Low-Cost High-Performance Transparent Conducting Oxide Films Fabricated by Combustion Chemical Vapor Deposition

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ABSTRACT

Transparent conducting oxides are needed for applications including solar cells, flat panel displays and electrochromic devices. Two leading candidate materials, tin doped indium oxide (ITO) and zinc oxide (ZnO), were deposited via the Combustion Chemical Vapor Deposition (CCVD) technique. CCVD is a low-cost flame based process that relies on using inexpensive precursor materials in solution to deposit thin films in open atmosphere. ITO and ZnO films were produced with and without dopants. The electrical, optical, and microstructural properties of the resulting films were characterized by four-point probe, van der Pauw and Hall measurements, transmission/haze, scanning electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy measurements. Results showed that the films' electro-optical properties and morphology varied as a function of process parameters and annealing conditions. High conductivity values ($> 10^3\ \Omega^{-1}cm^{-1}$) and high optical transmission (>85%) in the range of 400-800 nm were demonstrated for both ITO and ZnO films.

INTRODUCTION

Transparent conducting oxides (TCOs) are a group of wide-band-gap materials exhibiting metal-like conductivity and high optical transparency in the visible region. Due to their unique electro-optical properties, TCOs have been used in numerous areas such as solar cells, flat panel displays, and electrochromic devices as transparent electrodes; and in low emissivity (low-e) windows, electromagnetic shielding, static dissipation, and defrosting windows.

Oxides of Sn, Zn, In, and Cd, and their combinations are the leading TCO materials for the above-mentioned applications [1]. Various dopants have been added to these oxides to improve their electro-optical properties, such as F and Sb to SnO_2, B, Al, Ga, In, Si, Sn, Sc, Y, Ti, Zr, Hf and F to ZnO [2], and F to ITO. In recent years, along with the advance of technology, TCO materials with improved properties are in great demand. As an example of success in developing improved TCO materials, cadmium stannate (Cd_2SnO_4) films have been developed exhibiting one of the lowest resistivities of any TCO material [3]. Cd_2SnO_4 and zinc stannate (Zn_2SnO_4) have been used to replace the traditional SnO_2 front electrode in CdS/CdTe solar cells, resulting in a new world record efficiency of solar conversion of 16.4% [4-5]. $ZnSnO_3$ shows the highest work function (5.3 eV) which makes it an excellent electrode candidate for applications in organic electronics.

Low cost fabrication methods are required to enable widespread use of TCO materials. A number of thin film deposition techniques have been utilized to deposit TCO materials, such as chemical vapor deposition [6-8] (atmospheric/low pressure, plasma enhanced, metalorganic CVD), physical vapor deposition [9-13] (RF/DC sputtering, evaporation, ion plating), ion beam assisted deposition, pulsed laser deposition [14-15], spray pyrolysis [16-18], and sol-gel [19]. Among these techniques, spray pyrolysis and sol-gel are the least expensive techniques. In the present work, we present the use of a low cost CCVD technique to synthesize TCO films. The CCVD technique is a flame based deposition process, which uses low cost precursors to deposit thin film materials in an open-air atmosphere. This enables significant reductions in material and operation cost compared to vacuum based technologies. The CCVD process is scalable and can enable continuous production of coatings.

In this paper, the synthesis of two leading TCOs, ITO and ZnO thin films, using the CCVD technique will be presented, and their properties will be characterized. ITO shows the highest conductivity among all TCO materials, but is expensive due to the scarcity and high cost of indium metal. ZnO has superior properties and similar cost to the much-used SnO_2, and is a promising alternative. ZnO is an n-type, direct-band-gap semiconductor with a room temperature band gap of 3.3 eV and a hexagonal wurtzite structure, while In_2O_3 exhibits a cubic structure with a band gap of 3.75 eV.

