative permittivity. For ITO the m^* and ϵ_r values can be taken as 0.3 m_0 (Refs. 9 and 77) and 9,[9] respectively. μ_N and μ_I are the mobilities due to neutral and ionized impurities, and N_N and N_I are the density of neutral and ionized scattering centers, respectively. The total mobility μ_T can be taken as the reciprocal sum of μ_N and

$$\mu_I : 1/\mu_T = 1/\mu_N + 1/\mu_I. \tag{3}$$

The measured Hall mobility (solid line) of dip coated ITO films as a function of the carrier concentration is plotted in Fig. 1. The dotted and dashed lines approximate the calculated mobilities due to ionized impurities μ_I [Eq. (2)] assuming that the conducting carriers originate entirely from either doubly charged oxygen vacancies or singly charged tin, respectively. Within the experimental errors, the slopes of the calculated and experimental mobilities versus carrier
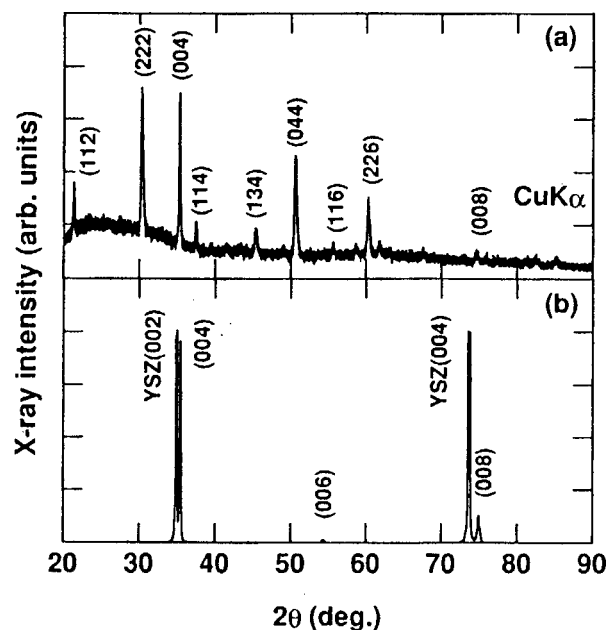
concentration are in good agreement. Therefore, scattering at ionized centers seems to be the most determinant and appropriate mechanism by which to elucidate the mobility behavior in the present films. The relatively lower measured mobilities, especially at high doping concentrations, might be due to the interaction of scattering centers[71] and/or formation of neutral scattering defects that should be taken into account.

2. Crystallographically oriented thin films

In order to improve the conductive carrier mobility, attention has been focused on developing preferentially oriented In$_2$O$_3$ and ITO thin films grown on insulating single crystal substrates such as MgO and yttria-stabilized zirconia (YSZ)[81–83] and on a semiconducting ZnO layer[84] coated on soda-lime glass. Since the crystal quality of heteroepitaxial film is far more idealized (excellent crystal orientation with no large angle grain boundaries) compared with that of randomly oriented polycrystalline films especially coated on amorphous substrates, it is very effective for clarifying the intrinsic conduction mechanism of ITO film. However, a proper substrate with lattice and thermal match is essential for the heteroepitaxial growth of thin films. In order to clarify the conduction mechanisms of ITO films, Kamei et al.[85] established heteroepitaxial growth. In their study, thin films of ITO (10 wt % SnO$_2$) were deposited on an optically polished single crystalline YSZ (Ref. 86) and SiO$_2$ coated soda-lime substrates using a conventional dc magnetron sputtering system.[87] The lattice matching between YSZ (cubic structure, lattice constant $2a_{YSZ} = 10.2$ Å) and ITO (cubic bixbyite structure, $a_{ITO} = 10.1$ Å) is excellent and the lattice mismatch is smaller than 1%. Hence, heteroepitaxial growth of ITO films could be realized on the single crystalline YSZ substrates. Figure 2 shows the x-ray diffraction XRD patterns of the ITO films deposited on both substrates.

TABLE I. Hall mobility, carrier density, and resistivity for the ITO films grown on glass substrate and single crystalline YSZ substrate under identical deposition conditions.

	Hall mobility ($cm^2/V\,s$)	Carrier concentration ($10^{20}\ cm^{-3}$)	Resistivity ($10^{-4}\ \Omega\ cm$)
Glass substrate	41	7.5	2.0
YSZ substrate	39	7.3	2.2

As clearly seen from Fig. 2, the ITO film on the (001) YSZ single crystal is perfectly oriented with the ⟨001⟩ axis normal to the substrate surface. In the case of the film on the SiO_2-coated soda-lime glass substrate the integrated intensity ratio of the (004) peak to the (222) peak was 1.0, while the values for the random orientation by the American Standard of Testing Materials (ASTM) was 0.33, which indicates a partially preferred orientation of the ⟨004⟩ axis normal to the substrate surface. The room-temperature resistivity ρ, Hall mobility μ, and carrier density n are shown in Table I for both ITO films. By comparing the electrical properties of the epitaxial ITO film with those of the polycrystalline film grown on the glass substrate, Kamei *et al.*[85] concluded that neither large angle grain boundaries[65] nor the crystalline orientation were revealed to be dominant electron scattering factors in ITO films. Electron scattering at point defects such as ionized impurity scattering and/or neutral impurity scattering is deduced as being the major obstacle for electrical conduction in ITO films. Recently, ITO films were epitaxially grown on the (100) face of yttrium-stabilized zirconia[88] by reactive dc magnetron sputtering of metallic indium with 9 mol % tin, and an unusual crystallite size of 270 nm was reported for the 300 nm thick film although the electrical properties were not given. Recently, the electrical properties of ITO films in association with the crystallite orientation were investigated.[84] The ITO films were deposited by a rf magnetron sputtering apparatus onto ZnO(001) precoated soda-lime glass and native glass substrates for comparison. Although the (111) preferred orientation could be achieved, there was no difference in resistivity, indicating the isotropic electrical properties of cubic In_2O_3. These results are consistent with those already reported.[85] The results obtained for ITO films deposited on single crystal Al_2O_3 (Ref. 89) by rf sputtering suggest that the electrical properties of the thin films do not depend significantly on the crystallographic orientation and the substrate material.[89,90]

