Sol – Gel Preparation, Characterization and Electrical Properties of Nanosized Gallium Doped Zinc - Oxide

ADLY A.,HANNA[1]*, SAHAR M.A.MOUSA[1], MARWA A. SHERIEF[1], GEHAN M.ELKOMY[2]

[1] Inorganic Chemistry Departement, National Research Centre, Dokki, Giza, Cairo, Egypt
[2] Electronic microscope and thin films department, National Research Centre, Dokki, Giza, Cairo, Egypt
a_hanna2006@yahoo.com

Abstract: Gallium – doped zinc oxide was prepared by using sol-gel method where different concentrations of Gallium 2-8 at % were used for doping zinc oxide. The formation of zinc gallate ($ZnGa_2O_4$) was investigated by x-ray diffraction. The thermal stability of both non doped and doped zinc oxide with gallium was studied by thermogravimetric analysis (TGA). The effect of doping by Ga on the crystallite size of zinc oxide was investigated by TEM. Also, the electrical conductivity of non doped and doped zinc oxide with gallium was measured. The results of this work indicates that the phases and the morphology of the produced samples depend on the method of preparation and the particle size controlled by the method of treatment and the doping. [Journal of American Science. 2010;6(10):296-300]. (ISSN: 1545-1003).

Keywords: preparation- characterization – electrical properties – sol-gel - doping

1. Introduction

The development of new and more efficient materials for gas sensors is a challenge of the near future, as the market of these devices continuous to grow [1]. Zinc oxide is an n-type semiconductor with wide band gab of 3.3 ev, which shows high transmittance and conductivity simultaneously [2]. Due to their physical properties, ZnO is used in many different applications such as transparent electrode for photovoltaic devices [3, 4], heat mirrors [5], pressure sensors [6] and gas sensors [7], among others is possible. Doped zinc oxide films have been extensively studied in the last years [8], because of their combined electrical and optical properties associated to their low material cost, resource availability, and high thermal mechanical stability [9], but non-doped zinc oxide usually presents a high receptivity due to low carrier concentration [10]. Al, In, and Ga have been reported as effective depend for zinc oxide based film [11,12]. Most of the works related to zinc oxide use Al as depend [13]. Al presents a very high reactivity leading to oxidation during the growth of the film with a deterioration of the electrical properties [14]. It is found that Ga is less reactive and more resistant to oxidation compared to Al [15]. It was demonstrated that doping of zinc oxide with gallium improves its electrical conductivity because Zn^{+2} ions is replaced by Ga^{+3} which is higher valance and causes a small lattice distortion due to the Zn and Ga similar tetrahedral radii, acting as an efficient shallow donor in ZnO. In addition the formation of $ZnGa_2O_4$ which has the cubic spinal crystal structure in which Zn+2 ions occupy tetrahedral sites and Ga^{+3} ions the octahedral ones. This compound might have interesting effects on the electrical and optical properties [15]. So the doping of ZnO with Ga led to low resistivity and high transmittance in the visible region [16]. For this interest, the work aimed to prepare zinc oxide doped with different concentration of gallium by using the sol-gel technique. Also, the aim of this work extend to characterized the produced samples to study the effects of doping on the crystallinity, thermal and electrical properties of the $ZnGa_2O_4$ powders

2. Material and Methods

Zn oxide was prepared by dissolving the appropriate weight of zinc acetate dehydrate in deionized water with continuous stirring and heating at 60° C. Citric acid and mono ethylene glycol were used as the monomers to form the resin. The doping was carried by adding to the solution an appropriate amount of gallium nitrate (Aldrich 99.9 %) in the ratios Ga : Zn = 0, 2,4,6 and 8 at %. The solutions have the molar ratio 1:3:16 of zinc acetate: citric acid: ethylene glycol. By heating the mixture at about 100° C a clear solution was achieved with a significant increase in its viscosity. The resin gives rise to fine powders after the heat treatment in air at 900° C for 2 h. Thermal stability of the produced resins after drying at 100° C were studied by using thermogravimetric analysis TGA [computerized

