Optimization of Transparent and Reflecting Electrodes for Amorphous Silicon Solar Cells

Final Technical Report

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TABLE OF CONTENTS

Abstract.....	1
Introduction.....	3
Experimental	3
Precursors	3
Experimental Procedure	4
Results and Discussion	6
Film Deposition	6
Composition and Crystal Structure	7
Electrical Properties	8
Optical Properties.....	10
Thermal Stability	11
Application to Amorphous Silicon Solar Cells.....	12
Summary.....	13
Acknowledgments	13
References.....	14
 Figure 1.....	 16
Figure 2.....	17
Figure 3.....	18
Figure 4.....	19
Figure 5.....	20
Figure 6.....	21
Figure 7.....	22
Figure 8.....	23
Figure 9.....	24
Figure 10.....	25
Figure 11.....	26
Figure 12.....	27
Figure 13.....	28
Figure 14.....	29
Figure 15.....	30
Figure 16.....	31
Figure 17.....	31
 Table 1	 32

ABSTRACT

Transparent conducting fluorine doped zinc oxide was deposited as thin films on soda lime glass substrates by atmospheric pressure chemical vapor deposition (CVD) at substrate temperatures of 460 °C to 500 °C. The precursors diethylzinc, tetramethylethylenediamine and benzoyl fluoride were dissolved in xylene. This solution was nebulized ultrasonically and then flash vaporized by a carrier gas of nitrogen preheated to 150 °C. Ethanol was vaporized separately, and these vapors were then mixed to form a homogeneous vapor mixture. Good reproducibility was achieved using this new CVD method. Uniform thicknesses were obtained by moving the heated glass substrates through the deposition zone. The best electrical and optical properties were obtained when the precursor solution was aged for more than a week before use. The films were polycrystalline and highly oriented with the c-axis perpendicular to the substrate. More than 90% of the incorporated fluorine atoms were electrically active as n-type dopants. The electrical resistivity of the films was as low as $5 \times 10^{-4} \Omega\text{cm}$. The mobility was about 45 cm^2/Vs . The electron concentration was up to $3 \times 10^{20}/\text{cm}^3$. The optical absorption of the films was about 3-4% at a sheet resistance of 7 ohms/square. The diffuse transmittance was about 10% at a wavelength of 650 nm. Amorphous silicon solar cells were deposited using the textured fluorine doped zinc oxide films as the front electrode. The short circuit current was increased over similar cells made with fluorine doped tin oxide, but the open circuit voltages and fill factors were reduced. The voltage was restored by overcoating the fluorine-doped zinc oxide with a thin layer of fluorine-doped tin oxide.

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INTRODUCTION

Zinc oxide is a large band gap semiconductor (3.3 eV) with a hexagonal wurtzite structure. As a thin film, zinc oxide has many practical applications, such as in solar cells, liquid crystal flat panel displays, energy efficient windows, gas sensors, surface acoustic wave devices, piezoelectric devices, ultrasonic transducers, etc.¹⁻³

Transparent conductors are materials with low electrical resistivity and high transmittance of visible light. Semiconducting metal oxides such as indium oxide, cadmium oxide, tin oxide and zinc oxide are transparent due to their large band gaps. They can be doped with impurity atoms to make transparent conductors. Zinc oxide has several advantages over the other transparent conducting oxides. Cadmium compounds are toxic and carcinogenic. Organotin precursors are toxic, while zinc compounds are generally non-toxic. Zinc metal is less expensive than tin, indium or cadmium. For solar cell applications, fluorine doped tin oxide currently is the most widely used front electrode. Tin oxide has the problem that it can be reduced during the plasma deposition process for making amorphous silicon solar cells. This results in elemental tin at the silicon interface which can cause optical loss or diffusion of tin into the silicon. These problems can lead to degradation in solar cell efficiency. Zinc oxide is more stable than tin oxide in a plasma reducing environment. Zinc oxide also has a higher optical transmittance than the other transparent conducting oxides. These two factors suggest zinc oxide may lead to higher solar cell efficiency than tin oxide. Zinc oxide is easier to etch than tin oxide and indium oxide. It can be etched easily in aqueous acids such as dilute hydrochloric acid. This makes it easier to produce patterns for liquid crystal flat panel displays. These advantages suggest that zinc oxide should be a technologically important material for transparent conducting applications.

Zinc oxide films have been successfully deposited by chemical vapor deposition (CVD),⁴⁻¹⁴ sputtering,¹⁵⁻¹⁸ vacuum evaporation,¹⁹ spray pyrolysis²⁰⁻²² and other thin film deposition techniques. CVD generally has higher growth rates and better uniformity than the other deposition processes. It is more suitable for large scale commercial applications. Conductive zinc oxide films have been made by adding impurity dopants such as fluorine²³, boron²⁴, aluminum²⁵⁻³¹, gallium³²⁻³⁴, and indium^{35,36}. The fluorine-doped zinc oxide films have the highest conductivity and transparency.

In this paper, we report the atmospheric pressure chemical vapor deposition of fluorine doped zinc oxide films using the tetramethylethylenediamine adduct of diethylzinc, $(C_2H_5)_2Zn(CH_3)_2NCH_2CH_2N(CH_3)_2$, as the zinc source, benzoyl fluoride (C_6H_5COF) as the fluorine dopant, and ethanol (C_2H_5OH) as the oxygen source. We also investigated the structural, electrical and optical properties of the films, and their applicability to amorphous silicon solar cells.

