Criteria for Choosing Transparent Conductors

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Introduction

Transparent, electrically conductive films have been prepared from a wide variety of materials. These include semiconducting oxides of tin, indium, zinc, and cadmium, and metals such as silver, gold, and titanium nitride. In this article, the physical properties of these materials are reviewed 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 materials having the highest figures of merit are fluorine-doped zinc oxide and cadmium stannate. Physical, chemical, and thermal durability; etchability; conductivity; plasma wavelength; work function; thickness; deposition temperature; uniformity; toxicity; and cost are other factors that may also influence the choice of transparent conducting material for any particular application.

Some Applications of Transparent Conductors

Transparent conductors (TCs) have a wide variety of uses. Their ability to reflect thermal infrared heat is exploited to make energy-conserving windows. These lowemissivity ("low-e") windows are the largest area of current use for TCs. Oven windows employ TCs to conserve energy and to maintain an outside temperature that makes them safe to touch. The electrical conductivity of TCs is exploited in front-surface electrodes for solar cells and flat-panel displays (FPDs). Automatically dimming rear-view mirrors for automobiles and electrically controlled "smart" windows incorporate a pair of TCs with an electrochromic (EC) material between them. Electric current is passed through TCs to defrost windows in vehicles and to keep freezer display cases frost-free. TCs dissipate static electricity from the windows on

xerographic copiers. Glass touch-control panels are etched from TC layers. TCs can also be formed into transparent electromagnetic shields, invisible security circuits on windows, and transparent radio antennas built into automobile windows.

It might appear reasonable to ask which transparent conducting material is the best. However, this question does not have a unique answer, since different TCs are best suited for different applications. Also, a given application may constrain the method of preparation and thereby affect

the choice of material. In the following, we first summarize the methods for preparing TCs. Then, we consider the various materials properties that can be important in choosing a TC. Finally, we show how these methods and properties lead to choices of different TCs that are best for different applications.

Processes Used in Making Transparent Conducting Materials

The properties of a TC layer depend not only on its chemical composition, but also on the method used for its preparation. These preparative methods include physical methods (sputtering, evaporation, pulsed laser deposition) and chemical methods (chemical vapor deposition, sol-gel, chemical bath deposition, electroplating). Some of the innovations in these deposition methods are listed in Table I.

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 1980s, chemical vapor deposition (CVD) has been widely adopted in the continuous production of glass coated with fluorine-doped tin oxide. ²³ By far the majority of TC films are currently produced in this way. Most of this material is used for energy-conserving "low-e" windows in buildings,

Table I: History of Processes for Making Transparent Conductors.

Materials and Process

Ag by chemical-bath deposition SnO_2 : Sb by spray pyrolysis

SnO₂:Cl by spray pyrolysis SnO₂:F by spray pyrolysis

In₂O₃:Sn by spray pyrolysis

In₂O₃: Sn by sputtering SnO₂: Sb by CVD

Cd₂SnO₄ by sputtering Cd₂SnO₄ by spray pyrolysis

SnO₂:F by CVD TiN by CVD

ZnO: In by spray pyrolysis

ZnO:Al by sputtering ZnO:In by sputtering

ZnO: In by spuπerin ZnO: B by CVD

ZnO: Ga by sputtering

ZnO:F by CVD ZnO:Al by CVD

ZnO: All by CVD

ZnO: In by CVD Zn₂SnO₄ by sputtering

ZnSnO₃ by sputtering

Cd₂SnO₄ by pulsed laser deposition

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Unknown Venetian

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with smaller amounts going into thin-film photovoltaics and other applications mentioned in the first section.

Although indium tin oxide (In₂O₃:Sn, ITO) was first made by spray pyrolysis, sputtering has become the preferred mode for its production. ITO is mainly used in FPDs.

Conductive zinc oxide films have been investigated more recently. One application in which zinc oxide is used is in photovoltaics. Because of its potential lower cost and easier etchability, zinc oxide may replace ITO in display applications.

Materials Properties Relevant to Transparent Conductors

A number of physical and chemical properties are related to the performance of a TC in any given application.

Optical and Electrical Performance of Transparent Conductors

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

$$\sigma/\alpha = -\{R_{\rm s}\ln(T+R)\}^{-1} \tag{1}$$

in which $R_{\rm s}$ is the sheet resistance in ohms per square, T is the total visible transmission, and R is the total visible reflectance. Thus σ/α is a figure of merit for rating TCs.²⁴ A larger value of σ/α indicates better performance of the TC.

