

Deposition Of Transparent Conducting Oxides For Solar Cells

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Abstract. Transparent conductors are needed as the front surface electrodes in all types of solar cells. The electrical and optical performance of a transparent conductor may be rated by a figure of merit defined as the ratio of the electrical conductivity to the optical absorption coefficient of the layer. Fluorine-doped zinc oxide is shown to have the highest figure of merit. ZnO:F films with a sheet resistance of 5 ohms per square can have a visible absorption of less than 3 per cent. This high performance makes zinc oxide a candidate for replacing tin oxide in thin film amorphous silicon solar cells, or for replacing part of the highly-doped silicon layer in crystalline silicon solar cells. A new, cost-effective process is described for the chemical vapor deposition of ZnO:F at atmospheric pressure.

BACKGROUND ON TRANSPARENT CONDUCTORS

The first transparent conductors to be used were based on tin oxide. During the second world war, tin chloride solutions were sprayed onto hot glass, to produce electrically conductive, chlorine-doped tin oxide coatings on glass. Electricity was passed through these coatings to heat aircraft windows.¹ Doping with antimony² and fluorine³ was found to give tin oxide films with even higher conductivity.

Conductive tin-doped indium oxide (ITO) films were also prepared by spray pyrolysis⁴ and sputtering⁵. Sputtering has been the preferred mode for its production. The high cost of ITO precludes its application to photovoltaics.

Chemical vapor deposition (CVD) was later shown to be a more effective process for making fluorine-doped tin oxide films⁶. Transparency, electrical conductivity and thickness uniformity are better for the CVD films than for the sprayed films. Since the 1980's, CVD has been widely adopted in continuous production of glass coated with fluorine-doped tin oxide.⁷ By far the largest area of transparent conducting oxide (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.

Conductive zinc oxide films were first produced by spray pyrolysis with indium doping⁸ and sputtering with doping by aluminum⁹, indium¹⁰ or gallium¹¹. CVD of conductive zinc oxide films has been achieved with doping by boron¹², aluminum¹³, gallium¹⁴, indium¹⁵ and fluorine¹⁶. Fluorine-doped zinc oxide was

found to have higher transparency for a given sheet resistance, than any of the other transparent conductors. The low cost of zinc, compared to that of indium or tin, gives zinc oxide the potential to be the least expensive TCO material, as well as the best performer.

What has been lacking is an inexpensive process for the manufacture of fluorine-doped zinc oxide. Industrial experience with tin oxide has shown that CVD at atmospheric pressure is the most cost-effective method for its production. We report in this paper a new atmospheric pressure CVD process for producing fluorine-doped zinc oxide, which has the potential to make this high-performance TCO at low cost.

DESIRABLE FEATURES OF A CVD PROCESS

There are many requirements for an effective CVD process. The reactants should be readily available and cheap, and easy to purify to the required level of purity. They should remain pure and stable during shipment and storage, and should not react with air or water. They should not be pyrophoric, flammable, toxic or corrosive.

The reactants should be gases or liquids at room temperature, because their use is easier than that of solid precursors. Gases can be metered into the process with standard flow-controllers. Liquids can be evaporated from bubblers, or pumped by a metering pump into a vaporizer. The viscosity of the liquid should be low enough so that it can be pumped and metered easily. The precursors should have a high enough vapor pressure (over about 1 Torr) at a temperature low enough (under about 200 °C) so that standard components and materials may be used in the vaporizer. The vaporization process should be rapid and reproducible. In order for this to happen, the liquid should not be associated or polymeric. The liquid should remain thermally stable during the vaporization process.

The CVD reaction should take place at a temperature above the vaporization temperature, but below a temperature that would damage the substrate or degrade the properties of the deposited film. If there are two or more reactant vapors, they should remain unreactive to each other at the vaporization temperature of the least volatile reactant, so that the vapors may be mixed to a uniform and homogeneous composition before they reach the CVD chamber. The use of a homogeneous reactant vapor mixture allows films to be deposited with more uniform composition and thickness, than in the case that the reactants react prematurely, so that they must be mixed near the surface of the substrate.

The reaction should be carried out at atmospheric pressure, rather than at low pressure, so that expensive vacuum chambers and pumps are not required. The yield of film should be high, with minimal production of gaseous byproducts or powder. This requirement is important not only for the economical use of the reactants, but also so that the CVD apparatus will require only infrequent cleaning, and so that the treatment of the byproduct gases will be simplified. The growth rate of the film must be high, so that the productivity of the apparatus is high.

