

# Boron-doped zinc oxide thin films prepared by sol-gel technique

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Multilayer transparent conducting boron-doped zinc oxide films have been prepared on glass substrates by the sol gel dip coating process. Zinc acetate solutions of 0.4 M in isopropanol stabilized by diethanolamine and doped with boron tri-*i*-propoxide were used. Each layer was fired at 400–650°C in a conventional furnace for 30 min. Selected samples were vacuum annealed at 400–450°C for 1 h to improve their electrical properties. The electrical resistivity curve with doping shows a minimum around 0.8 at.%. Excess boron caused a drop of the carrier mobility without acting as donors. Post-deposition annealing sequence was crucial for dopant partial regeneration. Films with an average optical transmittance exceeding 90% can be achieved reproducibly.

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## 1. Introduction

Transparent, electrically conductive films have been prepared from several metal oxides, including those of cadmium, indium, and tin, with special attention has been paid to In<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> (ITO) system. ITO films have been thoroughly investigated over the past two decades and their resistivities have reached a limit around 10<sup>-4</sup>Ω·cm regardless of the deposition technique. In addition, these films are essentially composed of indium which is one of the expensive and rare elements. Therefore, the increasing demand of TCO materials has promoted the development of inexpensive oxides, such as those based on Zinc. Zinc oxide holds considerable promise as an alternative to the commonly used indium tin oxide due to its low cost, higher abundance compared to other TCO materials, and stability in the presence of a hydrogen plasma.

The room temperature conductivity of the ZnO films can be changed by several orders of magnitude through the creation of intrinsic donors (oxygen vacancies or metal atoms on interstitial lattice sites) or by doping with Al, In, Ga, B, or group-VII elements such as fluorine. The extrinsic donors due to the dopant atoms are more stable than the intrinsic donors due to native defects especially when the films are subjected to higher temperatures. Considerable attention has been devoted to study the effect of Al, Sn, Ge, In and more recently Ga on the electrical and optical properties of zinc oxide. However, literature review shows relatively few reports on boron-doped zinc oxide (BZO) thin films that have been synthesized primarily by chemical vapor deposition [1–3], rf magnetron sputtering [4], atomic laser deposition [5], spray pyrolysis [6], and electrochemical

deposition [7]. We are not aware of attempts to deposit the material by sol-gel technique.

In this article we report on the physical properties of BZO films prepared by dip-coating technique. The electrical and optical properties were investigated according to various deposition parameters.

## 2. Experimental procedure

The starting reagents for BZO precursor solution synthesis were zinc acetate dihydrate [Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O], Boron tri-*i*-propoxide [B(O-*i*-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>] (99.999%, high purity chemicals), and diethanolamine (DEA). Isopropanol was used as an alcoholic medium in this sol-gel processing. The Zn precursor solution was prepared by dissolving zinc acetate dihydrate in isopropanol so as to prepare concentration of 0.4 mol/l. In this route, diethanolamine is used as a complexing agent to keep the metal ions in homogeneous solution without undergoing precipitation. The molar ratio DEA/Zn was fixed to 1. Finally, Boron tri-*i*-propoxide was added to provide a stock solution with specific molar ratio of boron to zinc. Part of the clear solution was transferred to a glass petri dish and allowed to gel at room temperature. The dried gel was transparent.

Crack free and highly adherent thin films were dip-coated on glass substrates (Corning #7059). After each deposition, samples were dried at 100°C for 10 min for solvent removal. Densification and crystallization were accomplished by subsequently annealing the layers at 400–650°C for 30 min in air. Deposition and heat treatment were repeated to build thicker coatings. Selected samples were subjected to vacuum annealing

( $\sim 10^{-3}$  Torr) at 400–450°C. The overall procedure for sol synthesis and film fabrication is summarized in Fig. 1.

The electrical properties were investigated by the Hall coefficient and by resistivity measurements. The optical properties were studied by measuring the transmittance, the reflectance, and by analyzing the relationship between the widening of band gap with carrier concentration.