Tarsa *et al.*[91] investigated the growth of preferentially oriented In_2O_3 films on InAs, GaAs, MgO, and yttria-stabilized zirconia substrates using pulsed laser deposition (PLD). Resistivities on the order of $5 \times 10^{-4}\ \Omega$ cm were measured for In_2O_3 deposited on both MgO and YSZ substrates. The Hall mobility measured for a 350 nm thick film on YSZ was about 50 cm^2/V s which corresponds to an electron concentration of around $5 \times 10^{19}\ cm^{-3}$. The low resistivity of the In_2O_3 oriented films was attributed to oxygen deficiency. Although the crystallographic orientation of the films prepared by sputtering did not affect the electrical properties, some improvement may be expected for ITO films prepared by less energetic methods, such as the sol–gel process.

III. DEPOSITION METHODS AND FILM PROPERTIES

A. Evaporation

1. Source material

For the preparation of ITO films using the evaporation method, many alternatives are available with respect to the source. For evaporating In_2O_3/SnO_2 powder using electron beam evaporation, thermal evaporation of metallic indium covered with In_2O_3 powder and direct thermal evaporation of metallic indium and tin in an O_2 ambient are commonly used. For the latter, since the indium has a significantly higher vapor pressure than that of tin, it will be preferentially vaporized, causing a change in the composition of the Sn+In liquid alloy with time. In turn, this will cause the vapor composition and consequently the ITO composition to change during the deposition. Therefore, in order to overcome this, Jan and Lee[92] proposed vaporizing a small amount of the sample each time, not enough to significantly change the composition of the vapor. Yao *et al.*[93] alternately evaporated pure indium and tin onto substrates kept at room temperature from two crucibles. The two crucibles were independently controlled to avoid stoichiometric deviation and other effects that can possibly occur when a single source is used. The as-deposited layers were subsequently annealed (at less than 200 °C) in air to improve their optical and electrical properties. Thus, an electrical resistivity of $4 \times 10^{-4}\ \Omega$ cm was obtained.

A mixture of In_2O_3 powder and metallic In (approximately 90% In_2O_3 and 10% In by weight) was also used as the source material. It was found that the incorporation of metallic indium in the evaporation source enhances the evaporation rate and significantly improves the electrical properties of the films. Pure indium oxide with electrical properties comparable to ITO films has been produced by thermal evaporation.[94] The roles that the additional metallic indium plays in the evaporation kinetics and its contribution to the film properties were not clarified. However, it can be argued that, if the coevaporated indium plays a nontrivial role in the evaporation kinetics, it is probably related to the quantitative ratio of the chemical species involved. This conclusion is supported by the work of Huang *et al.*[95] who deposited highly conductive ITO films using an In–Sn alloy plus In_2O_3.

2. Oxygen partial pressure

The oxygen partial pressure during deposition was found to play a crucial role in the growth process. Ovadyahu *et al.*[96] studied the electrical properties of pure In_2O_3 thin films deposited at different O_2 partial pressures. They noticed that a clear tendency towards a dendritic growth is observed once the O_2 partial pressure is lowered below the nominal pressure. This tendency was attributed to the lack of building material which forces the growing crystal to maximize its surface to volume ratio. The film with the dendritic structure had poor electrical properties. Powdery deposition of In_2O_3 with poor adhesivity[97] was recently observed when the O_2

partial pressure is lowered. On the other hand, too high O_2 pressure results in films with too few oxygen vacancies to act as charge carriers. The critical role of the partial O_2 pressure can, thus, be explained as resulting from the conflicting requirements of introducing enough oxygen vacancies without creating too many grain boundaries in the process. Banerjee *et al.*[98] investigated the effect of oxygen partial pressure on ITO films prepared by electron beam evaporation from a hot pressed powder of 90% In_2O_3–10% Sn_2O_3 by weight. For a fixed substrate temperature ($T_s = 250\,°C$), increasing the oxygen partial pressure up to 2×10^{-5} Torr resulted in (i) a decrease in resistivity and carrier concentration, (ii) enhanced Hall mobility, and (iii) improved transmittance. The decrease in carrier concentration might be due to the dissipation of oxygen vacancies.

3. Film thickness

When the film thickness decreases below a critical value, the electrical properties of the indium oxide and ITO films were found to deteriorate drastically. This value differs depending on the control parameters of the process. The film properties stabilize above a certain film thickness. Jan and Lee[92] deposited ITO films by direct coevaporating metallic indium and tin using a molybdenum (Mo) boat onto a heated glass substrate. A rapid increase of resistivity for decreasing film thickness below 50 nm was attributed to (i) increased importance of carrier scattering from the outer surface of the film due to surface roughness, (ii) greater density of grain boundaries due to decrease in grain size, and (iii) film discontinuities attributed to the formation of islands[99] and extensive voids. *In situ* measurement of thin film conductance showed that it significantly varies as a function of the substrate coverage.[100–103] *In situ* resistance measurement was used by Korobov *et al.*[103] who showed that the growth of ITO films goes through different stages of tunneling, percolation, and linear ohmic growth. Island formation from nucleation sites is proposed as the cause.[104,105] Sun *et al.*[105] observed that in the initial period of deposition the film does not conduct. This was attributed to the formation of sufficiently isolated islands of ITO. As the film thickness rises, a sudden onset of conductivity is noticed. The critical thickness was defined as the nominal thickness of the film at the onset of the conductivity. In line with these results, a topographic investigation[106] on ITO films deposited by reactive electron beam method revealed that the film surface has formed as a result of the coalescence of islands with varying sizes.