Finally, of course, the properties of the deposited film must be excellent, including high electrical conductivity and high transparency, good adhesion to the substrate. The morphology of the films is also important for solar cell applications. A rough, textured surface, on the scale of the wavelength of light, increases the amount of light absorbed by the cell.

SURVEY OF CVD REACTIONS USED FOR ZINC OXIDE TRANSPARENT CONDUCTORS

In this section, we will review the reactions previously reported for the CVD of zinc oxide films. Then we will report on a new CVD reaction which appears to overcome the main difficulties with the previously used reactions.

One commonly used precursor for zinc oxide films is diethylzinc. It reacts readily with water vapor to deposit zinc oxide films, at temperatures as low as about 150 °C:



This reaction is so fast that the reactant vapors must be mixed close to the surface of the substrate. It has been run successfully at atmospheric pressure and at low pressure. Textured films, with good light-trapping properties, are easily obtained from this reaction. The deposited zinc oxide film does contain a significant amount of hydrogen, probably in the form of zinc hydroxide. Because of this impurity, these films tend to desorb water vapor when heated.

Highly transparent zinc oxide films can be prepared by the CVD reaction of diethyl zinc vapor and ethanol vapor:



In the absence of other materials, however, this reaction does not begin spontaneously. If a small amount of water vapor is also present, it does begin the fast reaction (1), to deposit an initial small amount of zinc oxide. This initial deposit of zinc oxide then catalyzes on its surface the decomposition of ethanol into water and ethylene:



This decomposition reaction becomes rapid at surface temperatures above about 400 °C. The water thus produced then reacts with the diethylzinc according to reaction (1) to form more zinc oxide. The net effect of combining reactions (1) and (3) is the production of zinc oxide by the overall reaction (2). The water vapor acts as a catalyst for reaction (2).

The deposition of zinc oxide may also be initiated in a water-free vapor mixture by an already-deposited layer of zinc oxide, which then grows thicker. Other materials, such as a surface of aluminum oxide, also start the growth of zinc oxide, by catalyzing the decomposition of ethanol according to reaction (3).

An excess of ethanol vapor is necessary to make sure that the deposited zinc oxide is highly transparent. It is preferable to have a molar ratio of ethanol to diethylzinc of at least about 10. Using less ethanol produces zinc oxide films with a brown color due to absorption of visible light, probably from small amounts of carbon impurity in the film.

Dimethylzinc can also be used as a zinc source. The vapor of dimethylzinc, diluted in an inert carrier gas, such as nitrogen, may be mixed with oxygen or air for the CVD of zinc oxide films.¹⁷ At higher vapor concentrations, spontaneous burning produces powdered zinc oxide, rather than a film. The pyrophoric

properties of both dimethylzinc and diethylzinc make them somewhat dangerous precursors, requiring special care for their safe handling.

Another zinc precursor is zinc acetylacetonate. This material is stable in dry air, and is not pyrophoric. It does, however, absorb water vapor from humid air. The CVD reaction of zinc acetylacetonate with water vapor deposits zinc oxide at temperatures over about 400 °C, while the reaction with oxygen begins at about 500 °C. A considerable excess of oxygen is required to produce a highly transparent film from this reaction. Smaller amounts of oxygen leave a brown color in the film. The volatility of zinc acetylacetonate is low, so the growth rates from its CVD reaction are also low.

Table 1 summarizes the ratings of these reactions, with respect to the properties of an ideal CVD reaction. In summary, all of these previously-used CVD reactions for zinc oxide are less than ideal.

TABLE 1. CVD Reactions For Producing Zinc Oxide.
 *** = excellent, ** = good, * = fair, uns = unsatisfactory

Zn precursor	Et ₂ Zn	Et ₂ Zn	Me ₂ Zn	Zn(acac) ₂	Zn(acac) ₂	Et ₂ Zn(TEED)
O precursor	H ₂ O	EtOH	O ₂	H ₂ O	O ₂	EtOH
liquid precursor	***	***	***	*	*	***
inexpensive	***	***	*	***	***	***
stable 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	**	**	**	**	**	**

We have recently discovered a CVD reaction for zinc oxide which comes much closer to the ideal. In it, the diethylzinc is complexed with a diamine, such as tetraethylethylenediamine (TEED). The resulting liquid compound is not pyrophoric, although it still does react with water vapor. The vapor of this compound may be premixed with ethanol vapor, so that very uniform films can be deposited. Deposition becomes rapid at temperatures above about 400 °C.