Figures of merit for some TCs are given in Table II. The values given 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, and the cadmium stannate values, which we have taken from the literature.²⁵

The results in Table II show that fluorinedoped zinc oxide and cadmium stannate have the best figures of merit of these TCs. If the electrical and optical properties of a TC were independent of film thickness, then the figure of merit σ/α would not depend on film thickness, unlike other figures of merit that have been proposed.26 In fact, "bulk" properties of TCs, such as σ and α , do depend somewhat on film thickness. For example, they depend on crystallite grain size, which usually increases with film thickness. The figure of merit therefore generally increases with film thickness. The film thicknesses of the samples reported in Table II were chosen to be typical of those

Table II: Figures of Merit σ/α for Some Transparent Conductors.

		Visible		
	Absorption			
	Sheet Resistance	Coefficient	Figure of Merit	
Material	(Ω/\square)	α	(Ω^{-1})	
ZnO:F	5	0.03	7	
Cd ₂ SnO ₄	7.2	0.02	7	
ZnO:Al	3.8	0.05	5	
In ₂ O ₃ :Sn	6	0.04	4	
SnO ₂ :F	8	0.04	3	
ZnO:Ga	3	0.12	3	
ZnO:B	8	0.06	2	
SnO ₂ :Sb	20	0.12	0.4	
ZnO:In	20	0.20	0.2	

needed for low-resistance applications such as solar cells.

The results in Table II show that fluorine doping gives superior performance compared with 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 derived mainly 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.

A theoretical upper limit to the figure of merit may be estimated from the transport theory of electrons in metals²⁷ given by

$$\sigma/\alpha = 4\pi^2 \varepsilon_0 c^3 n(m^* \mu)^2 \lambda^{-2} e^{-2}, \qquad (2)$$

where ε_0 is the permittivity of free space, c is the speed of light in vacuum, n is the refractive index of the film, *m** is the effective mass of the conduction electrons, μ is the mobility, λ is a visible wavelength of light, and e is the electronic charge. The refractive index of TCs is close to 2.0 in the visible region, thus the highest figure of merit will be obtained from the material with the highest product of mobility and effective mass. For zinc oxide, 28 tin oxide, 29 and cadmium stannate, 30 m^* is close to 0.3 m. where m is the free-electron mass. Thus most of the variation in the figure of merit is due to differences in mobility. Note that the free-electron concentration does not enter into the figure of merit.

The electron mobility is determined by the electron-scattering mechanisms that operate in the material. First of all, some scattering mechanisms, such as scattering of electrons by phonons, are present in pure single crystals. In tin oxide29 and zinc oxide,31 these scattering mechanisms lead to mobilities of about 250 cm² V⁻¹ s⁻¹ at low doping levels, typically around 10¹⁶ cm⁻³. Practical TCs need much higher doping levels, usually $>10^{20}$ cm⁻³, in order to operate at reasonable thicknesses. For these high doping levels, scattering by the ionized dopant atoms becomes another important mechanism that alone limits the mobility to less than about 90 cm 2 V $^{-1}$ s $^{-1}$. 33 In the presence of both these scattering mechanisms, the mobility is limited to the value $(250^{-1} + 90^{-1})^{-1} =$ $66 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This maximum mobility is lowered still further by other scattering mechanisms such as grain-boundary scattering, present in polycrystalline thin films. The best TC films, ZnO:F and Cd₂SnO₄, have been prepared with mobilities in the range of $50-60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, closely approaching the theoretical upper limit.

Electrical Conductivity

In some applications of TCs, it is critical that the TC be as thin as possible. For example, in high-resolution displays, the required etched patterns in the TC create height variations in the device. To keep the topography as smooth as possible, the thinnest possible TC is desired. In this case, the important material parameter is the conductivity σ . The conductivity increases with the product of the concentration of free electrons and the mobility. For metals such as silver and titanium nitride, the free-electron concentration is fixed by the structure and electronic properties of the solid. For wide-bandgap semiconductors,

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the free-electron concentration is determined by the maximum number of electronically active dopant atoms that can be placed in the lattice. Attempts to place a larger number of dopant atoms in the lattice simply produce neutral defects that decrease the mobility. The maximum obtainable electron concentration and the maximum conductivity in TCs generally are found to increase in the following order: $ZnO:F < SnO_2:F < ZnO:Al < In_2O_3:Sn < TiN < Ag.$

Plasma Frequency

The plasma frequency for the conduction electrons in a TC divides the optical properties. At frequencies higher than the plasma frequency, the electrons cannot respond, and the material behaves as a transparent dielectric. At frequencies below the plasma frequency, the TC reflects and absorbs incident radiation. For most TC materials, the plasma frequency falls in the near-infrared part of the spectrum, and the visible region is in the higher, transparent frequency range. The plasma frequency increases approximately with the square root of the conduction-electron concentration. The maximum obtainable electron concentration and the plasma frequency of TCs generally increase in the same order as the resistivity, as shown in Table III. The corresponding plasma wavelengths decrease from about 2 μ m for Zn \ddot{O} :F to 0.7 μm (red light) for TiN (Table III).

