

# A Mini Review on Electrical properties of undoped and boron doped ZnO with their preparation methods:

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## ABSTRACT

The objective of this review paper is that the investigated reports and discussions about various syntheses of thin films and electrical properties of III A group Boron doped Zinc Oxide by using various syntheses. The synthesis of ZnO doped materials have been analyzed by many researchers by using X-Ray diffraction (XRD) and they have confirmed that the obtained crystal structure of doped film shows hexagonal wurtzite structure. Researchers use application of this material to increase the material's properties when they dope. The various synthesis techniques and electrical properties of doped thin films of III A group Boron and were analysed. ZnO material has very useful physical properties, which are sharply enhanced by doping. The properties of this material keep a very important place in electronics and optoelectronic devices. In this paper, the electrical properties of doped ZnO of III group Boron and its synthesis method have been discussed.

**Keywords:** ZnO, Electrical properties, 13<sup>th</sup> group, dip coating, sputtering, sol gel, boron doped.

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## INTRODUCTION

Zinc oxide (ZnO) is a very useful semiconductor material for optoelectronic application that comes to the fore among the II-VI because it has a direct wide band gap of 3.37 eV. ZnO usually exhibits n-type conductivity but its electrical and optical properties are not stable and the extrinsic doping process affects to control and improve the electro-optical and structural properties of ZnO nanomaterials. In III group (B, Al, In and Ga) doped ZnO reveals low resistivity and n-type conductivity but among these boron doping can be more suitable [1]. The studies about ZnO nanomaterial have been going on since the starting of 1900s [2]. These prepared films have various industrial applications and it can be prepared by various methods such as spray pyrolysis, thermal evaporation, r.f. magnetron sputtering and sol-gel method etc [3]. Chen et al. reported the degradation effect with time of ZnO and ZnO:B films grown by metal-organic chemical vapor deposition (MOCVD). Steinhäuser et al. reported that heavily doped ZnO:B films deposited by low pressure chemical vapor deposition (LPCVD) exhibited more stable resistivity after 800 h of damp heat treatment. Shah et al. also reported that LPCVD ZnO:B films passed the standard damp heat test [4]. In this review paper, 10 research papers have been collected for review so that it could be useful and only electrical properties have been discussed.

**Table 1 A Description of Various Terms Associated with Nanomaterial:**

Sn.	Term	Description
1.	Nanotechnology	Nanotechnology refers to technology at the Nanoscale level in which materials, devices, or systems are developed via controlling matter at the Nanoscale length to stimulate the unique
2.	Nano scale	Properties of the material at the Nano-level. A scale covering 1–100 nm.

3.	Nanomaterial	A material is called a nanomaterial if it has at least one dimension in the Nanoscale range of 1–100 nm.
4.	Nanoparticle	An object or particle is called a Nanoparticle when all of its dimensions are in the Nanoscale range.
5.	Nano rod	The term Nanorod is used when the shortest and longest axes have different lengths. Nano rod have a width in the range of 1 to 100 nm and an aspect ratio greater than 1.
6.	Nanofiber	A Nano-object with two dimensions in the Nanoscale range and a third dimension that is significantly larger.
7.	Nanowire	Nanowires are analogues to Nano rods, but with a higher aspect ratio.
8.	Nanotube	Hollow nanofibers are called nanotubes
9.	Nanostructured material	This is a term used for materials that have structural elements, molecules, crystallites, or clusters with dimensions in the range of 1–100 nm.