EXPERIMENTAL PROCEDURE

The CCVD Process

CCVD is a flame-assisted film deposition process that produces high quality thin films in open atmosphere [20,21]. In the process (Figure 1), precursors are dissolved in a solvent, which typically also acts as the combustible fuel. This solution is atomized to form submicron droplets by means of the Nanomiser™ technology proprietary to MicroCoating Technologies (MCT). These droplets are then convected by an oxygen stream to the flame where they are combusted. A

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substrate is coated by simply drawing it over the flame plasma. The heat from the flame provides the energy required to evaporate the droplets and for the precursors to react and to vapor deposit on the substrates.

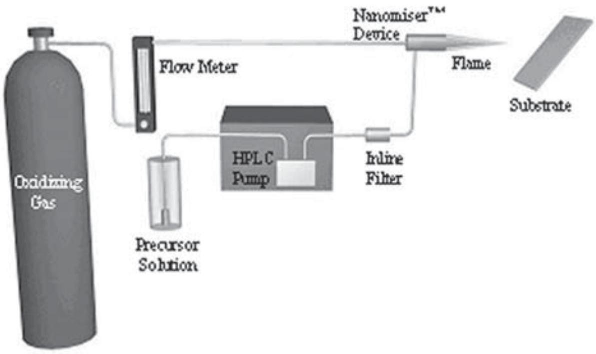


Figure 1: Schematic of the CCVD process.

By adjusting solution concentrations and constituents, a wide range of coating stoichiometries and compositions can be achieved. This is especially valuable for achieving the desired composition and thin film characteristics. Conventional CVD requires precursors with sufficiently high vapor pressures. This frequently necessitates the use of expensive materials and often produces toxic fumes which must be carefully treated ("scrubbed"). In contrast, the CCVD technique uses a wider range of inexpensive, soluble precursors that do not need to have a high vapor pressure. Hence, precursors for the CCVD process tend to be between 10 and 100 times less expensive than those used in traditional CVD processes.

Film Fabrication Procedure

Transparent conducting ZnO films doped with B, Al, Ga, In, and Sn, and their combinations, and ITO were deposited using the CCVD technique. 3"x3" borosilicate glass was used as the substrate. Low cost precursors such as acetylacetonates, ethylhexanoates, and nitrates were utilized as starting materials. These precursors were dissolved in suitable organic or inorganic solvents to form stock solutions. Typically, solutions with concentrations of 0.001 - 0.1 M were employed to produce films using the CCVD process.

Post-deposition annealing was conducted on as-deposited films to improve their electro-optical properties, and typical annealing conditions are given in Table 1.

Table 1: Post-deposition annealing conditions.

Annealing parameters	**Range**
Ambients	He, N_2, forming gas
Temperature (°C)	300-600
Duration time (minutes)	10-120

Film Characterization

Electrical, optical, and microstructural properties of the fabricated TCO films were characterized. The room temperature sheet resistance was measured by four-point probe and van der Pauw techniques. The Hall measurements (MMR) were carried out in the four-probe configuration with adjustable magnetic field and Hall current. For each sample, ten measurements were done, and an average Hall coefficient was used to calculate the carrier concentration and Hall mobility.

The film thickness was obtained using stylus profilometry (Veeco Dektek) or a variable angle spectroscopic ellipsometry (Jobin-Yvon) technique. The latter was also used to attain the refractive index and extinction coefficient of the films. Total and diffuse transmission and reflection were characterized by a UV/Vis/near IR Spectrophotometer (Perkin-Elmer Lambda 900), and a haze meter (BYK-Gardner) was used to measure the haze level.

Surface morphology was characterized by scanning electron microscopy (SEM, Hitachi S-800 field emission SEM) or optical profilometry (Burleigh Instruments). Phase and compositional information was determined by X-ray diffraction (XRD, Siemens general area detector diffraction system), X-ray photoelectron spectroscopy (XPS, Physical Electronics 5400), and energy dispersive X-ray spectroscopy (EDX).