Perkins Elmer 7-series(US) between 50 and 100° C with heating rate of 10 C /min]. The crystallinity of the produced samples of gallium doped zinc oxide were characterized by using x-ray diffractometry XRD using Bvukur D8 advanced diffractometer (Germany) using CuKα radiation where the produced phases were compared with JCPDS Table. The effect of doping by Ga on the morphology of ZnO was investigated by using TEM (Joel JEM 1230). Also the crystallite size was calculated from diffraction peaks according to Schrrer's equation. The electrical conductivity of both non doped and doped zinc oxide samples with gallium were measured by using a high impedance electrometer (keithely 6517). All the prepared samples which previously dried at 900° C were pressed to make pellets shape with dimension of 10 mm as diameter and 1.34mm as thickness. The electrical conductivity of measurements was performed inside a sealed glass tube. The measurements were carried out in the temperature range 300K- 473K, where the samples were heated with an electrical furnace inserted inside it. An electrical contact on both sides of the sample pellet was made with the help of special cooper holder.

3. Results and discussion

The TGA curves of pure ZnO and ZnO: GaO are shown in Fig 1 (a,b,c,d). This figure represents the thermal behavior of the prepared sample just dried at 100 °C and one sample (curve c) after thermal treatment at 900 °C. The same behavior for the samples except the sample heated at 900° C was observed where a small weight loss ranging from 1.16 to 3.36 was recorded on the TGA chart. This stage represents the evaporation of the moisture and the more volatile materials. A second stage of weight losses was start at 300 °C and ending at 500° C, this stage represents the conversion of the resions state to powder which accomlid by strong weight losses ending about ~600° C. After this temperature the weight losses is nearly negligible indicating that the produced pure oxide or the doped samples are thermal stable above ~600 °C [17]. From other hand the TGA of the sample exposed to heat treatment at 900° C for 2 h, no considerate weight loss was recorded indicating the thermal stabling of the sample.

The X-ray diffractograms (Fig 2) show that all samples (pure and Zn:Ga) have ZnO with hexagonal structure [JCPDS(80-0074)]. Also, it is observed that all gallium – doped zinc oxide samples (2-8 at %) present the cubic spinal crystal structure of $ZnGa_2O_4$ [JCPDS(38-1240)] where the amount of $ZnGa_2O_4$ increases as the doped concentration increases. The most intense peaks of zinc gallate ($ZnGa_2O_4$) related to the 311,511 and 440 reflections are clearly observed in the powder XRD patterns of ZnO: Ga(4,6 and 6 at %) for the doped zinc oxide sample with 2 at % gallium. The most intense peak of zinc gallate related to 311 is only observed.

The effect of doping by gallium on the crystallite size of ZnO was characterized as shown in Fig (3). TEM images indicate that the particle size of pure zinc oxide with hexagonal structure was (25-29nm). By doping the ZnO with Ga (ZnO:Ga = 2,4,6,and8 at %). The crystal size increases with increasing the dopant concentration. This increasing is non linear where the crystal size of ZnO: Ga becomes doublt when the dopant concentration is 2 at % of Ga. Then the increasing of crystal size will continue but with low values than that occurred at 2 at% of Ga.

The crystallite sizes which calculate from x- ray diffraction patterns has nearly the same values as observed at TEM image. Table (1) shows the variation of crystal size values which obtained from TEM images and x-ray diffraction patterns and dopant concentration of Ga.