EXPERIMENTAL

Precursors

The commonly used zinc precursors for chemical vapor deposition of zinc oxide include diethylzinc ($Zn(C_2H_5)_2$), dimethylzinc ($Zn(CH_3)_2$), and zinc acetylacetonate ($Zn(C_5H_7O_2)_2$). Both dimethylzinc and diethylzinc are difficult to handle because they burn spontaneously in air (pyrophoric). They are very reactive to oxygen and moisture, making a CVD process subject to disruption by leaks of air. The resulting films are frequently irreproducible and not uniform. Zinc acetylacetonate is a solid and has low solubility in the common solvents. It is difficult to vaporize as a precursor. Films made with zinc acetylacetonate also have relatively low growth rate and high resistivity ($>10^{-3} \Omega cm$).

The tetramethylethylenediamine (TMEDA) adduct of diethylzinc ($Et_2Zn(TMEDA)$) is synthesized by reacting diethylzinc with tetramethylethylenediamine. It is a compound with a chelate amine ligand attached to the diethylzinc. The zinc atom of the chelated precursor molecule is less accessible than in diethylzinc; therefore the chelated precursor is

much less reactive to oxygen and moisture, and is not spontaneously flammable. The new CVD process based on the chelated precursor is more controllable and reproducible, and the films are more uniform. $\text{Et}_2\text{Zn}(\text{TMEDA})$ is a solid that is easily dissolved in organic solvents such as xylene. Variants of the precursor are made by reacting diethylzinc with other amine ligands, such as tetraethylethylenediamine, $\text{N,N}'$ -dimethyl- $\text{N,N}'$ -diethylethylenediamine, N,N -dimethyl- N' -diethylethylenediamine, and $\text{N,N,N}'$ -dimethyl- N' -diethylethylenediamine. The resultant precursors are liquids at room temperature and have reactivity similar to $\text{Et}_2\text{Zn}(\text{TMEDA})$. Since tetramethylethylenediamine is less expensive than the other amine ligands, we used mainly $\text{Et}_2\text{Zn}(\text{TMEDA})$ as the zinc precursor.

An important advantage of these chelated diethylzinc precursors is that their vapors can be premixed homogeneously with ethanol vapor as an oxygen source. In our previous work²³⁻²⁵ with unchelated diethylzinc, the reaction with alcohol was so fast that premixing could not be used, and the vapors had to be mixed directly over the substrate from separate inlets. In a CVD process, homogeneously premixed vapors allow a much simpler injector design with a single inlet. Process reproducibility is also much improved with a homogeneous reactant vapor mixture, because the reactivity does not depend on the details of how the reactant vapors mix at the inlet to the reactor. We also tried other alcohols, such as isopropanol, but the results were not as good. The film conductivity was lower and the visible absorption was higher with isopropanol than with ethanol.

Finding an effective fluorine dopant source was difficult. We tried using several fluorine sources. Hexafluoropropene gas could be used as a dopant source for making conductive films, but large quantities are needed and thus it is not an efficient dopant source. Other gas phase fluorine sources such as hydrogen fluoride inhibited film growth at even low concentrations. We also tried acetyl fluoride. It has a boiling point of 20°C , so it is in between a liquid and a gas at room temperature. Various methods were used to introduce acetyl fluoride, but none were very reliable. Introducing acetyl fluoride as a gas from a heated cylinder did not lead to fluorine-doped films. Dissolving the acetyl fluoride in the zinc precursor solution was successful in producing fluorine-doping, but the concentration was not very reproducible because the very volatile acetyl fluoride escaped easily from solution. Benzoyl fluoride is a stable liquid at room temperature. It could be added to the zinc precursor solution, and it produced fluorine doping efficiency even at low concentrations. We found benzoyl fluoride to be convenient and reliable as a fluorine dopant, although the precursor solutions including benzoyl fluoride have a limited shelf life, as explained in the results section.

Experimental Procedure

The ZnO films were deposited with a BTU belt furnace. The experimental set up is schematically shown in Figure 1. The substrate temperature was varied from 450°C to 525°C . The injector consisted of a cylindrical shower head with small holes along its side, housed in a cylindrical chamber leading down to a slot 6 mm wide and 124 mm long. It was designed to make uniform films with all the precursors premixed before entering the injector. $\text{Et}_2\text{Zn}(\text{TMEDA})$ was synthesized by reacting diethylzinc in xylene with tetramethylethylenediamine. Benzoyl fluoride was mixed with $\text{Et}_2\text{Zn}(\text{TMEDA})$ dissolved in equal weight of xylene. Glass containers were not satisfactory for storage of the fluorine-doped solutions, because some precipitate gradually formed, probably from etching of the glass. Polyethylene containers were better for storage of the fluorine-doped solution, but they also tended to produce some residue, which may arise from leaching components of the plastic. Finally, we found that poly-fluorocarbon containers, such as Teflon, could be used to store the fluorine-doped solution in a dry nitrogen atmosphere without any precipitation or residue formation. Even with these precautions, there were gradual chemical changes within the clear solution, leading to CVD results that depended

on the time elapsed since the mixing of the benzoyl fluoride into the solution. These changes are noted in the sections on the results.

Anhydrous ethanol was obtained from Pharmco with a specification of less than 0.1 weight % water. The water content of this ethanol was determined using the Karl-Fischer titration method to be about 0.04 weight %.

The zinc precursor was pumped from a syringe pump to a SONOTEK ultrasonic nozzle that turned the solution into a fine mist of droplets of about 20 to 50 micron diameter. The precursor injection speed varied from 0.2 ml/min to 1.8 ml/min, corresponding to about 0.1 mol % to 1 mol % in the gas stream. Nitrogen carrier gas, preheated to about 150°C, met the precursor at the ultrasonic nozzle and vaporized the precursor droplets. The nitrogen gas was first purified by passing it through an oxygen purifier so that the oxygen content was in the parts per billion level. The nitrogen carrier gas flow rate varied from 8 L/min to 12 L/min. Ethanol was introduced through another line, also from a syringe pump. The injection speed varied from 1.0 ml/min to 6.0 ml/min, corresponding to about 3 mol % to 30 mol % in the gas stream. Ethanol was vaporized at a 1/16" Swagelok tee joint by nitrogen carrier gas heated to 80°C. The carrier gas flow rate for ethanol was set to 1.6 L/min.