4. Substrate temperature

The majority of the preparation methods currently used involve a relatively high substrate temperature ($\geqslant 300\,°C$) in order to obtain thin films with a reasonably good conductivity. This requirement may be restrictive for some applications, for example, for flexible electro-optical devices, heterojunction solar cells, and photovoltaic devices based on amorphous silicon which may seriously deteriorate at elevated temperature.[107] Reasonably good conductivity is easily and reproducibly obtained using pure In_2O_3 and ITO

TABLE II. Comparison of electrical properties of normal and zone-confining (5.1 at. % Sn) specimens.

Electrical properties	Normal specimen	Zone-confining specimen
Resistivity (Ω cm)	6.8×10^{-4}	4.4×10^{-5}
Carrier density (cm^{-3})	5.7×10^{20}	13.8×10^{20}
Mobility (cm^2/V s)	16	103
Mean free path (nm)	17	147

films for low substrate temperatures by electron beam evaporation. Increasing the substrate temperature to 250 °C has no apparent advantage for either the electrical conductivity or the transparency of the films.[96] It has been reported by Holland[108] that the vacuum species observed when In_2O_3 is evaporated from a nonreactive support such as an electron beam gun contain more In than its oxide. When In_2O_3 is evaporated from Al_2O_3 crucibles, In_2O, In, and O_2 in descending order of abundance were observed.[109] Motivated by the work of Pan and Ma[110] who attributed the high quality of their In_2O_3 films to the inclusion of metallic In in the thermal evaporation process, Agnihotry *et al.*[111] prepared pure In_2O_3 and ITO films by electron-beam evaporation at a relatively low substrate temperature of 200 °C. Good In_2O_3 and ITO films could be obtained at an even lower substrate temperature of 150 °C.[96,112–114] A rapid deterioration of the film properties takes place if the substrate temperature is further lowered.[113] The improvement in the film quality, although deposited at low temperature, was thought to be due to energetic particle bombardment of the substrate or a different vapor composition in the electron-beam case compared to that in thermal evaporation. Additionally, the relatively low resistivity observed for low substrate temperature films might be due to other factors such as good contact between crystallites.[42]

In contrast, for the ITO films prepared by activated reactive evaporation, Nath *et al.*[115] have shown that low deposition temperatures lead to stoichiometric oxide films. The decrease in resistivity with increasing deposition temperature may be due to the enhancement of oxygen vacancies in the film and/or to a change in the microstructure and crystallinity of the films.[116] In the case of ITO films, the effects of the substrate temperature and the tin concentration seem to be interdependent. Ovadyahu *et al.*[96] found that a high concentration of the dopant results in films of very poor quality unless the substrate temperature is increased to 300 °C. The source of the problem is connected with the presence of a quasiamorphous phase identified as Sn_3O_4. Either an increased substrate temperature or a reduced SnO_2 content was found to be effective in eliminating the problem. An increase in deposition temperature helps to increase the carrier concentration by favoring Sn^{4+} incorporation into the In^{3+} sites and as a result disorder induced by doping[42] is reduced, increasing the mobility.

Of special note are reports by Rauf,[3,117,118] who deposited ITO films by electron-beam evaporating indium and tin oxide powders using a zone-confining process. This process is based on the creation of a temperature gradient over various parts of the substrate. Table II shows the electrical prop-

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TABLE III. Experimental parameters used for evaporation technique. (RE—reactive evaporation; TE—thermal evaporation; EBE—electron-beam evaporation; ARE—activated reactive evaporation; and VE—vacuum evaporation.)

Film material	O_2 pressure (Torr)	Deposition rate (Å/min)	Source–substrate separation (cm)	Substrate temperature (°C)	Deposition method	References
In_2O_3	10^{-4}	⋯	30	400	TE	42
In_2O_3	$5-20\times10^{-5}$	15–30	⋯	320–350	TE	110
In_2O_3	$2-6\times10^{-4}$	30	50	~150	EBE	96
In_2O_3	1×10^{-3}	180	⋯	200–400	RE	144
ITO	10^{-4}	⋯	30	400	VE	42
ITO	10^{-4}	20–40	⋯	300	TE	92
ITO	0.08	40–50	⋯	250	EBE	3
ITO	0.08	50–50	⋯	300	EBE	3
				(average)		
ITO	1.5×10^{-4}	96	⋯	200	EBE	111
ITO	$2-6\times10^{-4}$	30	50	~150	EBE	96
ITO	3×10^{-4}	600	⋯	350	EBE	200
ITO	⋯	400	⋯	370	ARE	115
ITO	$1-2\times10^{-4}$	40–60	15	~300	RE	198
ITO	$1-2\times10^{-4}$	60–300	⋯	Room temperature-200	RE	199

erties of the zone-confined specimen and the normal specimen prepared under identical conditions with uniform substrate temperature distribution of 250 ± 3 °C. The specimen with 5.1 at. % tin prepared under zone-confining arrangements had a resistivity of 4.4×10^{-5} Ω cm, lower than the 7.0×10^{-5} Ω cm for ITO films prepared by reactive evaporation[115] and the 6.8×10^{-5} Ω cm for the films prepared by the magnetron sputtering technique.[119] Details regarding sample reproducibility were not given. The low resistivity was attributed to the considerably high mobility which is directly correlated to the microstructure. Grains within a zone are oriented in the same direction and boundaries separating them are twin boundaries or are of the type which are very relaxed and cause the least amount of scattering to the mobile electron.[3] This may explain the improvement in the distance that electrons can travel before being scattered and as a consequence the high mobility. Thilakan and Kumar[97] have recently examined the substrate-influenced effects on the structural and electrical properties of the reactive thermally deposited In_2O_3 and ITO thin films on InP substrates. Films with high porosity and low adhesivity were observed for films deposited at a substrate temperature of 50 °C. More compact and adherent films were obtained when the deposition temperature was raised. The substrate heating rate was found to affect the microstructure and thereby the electrical properties of the deposited films.