### Methods and electrical properties: Mini Review

S.D. Senol et al. They prepared Boron doped ZnO Nano powder by hydrothermal method via different concentration of boron doping (0-11) at % and electrical properties of doped ZnO has been investigated. As base materials Zinc acetate dehydrates ( $Zn(CH_3COO)_2 \cdot 2H_2O$ ) (Merck), hex methylene tetra amine (HMT) (Merck) and boric acid ( $H_3BO_3$ ) Merck) were taken. Zinc acetate and MT were made solution (equimolar aqueous). After it with different concentration boric acid were contributed which concentration quantities are ( $x=0.0, 0.05, 0.07, 0.11$ ) and those prepared solution for stirring kept it under magnetic for 1. Prepared solutions were transfers into Teflon-lined autoclave and kept if under oven at 95 95°C for 12 h. then using centrifuge B doped ZnO powders were separated from the solution and washed by deionized water and dried in air. The obtained powder was with boric acid sources of  $Zn_{1-x}B_xO$  ( $x=0.0, 0.05, 0.07, 0.11$ ) were labeled and calcined 750 °C to obtain white  $Zn_{1-x}B_xO$ . They reported the electrical properties (resistivity, carrier concentration, mobility) was measured by temperature dependent van der Pauw method with Ecopia HMS-5000 Hall-effect measurement system in the temperature range of 180–350 K. While electrical measurement's some values were applied sample size about  $1 \times 1 \text{ cm}^2$  and the four corners were soldered by silver blobs for the  $\Omega$  contacts magnetic field of 0.55 T and constant current of 5 mA were applied while electrical measurement. After investigating electrical properties of B doped ZnO ( $Zn_{1-x}B_xO$ ) powder. The carrier concentration increases from  $0.11 \times 10^{14} \text{ cm}^{-3}$  (0 at. %) to  $4.08 \times 10^{14} \text{ cm}^{-3}$  (11 at. %) as increases B doping concentration because of substitution of  $Zn^{+2}$  by  $B^{+3}$  ions and diffusion of  $B^{+3}$  into interstitial positions in the ZnO lattice, the Hall mobility decreased from  $5.61 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  to  $1.22 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and with increases B concentration 0 % to 7 % during the carrier concentration increases  $0.11 \times 10^{14} \text{ cm}^{-3}$  to  $2.06 \times 10^{14} \text{ cm}^{-3}$ . Electrical resistivity decreased from  $10.89 \times 10^4 \Omega \text{ cm}$  to  $1.25 \times 10^4 \Omega \text{ cm}$  while B doping concentrations increase and the electrical resistivity is observed to decrease with both the increase in dopant concentration and the temperature in the range of 180–350 K. [1]

T. Hurma He prepared solutions by dissolving of compound contain Zn and B element at 0.05 molarity in deionized water. For Zn and B source  $Zn(CH_3COO)_2 \cdot H_2O$  salt and  $H_3BO_3$  salt was used. For each film 150 ml of solution in all solution was mixed as given below :-

**Table1. Precursor solutions of the ZnO and ZnO:B films**

<i>Film</i> (ml) $Zn(CH_3COO)_2 \cdot H_2O$ (ml)	$H_3BO_3$

ZnS150.00		0.00
ZnO:B 3%	145.50	4.50
ZnO:B 6%	141.00	9.0
ZnO:B 9%	136.5	13.5

and 1 bar was used as carrier gas. The glass substrate temperatures were up to  $350 \pm 5^\circ\text{C}$  and prepared solution were sprayed on them for 30 min. Atomization velocity was set as 5cc/min. He observed that photovoltaic application its an importance another parameter for semiconductor films and for its electrical resistance value should be low. For electrical properties of undoped and B doped ZnO films were calculated at room temperature and for electrode and calculated impedances gold (Au) and ohm's law were used. Repetitions were done between 0 to 100 V range. From I-V rap it was obtained that all films showed ohmic conductivity. The resistance of ZnO films decreased as increases the dopant rate of B. Resistance of the un-doped ZnO film was found as  $1.37 \times 10^3 \Omega \text{ cm}$ . This value is around the same level of the values reported by Muiva et al. as  $5.39 \times 10^3 \Omega \text{ cm}$  and Bacaksiz et al. as  $2.23 \times 10^3 \Omega \text{ cm}$ . The B doped ZnO (3, 6, 9) % resistances were respectively obtained as  $9.28 \times 10^2 \Omega \text{ cm}$ ,  $3.97 \times 10^2 \Omega \text{ cm}$  and  $1.36 \times 10^2 \Omega \text{ cm}$ . Concentration of electron increased and might have decreased as a result of replacement of  $\text{Zn}^{+2}$  host atoms by  $\text{B}^{+3}$  atoms added in the ZnO films.[2]