Work Function

The work function of a TC is defined as the minimum energy required to remove an electron from the conduction band to the vacuum. Some work functions measured for TCs are collected in Table IV.

Thermal Stability of Transparent Conductors

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

In each case, the TC remained 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. The thermal stability of tin oxide films is currently limited more by the softening of glass substrates than by any thermal decomposition of the SnO₂:F film.

Table III: Approximate Minimum Resistivities and Plasma Wavelengths for Some Transparent Conductors.

	Resistivity	Plasma Wavelength
Material	($\mu\Omega$ cm)	(μm)
Ag	1.6	0.4
TiN	20	0.7
In ₂ O ₃ :Sn	100	>1.0
Cd ₂ SnO ₄	130	>1.3
ZnO:Al	150	>1.3
SnO ₂ :F	200	>1.6
ZnO:F	400	>2.0

Table IV: Work Functions of Some Transparent Conductors.

	Work Function	Electron Concentration
Material	(eV)	(cm ⁻³)
ZnO:F	4.2	2×10^{20}
ZnO	4.5	7×10^{19}
In ₂ O ₃ :Sn	4.8	>10 ²⁰
SnO ₂ :F	4.9	4×10^{20}
$ZnSnO_3$	5.3	6×10^{19}

Taken from Reference 33.

Table V: Thermal Stability of Some Transparent Conductors.

	Deposition Temperature	Stability Temperature
Material	(°C)	(°C)
LPCVD ZnO:B	200	<250
APCVD ZnO:F	450	< 500
APCVD SnO ₂ :F	650	<700

Cadmium stannate is deposited by sputtering at low temperatures in amorphous form. When annealed at high temperatures, it crystallizes into a crystalline form that is stable up to at least 1100°C.³⁴

Minimum Deposition Temperature

When TCs are deposited onto a substrate, the temperature of the substrate generally must be maintained at a sufficiently high temperature in order to develop the required properties in the TC. The required temperatures usually increase in the following order: Ag or ITO < ZnO < SnO $_2$ < Cd $_2$ SnO $_4$. Thus, silver or ITO may be preferred for deposition on thermally sensitive substrates, such as plastic, while cadmium stannate requires very refractory substrates to develop its best properties.

Diffusion Barriers between Transparent Conductors and Sodium-Containing Glass Substrates

When TCs are deposited on sodium-containing glass, such as soda-lime glass, sodium can diffuse into the TC and increase its resistance. This effect is particularly noticeable for tin oxide, because sodium diffuses rapidly at the high substrate temperatures (often >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 in-

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terference colors that would otherwise be shown by the TC film.³⁵ Alumina is a much more complete barrier against diffusion of sodium.³⁶

Etching Patterns in TCs

For some applications of TCs, such as displays, heaters, or antennas, parts of the TC must be removed. Table VI lists some chemicals that can be used to etch TCs. Zinc oxide is the easiest material to etch, tin oxide is the most difficult, and indium oxide is intermediate in etching difficulty. Series-connected thin-film solar cells also need to remove TCs along patterns of lines. This removal is usually carried out by laser ablation.

Chemical Durability

The ability of a TC to withstand corrosive chemical environments is inversely related to its ease of etching. Tin oxide is the most resistant, while zinc oxide is readily attacked by acids or bases. Silver is tarnished by air and moisture and can be used only in applications that are hermetically sealed.

Stability in Hydrogen Plasmas

In forming amorphous-silicon solar cells on TC superstrates, the TC 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.³⁷

Mechanical Hardness of TCs

The mechanical durability of TCs is related to the hardness of the crystals from which they are formed. Their hardness values may be ranked using the Mohs scale, in which higher values represent harder materials.³⁸ Table VII shows that titanium nitride and tin oxide are even harder than glass and can be used in applications that are exposed to contact. Zinc oxide is readily scratched, but can be handled with care. Thin silver films are so fragile that they cannot be touched and can be used only when coated with protective layers.

Production Costs

The costs of producing a transparent conducting material depend on the cost of the raw materials and the processing of it into a thin layer. The cost of the raw materials generally increases in this order: Cd < Zn < Ti < Sn < Ag < In. Indium is a rare and expensive element that is obtained as a byproduct of the mining of ores for their content of other metals such as zinc and lead. There are no "indium mines" because its concentration in minerals is too

Table VI: Etchants for Transparent Conductors.