From the above it can be concluded that the substrate temperature required to prepare ITO films with optimized electrical properties depends strictly on the deposition method. Although the reactive thermal and electron beam evaporation techniques are essentially the same in concept, there seem to be appreciable differences in the film properties. An anticipated advantage of the electron-beam technique over thermal evaporation is that the tin concentration in the film closely corresponds to that in the starting material.[61] A deposition temperature as low as 150 °C is enough in the case of electron-beam evaporation whereas a temperature higher than 300 °C is essential for thermally or reactively evaporated films. Owing to the low deposition temperature, the electron-beam evaporation technique may be suited to deposition onto plastics. Tables III and IV, respectively, give the process control parameters and electrical results reported by various authors.

B. Sputtering

The sputtering method is one of the most extensively used techniques for the deposition of ITO films. The properties of rf sputtered ITO films are sensitive to sputtering parameters, namely, oxygen content in the sputtering gas, target to substrate distance, substrate temperature, postdeposition treatment, film thickness, and target quality including its density and purity. The development of high performance magnetron sputtering sources that provide (i) relatively high deposition rates, (ii) large deposition areas,[66,87,120–127] and (iii) low substrate heating revolutionized the sputtering process by greatly expanding the range of feasible applications.[128] Films prepared by magnetron sputtering were found to be less damaged[129] than those prepared by ordinary diode sputtering methods. The relatively higher carrier concentration of sputtered films may be due to the knocking out of oxygen atoms by energetic neutrals. Table V gives the electrical properties of ITO films prepared by this technique.

1. Reactive sputtering

Reactive sputtering is more directional than reactive evaporation which limits the waste of expensive source materials. The sputtering rates are also relatively easy to control. Another important advantage of the sputtering process is that the composition of a sputter-deposited film tends to be the same as that of the target, provided that (i) the target is maintained sufficiently cool to avoid bulk diffusion of the constituents (especially severe in a low-melting alloy target like In–Sn), (ii) the target does not decompose, (iii) reactive

TABLE IV. Electrical properties of In_2O_3 and ITO films prepared by vacuum evaporation.

Film material	Resistivity (Ω cm)	Carrier mobility (cm^2/V s)	Carrier concentration ($\times 10^{20}$ cm^{-3})	Sheet resistance ($\Omega/\square$)	References
In_2O_3	4 ± 10^{-4}	72	4	···	42
In_2O_3	$\sim2\times10^{-4}$	70	4.69	6.75	110
In_2O_3	$8-16\times10^{-4}$	60–95	0.5–1.1	···	96
In_2O_3	$2-3\times10^{-3}$	25–60	0.35	···	114
ITO	2×10^{-4}	30	10	···	42
ITO	1.8×10^{-4}	30	10	15	92
ITO	6.8×10^{-4}	16	5.7	···	3
ITO	4.4×10^{-5}	103	13.8	···	3
ITO	2.4×10^{-4}	30	8	···	111
ITO	$1.5-10\times10^{-4}$	45–70	2–6	···	96
ITO	···	18	40	23	200
ITO	7.0×10^{-5}	20–30	~10	···	115
ITO	3×10^{-4}	···	···	···	198
ITO	···	···	···	50	199

contaminants are not present, (iv) the gas-phase transport of the components is the same, and (v) the sticking coefficients for the components on the substrate are the same.[130] Although the best ITO coatings are deposited using this technique, this procedure does not allow the control over the In/Sn ratio in the films that does chemical vapor deposition does.[41,121,131,132] Reduced yields in reactive sputtering attributed to compound formation are commonly observed. Sputtering in a pure O_2 produces a thin film of In_2O_3 and SnO_2 on the In–Sn target surface[133,134] especially at high oxygen partial pressure. The sputter rate substantially drops since oxides usually sputter more slowly than metals.[135,136] As a result of the difference in the volatility and sputter rates of these oxides, an enrichment of the film in indium is observed. Therefore, the film composition deviates from that of the target. Additionally, the surface topography that develops on the target can be significantly influenced by ions/surface interaction. Because of the difference in the sputter yields of metallic materials and their corresponding oxides, the deposition rate is very sensitive to the change in the oxidation state of the target. Therefore, control of the oxidation state of the target surface is a primary factor to be considered in the deposition of ITO thin films with good physical properties. The transition of the target state from oxidized to metallic strongly depends on the discharge parameters since the discharge power and the reactive gas partial pressure determine the sputter rate at the target surface and the oxidation rate of the target, respectively. Generally, oxygen is introduced near the substrate in order to reduce target oxidation. The problem of hysteresis due to the poisoning of the sputtering cathode by reactive gas and the instability of the system to simply control the flow of the reactive gas is now well documented and modeled.[137] Prior to the film deposition, a presputtering treatment[129,138–140] of the target surface is sometimes required to avoid eventual contamination.

Pure O_2 and a mixture of O_2 and Ar or N_2 are usually used as the sputtering gas. The use of inert gas ions avoids chemical reactions at the target and substrate. Accordingly, Ar is often used because of its mass compatibility with materials of engineering interest and its low cost.[130] A narrow range of partial pressures of oxygen which will allow the reactive sputtering of conducting and transparent oxide films from the In–Sn alloy was reported. Pure oxygen was used[141] to deposit insulating In_2O_3 using dc magnetron sputtering. Possible use of these films as barrier layers in tunnel junctions was investigated. H_2 and H_2O are sometimes introduced in order to reduce the target and/or the film. Rottmann and Heckner[142] deposited their films from a 80%–20%

TABLE V. Electrical properties of ITO films prepared by the sputtering technique. (DCMS—dc magnetron sputtering; RFMS—rf magnetron sputtering.)