### 3. Results and discussion

#### 3.1. Electrical properties

The in-plane electrical resistivity of the films ranges between  $\sim 10^{-3}$  and  $\sim 10^{-1}$   $\Omega\cdot\text{cm}$  depending on the firing profile and boron content in the film. Fig. 2. shows the room-temperature resistivity ( $\rho$ ), carrier concentration ( $n_e$ ), and Hall mobility ( $\mu_H$ ) of BZO thin films as

a function of the doping level. All the samples were prepared at the same deposition conditions with growing and annealing temperatures of 450°C. As the boron content in the film increases,  $n_e$  gradually increases and reaches a maximum value of  $1.3 \cdot 10^{20}/\text{cm}^3$  for 2 at.% B then declines for higher doping levels. The above  $n_e$  behavior suggests that not all the boron atoms are active. Excess boron above certain critical concentration seems to form neutral defects rather than generating carriers. Essentially the same behavior was observed for films doped with aluminum. The source of the problem seems to be connected with the appearance of additional phases. Sieber *et al.* [8] have studied the microstructure of sputtered aluminum-doped zinc oxide (AZO) films using high resolution transmission electron microscopy (HRTEM). They have identified the presence of tetragonal  $\text{Al}_2\text{O}_3$  (JCPDS 16-394) among

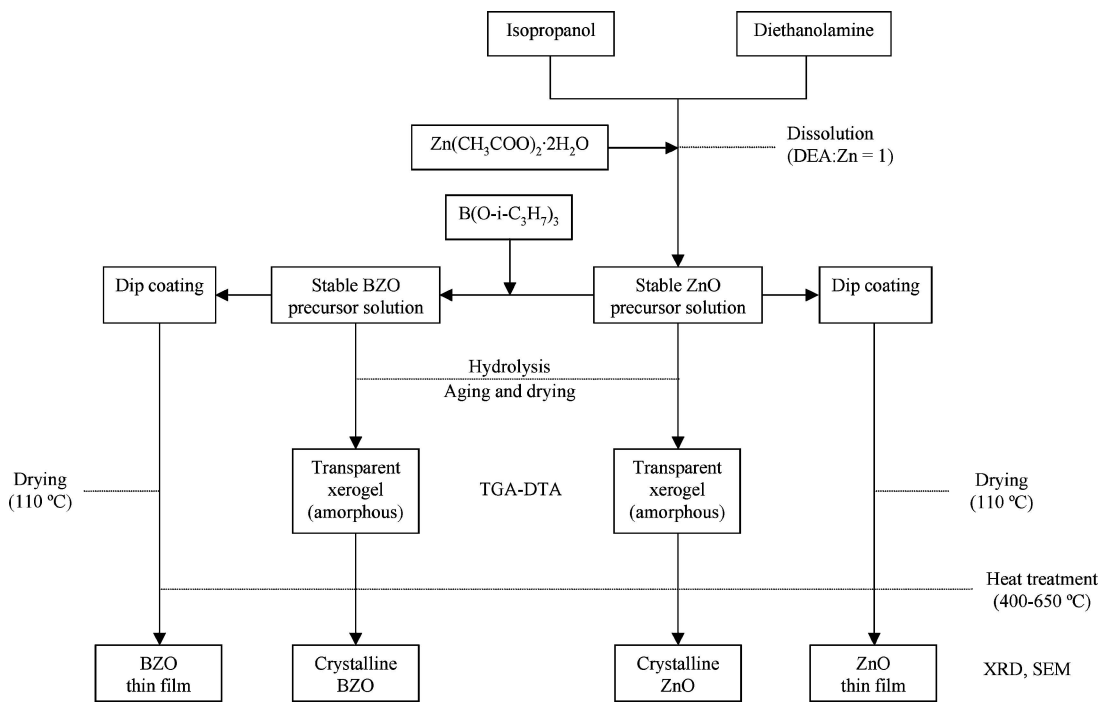


Figure 1 Flow chart for the sol-gel processing of ZnO-based thin films, dried gels, and calcined powders.