Two types of experiments were carried out. One was a static deposition where the substrates were stationary during the deposition. This was used to study the flow pattern and kinetics of the deposition process. The other type was a moving deposition where the substrates were moved by a belt at a constant speed across the reaction zone so that a uniformly thick film could be deposited. The belt speed varied from 0.5 to 10 inch/min.

Soda lime glass and silicon were used as the substrates. Soda lime glass was projector slide glass from Kodak. Silicon was 4 inch wafers from Silicon Sense Inc. The substrates were first cleansed with soap and water, then rinsed thoroughly with deionized water, then blown dry with dry air. The substrates were put on a substrate holder designed so that the substrate surface was level with the substrate holder surface. This produced a more uniform flow across the substrate surface and minimized edge effects. The substrate holder was made from either stainless steel or aluminum. The substrate surface temperature was profiled by cementing a thin thermocouple on the substrate. The substrate temperature was 30°C to 50°C below the furnace temperature.

Film thickness was measured with a Tencor Alpha-Step 200 profilometer. A step was generated by covering the film with Scotch tape and etching in 4M HCl. The sheet resistance was measured with a Veeco FPP-100 four point probe. The mobility and electron concentration of the films were measured using van der Pauw's method. A square pattern was generated by covering the film with 3/4 inch wide Scotch tape, then etching the uncovered part in 4M HCl, then the Scotch tape was peeled off, and a Scotch tape with the same width was placed perpendicularly on the film, and the uncovered parts etched off.

Optical properties in the near ultraviolet, visible and near infrared regions were measured with a Hitachi U-4001 spectrophotometer with an integrating sphere detector. Transmittance was taken as 100% when the two back holes in the sample beam and reference beam paths were covered with barium sulfate plates. Total transmittance was measured by placing the sample on the sample beam entrance of the integrating sphere. The sample beam hit the sample, then entered the integrating sphere, and was reflected by the barium sulfate plate. The diffuse transmittance was measured by removing the barium sulfate reflectance standard so that the perpendicular part of the light was passed through. Total reflectance was measured by placing the sample against the back hole of the integrating sphere in the sample beam path at an angle of about 10 degrees perpendicular to the incident beam.

For solar cell applications, the two most important optical properties are film absorption and texture. Film texture was characterized by measuring the diffuse transmittance. Film absorption was estimated by subtracting the total reflectance and total transmittance from 100%. For textured ZnO films on glass, since ZnO ($n=2.0$) has a

higher refractive index than glass ($n=1.52$) and air ($n=1$), some of the light is trapped inside the film by total internal reflection. This causes the measured absorption to be higher than the actual value. This effect is much reduced in a solar cell structure. Since silicon has a higher refractive index than ZnO, light in a solar cell would be trapped inside the silicon instead of the ZnO. To correct partially for this light trapping effect in our absorption measurements, an index fluid of $n=1.76$ was sandwiched between the film and a thin 7059 cover glass. The absorption of the cover glass/index fluid/film/substrate structure was measured. Since the soda lime glass substrate had about 2% absorption in the near infrared and the index fluid also had some absorption, the estimated film absorption was calculated by subtracting the absorption of the cover glass/index fluid/substrate structure.

X-ray diffraction spectra were obtained using a GE X-ray diffraction machine with iron K radiation. The X-ray wavelength was $1.93604\text{\AA}$. The operating voltage was 40 kV and the current was 10 mA. A manganese filter was used to filter out the iron $K\beta$ line, but a slight amount of $K\beta$ radiation still passed through, as could be seen from the small $K\beta$ line diffraction peaks in the X-ray spectra.

Rutherford backscattering spectra were obtained using a General Ionics Model 4117 spectrometer. The operating He^+ beam energy was 2.0 MeV. Since the fluorine concentration was very low in the film, and the fluorine signal sat on the silicon background, it was impossible to detect fluorine content using RBS. Two methods were used to measure the fluorine concentration. One was a nuclear reaction analysis method using the RBS machine. H^+ ions were used in the incident beam. Incident beam energy was varied in small increments. The γ radiation from the nuclear reaction with fluorine was measured. The nuclear reaction $^1\text{H}(^{19}\text{F},\alpha\gamma)^{16}\text{O}$ produced a strong resonance near 1.3 MeV. The total count was compared with a standard in order to obtain the fluorine concentration in the film. The standard for calibration was a Teflon tape. The other method used for measuring the fluorine concentration was electron microprobe analysis (EMA). It was done on a Cameca MBX electron microprobe using wavelength dispersive spectrometers. The operating beam voltage was 5 keV, beam current was 20 nA, and beam size was $32\mu\text{m} \times 32\mu\text{m}$. The standard for calibration was calcium fluoride.

Film morphology and crystallite size were studied with a LEO 982 Scanning Electron Microscope with GEMINI column.

RESULTS AND DISCUSSION

Film Deposition

Static depositions were first made to study the flow pattern and kinetics of the deposition process. On bare soda lime glass, results were not reproducible and sometimes no film was deposited, or film was only deposited on parts of the substrate. This was attributed to the inability of ethanol to react directly with the zinc precursor. A thin layer (a few tens of nm) of Al_2O_3 , TiO_2 , ZnO or SnO_2 precoated on the glass substrates did initiate reproducible ZnO growth, probably by catalyzing the dehydration of ethanol to water. As ZnO was grown and covered these oxides, its own surface also acted as a catalyst for the dehydration of ethanol to grow a next layer of ZnO on top. The results were reproducible when the substrates were precoated with any one of these oxides of aluminum, titanium, zinc or tin, all of which are known to catalyze the dehydration of alcohols. Alternatively, if a small amount of water vapor was introduced into the reaction zone just before the deposition began, it reacted with the zinc precursor to form a thin layer of ZnO on bare soda lime glass and initiated reproducible film growth.