Preparation method	Resistivity (Ω cm)	Carrier concentration (10^{20} cm^{-3})	Carrier mobility (cm^2/V^{-1} s^{-1})	Deposition temperature (°C)	Annealing temperature (°C)	References
DCMS	1.63×10^{-4}	9.28	41.0	350	···	87
DCMS	5.46 ± 10^{-4}	7.13	16	Room temp.	No annealing	159
DCMS	1.46×10^{-4}	10.1	~40	400	500	201
DCMS	3.7 ± 10^{-2}	7.0	24.5	235	No annealing	203
RFMS	6.8 ± 10^{-5}	36	27	370	No annealing	119
RFMS	6.9 ± 10^{-3}	···	···	···	···	38
RFMS	$\sim4\times10^{-4}$	···	···	Unheated	No annealing	123
RFMS	1.3×10^{-4}	···	···	300	350	202
RFMS	2.55 ± 10^{-4}	15.9	15.4	Unheated	400	165
RFMS	1.38×10^{-3}	2.6	17.39	Unheated	500	139

In–Sn target using pure H_2O vapor as the reactive dc sputtering atmosphere. The dc H_2O-sputtered ITO films exhibit their minimal resistivity of $\rho = 5 \times 10^{-4}$ Ω cm immediately after deposition at a substrate temperature of 350 °C. These films had a large amount of oxygen vacancies which were attributed to hydrogen produced during the sputtering process according to the following reaction:

$$2In + 6H_2O \rightarrow 2In(OH)_3 + 3H_2.$$
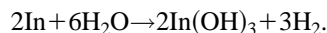
The hydrogen reduced the formed oxide and no postannealing was required. This might be due to the high deposition temperature. In contrast, the introduction of water to the arc plasma-assisted electron-beam evaporation process[143] resulted in a decrease in transmittance and an increase in resistivity due to the decrease in mobility. The films had low damage and a less oxidized structure.

When sputtered at low temperature substrates, the deposited films are usually amorphous and/or opaque with low conductivity because of their disordered structure.[9,96,144–146] Generally, to fabricate ITO films with satisfactory electrical and optical properties by reactive sputtering from a metal alloy target, either an increase in substrate temperature or a postpreparative annealing[60,120–123,138,139,146–148] in air or in an oxygen free environment is needed. With annealing, the ITO films become increasingly degenerate and more conductive. Meng and Dos Santos[139,149] rf sputtered an In–Sn (90–10) alloy target in an $Ar + O_2$ mixture. The deposited films were annealed at 500 °C for varying times. As the annealing time is varied, the x-ray peak intensity ratio of (222) to (400) varies. The film with higher intensity ratio has higher Hall mobility and hence lower resistivity. The carrier concentration was not affected by the annealing time.

However, certain kinds of flat panel display devices must be processed at low temperature. In the case of ITO films on a color filter in a liquid crystal display the deposition temperature is limited to 200 °C because of the low thermal resistance of the organic filter. The deposition temperature should not exceed 200 °C when polyethylene teraphythalate, acrylic, and other organic polymers are used as substrates. Furthermore, for applications involving the deposition of ITO onto silicon substrates the temperature related processing steps are a critical parameter that can result in poor electrical contact between the ITO film and the Si substrate;[150,151] formation of SiO_2 has been observed at the film–substrate interface at high temperature (~ 400 °C).[152] Chiou and Hsieh[140] rf sputtered ITO films onto acrylic substrates. The substrate temperature was kept below 65 °C and the sputtering power was 18 W to prevent deformation of the acrylic resin. The adhesion strength between the film and the substrate was ameliorated by reactive ion etching of the substrate. The film resistivity was 4.4×10^{-3} Ω cm which is more than 10 times higher than that generally obtained by sputtering. Karim et al.[153] used a modified reactive magnetron sputtering technique to deposit ITO films onto polymeric substrates at room temperature. For a given operating condition, the film electrical properties could be controlled by a dc probe voltage. Films prepared under optimized conditions have sheet resistances lower than 10 $\Omega/\square$ and resistivities of 6×10^{-4} Ω cm.

2. Sputtering of oxide targets

Sputtering from an oxide target allowed better control of the film stoichiometry and distinctly minimized diffusion problems. Hot-pressed target of pure or mixed oxides are generally used. The porosity of the target determines its susceptibility to contamination. Since In_2O_3 is quite a hygroscopic material, its contamination by water is likely to occur. Generally, less light scattering[154] was observed in ITO films obtained from the dense targets. The increase in target density was found to be very effective in suppressing black nodule formation[155] on the target and in ameliorating the composition uniformity.[156] Therefore, dense targets are required for the deposition of films with better qualities. Recently, Nadaud et al.[157] investigated the influence of TiO_2 additives on the sintering behavior of In_2O_3 ceramics. A density of 98% was obtained by adding 1 wt % TiO_2. The densification temperature was also lowered. The development of an ultrahigh density target of more than 99% in relative density has been lately reported.[158] Using this target, a resistivity as low as 1.5×10^{-4} Ω cm could be obtained by sputtering at a substrate temperature of 200 °C.