RESULTS AND DISCUSSION

ZnO Films

All the fabricated ZnO films exhibit n-type conductivity, and their electrical and optical properties were found to strongly depend on dopant species/concentration, substrate temperature, and solution flow rate. Table 2 gives the conductivity (σ), carrier concentration (n), hall mobility (μ), and optical bandgap (E_g) of the ZnO films using various dopants at their optimum concentrations. For these depositions, all the other process parameters were kept constant, including solution concentration, substrate temperature, zinc precursor, solvent, and annealing conditions (in N_2 ambient at 600°C for 1 hour). It can be seen that Al and Ga doped ZnO films have the highest conductivity. Hall measurements revealed that this was due to their much higher free electron concentration than those made using other dopants and high mobility. Furthermore, Sn and B doping contributed less electrons than other dopants, while B doping exhibits the highest mobility.

The typical transmission spectra of doped ZnO films are illustrated in Figure 2. All the films exhibited high transmission (> 85%) in the range of 450-1000 nm, and their fundamental absorption edges differed attributable to the Moss-Burstein (M-B) effect. The haze level of the films could be easily modified by adjusting process parameters, and most of the samples showed a haze level in the range of 1-5%.

Table 2: Conductivity, carrier concentration, electron mobility, and optical bandgap of doped ZnO films.

Material	σ (Ω^{-1}cm^{-1})	n (x10^{19} cm^{-3})	μ (cm^2/Vs)	E_g (eV)
ZnO:Ga	7.2x10^2	20.8	21.5	3.45
ZnO:Al	1.1x10^3	31.2	22.4	3.65
ZnO:B	1.1x10^2	2.9	24.2	3.35
ZnO:Sn	42.7	1.5	18.0	3.30
ZnO:In	1.3x10^2	6.3	13.0	3.35

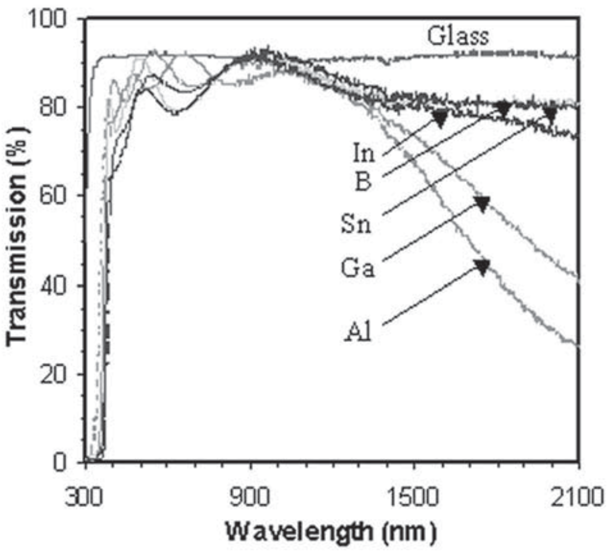


Figure 2: Optical transmission spectra of ZnO films doped with different elements.

Optical band gaps (E_g) were obtained by the extrapolation of the linear portion of $(\alpha h\nu)^2$ against $h\nu$ in the fundamental absorption region, where α is the absorption coefficient (cm^{-1}) calculated from the transmission/ reflection data and film thickness, and $h\nu$ is the photon energy (eV). Al and Ga doped ZnO films exhibited the highest E_g, which is in good agreement with their higher carrier concentration. All the other films showed band gaps near the band gap of intrinsic ZnO, suggesting they were little degenerated.