Because the zinc precursor and ethanol were premixed before entering the injector, and large amount of ethanol was used, it was important to use anhydrous ethanol. Even

trace amounts of water in the ethanol ($>0.1\%$) could react with the zinc precursor to form powder before entering the reaction zone. For example, 0.4% water in the ethanol reduced film thickness by 40% . The ethanol to zinc molar ratio was greater than 10. If lower amounts of ethanol were used, the films looked brown in transmission. Both the optical absorption and the film resistivity increased. These effects may be due to carbon incorporation in the films from incomplete reaction of the zinc precursor.

Below a substrate temperature of 450°C , very little film was grown. At a zinc precursor concentration of $0.3\text{ mol } \%$, the film growth rate increased with substrate temperature until 480°C . Above 480°C the growth rate remained the same. At a higher zinc precursor concentration of $0.9\text{ mol } \%$, the growth rate increased with substrate temperature until 510°C . Increasing the precursor concentration required a higher substrate temperature to achieve a similar deposition efficiency. The maximum growth rate was as high as 1000 nm/min near the gas injector slot. The ethanol concentration did not affect the film growth rate over a broad range. The benzoyl fluoride concentration in the precursor affected the growth rate, and its effect depended on how long the precursor mixture was aged after mixing in the benzoyl fluoride. If the precursor solution was not aged, a high benzoyl fluoride concentration ($\geq 3\text{ mole } \%$ relative to zinc) strongly inhibited film growth. If the precursor was aged for more than one week, the inhibition effect did not occur until a much higher fluorine concentration was reached. The dependence of the growth rate on fluorine concentration for the aged precursors is shown in figure 2.

Films made with static deposition usually had the maximum growth rate right under the inlet slot in the injector. As the precursor flowed along the substrate surface, it was gradually depleted, and the film growth rate became lower near the two exhaust slots. Looking at the film in reflectance showed stripes of interference color bands from the variation in thickness. Moving the substrate through the deposition zone produced uniformly thick films over the entire substrate. It was found that a precoated catalytic metal oxide was not necessary for uniform film growth during moving depositions on bare soda lime glass substrates. This effect was attributed to the nearby surface of the substrate holder, which already had ZnO deposited on it during previous depositions. The ZnO could catalyze the dehydration of ethanol into water and film growth could be initiated on the bare soda lime glass substrate. We confirmed this hypothesis by running depositions on bare soda lime glass substrates without using the substrate holder. The nucleation was poor without the substrate holder, indicating the necessity of an oxide layer to initiate growth. The maximum growth rate for moving deposition was about 240 nm/min .

The deposition efficiency of the reaction was calculated at the substrate temperature of 495°C , which was the optimum substrate temperature for obtaining good electrical conductivity. It was calculated from dividing the amount of zinc deposited in the film by the amount of zinc supplied in the precursor. The typical value was about 30% . The film growth rate could be varied by changing the precursor concentration. This was accomplished by varying the syringe pump speed. The growth rate increased with increasing precursor concentration, but the dependence was sub-linear. The deposition efficiency decreased with increasing precursor concentration. At $0.2\text{ mol } \%$, the deposition efficiency was 30% , at $0.4\text{ mol } \%$ it was 27% , at $0.6\text{ mol } \%$ it was 23% .

Composition and Crystal Structure

Rutherford back scattering (RBS) spectra were obtained for zinc oxide films deposited on silicon. RBS (figure 3) spectra showed the zinc oxide films had a Zn:O=1:1 stoichiometry. No carbon was detected in RBS. Since the fluorine content was very low and the fluorine signal sat on the silicon background, we could not detect the fluorine signal in the RBS spectra. The nuclear reaction method detected fluorine atoms one at a time, but the results were not consistent enough to be quantitatively useful. Electron microprobe analysis (EMA) with calcium fluoride as a standard gave fluorine concentration of 0.2 to

0.3 atomic percent. Since the fluorine concentration was near the detection limit, the results should only be taken as an estimate of the fluorine concentration.

X-ray diffraction patterns of all films grown in this study were crystalline with a hexagonal wurtzite structure. Figures 4 and 5 show the X-ray spectra of undoped and fluorine doped ZnO films grown at 495°C. Besides a small (103) peak in the undoped film, the main peaks were at (002) for both samples, indicating the crystallites had a strong orientation with the c-axis perpendicular to the substrate. The peaks near $2\theta=39.5^\circ$ were from iron $K\beta$ radiation in the X-ray source. Using the position of the (002) peak and the Bragg diffraction condition: $2d\sin\theta=n\lambda$, we calculated the lattice constant of undoped zinc oxide was $c=5.193\text{\AA}$. This is very closed to the published value $c=5.207\text{\AA}$.³⁷ The fluorine doped film had a very slight shift of $\Delta(2\theta)=0.02^\circ$ of the (002) peak towards the lower angles, corresponding to a small increase in the bond length. The n-type doping placed electrons in the anti-bonding conduction band, thereby weakening and lengthening the bonds.

The full width at half maximum of the (002) peaks of both the undoped and fluorine doped ZnO films were the same. This indicated the crystallite sizes along the c-axis for both films were the same. An estimate of the crystallite size in the direction perpendicular to the substrate was calculated using the Scherrer equation³⁸:

$$t=9\lambda/\beta\cos\theta \quad (1)$$

where λ is the wavelength of the X-ray, θ is the angular diffraction peak position, and β is the FWHM of the peak. The calculated crystallite thickness was about 0.3 micron for a film 0.8 micron thick.