Beside O_2 and Ar, H_2O and H_2 were also introduced in certain proportions. Ishibashi et al.[159] reported that the partial pressure of H_2O affects the properties of ITO films prepared by dc magnetron sputtering. The addition of 2 $\times 10^{-5}$ Torr H_2O gas during ITO sputtering onto 200 °C or lower substrate temperatures increases the carrier concentration and improves the reproducibility. The addition of oxygen has been found to enhance the crystallization[129] of the films regardless of the substrate temperature. Conforming to solar cell processing technology, Aperathitis et al.[160] deposited antireflective ITO coatings by rf sputtering on room temperature GaAs substrates substrates and without the introduction of O_2 into the plasma. At a given pressure, higher rf power delivered to the target (90% In_2O_3 + 10% SnO_2) resulted in films with lower electrical resistivity. This might be due to the removal of oxygen from the forming oxide.[138,160–162]

As a consequence of the high kinetic energies of the sputter-ejected species, the substrate and also the growing film may be subjected to the bombardment of low-energy particles of accelerated host lattice species, dopants, and energetic particles being backscattered from the target. Thus, ion/surface interactions are not only important at the target, but they can also play a decisive role in determining film nucleation and growth kinetics, microstructure evolution, dopant incorporation, and hence the electrical properties of the films.[130] In addition, the heating associated with electron bombardment often prohibits the use of thermally sensitive substrates. Shigesato et al.[87] prepared ITO films by conventional dc magnetron sputtering. The films had many crystallographic faults caused by the bombardment of high energy particles increasing the electrically inactive dopants trapped at structural defects. Films with lower damage and resistivity of 1.34×10^{-4} Ω cm were obtained by applying a stronger magnetic field. Ishibashi et al.[163] reported that the lower the sputtering voltage, the less the damage is in ITO films. Bullette and Kelley[164] related the number of defect sites to the

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method of deposition and especially to the deposition temperature. Nanto et al.[165] studied the electrical and optical properties of rf sputtered ITO films from pressed powder in an Ar+O$_2$ mixture under an applied external magnetic field. Under optimum sputtering conditions, the films had high carrier concentration and were highly conducting as deposited. When deposited on high-temperature substrates (350 °C), the lower resistivity was obtained when using an In$_2$O$_3$-10 wt % SnO$_2$ target, whereas in the deposition on low-temperature substrates (below 140 °C), the film with lowest resistivity was obtained from an In$_2$O$_3$-5 wt % SnO$_2$ target. The characteristic feature of the films deposited on high-temperature substrates is a relatively high mobility although the films deposited on low-temperature substrates had high carrier concentration and relatively low mobility. Lee et al.[151] deposited ITO films from a sintered mixture of 10% SnO$_2$ and 90% In$_2$O$_3$ by weight using the magnetron sputtering system. The room-temperature deposited films were found to be sensitive to the oxygen concentration and the total sputtering pressure. ITO films deposited in 0.7% oxygen had a resistivity of 8.2×10^{-4} Ω cm.

When ejected, the target atoms or molecules are subjected to collisions with ambient gas atoms and with other sputtered atoms resulting in a partial loss of energy and direction during their transit to the substrate. The motion of both ions and sputtered atoms is thus impeded by the working gas atmosphere. When their energy is reduced to thermal energy (kT) the sputtered species are said to be thermalized. The transport of atoms from the thermalization region to the substrate is achieved by diffusion under a concentration gradient. Therefore, the adjustment of the target to substrate distance strongly affects the deposition rate. Several researchers[123,161] have discussed the effect of target–substrate distance on the physical properties of rf sputtered ITO films under various deposition parameters. They concluded that the thermalization distance increases by increasing the rf power since it results in sputtered neutrals of higher initial energy. At a given rf power the thermalization region shifts towards the target by increasing the sputtering pressure. The same trend was observed when O$_2$ partial pressure was increased. This resulted in the oxidation of the target,[166,167] possible resputtering of the film,[168] and/or stoichiometry deviation.[168] Ray et al.[119] deposited ITO films using a disk of hot-pressed powder with the composition 90% In$_2$O$_3$–10% SnO$_2$. They found that a variation of the spacing between the substrate and target from 5 to 15.5 cm did not lead to significant change in the resistivity of the magnetron sputtered ITO films.

C. Chemical vapor deposition

Chemical vapor deposition (CVD) is a process in which a chemical reaction involving gaseous reacting species takes place on, or in the vicinity of, a heated substrate surface. Materials with different properties can be grown by varying the experimental conditions. The main controlling parameters are the substrate temperature, substrate material, composition of the reaction gas mixture, gas flow, total pressure, and the geometry of the deposition system. The gas flow and the apparatus geometry determine the uniformity of the deposited films over large areas. The substrate temperature and gas flow control the deposition rate. Organometallic reagents are sometimes used as the vapor source. InCl$_3$ (Refs. 169 and 170) is also used as indium precursor for the preparation of ITO films. These starting materials should be volatile, stable, preferably low cost, have high vapor pressure below the decomposition temperature and decompose at higher temperatures. The properties of different transparent conducting oxides prepared by CVD were recently compared.[171]

The CVD technique has the advantage of being cost effective with respect to the apparatus. It enables the production of coatings with good properties even on substrates of complicated shapes without the use of high vacuum. In particular, atmospheric pressure CVD (APCVD) is attractive in many applications in the sense that it offers high deposition rates and hence short process time. However, since CVD processes are based on interfacial chemistry, they are sensitive to contamination. The major limitations of the process are the small areas of uniform coatings and the cost of the starting reagents as in the case of indium compounds. The reaction mechanisms in CVD processes are very complicated and detailed understanding is not available.