Film microstructure and morphology were also found to greatly depend on the dopants (Figure 3). As can be seen from the SEM micrographs of the doped ZnO films, all the CCVD fabricated films demonstrate small grain size, which is attributed to the unique design of the Nanomiser™ atomizer. For Ga and Sn doped ZnO films, a cauliflower-like structure is the dominant microstructure, while granular microstructure governs for In doped ZnO, and flake-like structure prevails for Al-doped ZnO. Among the doped films, B doped ZnO exhibited the least root mean square roughness (RMS < 1 nm) measured from optical or stylus profilometry, which is associated with the low melting point of boron. The larger grain of ZnO:B films is believed to contribute to their relatively high mobility. Multiple dopants did not aid higher conductivity; however, it was observed that triply doped films produced nanosized grains (Figure 3g). This can have utility in gas sensing, catalysis, energy conversion, and electronics.

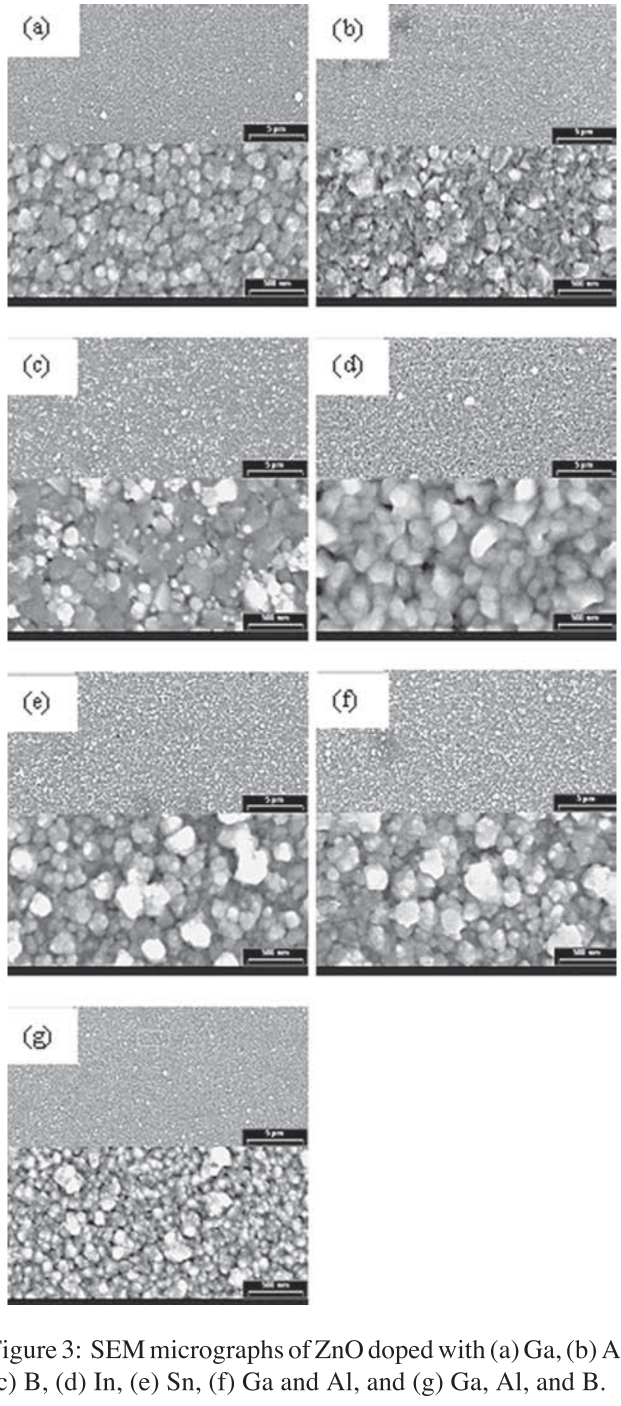
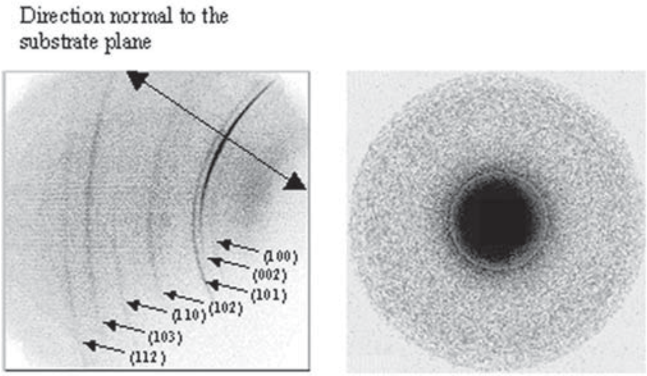


Figure 3: SEM micrographs of ZnO doped with (a) Ga, (b) Al, (c) B, (d) In, (e) Sn, (f) Ga and Al, and (g) Ga, Al, and B.