Material	Etchant
ZnO	Dilute acids
ZnO	Ammonium chloride
TiN	$H_2O_2 + NH_3$
ln_2O_3	HCl + HNO ₃ or FeCl ₃
SnO ₂	Zn + HCl
SnO ₂	CrCl ₂

Table VII: Hardness of Some Transparent Conductors.

Material	Mohs Hardness
TiN	9
SnO ₂	6.5
Soda-lime glass	6
ln_2O_3	~5
ZnO	4
Ag	low

low to allow economic extraction only for the value of the indium. Thus the supply of indium cannot be increased significantly without a large increase in price sufficient to make "indium mines" profitable.

The costs of the deposition methods typically increase in the following order: atmospheric-pressure CVD < vacuum evaporation < magnetron sputtering < low-pressure CVD < sol-gel < pulsed laser deposition. This ranking was estimated by considering the lowest-cost product made by each process. The speed of the process is very important in the cost. Atmospheric-pressure CVD, vacuum evaporation, and magnetron sputtering have high deposition

rates and have been scaled up to large areas. Low-pressure CVD has higher equipment costs than atmospheric-pressure CVD. Solgel suffers from slow drying and reheating steps, while pulsed laser deposition is only suitable for small areas. This ranking can give only a rough comparison of production costs because many other factors enter into a full economic analysis, including the production volume and the tolerances for variations in the properties of the product.

Toxicity

Some of the elements used in TCs are toxic. This increases the cost of processing them because of the need to protect workers and prevent the escape of toxic materials into the environment. Additional encapsulation during use may be needed, as well as a provision for recycling at the end of the product's lifetime. Toxicity of the elements generally increases in the following order: Zn < Sn < In < Ag < Cd. Cadmium compounds are carcinogens and thus are heavily regulated and even prohibited from some applications.

Choice of Transparent Conducting Oxides

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

Examples of Applications and the TCs Chosen for Them

We will now see how these criteria apply to a number of applications in which TCs are used.

Table VIII: Choice of Transparent Conductors.

Property	Material
Highest transparency	ZnO:F, Cd ₂ SnO ₄
Highest conductivity	In ₂ O ₃ :Sn
Lowest plasma frequency	SnO_2 : F, ZnO : F
Highest plasma frequency	Ag, TiN, In ₂ O ₃ :Sn
Highest work function, best contact to <i>p</i> -Si	SnO ₂ :F, ZnSnO ₃
Lowest work function, best contact to <i>n</i> -Si	ZnO:F
Best thermal stability	SnO ₂ :F, TiN, Cd ₂ SnO ₄
Best mechanical durability	TiN, SnO ₂ :F
Best chemical durability	SnO_2 :F
Easiest to etch	ZnO:F, TiN
Best resistance to H plasmas	ZnO:F
Lowest deposition temperature	In ₂ O ₃ :Sn, ZnO:B, Ag
Least toxic	ZnO:F, SnO ₂ :F
Lowest cost	SnO_2 :F

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Low-Emissivity Windows in Buildings

TCs on window glass improve the energy efficiency of the window because the free electrons reflect infrared radiation for wavelengths longer than the plasma wavelength. The effect is similar to that of the silver coating in a Thermos bottle. In cold climates, the plasma wavelength should be fairly long, about 2 μ m, so that most of the solar spectrum is transmitted into heat inside the building. Fluorine-doped tin oxide is the best material for this purpose because it combines a suitable plasma wavelength with excellent durability and low cost. Billions of square feet of TCcoated window glass have been installed in buildings around the world.

In hot climates, a short plasma wavelength, $\leq 1 \mu m$, is desirable, so that the near-infrared portion of incident sunlight can be reflected out of the building. The metals silver and titanium nitride have sufficiently short plasma wavelengths for this application. Silver is widely used for this application despite its poor durability; it is sealed inside double-glazed panes for protection from air and moisture. Titanium nitride is much more durable and can be used on exposed surfaces, even on singleglazed windows. The reflective gold color of TiN-coated glass can frequently be seen on large office buildings, but it is not popular for residential windows.

Solar Cells

The front surfaces of solar cells are covered by transparent electrodes. In singlecrystal silicon cells, a highly doped layer of the silicon itself serves as the front electrode. In thin-film cells, a TC layer serves as the front electrode. Cadmium telluride and some amorphous-silicon solar cells are grown on a SnO₂: F-covered glass superstrate. Thermal stability and low cost are the primary factors in this choice. The high work function of SnO₂: F is also helpful in making low-resistance electrical contact to the p-type amorphous-silicon layer. Other amorphous-silicon cells are grown on flexible steel or plastic substrates; in this case, the top TC must be deposited at low temperature on thermally sensitive cells. ITO or ZnO is chosen for this purpose because both compounds can be deposited successfully at low temperatures (typically ≤200°C).

