Military Technical College
Kobry Elkobbah,
Cairo, Egypt

2nd International Conference
on Electrical Engineering
ICEENG 99

NOVEL SYNTHESIS OF DOPED AND UNDOPED ZINC OXIDE SEMICONDUCTOR VIA SOL-GEL TECHNIQUE UNDER ULTRASONIC WAVES EFFECTS

Fayed* M. Sh., Gouda* Sh. R., Awwad* S. A.

ABSTRACT

Research on advanced materials continues to develop along lines related to specific applications. Being the cheapest material with diverse applications in electronics, zinc oxide was selected to synthesize via the sol-gel technique under the effect of ultrasonic waves. It was prepared from the hydrolysis reaction of zinc acetate dihydrate in ethanolic solution at 80°C, followed by the condensation step catalyzed by lithium hydroxide under the effect of ultrasonic waves. Formamide in 30% by volume was used as a drying control chemical additive. Zinc oxide thin films were doped by antimony oxide resulting from the incorporation of $SbCl_3$ with variable concentrations during the preparation of zinc oxide colloidal system. The thin zinc oxide films were made on glass microscope slides and calcined at 600°C. The characteristics of these films were studied via the IR, SEM, near IR transmittance and electric conductivity.

INTRODUCTION

The semiconducting property of a great variety of glasses and ceramics is based on their zinc oxide content. Zinc oxide ceramic varistors are primarily used for protection of electronic equipment against transient over voltages due to switching surges or lighting. They offer nanosecond switching response to surges, and require very little standly power when surges don't occur [1].
Zinc ferrites are basically zinc-ferrite oxide spinels, which are highly magnetic. Usually they also contain other oxides, e.g., nickel and manganese oxides. Ferrites are used in many electrical and electronic devices [2]. ZnO is an n-type semiconductor in which deviations from stoichiometry, in the form of a zinc excess, are electrically active. Thus it is possible to achieve a control of its electrical properties by making a suitable choice of the parameters of the synthesis process, which affect its stoichiometry. The ZnO structure is relatively open, with all of the octahedral and half of the tetrahedral sites empty. It is, therefore, relatively easy to incorporate external dopants into the ZnO lattice.

---

* Egyptian Military forces.

The open structure also influences the nature of defects and the mechanism of diffusion. Single crystals of ZnO exhibit n-type conductivity, so that ZnO is an n-type rather than an intrinsic semiconductor. The reason for this is excess zinc, which acts as a donor [3]. Low resistivity ZnO films have been prepared using several techniques: spray pyrolysis, sputtering, evaporation and organometallic chemical vapor deposition [4]. Zinc oxide has many modern applications due to its semiconductor behavior. The use of ZnO as a varistor and its fabrication was reported by Nobrega [5]. ZnO ceramic powder used for the manufacture of varistors is produced using colloidal-gel powder [6]. Tsuneeharu N. et al [7], prepared ZnO-ZnS type composite ceramics containing 0.01-2 wt. % Sb_2O_3. The addition of antimony oxide lowers the electrical resistance of the ZnO, and hence, gives various electronic devices such as electroluminescent and photoelectric devices having lower operational voltages.

In this work zinc oxide colloid was prepared via sol gel technique using zinc acetate as a precursor. Antimony chloride $SbCl_3$, as a source of antimony oxide [8], was added to ZnO colloidal samples with different percentages. The colloids formed, doped and undoped, were used to form thin films prepared by dip coating of glass microscope slides into colloidal solution. The formed films were calcined to 600°C. IR was used to characterize the formed bulks.
The thickness, transmittance of the formed films as well as electrical conductivity were measured. The morphological analyses of the formed films were studied by scanning electron microscope. The factors affecting the formation were studied (drying temperature and the use of drying control chemical additives).

EXPERIMENTAL SECTION

The source, origin and specifications of the used chemicals are listed in the following table: They were used in the experimental work without further purification.