Electrical Properties

Film resistivity was measured from the sheet resistance and the film thickness. The films deposited using moving substrates had good uniformity in both the film thickness and sheet resistance, usually with a variation of less than 10% over the entire substrate area. Variation mainly occurred near the edges. The edge area usually had slightly higher sheet resistance and lower growth rate. This could come from a small variation of the temperature over the substrate. Deposition parameters such as the substrate temperature, dopant concentration, precursor aging time, and ethanol concentration were varied to optimize the film resistivity.

The lowest resistivity was found for substrate temperatures around 480°C to 500°C. At temperatures below 500 °C, the electron mobility of the films generally increased with increasing substrate temperature because of the larger grain sizes and better crystallinity. At substrate temperatures above 500°C, the mobility and the electron concentration started to decrease. Either the dopant was less efficiently incorporated into the film or the dopant was not as electrically active at the higher deposition temperatures. The mobility could become lower from increased defect scattering if sodium diffused into the film at the higher temperatures from the soda lime glass substrate. The dependence of the film thickness and the electrical properties on substrate temperature is shown in figure 6.

The aging time of the fluorine and zinc precursors affected the film resistivity. Benzoyl fluoride was premixed with $\text{Et}_2\text{Zn}(\text{TMEDA})$ in xylene solution and stored in a glove box for up to 2 months. Films made with the precursor aged for more than one week, but less than five weeks had film resistivity about 30% lower than the films made with precursor aged for less than one week. This was probably because the fluorine exchanged with the ethyl group and attached to the zinc atom, resulting in more efficient doping during film deposition. However, aging the precursor for more than five weeks

resulted in higher film resistivity. It was found that both the electron concentration and mobility were lower. This could be due to the formation of zinc fluoride in the precursor or in the film. NMR spectra showed there was a reaction between the zinc and the fluorine precursors over time, but the precise mechanism was not clear.

If the precursor solution was used soon (less than a week) after adding the benzoyl fluoride, the film resistivity was very sensitive to the precise concentration of fluorine in the precursor. Even a few percent change in the fluorine concentration resulted in large change of the resistivity. The results were difficult to reproduce. For precursor solutions aged more than a week, the resistivity was much less sensitive to the fluorine concentration in the precursor, and the optimum fluorine concentration had a wider range. The optimum molar ratio of fluorine to zinc was in the range 1:20 to 1:30. The deposition process was more controllable and reproducible when the precursor was aged for a week or more before use. The dependence of several electrical properties on fluorine concentration in the precursor solution is shown in figures 7 to 9.

Ethanol concentration also affected the film resistivity. When ethanol concentration was low (below 10:1 ethanol to zinc molar ratio), the films had higher resistivity. This was probably due to carbon contamination in the film from the incomplete decomposition of the zinc precursor. The resistivity was optimized over a relatively wide range of ethanol concentration. The optimum molar ratio of zinc to ethanol was about 1 to 20. When the ethanol concentration was too high, the resistivity increased. The increase in resistivity mainly came from a decrease in the carrier concentration, indicating doping was less efficient when the ethanol concentration was high.

The resistivity also depended on the film thickness. Thinner films had higher resistivity. Generally, the mobility of thinner films was lower because of the smaller grain size. This resulted in larger grain boundary scattering of the free electrons. We found that both the mobility and electron concentration were lower for thinner fluorine doped zinc oxide films. The decrease in electron concentration could be attributed to the increase of trapping states at the grain boundaries when the grain sizes were smaller. Figure 10 shows the dependence of the resistivity on film thickness. The thickness of these films was varied by changing the speed at which the substrate moved across the reaction zone. For films with thickness less than 300 nm, film resistivity depended very strongly on the film thickness, since grain boundary scattering was important for thinner films with small crystallite sizes. For films with thickness greater than 300 nm, film resistivity depended only weakly on the film thickness. Grain boundary scattering was less important when the crystallite sizes were large. The mobility of the thicker films was dominated by ionized impurity scattering. For amorphous solar cell applications, we wanted films with low sheet resistance ($<15 \Omega/\text{square}$) and a high diffuse transmittance ($>10\%$ near 650 nm); both of these qualities required thick films. We concentrated on investigating films with thickness in the range of 700 nm to 900 nm.

The electrical properties of undoped and fluorine doped zinc oxide films were measured for comparison. Undoped ZnO films were deposited under the same conditions as fluorine doped ZnO films except no benzoyl fluoride was added. The optimized fluorine to zinc molar ratio in the precursor for making the doped films was 1:27. The substrate temperature was 495°C . The zinc precursor concentration was 0.6 mol% in the gas phase. The ethanol vapor concentration was 12 mol%. The total carrier gas flow was 12 L/min. The exhaust flow was 24 L/min. The belt speed was 2 inch/min. Hall mobility and electron concentration were measured using van der Pauw's method. Both the undoped and doped films had similar mobility of about $45 \text{ cm}^2/\text{Vs}$. This was higher than other transparent conductors such as indium tin oxide and fluorine doped tin oxide. Doping increased the electron concentration by two orders of magnitude. The undoped films had electron concentration of the order of $10^{18}/\text{cm}^3$, and the fluorine doped films had electron concentration of around $2 \times 10^{20}/\text{cm}^3$. The film resistivity of the fluorine doped zinc oxide

films was as low as $5 \times 10^{-4} \Omega\text{cm}$. The doping efficiency was calculated from the electron concentration divided by the fluorine concentration in the film. The doping efficiency was around 90%.

