PREPARATION AND PROPERTIES OF TRANSPARENT CONDUCTORS

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ABSTRACT

Transparent, electrically conductive films have been prepared from several different metal oxides, including those of tin, indium and zinc. Deposition methods for these materials are reviewed, and their properties summarized and compared. A figure of merit for a transparent conductor may be defined as the ratio of the electrical conductivity to the optical absorption coefficient of the film. The figure of merit for fluorine-doped zinc oxide is shown to be larger than that of other transparent conductors, such as boron-doped zinc oxide, fluorine-doped tin oxide, and tin-doped indium oxide. Physical, chemical and thermal durability, deposition temperature, and cost are other factors which may also influence the choice of material for a particular application.

SOME APPLICATIONS OF TRANSPARENT CONDUCTING OXIDES

Transparent conducting oxides (TCOs) have a wide variety of uses. Their ability to reflect thermal infrared heat is exploited to make energy-conserving windows. These low-emissivity windows are the largest current use for TCOs. Oven windows employ TCOs to maintain an outside temperature which is safe to touch, and also to conserve energy.

TCO's electrical conductivity is exploited in front-surface electrodes for solar cells and flat-panel displays. Automatically dimming rear-view mirrors for automobiles and electrically-controlled "smart" windows incorporate a pair of TCOs with an electrochromic material between them. Electric current is passed through TCOs to defrost windows in vehicles, and to keep freezer display cases free of frost. TCOs dissipate static electricity from the windows on Xerographic copiers. Glass touch-controls panels are etched from TCO layers. Transparent electromagnetic shields can be formed from TCOs. Invisible security circuits can be placed on windows. Transparent radio antennas can be built into automobile windows.

Abrasion-resistant tin oxide coatings are used to protect the covers over optical bar-code readers. Acid-resistant tin oxide coatings are protecting windows from graffiti etched by acids sold for putting identifying marks on car windows.

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PROCESSES USED FOR MAKING TRANSPARENT CONDUCTING OXIDES

Production of TCO layers has been carried out by a variety of methods. Innovations in these deposition methods are listed in Table I.

Table I. History Of Processes For Making Transparent Conducting Oxides

SnO_2:Sb by spray pyrolysis	J. M. Mochel (Corning), 1947[1]
SnO_2:Cl by spray pyrolysis	H. A. McMaster (LOF), 1947[2]
SnO_2:F by spray pyrolysis	W. O. Lytle and A. E. Junge (PPG), 1951[3]
In_2O_3:Sn by spray pyrolysis	J. M. Mochel (Corning), 1951[4]
In_2O_3:Sn by sputtering	L. Holland and G. Siddall, 1953[5]
SnO_2:Sb by CVD	H. F. Dates and J. K. Davis (Corning), 1963[6]
SnO_2:F by CVD	R. G. Gordon (Harvard), 1979[7]
ZnO:In by spray pyrolysis	Major, Banerjee and Chopra (Delhi), 1984[8]
ZnO:Al by sputtering	Minami, Nanto & Takata (Kanazawa),1984[9]
ZnO:In by sputtering	S. N. Qiu, C. X. Qiu and I. Shih, 1987)[10]
ZnO:B by CVD	P. S. Vijayakumar et al (Arco Solar), 1988[11]
ZnO:Ga by sputtering	Choi, Im, Song and Yoon, 1990[12]
ZnO:F by CVD	J. Hu and R. G. Gordon (Harvard), 1991[13]
ZnO:Al by CVD	J. Hu and R. G. Gordon (Harvard), 1992[14]
ZnO:In by CVD	J. Hu and R. G. Gordon (Harvard), 1992[15]
ZnO:Ga by CVD	J. Hu and R. G. Gordon (Harvard), 1992[16]

Spray pyrolysis was first used commercially more than half a century ago to deposit conductive tin oxide films on heated glass plates, in batch processes. Since the 1980's, chemical vapor deposition (CVD) has been widely adopted in continuous production of glass coated with fluorine-doped tin oxide.[17] By far the largest area of TCO films are currently produced in this way. Most of this material is used for energy-conserving ("Low-Emissivity") windows in buildings, with smaller amounts going into thin-film photovoltaics and other applications mentioned in the first section.

Although In_2O_3:Sn (ITO) was first made by spray pyrolysis, sputtering has been the preferred mode for its production. ITO is mainly used in flat panel displays.

Conductive zinc oxide films have been investigated more recently. Some use of it is made in photovoltaics. Because of its potential lower cost and easier etchability, zinc oxide may replace ITO in display applications.