Table 1. Chemicals used and their specifications

Name	Formula	M wt. g/mole	Grade %	Source
Zinc acetate dihydrate	$Zn(CH_3COO)_2.2H_2O$	219.49	98	May & Baker, England
Ethanol	C_2H_5OH	46.07	>99	Merck Germany
Lithium hydroxide monohydrate	$LiOH.H_2O$	41.96	99	BDH, England
Formamide	$HCONH_2$	45	Pure	Prolab.
Antimony chloride	$SbCl_3$	228.11	Pure	Prolab.

The preparation procedure followed in this study was essentially the same as that of Spanhel [9].
The procedure consists of three major steps:

(1) Preparation of precursors: -

A 0.1M ethanolic solution of zinc acetate was prepared by dissolving 0.05 mol of zinc acetate in 0.5 L of ethanol in a 1-L round-bottom flask. The flask was fitted with condenser and calcium chloride moisture trap and refluxed while stirring (with a magnetic stirring bar) for 180 min at 80°C. The condensate was collected continuously at the end of this procedure, 0.2 L of reaction product (precursor) and 0.3L of condensate (which was discarded) were obtained.
At this point, the synthesis, the precursor, likely contains a zinc ethoxide-type compound (and the reaction by products such as acetic acid derivatives), although we did not determine their structures [9,10].

(2) Hydrolysis of the precursor to form the colloid: -

The 0.2L of precursor was diluted back to the original volume of 0.5 L with absolute ethanol. Then, 0.07 mol of lithium hydroxide powder ($LiOH.H_2O$) was added to this precursor to give a final lithium concentration of 0.14 M.
The mixture was then hydrolyzed in an ultrasonic bath to accelerate the reaction. This hydrolysis reaction was continued at room temperature until lithium hydroxide powder no longer visibly present (about 1h).
The ZnO colloidal suspension was filtered to remove any undissolved lithium hydroxide that might remain.

(3) Concentrating the colloid to form the final sol: -

This colloid was then concentrated by evaporation from 0.1 M to 0.5 M (with respect to zinc concentration) by heating at 80°C with stirring, the product is a colorless liquid, and if it remains in open atmosphere more than 3 days, the white bulk of ZnO will appear.

Antimony chloride $SbCl_3$, was added to ZnO colloidal sample after the hydrolysis reaction with different percentages 0.01, 0.02, 0.03, 0.1 %, to the same reaction mixture used before. The colloidal formed was used to form thin film by dip coating of a glass substrate in the solution for 20 sec and elevated by 1 cm/sec. The formed thin films were calcined to 600°C. Thickness, transmittance, conductivity and SEM were measured for the thin films formed. IR was used to characterize the formed bulks. Comparison of the results was discussed. Formamide was added as a drying control chemical additive to ZnO colloidal with 30 % (volume percentage).

RESULTS AND DISCUSSION

Transmittance of zinc oxide thin films: -

The films formed at room temperature (25°C) and dried at 50,100,120,150°C can be removed by thumbnail, they are neither homogeneous nor uniform. The films formed at 50°C were more adhesive than the thin film formed without doping but it can still be removed by hand and are not well adhered to the substrate. The samples were thermally treated putting the thin films formed in an oven at room temperature and the temperature was elevated gradually by 1°C/sec. up to 600 °C. It was noted that the rate of heating had an effect on the formed film. If the samples were heated

spontaneously or started to be heated above 60°C the thin film was burned and black color of burning organic compounds residues appeared.
Fig.1 shows the average transmittance of the thin films in a region 900 to 1200nm formed with 30% formamide doped with 0.02% $SbCl_3$ thermally treated at 50°C and 600°C. The transmittances of the thin films formed were lower than that formed without doping. The thickness of the formed films ranged from 8-19μm. We added formamide as drying control chemical additive, DCCA, with 30% volume percentage in order to obtain more uniform surface since it affects the rate of drying contributes with different evaporation rate [11]. The percentage transmittance always decreased (in all cases) with the increase in film thickness specially in the region above 1μm.