Fluorine dopant can be introduced into the films using a variety of fluorocarbon gases. Acetyl fluoride is particularly effective as a source for fluorine doping. Using this new reaction, films of ZnO:F were prepared with sheet resistance as low as 8 ohms per square, along with an absorption of visible light less than 2%.

COMPARISON OF THE OPTICAL AND ELECTRICAL PERFORMANCE OF TRANSPARENT CONDUCTORS

The best transparent conductor should combine a high electrical conductivity with a low loss of light through absorption. In order to measure the performance of a transparent conductor, we proposed¹⁸ the use of a figure of merit defined by the ratio of the electrical conductivity, σ , to the visible absorption coefficient, α :

$$\sigma/\alpha = -\{R_{\square}\ln(T+R)\}^{-1} \quad (4)$$

This ratio can be evaluated by measuring the sheet resistance R_{\square} , in ohms per square, and using an integrating sphere spectrometer to find the total visible transmission T, and the total visible reflectance R, expressed as fractions. 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. This figure of merit is independent of film thickness, to the extent that the material properties of a film are independent of its thickness.

TABLE 2. Figure of Merit for Some Transparent Conductors

Material	Sheet Resistance (ohms/square)	Visible Absorption	Figure of Merit (inverse ohms)
ZnO:F	5	0.03	6.6
ZnO:Al	3.8	0.05	5.1
In ₂ O 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

Figures of merit for some transparent conductors are given in Table 2. 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.

These results show that fluorine-doped zinc oxide gives the best figure of merit among the known transparent conductors.

COMPARISON OF AMORPHOUS SILICON SOLAR CELL PERFORMANCE ON DIFFERENT TCO MATERIALS

Samples of fluorine-doped zinc oxide were deposited on glass substrates at a temperature of about 450 °C by the new APCVD process. Some were sent to the Institute for Energy Conversion, University of Delaware and to the Thin Film Division of Solarex, for evaluation of their use in superstrate amorphous silicon solar cells. Optical measurements at Solarex confirmed the high visible transmission of these films. Visible haze values ranged up to 12%, just at the lower end of the desired range of 12 to 18%. The thicknesses of the films were considered to be quite uniform over their 10 cm by 10 cm areas, with thicknesses around 800 nm. Future samples will be made slightly thicker in order to increase the haze values.

An amorphous silicon solar cell was made on ZnO:F at IEC, Delaware. Figure 1 shows the quantum efficiency for this cell as a function of wavelength. As expected from the optical measurements, the current is higher for zinc oxide than for tin oxide at all wavelengths, with the smallest increases in the red end of the spectrum. When ZnO:F samples with higher haze levels are prepared, even higher currents should be found for the red wavelengths.