DESIRABLE FEATURES OF A CVD PROCESS

Because of the importance of CVD as a production method for TCO materials, we will review some of the CVD methods. Before mentioning the specific processes, we note that an ideal CVD reaction should satisfy many requirements.

Properties of the precursors:

- The precursors should be fluids (gases or liquids), not solids, at room temperature, in order to facilitate handling and metering.
- The precursors should be inexpensive to manufacture and to purify.
- They should remain stable during storage, and not react with air.
- They should be non-flammable, non-toxic, and non-corrosive.

Vaporization of the precursors:

- Their vapor pressures should be sufficiently high (e.g., 1 Torr) at a relatively low temperature (e. g., less than 200 °C).
- They should be thermally stable at their vaporization temperature.
- They should vaporize rapidly and reproducibly, which is usually the case if it is a non-associated liquid (not a solid) at its vaporization temperature.

CVD reaction:

- The reaction should take place at a temperature low enough not to damage substrates.
- The reactant vapors should not react with each other prematurely, in order to allow mixing into a uniform vapor composition.

- The reaction should produce a pure film, with high conductivity and good step coverage.

- A high percentage of the precursor should be converted to film.

Byproducts:

- The byproducts of its CVD reaction should be stable and non-reactive.

- The reaction byproducts should be non-flammable, non-toxic and non-corrosive.

In the next sections, we will see how well these ideals are approached by CVD reactions for tin oxide and zinc oxide. Reactions run at atmospheric pressure are emphasized, because these are the basis for commercial large-scale coating operations.

SURVEY OF CVD REACTIONS USED FOR TIN OXIDE TRANSPARENT CONDUCTORS

Several different CVD reactions have been used to deposit tin oxide. A commonly used precursor is tin tetrachloride, $SnCl_4$. When reacted with water vapor, according to Eq. (1),

$$SnCl_4 + 2\ H_2O \rightarrow SnO_2 + 4\ HCl \qquad (1)$$

tin oxide is rapidly deposited at substrate temperatures as low as 250 °C. The main disadvantage of this reaction is that the reagents must be mixed immediately over the substrate surface. If the tin chloride and water vapor are mixed more than a few centimeters from the substrate surface, most of the film forms on the apparatus, and very little film covers the substrate. At atmospheric pressure, turbulent mixing is needed to combine the reagents quickly, and the resulting inhomogeneous gas concentrations of the reactants leads to somewhat non-uniform coating thicknesses.

By adding organic ligands to the tin precursor, premature reactions are suppressed, and the reactants can be combined into homogeneous gas mixtures prior to their introduction to the substrate surface. For example, tetramethyltin vapor and oxygen do not react at temperatures below about 400 °C, so that they can be combined into a homogeneous gas mixture which then reacts at a hotter glass surface to deposit tin oxide:

$$Me_4Sn + O_2 \rightarrow SnO_2 + \ldots . \qquad (2)$$

This reaction can produce uniform coatings, but its deposition rate is too low for use on-line in a glass plant. Another disadvantage of tetramethyltin is its high toxicity.

Organo-tin chlorides, such as dimethyltin dichloride and butyltin trichloride, can form premixed vapors that provide uniform coatings at high coating rates, along with lower toxicity than tetramethyltin. The various advantages and disadvantages of these CVD reactions are summarized in Table II.

Table II. CVD reactions for producing tin oxide.
*** = excellent, ** = good, * = fair, uns = unsatisfactory.

Sn precursor	Me_4Sn	Me_2SnCl_2	$BuSnCl_3$	$SnCl_4$	Bu_2SnF_2
O precursor	O_2	O_2, H_2O	O_2, H_2O	H_2O, MeOH	O_2
liquid precursor	***	**	***	***	*
inexpensive	*	**	**	***	**
stable in storage	***	***	***	***	*
non-flammable	*	**	**	***	**
non-toxic	uns	*	**	***	**
non-corrosive	***	*	*	*	**
volatile	***	**	**	***	*
fast vaporizing	***	***	***	***	*
stable vapor	***	***	***	***	*
low CVD temp.	**	**	**	***	**
deposition rate	*	***	***	***	***
uniformity	***	***	***	**	**
film purity	***	***	***	***	**
transparency	***	***	***	***	**
conductivity	***	***	***	***	**
light-trapping	***	***	***	***	**
byproducts	*	**	**	**	**

SURVEY OF CVD REACTIONS USED FOR ZINC OXIDE TRANSPARENT CONDUCTORS

Several different CVD reactions have been used to make zinc oxide. The most commonly used precursor is diethylzinc, $Zn(C_2H_5)_2$. When reacted with water vapor, according to Eq. (3),

$$Zn(C_2H_5)_2 + H_2O \rightarrow ZnO + 2\,C_2H_6 \qquad (3)$$

zinc oxide is deposited at appreciable rates for temperatures as low as 150 °C. This CVD process may be carried out either at low pressure, or at atmospheric pressure.