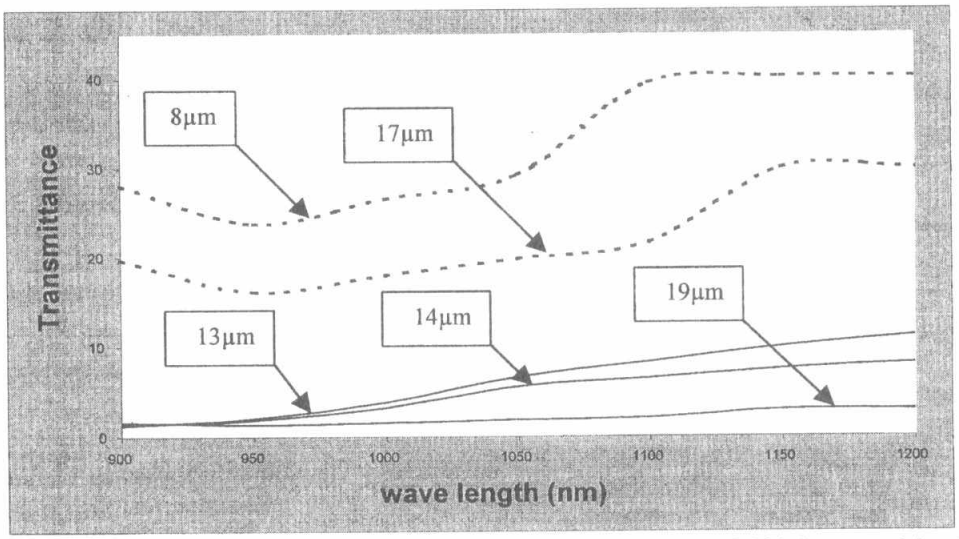

Fig.1. The change of transmittance of thin films formed with 30% formamide doped with 0.02% $SbCl_3$ thermally treated at
(a) (----- series) 50°C and (b) (— series) 600°C.

IR analysis of the formed bulks: -
The optimum percentage of $SbCl_3$ under the test conditions was found to be from 0.01 to 0.02 wt. %. The high concentrations of $SbCl_3$ turbid the zinc oxide colloid formed and the final solution formed is not suitable in the formation of thin film (the formed films are not homogeneous). The bulks formed by adding 0.01 to 0.02 wt. % of $SbCl_3$ to zinc oxide colloid were analyzed in order to determine the effect of adding antimony chloride.
Fig.2 shows the IR spectra of samples prepared with different $SbCl_3$ percentage (0.01 and 0.02) respectively. It is reported in literature that, there are three characteristic peaks for antimony oxide (sharp peak at 690, 590 and very broad peak at 550cm^{-1}) [12].

From IR spectra, there are two sharp peaks at 690 and 590 cm^{-1} characteristic for antimony oxide. That proved the formation of antimony oxide, and confirmed the successful use of antimony chloride as its source [8].
There was no difference between the two spectra except, the intensity of the peak appeared at 490 cm^{-1} more sharply in higher $SbCl_3$ concentrations.