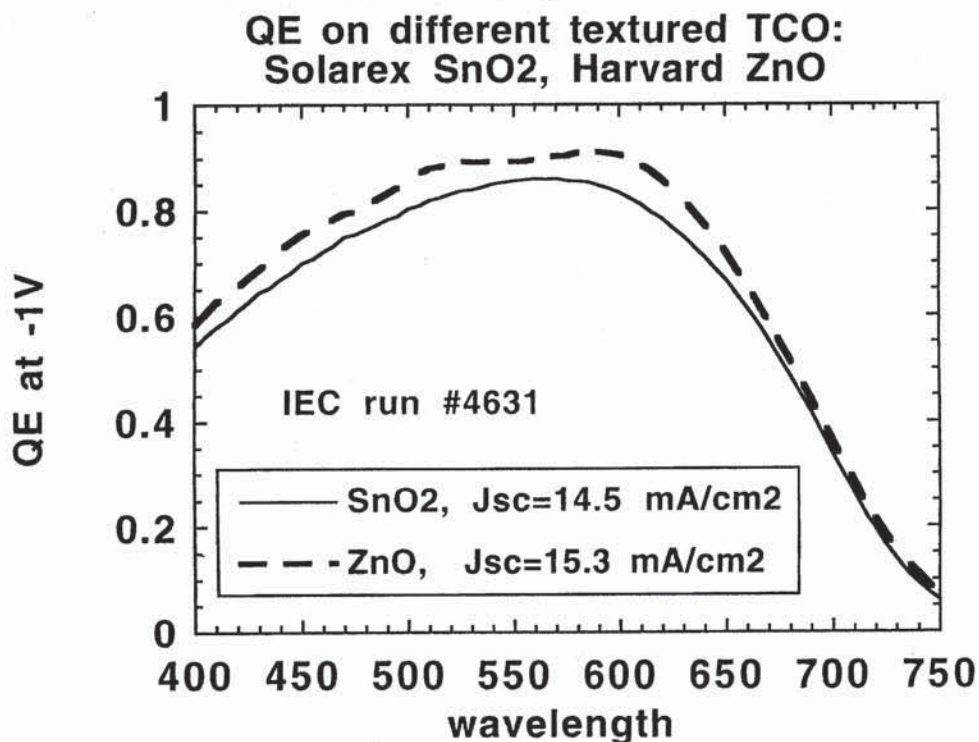


FIGURE 1. Quantum efficiency as a function of wavelength (nm) for amorphous silicon solar cells produced at IEC, Delaware on fluorine-doped tin oxide and zinc oxide.

Electrical parameters for the IEC single-junction cell are given in Table 3.

TABLE 3. Solar Cell Parameters for IEC Amorphous Silicon Solar Cells on Different TCO Films.

TCO Type	Voc V	FF %	Jsc mA/cm ²	Effic. %	Roc Wcm ²
APCVD ZnO:F	0.856	60.5	15.3	7.9	12.5
Solarex SnO ₂	0.875	67.0	14.5	8.5	7.0

Similar results are given in the table 4 for a superstrate tandem cell made at Solarex, in comparison with two of their TCO materials.

TABLE 4. Solar Cell Parameters for Solarex Tandem Amorphous Silicon Solar Cells on Different TCO Films.

TCO Type	Voc V	FF %	Jsc mA/cm ²	Effic. %	J1 mA	J2 mA
APCVD ZnO:F	1.45	67.3	10.22	9.97	9.72	10.3
LPCVD ZnO:B	1.45	70.2	9.62	9.79	9.12	10.55
SnO ₂	1.47	70.5	9.82	10.18	9.32	9.74

The voltages of the cells prepared on ZnO are about 20 mV lower than those prepared on SnO₂. The fill factors are also significantly lower, by an average of 5%. These deleterious factors negate the advantage of the higher currents found for the ZnO. Both of these deleterious effects relate to an electrical contact between the p-type amorphous silicon and ZnO that is more resistive than that with SnO₂. On the other hand, many other groups have reported that amorphous zinc oxide makes low-resistance electrical contact to n-type amorphous silicon.

These observations about contact resistance can be rationalized if (n-type) tin oxide has a higher work function (lower conduction band energy) than that of (n-type) zinc oxide. Thus the conduction band of tin oxide is closer to the valence band energy of silicon, and has a lower electrical barrier in contact with p-type silicon. The conduction band energy of zinc oxide is further above the valence band energy of silicon, and forms a higher-resistance contact.

The opposite situation holds for contacts to n-type silicon. The conduction band of zinc oxide lies closer to the conduction band of n-type silicon, forming a low-barrier, low-resistance contact. The conduction band of tin oxide lies further below the conduction band of silicon, resulting in a higher barrier and larger contact resistance to n-type silicon.

It is planned to prepare transparent conductors with the structure thin SnO₂:F/thick ZnO:F/glass. This structure should combine the best features of the two materials for use in superstrate amorphous silicon solar cells. The thick ZnO:F should provide high transparency, and the thin SnO₂:F should provide good electrical contact to the silicon.

PROPOSED USE OF TCO MATERIALS IN CRYSTALLINE OR POLYCRYSTALLINE SOLAR CELLS

Fluorine-doped zinc oxide may also have a beneficial role to play in crystalline and polycrystalline silicon solar cells, because the transparency of ZnO:F is higher than that of the doped silicon layer on the front surface of conventional cells. If the diffused n-silicon layer were made thinner and a layer of fluorine-doped zinc oxide were applied to the front surface, a more efficient cell should result. Figure 2 shows a schematic cross section of this structure. Because the ZnO:F would greatly reduce the sheet resistance of the surface, fewer metal grid lines would be needed, thereby reducing the surface recombination velocity and increasing the voltage. The current should be increased, both because of the reduced shading from fewer grid lines and the reduced absorption in the thinner diffused layer. The textured surface of the polycrystalline ZnO:F will also help provide broadband antireflection to the cell.