Films with higher conductivity and transparency have been prepared using ethanol as the main oxygen source, according to the reaction

$$Zn(C_2H_5)_2 + C_2H_5OH \rightarrow ZnO + 2\,C_2H_6 + C_2H_4 \qquad (4)$$

In order to initiate the ethanol reaction, a small amount of water vapor must be present. Alternatively, a thin initial coating of zinc oxide may be deposited by the water reaction (3), after which dry ethanol will continue to react by equation (4) even in the absence of added water vapor. The main disadvantage of the alkylzinc precursors is that they burn spontaneously if accidentally exposed to air. Also, even small, accidentally introduced amounts of oxygen can disrupt a CVD process using alkylzinc precursors.

Zinc acetylacetonate is stable in dry air, but its volatility is not as high as desired in a CVD precursor.

Table III. CVD reactions for producing zinc oxide.
*** = excellent, ** = good, * = fair, uns = unsatisfactory

Zn precursor	Et_2Zn	Et_2Zn	Me_2Zn	$Zn(acac)_2$	$Zn(acac)_2$
O precursor	H_2O	EtOH	O_2	H_2O	O_2
liquid precursor	***	***	***	*	*
inexpensive	***	***	*	***	***
stable in storage	***	***	***	***	***
non-flammable	uns	uns	uns	**	**
non-toxic	***	***	***	***	***
non-corrosive	***	***	***	***	***
volatile	***	***	***	*	*
fast vaporizing	***	***	***	**	**
stable vapor	***	***	***	**	**
low CVD temp.	***	**	***	**	*
deposition rate	***	**	***	**	**
uniformity	**	**	***	**	***
film purity	**	***	**	**	**
conductivity	**	***	**	**	**
transparency	***	***	***	***	**
light-trapping	***	***	**	**	**
byproducts	**	**	**	**	**

Table III summarizes these CVD reactions for forming zinc oxide. None of them fully meets all the criteria we have discussed as being desirable in a CVD reaction for producing ZnO.

OPTICAL AND ELECTRICAL PERFORMANCE OF TRANSPARENT CONDUCTORS

An effective transparent conductor should have high electrical conductivity combined with low absorption of visible light. Thus an appropriate quantitative measure of the performance of transparent conductors is the ratio of the electrical conductivity σ to the visible absorption coefficient, α,

$$\sigma/\alpha = \{R_{\square}\ln(T+R)\}^{-1} \qquad (5)$$

in which $R_{\square}$ is the sheet resistance in ohms per square, T is the total visible transmission, and R is the total visible reflectance. σ/α is thus a figure of merit for rating transparent conductors. A larger value of σ/α indicates better performance of the transparent conductor. Figures of merit for some transparent conductors are given in Table IV. The values are for the best samples that we have prepared in our laboratory by CVD at atmospheric pressure, except for the indium oxide value, which is the best that we have measured for a commercially available film.

Table IV. Figure of Merit for Some Transparent Conductors

Material	Sheet Resistance	Visible Absorption	Figure of Merit
	(ohms/square)		(inverse ohms)
ZnO:F	5	0.03	6.6
ZnO:Al	3.8	0.05	5.1
In_2O_3:Sn	6	0.04	4.1
SnO_2:F	8	0.04	3.1
ZnO:Ga	3.2	0.12	2.5
ZnO:B	8	0.06	2.0
SnO_2:Sb	20	0.12	0.4
ZnO:In	20	0.20	0.2

These results show that the fluorine-doped zinc oxide gives the best performance of these transparent conductors.

If the electrical and optical properties of a transparent conductor were independent of film thickness, then the figure of merit σ/α would not depend on film thickness. In fact, properties of transparent conductors do depend somewhat on film thickness, for example because they depend on crystalline grain size, which increases with film thickenss. Thus the figure of merit generally increases with film thickness. The film thicknesses of the samples reported in Table IV were chosen to be typical of those needed for low-resistance applications such as solar cells.