Fluorine was expected to replace oxygen in the zinc oxide lattice and contribute free electrons, but they also acted as ionized impurity scattering centers. SEM micrographs (figure 11) showed that when the fluorine concentration was high, the grain size decreased. Grain boundary scattering increased when the grain size decreased. Therefore, the mobility of films with high fluorine concentration decreased due to both the increase in ionized impurity scattering and grain boundary scattering. A high fluorine concentration in the films did not necessarily lead to a higher electron concentration. The fluorine atoms needed to replace the oxygen atoms in the zinc oxide crystal structure if they were to contribute free electrons. If the fluorine atoms did not occupy the proper oxygen sites or if they formed zinc fluoride, they would not provide free electrons and could change the morphology and grain size of the films. The SEM micrographs (figure 11) showed the undoped films had large grain size with a hexagonal structure. The crystallites were plate-like and thin in one of the dimensions. The plates were randomly tilted, indicating the crystallites were not completely oriented with the c-axis perpendicular to the substrate surface. Fluorine doped films with the optimum fluorine concentration for low resistivity had a hexagonal columnar structure. The crystallites were thick and shrank near the top. The columns were highly oriented with the c-axis perpendicular to the substrate surface. The optimal doped films were more oriented than the undoped films. Films with higher than optimum fluorine content had a plate-like morphology similar to the undoped films but with smaller crystallite sizes.

Optical Properties

Transmission and reflection spectra were obtained in order to study the optical properties of the films. The total transmittance and reflectance of a ZnO film with optimum fluorine doping is shown in figure 12. The film thickness was about 800 nm and the sheet resistance was about $7 \Omega/\text{square}$. Optical absorption and texture were the two main optical properties we tried to optimize. For solar cell applications, a low optical absorption is desired to allow more photons to enter the active cell region and generate electron-hole pairs. Film texture is desired to provide light trapping in the cell in order to lengthen the light path in the cell. This is especially important for silicon in the near infrared region of the spectrum, since silicon does not absorb strongly in this region.

Deposition conditions such as the substrate temperature, dopant concentration, and ethanol concentration were varied to study the optical absorption of the films. Film absorption was mainly affected by the ethanol concentration. Low ethanol concentrations resulted in brown films with high absorption. This may be due to carbon contamination from incomplete decomposition of the zinc precursor. Optical absorption decreased with increasing ethanol concentration. This must be compromised with electrical resistivity, since a higher than optimum ethanol concentration increased the film resistivity.

Doping the films with fluorine generated free electrons, which modified the optical properties of the films. Increasing the electron concentration in the film also led to increased absorption in the visible region from free electron absorption. The absorption coefficient α in the visible region is given by³⁹:

$$\alpha = 4\pi k / \lambda = (e^3 / 4\pi^2 \epsilon_0 c_0^3) (\lambda^2 n_e / m^{*2} \mu) \quad (2)$$

where n and k are the real and imaginary parts of the refractive index, λ is the wavelength, n_e is the free electron concentration, m^* is the effective mass, and μ is the mobility. Since the fluorine doped zinc oxide films had high mobility and low electron concentration, film absorption was lower than other transparent conductors such as indium tin oxide and fluorine doped tin oxide. The solar weighted average absorption in the wavelength region

400 nm to 700 nm was as low as 3-4% for films with a sheet resistance about 7-8 Ω /square.

Figure 13 shows the absorption spectra of undoped and doped zinc oxide films. The doped zinc oxide film showed increased absorption in the near infrared region due to the increase in free electron concentration. The doped zinc oxide films had lower absorption in the near ultra-violet region because of the Moss-Burstein effect. When the semiconductor was heavily doped, the Fermi level shifted into the conduction band and the bottom of the conduction band became filled. The valence electrons could only be excited to the unoccupied states in the conduction band. The effective optical band gap was increased. The Moss-Burstein effect is partly offset by a band gap narrowing effect due to carrier-carrier interactions and carrier-impurity interactions. For heavily doped films such as the fluorine doped zinc oxide, the Moss-Burstein effect is dominant and the absorption edge shifted to the lower wavelengths. As a result, the doped films had lower absorption in the near ultra-violet regions. This effect is advantageous in solar cell applications to allow more photons in the near ultra-violet region to enter the cell. It can also be useful in some optoelectronic devices where band gap tailoring is required.

Film texture was measured by the diffuse transmittance of the films. For effective light trapping, about 5% diffuse transmittance at 650 nm is adequate to enhance cell performance.⁴⁰ We found that the film texture depended on the substrate temperature, ethanol concentration, and dopant level. Texture increased with the substrate temperature. This was due to the increase in grain size at the higher temperatures. Texture decreased when the ethanol concentration was high. The nucleation density was probably higher when the ethanol concentration was high, leading to smaller crystallite sizes and smoother films. Texture also decreased with increasing fluorine dopant concentration. Figure 14 shows the diffuse transmittance spectra of undoped, optimally doped and highly doped films. For the optimally doped films, more than 10% diffuse transmittance was achieved at a wavelength of 650 nm.

Thermal Stability

The fluorine doped zinc oxide films were stable at room temperature. The electrical and optical properties did not change with time. The thermal stability of the films was studied by annealing the films at 400°C to 500°C in the furnace for half an hour (Table 1). At 400°C, the resistivity was relatively unchanged after annealing. At higher temperatures, the resistivity increased after annealing. The percent increase in resistivity was higher at the higher annealing temperatures. At 500°C, the resistivity was increased by at least an order of magnitude. The more resistive films showed larger increases in resistivity.