Fig (4) shows the conductance- temperature behavior of both pure zinc oxide and doped with different concentration of Ga (2-8 at%). All samples showed two conductance regions. The first between 200° C and 60 °C may due to extrinsic conduction, since ZnO is an n-type semiconductor and its conduction mechanism is due to free electrons in donor level lying near to conduction band. At low temperature between 60° C and 30 °C, the conductance decrease due to the process of adsorption on the surface states of such oxides. The free electrons can be trapped by the surface states. The adsorption process can illustrate by the following equation

$O_2 + \bar{e} === O_2$

Where O_2 is the gaseous oxygen and O_2 is the chemisorbed oxygen acts as an electron acceptor. So, the potential barrier is built up and hence the conductivity decreases. Depending on this result, the conduction in the first region is extrinsic due to adsorption process. With increasing of temperature, the oxygen is desorbed and the conduction mechanism is intrinsic. As a result of desorption process, the conductance increases gradually with temperature due to release of trapped electrons and back to conduction band [18].

There are an increasing of conductivity with doping reaches a maximum value at a doping level of 2 at% of Ga and then decrease with increasing doping concentration. This behavior was explained by Poul et al [19]. By introducing a small amount of Ga, it is ionized as a Ga^{+3} and replaces Zn^{+2}. The atomic radii of zinc (1.225Å) are equal and gallium can be easily substituted for zinc without much lattice distortion.

The electronegativity of gallium (1.13) and zinc (0.99) are also close as compared to other impurities. So the localization of conduction electrons by gallium is also small. Hence, the carrier concentration initially increases with doping. But at higher Ga concentration, free electrons density decreases because increasing dopant atom produces some kind of neutral defects [20], which do not contribute to conductivity. On the other hand the neutral atoms may be segregates at the grain boundaries. This reduces the mobility. So, the mobility of free electrons is highest for 2 at % doped sample.

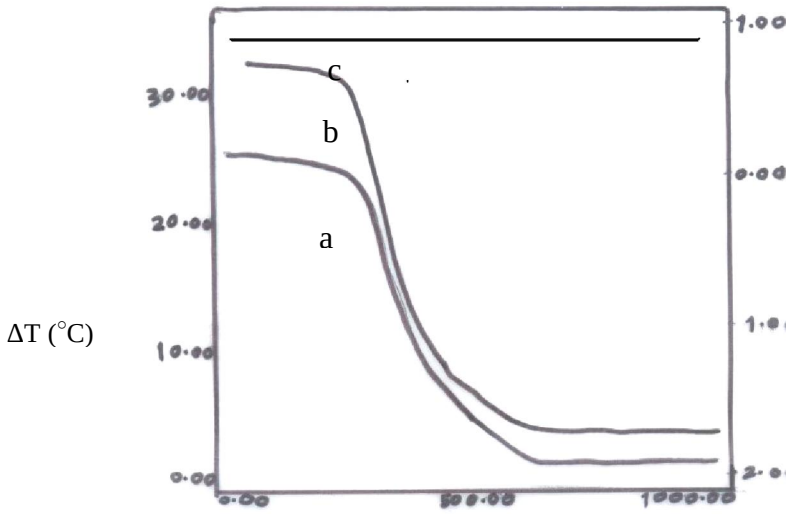


Fig 1: TGA of pure and doped ZnO samples (a) pure ZnO sample (b) samples doped with different percentage of Ga (c) sample heated at 900 °C for 2h