The results in Table IV show that fluorine doping gives superior performance compared to metallic dopants, in both zinc oxide and tin oxide. A theoretical understanding of this advantage of fluorine can be obtained by considering that the conduction band of oxide semiconductors is mainly derived from metal orbitals. If a metal dopant is used, it is electrically active when it substitutes for the primary metal (such as zinc or tin). The conduction band thus receives a strong perturbation from each metal dopant, the scattering of conduction electrons is enhanced, and the mobility and conductivity are decreased. In contrast, when fluorine substitutes for oxygen, the electronic perturbation is largely confined to the filled valence band, and the scattering of conduction electrons is minimized.

THERMAL STABILITY OF TRANSPARENT CONDUCTORS

TCOs will generally increase in resistance if they are heated to a high enough temperature for a long enough time. For example, some of the TCOs were tested in my laboratory by heating them in air for a period of 10 minutes, to successively higher temperatures. Table V gives as the "stability temperatures" the temperature range within which no increase of more than 10% in sheet resistance was noted.

Table V. Thermal Stability of Some Transparent Conductors.

Material	Deposition Temperature °C	Stability Temperature °C
LPCVD $ZnO:B$	200	<250
APCVD $ZnO:F$	450	<500
APCVD $SnO_2:F$	650	<700

In each case, the TCO remains stable to temperatures slightly above the optimized deposition temperature. The high-temperature stability of tin oxide films allows coated glass to be reheated in order to strengthen it by tempering. Deposition of CdTe solar cells on tin oxide coatings also requires their high-temperature stability.

DIFFUSION BARRIERS BETWEEN TCOs AND SODIUM-CONTAINING GLASS

When TCOs are deposited on sodium-containing glass, such as soda-lime glass, sodium can diffuse into the TCO and increase its resistance. This effect is particularly noticable for tin oxide, because sodium diffuses rapidly at the high substrate temperatures (often over 550 °C) used for its deposition. It is common to deposit a barrier layer on the glass prior to the deposition of tin oxide. Silica is most commonly used as the barrier layer between soda-lime glass and tin oxide, even though silica is only partially effective in blocking the transport of sodium. The silica layer usually serves a second purpose, that of eliminating the interference colors that would otherwise be shown by the tin oxide film.[18]

STABILITY IN HYDROGEN PLASMAS

In forming amorphous silicon solar cells on TCO superstrates, the TCO is exposed to a plasma containing hydrogen atoms. These plasma conditions rather easily reduce tin oxide, causing an increase in the optical absorption by the tin oxide. Zinc oxide is much more resistant to hydrogen plasma reduction, and may be preferred for applications such as amorphous silicon solar cells.[19]

ETCHING PATTERNS IN TCOs

For some applications of TCOs, such as displays, heaters or antennas, parts of the TCO must be removed. Table VI lists some chemicals which may be used to etch TCOs. Zinc oxide is the easiest material to etch, tin oxide is the most difficult, and indium oxide is intermediate in difficulty.

Table VI. Etchants For
Transparent Conducting Oxides

Material	*Etchant*
ZnO	Dilute acids
ZnO	Ammonium chloride
In_2O_3	$HCl + FeCl_3$
SnO_2	$Zn + HCl$
SnO_2	$CrCl_2$
SnO_2	proprietary (Feldman)

Thin film solar cells also need to remove TCO along patterns of lines. This removal is usually carried out by laser ablation.

CHOICE OF TRANSPARENT CONDUCTING OXIDES

It is apparent from the diversity of applications for TCOs that no one material is most suitable for all uses. Depending on which material property is of most importance, different choices are made. Table VII lists some of the most important criteria which may influence the choice of a TCO material.

Table VII. Choice Of Transparent Conducting Oxides

Property	Material
Highest Transparency	ZnO:F
Best Thermal Stability	SnO_2:F
Most Durable	SnO_2:F
Most Easily Etched	ZnO:F
Best Resistance to H Plasmas	ZnO:F
Lowest Deposition Temperature	In_2O_3:Sn, ZnO:B
Lowest Cost	SnO_2:F

CONCLUSIONS

Transparent conducting oxides have many applications. Fluorine-doped tin oxide is the most widely used TCO, while tin-doped indium oxide remains preferred for displays. Zinc oxide is seeing expanding use in solar cells. All of these commonly-used TCO materials and their production methods have advantages and disadvantages, which must be carefully weighed for each new application. The information in this paper may assist in making rational decisions about the use of TCO materials.

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