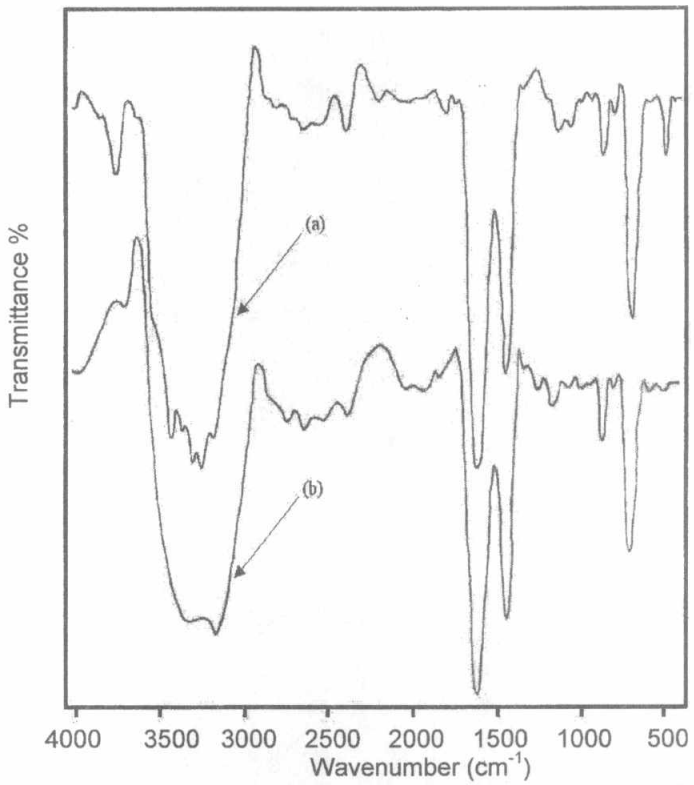

Fig.2. IR spectrum of the samples prepared with different $SbCl_3$ (a) 0.01 and (b) 0.02 wt. %.

Morphology analysis: -
Fig. 3, 4, 5 and 6 show the morphology analysis of the formed thin films
Fig.3 and 4 show the SEM of thin film undoped zinc oxide calcined at 600 °C with and without formamide respectively. The thin film uniformity increased by adding of formamide as a drying control chemical additive. The optimum percentage of formamide was shown to be 30 % by volume [13]
Fig.5 and 6 show the SEM of thin film doped with 0.02 wt. % $SbCl_3$ calcined at 600 °C with and without formamide respectively.

The SEM in Fig.5 shows that, the surface was irregular and cracking appears and the films formed were not uniformly distributed. While in Fig.6 the addition of formamide with 30% increased the regularity of the surface and the cracking disappeared and some crystals appeared on the surface. The crystals may be formed after calcination while the film was cooling to room temperature.

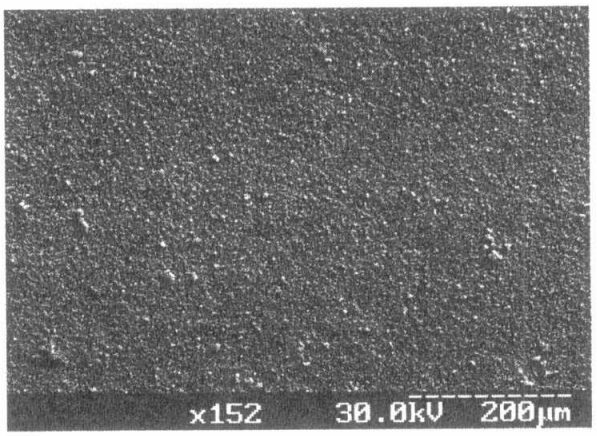

Fig.3. The SEM of thin film calcined at 600 °C
(Thickness 19µm).

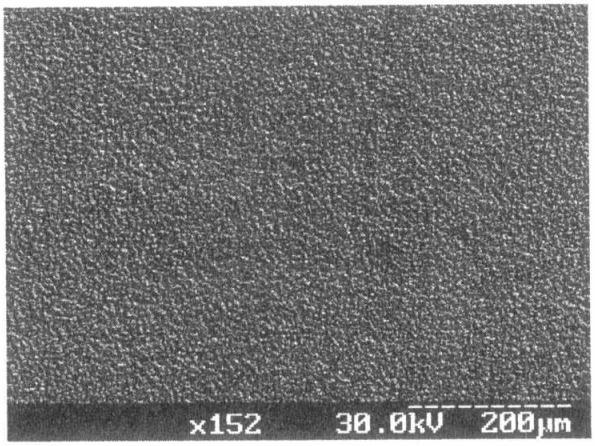

Fig.4. The SEM of thin film calcined at 600 °C
with 30% formamide
(Thickness 21µm).