Despite the morphological distinction of the ZnO films with different dopants, the XRD analyses indicated that all the films exhibited similar polycrystalline structure with a dominant in-plane (002) orientation (Figure 4a). The (002) peak intensities remained unchanged before and after annealing in N_2, forming gas, or He ambients, and no additional peaks were found besides those for ZnO, indicating that there were no new phases formed during the deposition and annealing. The pole figure measurements using the ZnO (002) reflection have been performed, and the result for an Al doped ZnO is depicted in Figure 4b. The result, however, indicates that the film is randomly oriented in the substrate plane.



(a) (b)

Figure 4: (a) An area detector XRD pattern and (b) a (002) pole figure of an Al doped ZnO film.

It should be noted that the resistivity of the annealed films is typically several thousandths that of as-deposited films, and a significant increase in free electron concentration was found to contribute to this remarkable improvement. To identify the source of the extra electrons, surface and depth profile XPS characterizations were performed, which provides useful information in elemental compositions and their oxidation states. A zinc depletion layer on the surface was found for the annealed films compared to the near stoichiometric composition for as-grown films, leaving a dopant (Al in the case of ZnO:Al) rich layer which contributed additional free electrons. The loss of zinc is due to the high vapor pressure of ZnO at high temperature during annealing.

The refractive index (n) and extinction coefficient (k) of the films were obtained from ellipsometry measurements. It was found that n values varied in the range of 1.7-1.95 at 632.5 nm compared to n = 2.0 for crystal ZnO, depending upon process parameters such as dopant species and concentration, solution concentration, and substrate temperature. It can be concluded that films with differing microstructures from porous to dense were achieved using the CCVD process.

ITO Films

ITO films have been deposited using optimized CCVD process parameters with tin concentration (Sn/[In+Sn] in atomic ratio) being the only variable, and their sheet resistance is plotted as a function of Sn% in Figure 5. All the films were annealed at 600°C for 1 hour in N_2 ambient, and had thicknesses of 300±30 nm. It is evident that a sheet resistance of lower than 10 Ω/sq can be achieved at a wide range of Sn concentration (2-9 at%). The lowest resistivity for ITO films obtained so far is 1.5×10^{-4} Ω-cm, which matches the state-of-the-art value. Hall measurements revealed that the higher electron mobility of ITO (30-35 cm^2/V-sec vs < 25 cm^2/V-sec for ZnO) and larger free electron concentration ($7\text{-}8\times10^{20}$ cm^{-3} vs $2\text{-}3\times10^{20}$ cm^{-3} for ZnO) contribute to the superior electrical conductivity of the ITO films. The optical transmission of the films in the visible range of all the ITO films is greater than 90%, as depicted in Figure 6 (in the figure, transmission is measured without the deduction of glass substrate). Sn doping shifts the transmission to UV region due to the M-B effect. Furthermore, as can be seen in Figure 6, the fundamental absorption edge of the ITO films is larger than the doped ZnO films (Figure 2), in accordance with the larger band gap.