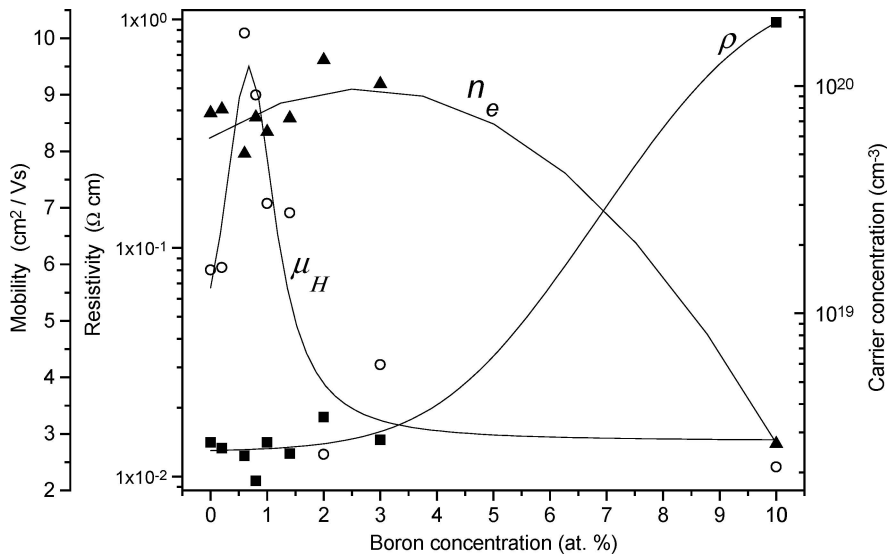


Figure 2 Hall mobility, carrier concentration, and resistivity as a function of boron concentration for the vacuum annealed BZO thin films.

TABLE I Cationic radii, electronegativities, and Lewis acid strengths of boron, aluminum, and zinc

Element	Cationic radius (Å)	$\frac{Z}{r^2}$	Electro-negativity	Lewis acid strength
Boron	0.23 (B <sup>3+</sup> )	17.85	2.0	10.7 (B <sup>3+</sup> )
Aluminum	0.56 (Al <sup>3+</sup> )	6.58	1.5	3.04 (Al <sup>3+</sup> )
Zinc	0.74 (Zn <sup>2+</sup> )	3.66	1.6	0.66 (Zn <sup>2+</sup> )

other phases. Previously Al<sub>2</sub>O<sub>3</sub> was also detected by Privato *et al.* [9] above 1.6 at.% Al-doping near the surface of the films.

The mobility initially increases on raising the boron content to about 1 at.% B, passes through a maximum ( $\mu_H \approx 10 \text{ cm}^2/\text{Vs}$ ), then abruptly drops. The initial increase in  $\mu_H$  may be attributed to the donor scattering power of B<sup>3+</sup> ions. In fact boron atoms having a value of  $Z/r^2$  higher than that of Zn (see Table I) will polarize the electron cloud of the oxygen more strongly thereby screening its charge so as to weaken it as a scattering center. Similar result have been reported by Campet *et al.* [10] for tin and germanium doped indium oxide semiconductors. The sharp decrease in mobility above 1 at.% B cannot be accounted for by an increased contribution of ionized impurity scattering: indeed for this scattering mechanism the mobility varies as the inverse of the carrier concentration. Therefore, this can be qualitatively explained on the basis of cluster formation by the segregated atoms at higher concentrations. In a previous article [11] we have demonstrated that the scattering at neutral impurities dominates the mobility at high dopant concentration, and thereby lowering the conductivities of the sol-gel processed AZO thin films.

Since the resistivity depends on the product of  $n_e$  and  $\mu_H$ , it incorporates the variation of these two parameters. The minimum value of resistivity of  $9.5 \times 10^{-3} \Omega \cdot \text{cm}$  is obtained at 0.8 at.% B.

A comparison of the electrical properties measured for ZO, BZO and AZO films is shown in Table II. The small increase in carrier concentration in undoped ZnO film with vacuum annealing is attributed to the increase in the number of oxygen vacancies. Very low mobility

values are obtained for the as-deposited films even when deposited at relatively high temperature of 650°C. Vacuum annealing at moderate temperatures (400–450°C) results in a significant increase in both the electronic mobility (up to 15 times) and electron concentration. This indicates the importance of the annealing stage for the sol-gel processed thin films with respect to dopant regeneration. The dopant activation was partially accomplished through oxygen out-diffusion. Despite this improvement, the mobility values are still smaller than that obtained in single crystals (180 cm<sup>2</sup>/Vs) [12].

Of special note are the relatively large carrier densities (almost double) measured for AZO films compared to those observed for BZO coatings that were prepared at the same conditions including the dopant level, Table II. The difference in the doping performance may be analyzed on the basis of the electronegativities and the Lewis acid strengths of the cations. Zhang [13] established the following relation that relates the Lewis acid strength “L” of a cation to its electronegativity “ $\chi$ ” and  $\frac{Z}{r^2}$ :