#### Mujdat Caglara et al.

They prepared undoped and B doped ZnO films, using sol-gel method onto indium tin oxide (ITO) coated glass substrate. Using as starting materials and solvent and stabilizer, Zinc acetate dehydrate [ $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ] (ZnAc), 2-Methoxyethanol ( $\text{C}_3\text{H}_8\text{O}_2$ ) and ethanolamine [ $\text{C}_2\text{H}_7\text{NO}$ ] (MEA) were used. Trimethyl borate [ $\text{B}(\text{OCH}_3)_3$ ] used as dopant source of boron. The ratio of molar was 1:1 of MEA to ZnAc and TMB. The boron and Zn normal ratio was 1% and 5%. Using magnetic stimulating solution was stirred at  $60^\circ\text{C}$  to yield (et) homogeneous and transparent solution. using an ultrasonic cleaner the ITO substrates were cleaned by detergent then methanol and acetone. The coated solution was dropped into ITO substrate and rotate at 3000 rpm for 30s by spin coater and after it films were dried at  $300^\circ\text{C}$  for 10 min in a furnace to evaporate the solvent and for removing organic residuals it repeated for 10 times and finally annealed at  $500^\circ\text{C}$  for 1 in air. This process was repeated for all the films. Film thickness was obtained with mettler Toledo MX5 microbalance by weighting method and got 546, 487 and 640nm for ZnO, 1% B doped ZnO (ZnO:1% B) and 5% B doped ZnO (ZnO:5% B), respectively. They determined Electrical conductivity of boron doped ZnO (5%) in dark and furnace at 300 to 460 K temperatures. The conductivity with temperature dependency shows two different regions because of concentrations. If temperature increases the conductivity also increases for B (5%) doped ZnO because as donor carrier electron. As temperature increase more carrier electron increases. The temperature dependent of the conductivity can be represented by the formula

$$\sigma = \sigma_0 \exp(-E/kT)$$

where  $\sigma_0$  is the pre-exponential factor, T is absolute temperature. The activation energies of shallow and deep donor levels were obtained as 0.160 eV and 0.850 eV, respectively. From the forward bias I-V measurements, k is Boltzmann constant and E is the activation energy corresponding to the energy difference between donor level and conduction level.[3]

#### Chien-Yie Tsay et al.

They took as starting materials, solvent and stabilizer, Zinc acetate dehydrates (ZnAc), 2-methoxyethanol (2-ME), and di-ethanolamine (DEA), respectively. Trimethyl borate (TMB) was used as boron source. By dissolving ZnAc and TMB in a mixture of 2-ME and DEA, the precursor solution was prepared with varied B doping concentrations 0 to 5 at% ( $[\text{B}]/[\text{ZnO:B}]$ ). The molar ratio was kept 1.0 between sol stabilizer and metal ions with 0.5 M concentration of metal ions. Each solution was stirred in  $60^\circ\text{C}$  with help of magnetic stirrer for 2 to yield a clear and homogeneous solutions after that to adjust PH values to 7.0 glacial acetic acid was added. Now the resultant solution was kept in air for 72 hours at room temperature. Doped and boron doped (ZnO: B) films were prepared by spin coating the precursor solution onto pre-cleaned alkali-free glasses (NEGOA-10, dimensions: 50mm X 50 mm X 0.7 mm) at 1000 rpm for 30s. They found that the electrical conductivity of doped ZnO films is more stable than pure ZnO films at high temperature. For 1% doping film shows best electrical properties. Hall mobility ( $\mu$ ) of  $17.9 \text{ cm}^2/\text{Vs}$ , electron concentration (n) of  $1.2 \times 10^{15} \text{ cm}^{-3}$ , and resistivity ( $\rho$ ) of  $2.2 \times 10^2 \Omega \text{ cm}$ . In doped ZnO films  $\text{B}^{3+}$  into  $\text{Zn}^{2+}$  site, provide a carrier as donor for conduction between ZnO lattices even all mobility and electron concentration decreases as increases B doping up to 1 to 5 at% and for resistivity it just opposite effect because n type semiconductor materials are having an inverse relationship electron concentration ( $\rho \propto 1/n$ ). The reason of decreasing the electron concentration higher than 1% can be explained. The Nano structural prepared tin films were passed via to trap electron through greater number of grain boundaries and excess B doping concentration from neutral defect (such as clusters and precipitates) rather than generating carriers. The polycrystalline conducting oxide and oxide semiconductor tin film depend upon grain size and it is an important mechanism specially if grain size is small. The barrier potential from grain boundary and trapped electron or mobility

of cares decreasing conductivity. Hall mobility of  $17.9 \text{ cm}^2/\text{V}$  and the lowest electrical resistivity of  $2.2 \times 10^2 \Omega \text{ cm}$  were obtained at the optimal boron doping concentration of 1%. Such as-prepared transparent oxide semiconductor thin films could be used as the active layer in functional transparent electronics.[4]