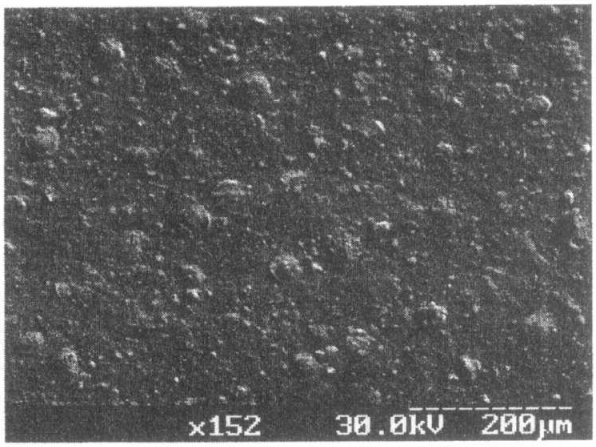

Fig.5. The SEM of thin film calcined at 600 °C doped with 0.02 wt. % $SbCl_3$ (Thickness 8µm)

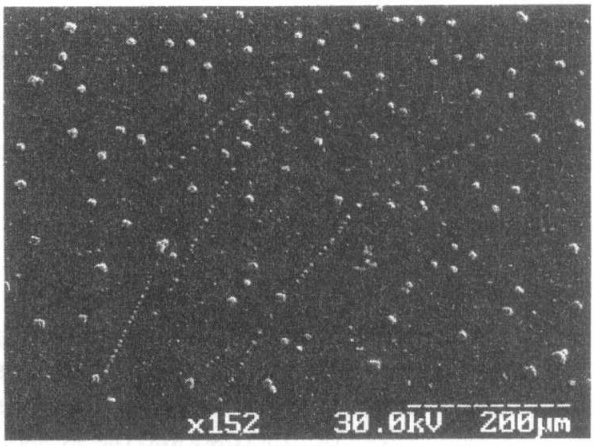

Fig.6. The SEM of thin film calcined at 600 °C doped with 0.01%$SbCl_3$ with 30 % formamide (Thickness 17µm).

Electrical conductivity of the thin films: -

C. J. Mullem et al [14], found that the electrical resistivity of zinc oxide thin films (deposited by sputtering) generally is low (0.01 Ωcm), but can be increased to higher than 10^9 Ωcm by optimization of the sputtering parameters or annealing procedures. The highest achievable piezoelectric strain constants are about 70 % of the bulk value. Several devices have been fabricated with these films, like surface acoustic wave sensors, resonant force sensors, bulk acoustic wave sensors and optical waveguides [15-17]. The electrical resistivity of the films was characterized as a function of deposition parameters and the thermal treatment temperature. Also it depends on the homogeneity of the formed films and its thickness [18].

Table 2 shows the electrical conductivity of the formed films. The use of formamide leads to an appreciable decrease in thin film resistivity. While the doping with antimony oxide depends on the used concentration of $SbCl_3$. With 0.02 % $SbCl_3$ the conductivity increased but it decreased with 0.01% $SbCl_3$.

Table 2. The electrical conductivity of the formed films

Specification of zinc oxide thin films	Resistance (Ω)	Resistivity (Ω cm)	Conductivity $(\Omega\ cm)^{-1}$
calcined at 600°C	$78.847\ 10^6$	$131.41\ 10^4$	$7.6\ 10^{-7}$
calcined at 600°C with 30% formamide	$13.792\ 10^6$	$14.94\ 10^4$	$6.6\ 10^{-7}$
doped with 0.02 wt. %$SbCl_3$ calcined at 600°C	$8.784\ 10^6$	$13.9\ 10^4$	$7.1\ 10^{-6}$
doped with 0.02 $SbCl_3$ calcined at 600°C,with 30 % formamide	$65.984\ 10^6$	$61.8\ 10^4$	$1.6\ 10^{-6}$

CONCLUSION

Zinc oxide thin films were successfully prepared via the sol-gel technique using zinc acetate dihydrate as a starting material, hydrolyzed under basic conditions using lithium hydroxide and ultrasonic waves. The thin film was deposited from the colloidal solution obtained under ultrasonic effect on microscopic glass slides.
The transmittance measurement in the near infrared region from 900 to 1200 nm showed a decrease with the increase in calcination temperature. The more uniform film formed at higher calcination temperature, at about 600°C, with the addition of about 30% by volume of formamide as a drying control chemical additive improved the surface regularity of the formed thin film. The addition of formamide increased the electrical conductivity of the formed films, while the addition of antimony chloride may increase or decrease its value depending on the concentration of precursor.