Flat-Panel Displays

The many different styles of FPDs all use TCs as a front electrode. Etchability is a very important consideration in forming patterns in the TC electrode. The easier etchability of ITO has favored its use over tin oxide, which is more difficult to etch. The low deposition temperature of ITO is

also a factor for color displays in which the TC is deposited over thermally sensitive organic dyes. Low resistance is another factor favoring ITO in very finely patterned displays, since the ITO layer can be made very thin, thus the etched topography remains fairly smooth. ZnO is lower in cost and easier to etch than ITO is, so ZnO may replace ITO in some future displays.

Electrochromic Mirrors and Windows

Automatically dimming rear-view mirrors are now installed in millions of automobiles. They include a pair of SnO₂: F-coated electrodes with an electrochemically active organic gel between them. The main considerations are chemical inertness, high transparency, and low cost. "Smart" windows with electrically controllable transmission are just entering the market-place. Tin oxide appears to be the material of choice, for the same reasons that it is chosen for electrochromic mirrors.

Defrosting Windows

Freezers in supermarkets pass electric current through TCs on their display windows in order to prevent moisture in the air from condensing on them and obscuring the view. Low cost and durability are the main factors that have led to the choice of tin oxide for this application.

Defrosting windows in airplanes was the first application of TCs, permitting highaltitude bombing during World War II. The discovery of TCs was kept secret until after the war. Originally tin oxide was used, but now ITO has replaced it in modern cockpits because its lower resistance permits defrosting larger window areas with relatively low voltage (24 V). Some automobile windshields use silver or silver-copper alloy TCs for electrical defrosting because the 12-V systems in automobiles require very low resistance, combined with the legal requirement of a minimum transmission of 70%. The metal layers are protected in the windshield by laminating them between two sheets of glass.

Oven Windows

Tin oxide coatings are placed on oven windows to improve their safety by lowering the outside temperature of the glass to safe levels. This permits the use of windows even in self-cleaning ovens that reach very high temperatures. The tin oxide coating also improves the energy efficiency of the ovens. The main criteria for this choice of material are high temperature stability, chemical and mechanical durability, and low cost.

Some transparent laboratory ovens are constructed entirely of TC-coated glass,

which also serves as the electrical resistor for heating the oven.

Static Dissipation

TCs are placed on glass to dissipate static charges that can develop on xerographic copiers, television tubes, and CRT computer displays. Only relatively high resistances ($\geq 1~\mathrm{k}\Omega/\Box$) are needed, so the main concern is mechanical and chemical durability. Tin oxide is the material of choice for these applications.

Touch-Panel Controls

Touch-sensitive control panels, such as those found on appliances, elevator controls, and ATM screens, are formed from etched TCs on glass. They sense the presence of a finger either by direct contact or capacitively through the glass. The durability and low cost of tin oxide make it a good choice for these applications.

Electromagnetic Shielding

It is apparently possible to eavesdrop on computers and communications by detecting electromagnetic signals passing through windows. These stray signals can be blocked by TCs with low sheet resistance. Silver and ITO are the best materials for this purpose.

Invisible Security Circuits

TC-coated glass can be used as part of invisible security circuits for windows or on glass over valuable works of art. Some protection from fading by UV light is also provided by the TC. Any TC (except for colored TiN) could be used. Silver/ZnO multilayers provide the best UV protection.

Improving the Durability of Glass

Some tin oxide coatings are used solely to take advantage of tin oxide's extraordinary durability and have nothing to do with its electrical conductivity. Tin oxide coatings are used on the windows of barcode readers to improve their abrasion resistance. Hydrofluoric acid etches glass, but does not affect tin oxide. Some vandals have used hydrogen-fluoride etching kits (designed to etch identifying marks on automobile windows) to etch slogans on windows. Tin oxide coatings are used to protect windows from these attacks.

Conclusions

Transparent conductors have many applications. There is no one TC that is best for all applications. Fluorine-doped tin oxide is the most widely used TC, while tin-doped indium oxide (ITO) remains preferred for flat-panel displays. Zinc oxide has potential for use in more efficient and less expensive solar cells. All of these com-

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monly used transparent conducting materials and their production methods have advantages and disadvantages that must be carefully weighed for each new application. The information in this article may help in choosing the most appropriate transparent conducting material for a new use.

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