The deposition of ITO films by the CVD method generally faces difficulties due to a lack of volatile and thermally stable source materials. The materials that fulfill the requirements of volatility, thermal stability at a temperature sufficiently high to produce an adequate vapor pressure, and decomposition kinetics at the CVD temperature range are limited almost entirely to the chelates of β-diketones. Therefore, photons, electrons, and ions or a combination of them may be used to induce and maintain CVD reactions. dc[172] and rf[173] plasma CVD from trimethylindium and O$_2$ has been already attempted. Typical samples had a relatively high resistivity of 2.83×10^{-3} Ω cm. Kane and Schneizer[174] carried out one of the earliest and most successful investigations on the preparation of ITO films by the CVD method. The starting compounds were indium chelate, tris (2, 2, 6, 6-tetramethyl-3, 5-heptane-dionato) indium,[175] commonly referred to as In(DPM)$_3$, derived from dipivaloyl methane and dibutyl tin diacetate. Films with resistivities as low as 2.2 $\times10^{-4}$ Ω cm could be obtained for tin concentrations of 8.0 at. %, although the resistivities of typical samples were in the range 4.8–5.8×10^{-4} Ω cm. The layers deposited at 400–500 °C exhibited very smooth surfaces but at a higher substrate temperatures the film surfaces became rougher with an increase in crystallite size. Maruyama and Tabata[176] deposited ITO films using the APCVD technique without an oxygen supply. The precursor materials were indium acetate and tin diacetate. Although the transmittance in the visible region exceeded 90%, the films had a relatively high electrical resistivity of 6.93×10^{-3} Ω cm which was attributed to the small crystallite size (15–20 nm). Maruyama and Fukui[131] reported the fabrication of ITO films with better electrical properties using indium acetylacetonate and tin (II) acetylacetonate. The films had much lower resistivity (1.8 $\times10^{-}$ Ω cm) and no postannealing was necessary. However, in this case oxygen gas was introduced. Indium acetylacetonate was previously used by Ryabova and

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TABLE VI. Electrical properties of ITO films prepared by the CVD technique.

Starting reagents	Resistivity (10^{-4} Ω cm)	Carrier concentration (10^{20} cm^{-3})	Carrier mobility (cm^2/V^{-1} s^{-1})	Reaction temperature (°C)	Gas flow rate (l min^{-1})	References
Indium and tin acetylacetonates	1.6–1.8	9	43	350–450	450	46
Indium acetate and tin diacetate	69.3	···	···	300	700	176
Indium and tin acetylacetonates	1.8	···	···	450	···	131
InCl$_3$ and SnCl$_2$	···	~1	5–22	450	···	170
Indium chelate and dibutyl tin diacetate	5	···	···	500	···	174
···	10	···	···	900	···	180
Trimethyl indium	···	···	···	···	···	173
Trimethyl indium	28.3	···	···	260	···	172
Indium 2-ethylhexanoate and tin (IV) chloride	2.9	···	···	400	···	179
In(DPM)$_3$ and dibutyl tin diacetate	~2	···	40–70	510	···	175

co-workers[177,178] for the deposition of pure In$_2$O$_3$. Indium 2-ethylhexanoate and tin (IV) chloride were recently proposed[179] as precursor materials for obtaining In$_2$O$_3$ and ITO films by APCVD without a supply of oxygen. The ITO film obtained at a reaction temperature of 400 °C and an atomic ratio Sn:In = 0.086 had a resistivity of 2.9 $\times 10^{-4}$ Ω cm. Using the same procedure described by Manifacier,[6] Privman *et al.*[180] prepared ITO films in order to use them as a electrodes for high temperature fuel cells. Their study mainly focused on structural aspects, and film resistivity of 1×10^{-3} Ω cm was reported.

It is clear from the preceding results that the resistivities obtained at optimum conditions differ by about one order of magnitude. The starting precursors for indium and tin appear to have a critical effect on the film's electrical properties. In this regard, acetylacetonate derivatives seem to be more suitable. Typical electrical properties of CVD ITO films are given in Table VI.

D. Sol-gel process

Compared to conventional thin film forming processes, films prepared by the sol–gel[181–183] route require considerably less equipment and are potentially cost effective. This method offers many other advantages:

(1) intimate mixing, at the molecular level, of the starting materials resulting in an high degree of film homogeneity even for multicomponent systems;

(2) low processing temperature which allows the use of volatile components and avoids the formation of undesired phases;

(3) dopants, even at a trace level, can be introduced with relative ease;

(4) easy adjustment of the viscosity, and thereby the thickness per coating, by adequate choice of the solvent, chelating organic ligands, concentration, etc.;

(5) large area coatings of desired thickness and composition are obtainable.

Although, ITO coatings prepared by sputtering and evaporation methods have received much attention in literature, reports on their preparation by other techniques like dip coating[184] using the sol–gel process are rather rare. The electrical, chemical, optical, and mechanical properties of sol–gel derived ITO films were described by Arfsten and co-workers.[185] These authors[186] have showed that ITO films with satisfactory electrical and optical properties could be prepared by the sol–gel method. Gallagher and co-workers[187,188] prepared ITO films by dip coating them from an acetylacetone solution of indium and tin acetylacetonate. The use of an acetylacetone solution of indium nitrate [In(NO$_3$)$_3$]$\times$H$_2$O and tin chloride (SnCl$_4$) was also investigated. These researchers[187,188] mainly studied the solution chemistry and the thermal decomposition of ITO
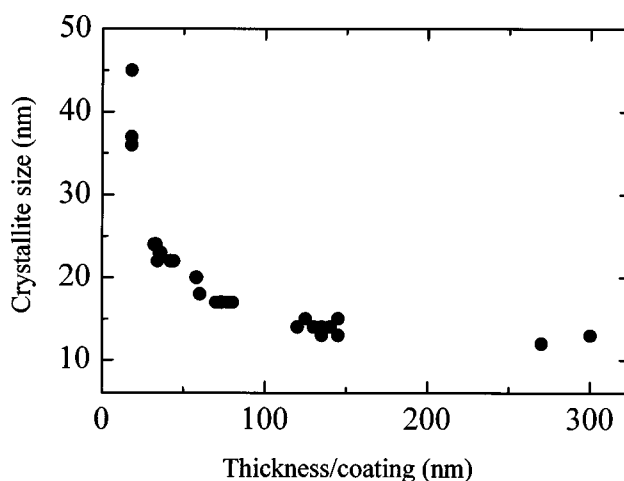
FIG. 3. Crystallite size of ITO films prepared by the dip coating method vs thickness per coating.