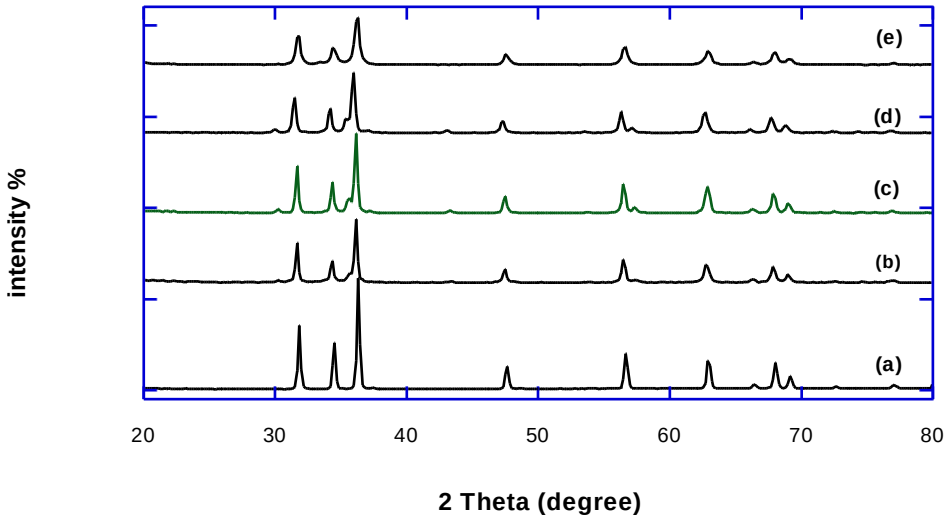
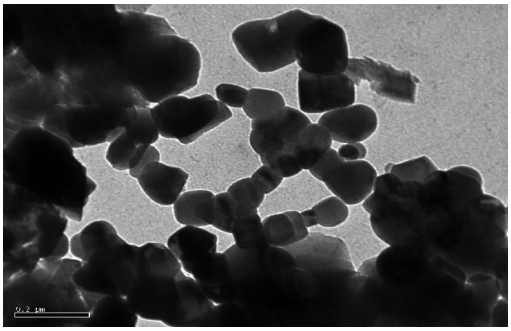
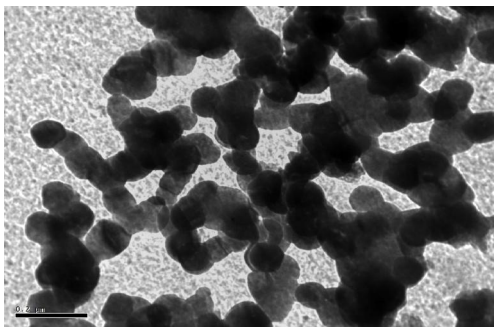


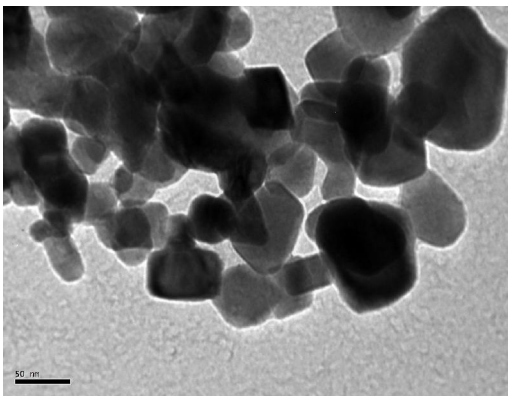
Fig 2.X-ray of the ZnGaO samples, a) Pure ZnO, b) with 2% Ga, c) with 4% Ga, d) With 6% Ga, e) with 8% Ga