Some of these effects could be due to the free electrons in the film contributed by oxygen vacancies. Annealing in an oxygen containing environment would cause oxygen to enter the film and fill some of the oxygen vacancies. This would reduce the carrier concentration and increase the resistivity. Nitrogen was used to fill the annealing furnace, but since the muffle had open ends, there was a small concentration of oxygen in the furnace. At high annealing temperatures, oxidation was more efficient. Films with lower resistivity had more fluorine in the film. The fluorine atoms replaced the oxygen sites. Therefore there should be fewer oxygen vacancies in the more conductive films, agreeing with the fact that they were more stable under annealing. Films with higher resistivity had less fluorine and more oxygen vacancies. Their resistivity increased more rapidly when the oxygen vacancies were filled by the ambient oxygen during annealing. Another effect could be sodium diffusion from the soda lime glass substrate at higher temperatures. Sodium in the film could increase defect scattering, lower the mobility and increase the resistivity.

Films were also annealed in 10% oxygen and 90% nitrogen at 400°C to study their stability in an oxygen environment. These films were annealed for about 10 minutes to

simulate the deposition of another layer on the film. The resistivity did not change for films with resistivity less than $8 \times 10^{-4} \Omega \text{cm}$. The resistivity increased for films with higher resistivity. The percent increase in resistivity was higher when the film resistivity was higher.

Application to Amorphous Silicon Solar Cells

To test the applicability of fluorine doped zinc oxide as a front electrode on amorphous silicon solar cells, solar cells were deposited on the textured fluorine doped zinc oxide films at Solarex and the University of Delaware. The structure of the cells is shown in figure 15. Cell parameters were measured and compared with the control cells made using Solarex's standard fluorine doped tin oxide as the front electrode. Both groups reported an increase of around 5% in the short circuit current using fluorine doped zinc oxide, consistent with the higher transparency of the zinc oxide films compared with the tin oxide films.

The open circuit voltages of the cells made on fluorine-doped zinc oxide were, however, from 10 to 100 mV lower than control cells made in the same runs on tin oxide. The lower open circuit voltages can be explained if zinc oxide has a lower work function than tin oxide does. In fact Kelvin probe measurements have recently shown that zinc oxide has a work function about 35 mV lower than tin oxide.⁴¹

The fill factors of ZnO:F cells were also lower, by 3 to 10 %, than cells made on SnO_2 :F. Since the oxide front electrodes are n-type, there is a rectifying effect at the interface with the adjacent p-type amorphous silicon. This p-n junction creates a resistance impeding carrier flow. Two factors determine the contact resistivity. One is the barrier height. This is determined by the difference in work function of the two materials. A transparent electrode with a high work function can effectively lower the barrier height, thereby lowering the contact resistivity. Tin oxide has a slightly higher work function than zinc oxide, and thus a lower barrier and lower contact resistivity. The other factor is the carrier concentration. If the transparent conductor has a high carrier concentration, the barrier width is reduced for electrons tunneling through the barrier in the oxide. Fluorine doped zinc oxide has lower electron concentration (about $2 \times 10^{20} \text{ cm}^{-3}$) compared to fluorine doped tin oxide (about $5 \times 10^{20} \text{ cm}^{-3}$). Both the lower work function and the lower electron concentration contributed to the increase in contact resistivity when using fluorine doped zinc oxide films. This led to the lower fill factors.

A solution was proposed to solve the voltage and contact resistivity problems of zinc oxide: a thin layer (a few hundred angstroms) of heavily doped tin oxide deposited between the zinc oxide and the p-type amorphous silicon layer. Since a large electron concentration leads to increased optical absorption, the tin oxide layer needs to be as thin as possible to keep the light transmission high. At the same time, the tin oxide must be thick enough so that its contact properties approach those of thicker layers. These transparent conductors with the structure thin SnO_2 :F/thick ZnO:F/glass should combine the best features of the two materials for amorphous silicon solar cells. The thick ZnO:F should provide high transparency, and the thin SnO_2 :F should provide good electrical contact to the silicon.

In order to deposit SnO_2 :F by CVD, we normally use substrate temperatures over 500 °C. However, when we heated the ZnO:F films to temperatures over 480 °C, their sheet resistance increased. Thus we studied SnO_2 :F deposition at various temperatures, and found that substrate temperatures as low as 460 °C could be used for the depositing SnO_2 :F by the reaction of tetramethyltin, oxygen and hexafluoropropene. The same 460 °C substrate temperature was found to be suitable for the ZnO:F deposition. Thus this common temperature was adopted for making the thin SnO_2 :F/thick ZnO:F/glass electrodes.

Transparent conductors with this structure were deposited at about 460 °C, which is in the optimum temperature range for ZnO:F deposition using the CVD method described

above. This temperature is below the optimum for depositing fluorine-doped tin oxide, so the free electron concentration in the tin oxide was measured to be only about $5 \times 10^{19} \text{ cm}^{-3}$, an order of magnitude lower than the values usually found for optimized tin oxide deposited at higher temperatures. Unfortunately, because the ZnO:F films increase their electrical resistance when they are reheated to temperatures above their original deposition temperature, higher substrate temperatures could not be used for the SnO₂:F overcoating.

Samples of the thin SnO₂:F/thick ZnO:F/glass transparent conductors were sent to Steven Hegedus at IEC, Delaware. He deposited amorphous silicon solar cells using three different dopant levels in the p-Si layer contacting the tin oxide. The lowest diborane flow is typical of what they used for standard tin oxide substrates. Figure 16 shows that the standard boron doping level gave lower open-circuit voltages on the zinc oxide substrate than on tin oxide. Even the thin, lightly doped tin oxide layer on the composite SnO₂:F/ZnO:F was able to raise the voltage back to the level found in the same run for standard tin oxide. This result supports the potential of using the composite SnO₂:F/ZnO:F to increase cell efficiency.

At the higher levels of boron doping, the voltages became equivalent for all of the substrates. The fill factors increased with boron doping level, but, unfortunately, remained lower for both ZnO-containing substrates, at all boron doping levels (Figure 17). Apparently, a higher free electron concentration will be needed in the tin oxide contact layer, if higher fill factors and efficiencies are to be attained with the composite SnO₂:F/ZnO:F transparent conductor.