TABLE VII. Electrical properties of ITO films prepared by the sol–gel process.

Starting reagents	Resistivity (Ω cm)	Carrier concentration (10^{20} cm^{-3})	Carrier mobility (cm^2/V^{-1} s^{-1})	Preparation method	References
In$_2$(SO$_4$)$_3$$nH_2$O and SnSO$_4$	$6-8\times10^{-4}$	6	14	Dipping	190
InCl$_3$ and SnCl$_4$	1.2×10^{-3}	1.2	7	Dipping	204
In(NO$_3$)$_3$3H$_2$O and SnCl$_4$	4.23×10^{-4}	⋯	⋯	Dipping	189
Indium 2-ethylhexanoate and tin 2-ethylhexanoate	$3-5\times10^{-3}$	⋯	⋯	Dipping	191
Indium and tin acetylacetonate	1.01×10^{-3}	⋯	⋯	Dipping	187
Indium acetate and tin isopropoxide	3.3×10^{-4}	10.0	21	Dipping	194
Indium acetate and tin octylate	5.8×10^{-4}	5.6	19	Dipping	196
Indium 2-ethylhexanoate and tin 2-ethylhexanoate	4.21×10^{-3}	1.62	9.14	Spinning	192

precursors. The best resistivity value was 1.01×10^{-3} Ω cm obtained for the film doped with 8 wt % SnO$_2$ and postannealed in forming gas. For ITO films prepared in a similar way, Maruyama and Kojima[189] obtained much lower resistivity of 4.23×10^{-4} Ω cm. In the latter case the films were heated directly in an inert gas. Further vacuum annealing resulted in an increase in the resistivity. A slightly higher resistivity of 6×10^{-4} Ω cm could be obtained[190] from an aqueous system by hydrolysis of indium and tin sulfates. Furusaki *et al.*[191] used indium 2-ethylhexanoate or indium acetylacetonate, and tin 2-ethylhexanoate as starting materials for indium and tin. A relatively high resistivity in the range of $3-5\times10^{-3}$ Ω cm was obtained after annealing in vacuum at 550 °C. Using the same precursors, Xu *et al.*[192] obtained comparable resistivity values for spin coated ITO films without annealing in reducing conditions. Better uniformity is reported for the films fired directly at 550 °C. The intent of the experiments of Bommel and co-workers[193] was to clarify the dependence of the electrical properties on the processing parameters of spin coated ITO films. Indium isopropoxide and tin isopropoxide were used as precursors for indium and tin. Prior to the addition of water, a complexing agent (triethanolamine) was added to control the rate of hydrolysis and to avoid precipitation. Lower resistance was obtained at higher water content and oxidation temperature, 0.06–0.08 Sn/In molar ratio, and short hydrolysis time.

Similar to the CVD technique, the preparation of ITO films with satisfactory electrical and optical properties by the sol–gel process is restrained to a limited range of precursors mainly because of the (i) high cost of alkoxides which are commonly used and (ii) lack of sufficient solubility. Additionally, when different alkoxides of different elements are used, as for the case of ITO, the reactivity toward water may differ resulting in inhomogeneity of the gel. This can be solved by using chelating organic ligands to judiciously control or suppress the hydrolysis. Ethanolamine stabilized sols were successfully prepared[194] from both alkoxide (indium triisopropoxide) and indium acetate.[195,196] The ITO films prepared from the acetate system had higher conductivity which was correlated to the difference in purity. The fabrication of pure In$_2$O$_3$ thin films from aqueous sol and organic solution by the dip coating method has been reported.[58] Their electrical properties were discussed based on their morphologies. The electrical resistivity of In$_2$O$_3$ films from organic solution was lower than that from aqueous sol. This was attributed to the difference in the film density. A distinctive characteristic of the dip coated ITO films is the change in their electrical properties with time. In particular, the electrical resistivity was reported[58,194] to significantly decrease for up to two weeks from the deposition time before it stabilizes. This was attributed to the film relaxation and/or porosity and/or progressive adsorption of moisture[195,196] on the film surface. Recently it was shown[197] that multiple coatings of very thin layers using a diluted solution and/or a slow substrate withdrawal speed result in films of large crystallite size and improved mobility. This result is very interesting since it allows some flexibility in adjusting the crystallite size which is a determinant factor for the film's electrical properties. The variation of the crystallite size versus the thickness per coating is illustrated in Fig. 3. Representative electrical data on ITO thin films prepared by the sol–gel process are listed in Table VII.

From the brief summary of the results presented above, it is clear that better understanding of the sol chemistry, film thermal decomposition and reduction, and control of film microstructure are important in the preparation of low electrically resistive films by the sol–gel method.

IV. CONCLUSION

The electrical properties of ITO thin films depend on the preparation method, the deposition parameters used for a given deposition technique, and the subsequent heat treatment in various ambients at different temperatures. Regardless of the fabrication method, comparable conductivity values were obtained by an appropriate adjustment of the deposition parameters. The key factors for the low resistivity have not been clearly elucidated because of the complex

structure of the unit cell of crystalline In_2O_3 formed by 80 atoms and the complex nature of the conducting mechanisms in polycrystalline films. Due to the large number of processing parameters, even for a single technique, a standard procedure for depositing ITO films is not yet established. Therefore, a coherent understanding is yet to be reached. Precise control and tailoring of the microstructure together with better understanding of the scattering mechanisms are essential to fill the gap between science and technology in the field of transparent electrically conducting oxide films.

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