REFERENCES

[1] Bever M. B., Encyclopedia of materials science and engineering, vol.7, A.Whealon and Co. Ltd. Exeler, U.K., (1986).
[2] Othmer D. F., Encyclopedia of chemical technology, 3rd edition, vol.24, p.851-863, New York, (1984).
[3] HIRSCHWALD W. H.," Zinc Oxide: An Outstanding Example of a Binary Compound Semiconductor"; Accounts of Chemical Research, vol. 18, p. 228-234, (1985).
[4] Mancini A. M., Pierini P., Valentini A. and Vasanelli L., " ZnO/CdTe heterojunctions prepared by R.F. sputtering ", Thin Solid Films, vol.124, p.85-92, (1985).

[5] Nobrega M. C., Zolotar M. S., Mannheimer W. A., and Espinola A., " ZnO varistors produced using colloidal-gel powders ", J. Non-Cryst. Solids, vol.147and148, p. 803-807, (1992).

[6] Shimura M., Yasuno Y., Iwakura M., Sakai S., Suzuki K., and Sakamoto S., " A new monitor with a zinc-oxide thin film semiconductor sensor for the measurement of volatile sulfer compounds in mouth air ", Journal of Periodontal, Vol.67, p.396-402, (1996).

[7] Tsuneharu N., Yukio K., Jiro T., and Shigeru H., " Zinc oxide-Zinc Sulfide type composite ceramics for electroluminescence and photoelectric devices ", Chemical Abstract, no.16118y, vol.83, p.571, (1975).

[8] Parlog C., Gartner M., Vasilescu A., and Dragan N., " Preparation and characterization of SiO_2-Sb_2O_3 films obtained by a sol-gel method ", J. Non-Cryst. Solids, vol.151, p. 109-114, (1992).

[9] Sakohara S., Tickanaen L. D., and Anderson M. A., " Luminescence properties of thin Zinc Oxide membranes prepared by the sol-gel technique: change in visible luminescence during firing," J. Phys. Chem., vol.96, p.11086-11091, (1992).

[10] Spanhel L. and Anderson M. A., " Semiconductor cluster in the sol-gel process: quantized, aggregation, gelation, and crystal growth in concentrated ZnO colloids," J. Amer. Chem. Soc., vol. 113, P.2826-2833, (1991).

[11] Lloyd T. B., Kirk-Othmer, Encyclopedia of chemical technology, 3rd edition, vol.24, p.851-863, New York, (1984).

[12] Gadsden J. A., "Infrared spectra of minerals and related inorganic compound ", Butterworth group, USA, (1975).

[13] Fayed M. Sh., Gooda Sh. R. and Awwad S. A., " Deposition and characteristic of zinc oxide thin films ", 8th International Conference on Aerospace Sciences and Aviation technology, CA-06, p.765-776, (1999).

[14] Mullem C. J., Blom F. R., Fluitman J. H. and Elwenspoek M., "Piezoelectrically driven silicon beam force sensor ", Sensors and Actuators A 25-27, p.379-383, (1991).

[15] Burger G.J., Lammerink T. S., Fluitman J. H., Imai S., Tokuyama M. and Hirose S., " Piezoelectric impact force sensor array for tribological research on rigid disk storage media ", Proc. IEEE Workshop on Micro Electro Mechanical Systems, Amsterdam, The Netherlands, p. 294-299, (1995).

[16] Heideman R. G., Lambeck P.V. and Gardeniers J. G., " High quality ZnO layers with adjustable refractive indices for integrated optics applications ", Optical Materials, vol. 4, p.741-755, (1995).

[17] Gardeniers J. G., Rittersma Z. M. and Burger G. J., "Preferred orientation and piezoelectricity in sputtered ZnO films ", J. of Appl. Phys., vol. 83, p. 7844-7854, (1998).

[18] Roseberg H. M., The solid state, Oxford University Press, (1988).