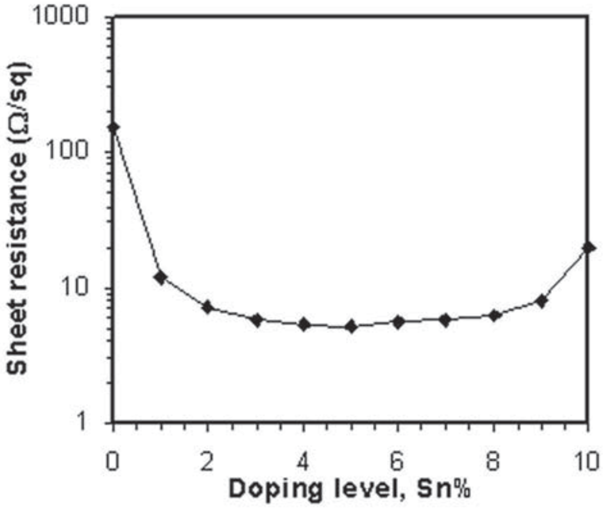


Figure 5: Sheet resistance of ITO films as a function of Sn concentration.

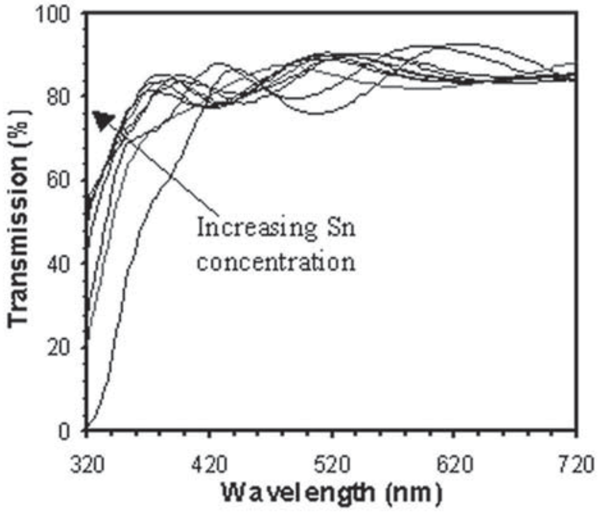


Figure 6: Optical transmission spectra of CCVD ITO films with various Sn contents (0-8 at%).

XRD analysis showed polycrystalline microstructure of the ITO films, which had almost identical pattern to the powder diffraction of In_2O_3. The ITO films also showed larger grain size than the ZnO films, as shown in Figure 7. This is believed due to the low melting point of indium metal, therefore greater diffusion promoting the growth of ITO crystallites. Ellipsometry measurements showed that the n values for ITO films were in the range of 1.9-1.95 at 632.5 nm, close to the values of sputtered films [22].

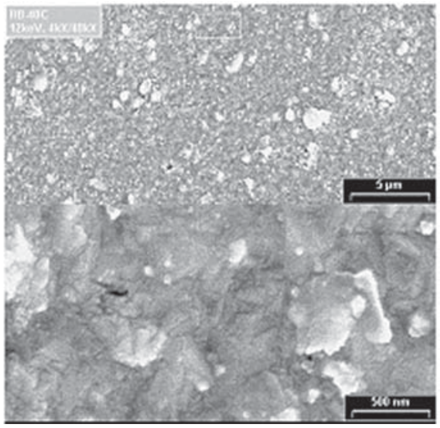


Figure 7: SEM micrograph of an ITO film.

CONCLUSIONS

Highly conductive and transparent doped ZnO and ITO films have been fabricated by the CCVD technique which is low-cost, scalable, and environment friendly. The electro-optical properties of the ZnO films depended on dopant species/concentration and other process parameters. Al and Ga doped ZnO films demonstrated the highest conductivity attributed to their high carrier concentration. Synthesized films exhibited polycrystalline structure with a textured orientation of (002) and microstructure varying from porous to dense. Film roughness can be modified by adjusting process parameters, and one can achieve various haze levels as a result. ITO films showed much higher conductivity than ZnO films due to their higher electron concentration and mobility, and a state-of-the-art value ($1.5x10^{-4}$ Ω-cm) has been achieved. Further optimization of the film properties and equipment scale-up are underway.

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