#### **Soaram Kim et al.**

Sol-gel dip-coating technique was taken, to prepare un-doped and Boron doped ZnO thin films. quartz glass substrates were used. Zinc acetate dehydrate ( $[\text{Zn}(\text{CH}_3\text{-COO})_2 \cdot 2\text{H}_2\text{O}]$ ), M $\ddot{u}$ n ethanolamine (MEA,  $[\text{C}_2\text{H}_7\text{NO}]$ ), and 2-methoxyethanol ( $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}]$ ) were used as a starting material, stabilizer, solvent respectively. Triisopropyl borate ( $[\text{((CH}_3)_2\text{CHO)}_3\text{B}]$ ) was used as source of dopant. They dissolved the 0.6 M zinc acetate dehydrate and Triisopropyl borate in the mixture of solvent and stabilizer and the molar ratio of B/ZO was varied 0-2.5 at%. The solution was stirred at  $60^\circ\text{C}$  for 2 h then aged at RT for 24 h then cleaned the substrate by distilled water, acetone and ethanol respectively under ultrasonic irradiation and dried by  $\text{N}_2$  then dip-coated and BZO films were grown on the glass substrate. They reported the resistivity ( $\rho$ ) of un-doped and boron doped ZnO thin films with various doping concentration. The  $\rho$  depended on the Boron doping concentration that was lower than of un-doped ZnO thin films. The  $\rho$  values were 1411, 74.3, 105.7, 371, 510, and 649 X cm for 0, 0.5, 1.0, 1.5, 2.0, and 2.5 at.% B, respectively. These results were different from Tahar et al.[5]

#### **Li Gao et al.**

They used radio frequency-magnetron sputtering (RF-MS) method and reported that they wanted to obtain target material with about 2 wt%  $\text{B}_2\text{O}_3$  and the target were prepared from ZnO powder then doped  $\text{B}_2\text{O}_3$  with 4wt%. They compared resistivity of un-doped ZnO films that was  $6.3 \times 10^2 \Omega$  and obtained low resistivity of BZO films which were  $9.2 \times 10^{-3} \Omega$  and  $7.5 \times 10^{-3} \Omega \text{ cm}$  respectively due to increase in carrier concentrations.[6]

#### **Lian-Hong Wong et al.**

In this work they studied BZO films at temperature from  $300^\circ\text{C}$  to  $600^\circ\text{C}$ . Reagent-grad zinc oxide and boron oxide, using this BZO ceramic target prepared and mixed with weight ratio of 97:3. Ball milling of ZnO/ $\text{B}_2\text{O}_3$  mixture was carried out in alcohol for 0.5 h and the dried mixture was pressed into stainless-steel mold. They reported Hall measurement identified all the films as n-type and obtained the lowest resistivity  $0.64 \times 10^{-3} \Omega \text{ cm}$  of BZO films at  $400^\circ\text{C}$ . [7]

#### **Gilho Kim et al.**

Using liquid source misted chemical vapor deposition (LSMCD) method, un-doped and B doped ZnO films were grown. They use Zinc acetate ( $(\text{C}_2\text{H}_3\text{O}_2)_2\text{Zn}$ ) and boric acid  $[\text{B}(\text{OH})_3]$  as precursor. These were dissolved into  $\text{H}_2\text{O}$ : methanol (15:85 v/v) mixture and stirred at room temperature and the B concentration were varied from 1 to 4 at%. they found 2 at% concentration the film had lower resistivity ( $\approx 10^{-2}$ ) than ZnO.[8]

#### **Snigdha Bhattacharjee et al.**

They studied boron doped ZnO nanostructure thin films and used zinc acetate dehydrate, 2-methoxyethanol and ethanolamine as starting material, solvent and stabilizer sequentially. Boric acid was used as dopant source. The molar ratio of zinc acetate with 2-methoxyethanol and ethanolamine and boric acid were maintained 1:1. The concentrations of B/ZO were 0, 1, 1 and 5 at % and ITO substrate with spin coating at 3000 rpm for 30s, used. They reported the linear current-voltage (I-V) characteristics under both forward and reverse bias exhibit ohmic metal-semiconductor contacts.[9]

#### **Dojalisa Sahu et al.**

Zinc acetate and Boric acid were taken to grow the films as starting and doping source materials then dissolved them into deionized water and stirred for 30 min. The doping concentrations were 0.001, 0.002, 0.003, 0.004 and 0.005 and using ultrasonication method the samples were obtained. They reported the Hall measurement showed interesting properties like with initial boron doping concentration as resistivity decreased, conductivity and mobility increased but obtained for higher doping concentration it seemed reverse in the film samples.[10]

## **CONCLUSION**

In this review various types of methods have been summarized to prepare un-doped and boron doped zinc oxide (ZnO). Zinc oxide is a low cost and non-toxic semiconductor materials which is very useful for many applications. In this review the electrical properties of un-doped and boron doped ZnO materials prepared by various methods have been investigate with various dopant concentration.

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