SUMMARY

We were able to successfully deposit highly transparent conducting textured fluorine doped zinc oxide films from Et₂Zn(TMEDA), ethanol, and benzoyl fluoride. The new precursor and injector design produced uniform films with good reproducibility. A catalytic oxide was needed to dehydrate the ethanol and start film growth on bare glass substrates. The film growth rate increased with precursor concentration, but the deposition efficiency became lower. The growth rate decreased with fluorine dopant concentration. The films were polycrystalline and highly oriented with the c-axis perpendicular to the substrate. The crystallites were pointed columnar with diameters between 100 nm and 500 nm and height of about 280 nm. The resistivity decreased with the film thickness. The aging time of the zinc and fluorine precursor solution affected the electrical and optical properties of the films. The mobility decreased with dopant concentration and was optimized at about 480°C to 500°C. The mobility was about 45 cm²/Vs. The electron concentration increased with dopant concentration and decreased after a maximum was reached. The electron concentration was up to $3 \times 10^{20} \text{ cm}^{-3}$. The resistivity was as low as $5 \times 10^{-4} \text{ } \Omega \text{ cm}$. Film absorption decreased with increasing ethanol concentration, but the conductivity and the texture of the films decreased when the ethanol concentration was too high. The optimum zinc to ethanol molar ratio was about 1:20. Visible absorption was only 3-4% for a sheet resistance of 7 Ω /square. The diffuse transmittance can be varied from about 1 to 10% at 650 nm. We conclude that the excellent electrical and optical properties of the fluorine doped zinc oxide films, together with good uniformity and reproducibility, makes it an attractive candidate for many applications as a transparent conductor. Application to improved amorphous silicon solar cells will require a thin contact layer of highly-doped tin oxide.

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Figure 1. Schematic drawing of the experimental setup

Figure 2. Dependence of the growth rate on fluorine concentraion in the precursor

Figure 3. RBS spectrum of a ZnO:F film

Figure 4. X-ray spectrum of undoped ZnO(deposition temperature 495 °C)
X-ray source: Mn-filtered Fe K lines

Figure 5. X-ray spectrum of ZnO:F (deposition temperature 495 °C)
X-ray source: Mn-filtered Fe K lines

Figure 6. Electrical properties of ZnO:F films made at different substrate temperatures with other deposition conditions the same

Figure 7. Dependence of the resistivity of ZnO:F on the fluorine concentration in the precursor

Figure 8. Dependence of the mobility of ZnO:F on the fluorine concentration in the precursor

Figure 9. Dependence of electron concentration of ZnO:F films on the F concentration in the precursor

Figure 10. ZnO:F film resistivity vs. thickness

(a)

(b)

(c)

Figure 11. SEM micrographs of ZnO films (a) undoped, (b) optimal F concentration, (c) high F concentration

Figure 12. Total transmittance and reflectance spectra of a ZnO:F film
sheet resistance: $7 \Omega/\text{square}$; thickness: $8000 \text{\AA}$

Figure 13. Optical absorption of undoped and fluorine doped ZnO films

Figure 14. Diffuse transmittance spectra of undoped and F doped ZnO films

Figure 15. Structure of an amorphous silicon solar cell with ZnO:F as the front electrode

Figure 16. Open circuit voltages for amorphous silicon solar cells grown on three different transparent conductors, as a function of the boron doping level in the p-layer.

Figure 17. Fill factors for amorphous silicon solar cells grown on three different transparent conductors, as a function of the boron doping level in the p-layer.

original sheet resistance (ohms per square)	sheet resistance after annealing for 30 minutes				
	400 C	425 C	450 C	475 C	500 C
10.1	10.1	12.0	13.9	29.4	527
12.9	13.6	18.9	21.7	51.0	1900
13.6	14.6	22.4	27.8	76.4	6600

Table 1. Sheet resistances of ZnO:F films annealed in one atmosphere of nitrogen gas for 30 minutes at various temperatures

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13. ABSTRACT (Maximum 200 words) Transparent conducting fluorine-doped zinc oxide was deposited as thin films on soda-lime glass substrates by atmospheric pressure chemical vapor deposition (CVD) at substrate temperatures of 460° C to 500° C. The precursors diethylzinc, tetramethylethylenediamine and benzoyl fluoride were dissolved by xylene. This solution was nebulized ultrasonically and then flash vaporized by a carrier gas of nitrogen preheated to 150° C. Ethanol was vaporized separately, and these vapors were then mixed to form a homogeneous vapor mixture. Good reproducibility was achieved using this new CVD method. Uniform thicknesses were obtained by moving the heated glass substrates through the deposition zone. The best electrical and optical properties were obtained when the precursor solution was aged for more than a week before use. The films were polycrystalline and highly oriented with the c-axis perpendicular to the substrate. More than 90% of the incorporated fluorine atoms were electrically active as n-type dopants. The electrical resistivity of the films was as low as $5 \times 10^{-4} \Omega \text{cm}$. The mobility was about $45 \text{ cm}^2/\text{Vs}$. The electron concentration was up to $3 \times 10^{20}/\text{cm}^3$. The optical absorption of the films was about 3%-4% at a sheet resistance of 7 ohms/square. The diffuse transmittance was about 10% at a wavelength of 650 nm. Amorphous silicon solar cells were deposited using the textured fluorine-doped zinc oxide films as the front electrode. The short-circuit current was increased over similar cells made with fluorine-doped tin oxide, but the open-circuit voltages and fill factors were reduced. The voltage was restored by overcoating the fluorine-doped zinc oxide with a thin layer of fluorine-doped tin oxide.				
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