$$L = \frac{Z}{r^2} - 7.7\chi + 8.0,$$

where  $r$  is the empirical ionic radius and  $Z$  is the charge number of the atomic core. The values of  $L$ ,  $\chi$ , and  $\frac{Z}{r^2}$  for B<sup>3+</sup>, Al<sup>3+</sup>, and Zn<sup>2+</sup> are shown in Table I. A remarkably high  $L$  and  $\chi$  values are observed in the case of boron indicating that this atom is relatively more tightly bonded to oxygen. Thus, relatively more oxygen is expected to remain in the BZO thin film even after annealing. The excess oxygen atoms neutralize the dopants and provide additional neutral scattering centers and, therefore, limiting the carrier density and mobility. This was further confirmed by analyzing the doping level dependence of the carrier density and mobility of the BZO thin films as discussed above. Thus, future research in the field of transparent conductors should focus on minimizing the density of neutral compounds by optimizing the parameters involved in the post-deposition annealing. In this respect, lower oxygen pressure may help in the donor regeneration.

TABLE II Electrical properties of pure ZnO, BZO, and AZO thin films that were prepared at various conditions

Dopant	Coating parameters			Electrical properties			
	Doping conc. (at.%)	Growth temperature (°C)	Vacuum annealing temperature (°C)	Resistivity ( $\times 10^{-3} \Omega \text{ cm}$ )	Carrier concentration ( $\times 10^{19} \text{ cm}^{-3}$ )	Carrier mobility (cm <sup>2</sup> /Vs)	Sheet resistance ( $\times 10^4 \Omega$ )
None (pure ZnO)	0	450	Not annealed	2100	0.47	0.63	6.69
None (pure ZnO)	0	450	450	149	0.80	5.18	0.74
Boron	0.8	450	Not annealed	2219	1.52	0.19	9.13
Boron	0.8	450	400	15.4	6.98	5.82	0.06
Boron	0.8	450	450	9.5	7.26	9.00	0.05
Boron	1.0	650	Not annealed	1632	0.41	0.93	7.25
Boron	1.0	650	450	14.6	2.82	15.18	0.07
Aluminum	0.8	450	Not annealed	1432	0.18	2.08	5.26
Aluminum	0.8	450	400	3.8	13.50	12.19	0.01
Aluminum	0.8	450	450	3.3	14.95	12.69	0.02

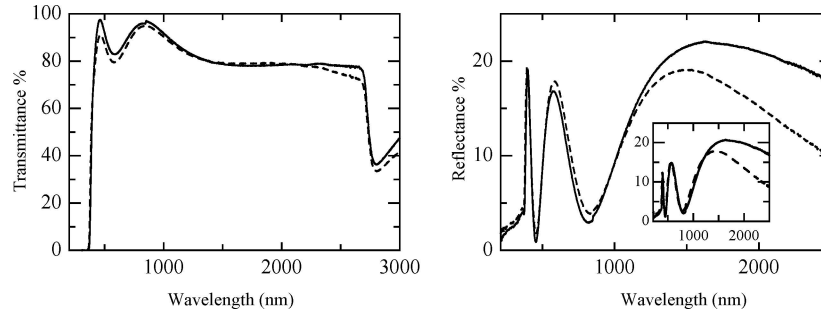


Figure 3 Plots of transmittance and reflectance of BZO thin film that was doped with 1.4 at.% B (solid line) before and (dashed line) after vacuum annealing at 450°C.

### 3.2. Optical properties

Fig. 3 shows the spectral transmittance and reflectance of 1.4 at.% doped ZnO film before and after vacuum annealing. The average transmission through both the BZO film and the glass substrate across the visible spectrum exceeds 95%. This value is significantly higher than those of most TCOs. The luminous performance is sensibly unaffected by annealing. However, the infrared reflectance of the films unexpectedly decreases on annealing despite the significant improvement in carrier mobility and density, Table II. As seen in the inset of Fig. 3, the film doped with 3 at.% also follow the same trend. This is probably due to a drastic change in the film morphology and particularly in enhanced surface roughness, and to the decrease in film thickness (see Table III).

The transmission data were used to evaluate absorption coefficients of the BZO films at different wavelengths. At the absorption edge, the absorption coefficient,  $\alpha$ , is given by the following relation [14]:

$$T \approx \exp(-\alpha d),$$

where  $d$  is the film thickness.

The absorption coefficient data were used to determine energy gap,  $E_g$ , using the relation [15]:

$$\alpha h\nu \approx (h\nu - E_g)^{1/2},$$

where  $h\nu$  is the photon energy.