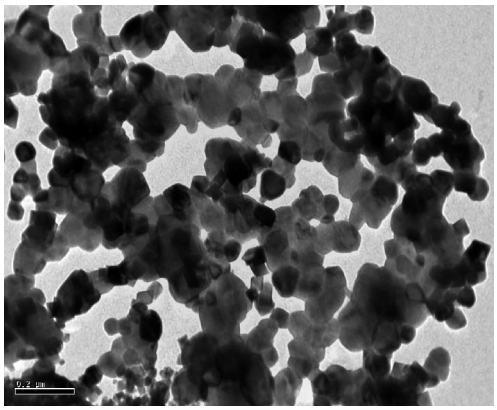
Pure ZnO



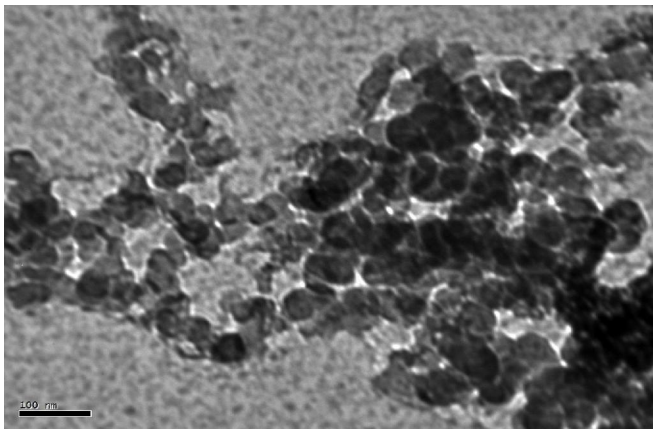
with 2% Ga



With 4% Ga



with 6 % Ga



With 8% Ga

Fig 3. TEM of the ZnGaO samples

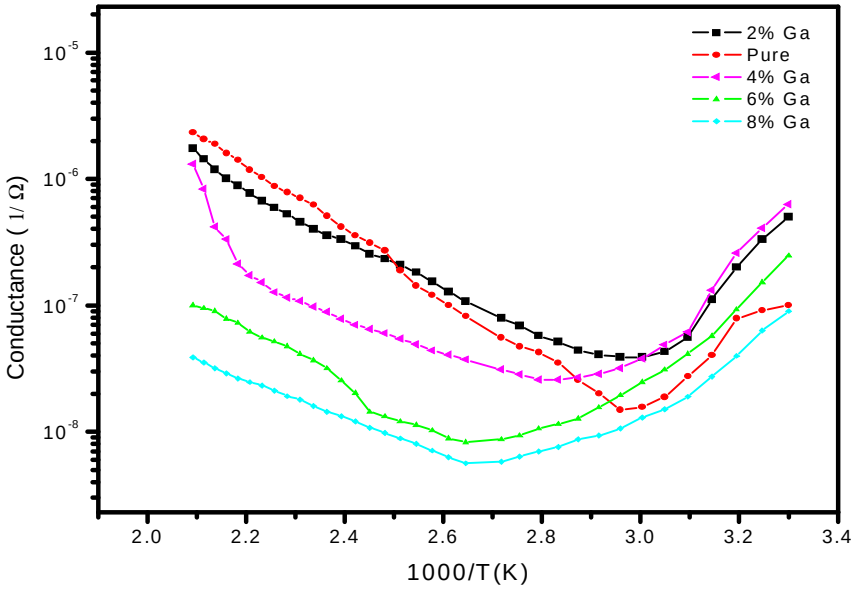


Fig 4. Relation between the conductivity and temperature of all samples

Table (1): The variation of crystal size values, obtained from TEM images and x-ray diffraction patterns

ZnO:Ga at%	Crystal size obtained from TEM (nm)	Crys.size obtained from xrd patterns
Pure ZnO	25-28	24
2	39-50	46
4	56-65	60
6	75-88	80
8	90-104	100

4. Conclusion

Zinc oxide with different concentration of gallium was prepared by using sol-gel method TGA curves of pure and doped zinc oxide indicated that all prepared samples have the same behavior and should be expired to heat treatment higher than 600 °C, to avoid the presence of the organic results. The x-ray diffractograms show, that all samples (pure and doped) have ZnO with hexagonal structure. Also, it observed that all gallium – doped zinc oxide samples (2- 8 at %) presents in the cubic spinel crystal structure of $ZnGa_2O_4$. TEM images indicated that the crystal size of gallium – doped zinc oxide increased with increasing the dopant concentration. There are an increasing of electrical conductivity with doping by Ga reaches a maximum value at a doping level of 2 at % of Ga and then decrease with increasing doping concentration.

Corresponding Author:
Dr. ADLY A.,HANNA
Inorganic Chemistry Departement, National Research Centre, Dokki, Giza, Cairo, Egypt
E-mail: a_hanna2006@yahoo.com

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5/1/2010