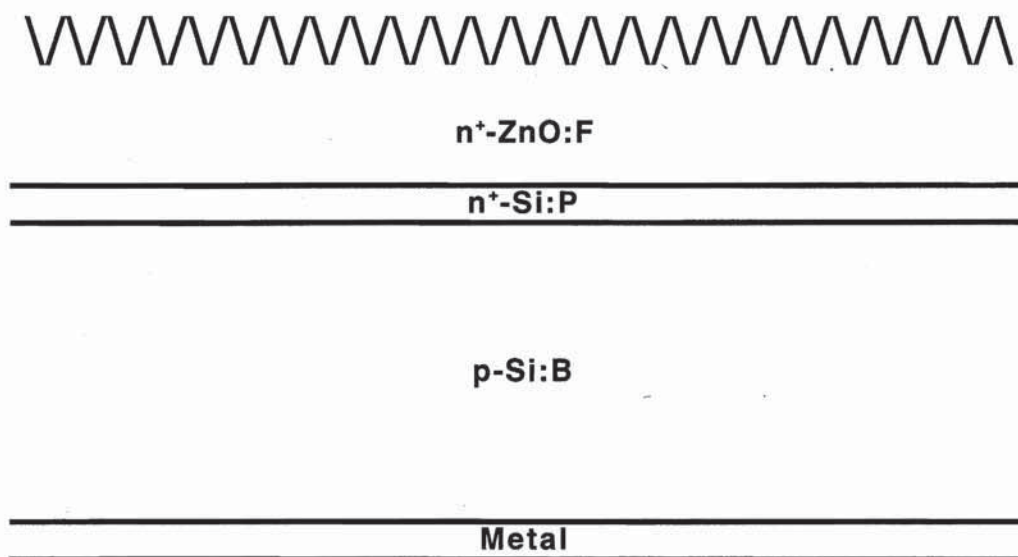


FIGURE 2. Proposed design for a more efficient crystalline or polycrystalline silicon solar cell.

STABILITY OF TCO MATERIALS

The stability of TCO materials during their formation and use must also be considered. Regarding thermal stability, the TCOs are usually found to be stable at least up to their deposition temperature. Because tin oxide is usually deposited at temperatures around 550 °C or higher, it is stable at least up to these high temperatures. APCVD fluorine-doped zinc oxide is deposited between 400 to 500 °C, and is usually stable up to about 500 °C. LPCVD boron-doped zinc oxide

increases its resistance when heated above its deposition temperature of around 200 °C.¹⁹

Zinc oxide is much more resistant to hydrogen plasma reduction than is tin oxide.²⁰

Sodium in soda-lime substrates is another factor affecting TCO materials. Sodium can diffuse out of a soda-lime substrate into the TCO and increase its resistance. This effect can be important for tin oxide, because the sodium is particularly mobile at the high substrate temperatures used in the CVD of tin oxide. In order to retard the diffusion of sodium out of the glass, a diffusion barrier of silica is usually deposited on the glass before the CVD of the tin oxide. Even though the silica does not entirely prevent the diffusion of sodium, it does reduce the amount of sodium reaching the tin oxide.²¹ The silica layer usually serves a second purpose, that of eliminating the interference colors that would otherwise be shown by the tin oxide film.²²

Because the CVD zinc oxide processes operate at lower glass temperature, under 500 °C, sodium diffusion from the glass is negligible, and the extra step of applying a sodium diffusion barrier is not needed. The low glass temperature also helps to avoid warping the glass substrates during the CVD process.

CONCLUSIONS

Because of the many requirements for a TCO, many factors must be taken into account in the choice of the most appropriate material. Table 5 summarizes the relative properties of the most widely used TCO materials.

TABLE 5. Criteria for the Choice of a Transparent Conductor.

***=excellent, **=good, *=fair.

MATERIAL	TRANS-PARENCY	STABILITY TO H PLASMA	THERMAL STABILITY	CONTACT RESIST-ANCE	COST	ABUN-DANCE
ZnO:F	***	***	**	***(n-Si)	***	***
SnO ₂ :F	*	*	***	***(p-Si)	***	**
In ₂ O ₃ :Sn	**	**	*	**	*	*

It is clear that no one material is best in all respects. For the highest currents in solar cells, the high transparency of zinc oxide is the most important factor. Low contact resistance is also essential for high voltages and fill factors, so the optimum choice for a transparent electrode over p-type amorphous silicon may require a composite of a thick zinc oxide layer and a thin tin oxide layer in contact with the p-type silicon.

Applying a layer of conductive ZnO:F to the front surface of crystalline or polycrystalline silicon solar cells should allow thinner diffused layers and fewer metal grid lines, increasing both the current and the voltage of the cells.

For large-scale use in photovoltaics, abundance in the Earth's crust will eventually favor the use of zinc, over less abundant tin, which is mined in only a few areas, and indium, a rare metal in limited supply.

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