Fig. 4 shows  $\alpha^2$  versus a plot of photon energy ( $h\nu$ ) curves for pure and BZO samples before and after vac-

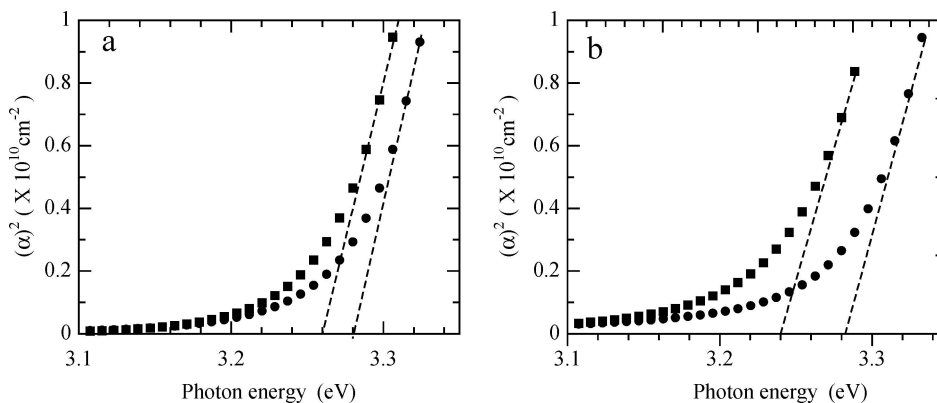


Figure 4 Plots of  $(\alpha^2)$  against  $(h\nu)$  for (a) pure and (b) 1.4 at.% B doped ZnO thin films before (■) and after (●) vacuum annealing at 450°C for one hour.

TABLE III Dependence of the thicknesses and the refractive indices of the films on dopant concentration and vacuum annealing

Doping level (at.% B)	Film thickness (nm)		Refractive index (wavelength) (nm)	
	As-deposited	Annealed	As-deposited	Annealed
0.0	284	272	1.82 (494)	1.86 (496)
0.2	253	228	1.76 (577)	1.79 (572)
0.6	295	257	1.68 (580)	1.72 (584)
0.8	243	210	1.72 (540)	1.84 (532)
3.0	240	227	1.71 (561)	1.76 (556)
10.0	277	212	1.63 (580)	1.79 (553)

TABLE IV Energy-gap values measured from transmission spectra for pure and Boron-doped ZnO thin films before and after vacuum annealing

Doping level	Band gap (eV)	
	As-deposited film	Annealed film
Undoped	3.26	3.28
1.4 at.% B	3.24	3.28

uum annealing. The values of the direct optical band gap  $E_g$  were determined by extrapolations of the linear regions of the plots to zero absorption ( $\alpha h\nu = 0$ ). It was observed (Table IV) that, after vacuum annealing, the direct band gap of the films slightly increased from 3.26 to 3.28 eV and from 3.24 to 3.28 eV for pure and 1.4 at.% boron doped films, respectively. This increase in band gap is due to increase in carrier concentration

of the films. The shift of the band gap with change in carrier concentration can be explained by the Burstein–Moss (B–M) shift [16]. The bandgap widening between the undoped and the doped films could not be detected experimentally because of its low value [17], which is a consequence of the relatively low carrier densities.

The effect of boron doping and post-deposition annealing were also found to affect the refractive index,  $n$ . In Table III, the values of  $n$  and the film thickness are presented. The refractive index decreases with boron content. Slightly higher  $n$  values were measured for the vacuum annealed samples. The refractive index reported for zinc oxide single crystal is  $n = 2.02$  (Ref. 18). The low refractive indices that are reported for the present films are due to the porous nature of the sol-gel deposited films, the relatively low firing temperature (450°C), and the incorporation of the dopant.

#### 4. Conclusion

BZO sol gel coatings have been prepared with electrical resistivity as low as  $9 \times 10^{-3} \Omega\cdot\text{cm}$  and good optical properties. An optimum doping concentration of 0.8 at.% boron, and firing and post-deposition annealing temperatures of 450°C were found to be the best conditions in terms of maximum conductivity. Boron-doped zinc oxide films show lower carrier concentrations compared to those doped with aluminum. Highly doped and/or unannealed films had very poor quality. Electrically inactive boron atoms negatively affected the carrier density and mobility. The present results suggest that vacuum annealing at 450°C but at rather lower pressure is one possible means for obtaining improved films. The optical energy gap of BZO films for direct

transition is 3.28 eV and no deviation from the value for ZnO by boron doping is observable.

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