Effect of Transition Metal Dopant on the Electrical Properties of ZnO-TiO$_2$ Films Prepared by PLD Technique

Hussein J. Abdul Karim, Ghuson H. Mohammed

Department of Physics, Collage of Science, University of Baghdad, Iraq

E-mail: ghuson1975@gmail.com

Corresponding author: h.j.59hh@gmail.com

Abstract

In this work, the influence of group nano transition metal oxides such as MnO$_2$, Fe$_2$O$_3$ and CuO on the electrical properties of ZnO-TiO$_2$ thin films has been studied. The prepared films were deposited on glass substrate by laser Nd-YAG with wavelength 1064 nm, energy of 800 mJ and constant number of shots 400. The thickness of the film was 200 nm at room temperature and annealing temperature (573K). The electrical properties such as DC conductivity and Hall Effect were obtained. The results of DC conductivity showed that the high activation energies occurs when doping with MnO$_2$ corresponding to the lower values of DC conductivity (σ_{RT}). After annealing the films to 573 K the activation energy increased while the DC conductivity decreased for all metal oxides doping. Hall effect measurement showed films have either n-type or p-type conductivity depending on the type of the metal dopant.

تأثير التطعيم بالمعادن الانتقالية على الخواص الكهربائية لأغشية ZnO-TiO$_2$ المحضرة بواسطة تقنية PLD

حسين جمال عبد الكريم، غصون حميد محمد

قسم الفيزياء، كلية العلوم، جامعة بغداد، العراق

الخلاصة

في هذا العمل تم دراسة تأثير مجموعة أكاسيد المعادن الانتقالية النانوية مثل MnO$_2$ وFe$_2$O$_3$ و CuO على الخواص الكهربائية للأغشية الرقيقة ZnO-TiO$_2$. رسبت الاغشية المحضرة على قواعد زجاجية بواسطة الليزر Nd-YAG بطول موجة 1064 نانومتر وطاقة 800 مللي جول وعدد ثابت للنبضات 400. سمك الغشاء 200 نانومتر عند درجة حرارة الغرفة ودرجة حرارة التلدين (573 كلفن). درست الخواص الكهربائية مثل التوصيلية المستمرة وتأثير هول. بينت نتائج التوصيلية المستمرة أن طاقات التنشيط العالية تحدث عند التطعيم بـ MnO$_2$ المقابلة للقيم المنخفضة لموصلية المستمرة (σ_{RT})، وبعد تلدين الأغشية إلى 573 كلفن تزداد طاقة التنشيط بينما تنخفض التوصيلية المستمرة لجميع منشطات أكاسيد المعادن. أظهر قياس تأثير هول ان للغشاء موصلية من النوع n أو النوع p اعتمادًا على نوع التطعيم المعدني.

Introduction

The family of nonmaterial consists of nanostructure films for intermediate metal oxides such as MnO$_2$, ZnO, CuO, Fe$_2$O$_3$ and TiO$_2$. The physical, chemical and favorable capacitive properties of these metal oxide films are highly interesting and

have led to an increase in the performance of various equipment. The environmentally sustainable construction in use these materials in a variety of research fields motivating further development [1-5]. Because of their fascinating physical and chemical properties (ZnO NP$_s$) have gained considerable importance [6]. They are essential for applications in science and technology, nonlinear optics, electrical tools, catalysis, therapeutic technology and novel methods of antimicrobials. ZnO NP's are used to inhibit low toxicity or heat resistance to microbial pathogens in strains resistant to microbial pathogens [7]. (TiO_2) powder is commonly known to be one of the major semiconductor substances [8]. (TiO_2) material possesses high chemical stability, non-toxicity and fairly high visible spectrum transmittance [9]. (TiO_2) however has a high recombination rate in solar cells which decreases its efficiency [10]. The materials related to Manganese Oxide (MnO_2), because of their low cost due to their low natural surplus, are environmentally friendly and their diverse chemical / physical attributes such as many crystals and the oxydency, have acquired considerable interest in the wide areas of catalysis, magnetism, detecting chemical and electric chemistry(lithium-ion, super capacities, etc). [11]. (MnO_2) has been extensively studied as systematic oxidation heterogeneous catalysts of liquid phases [12]. The Iron (hematite) is considered one of the most important oxide transition elements, and the ferric oxide of all other iron oxides is the most stable one. It is one of iron's thermodynamic phases and one of trivalent iron compounds, which can be derived through extreme heating of ferrous sulfate or through ferrous oxidation by adding alkali to ferrous sulphate. It is a n-type semiconductor that adopts a crystalline hexagonal structure [13]. It has an energy gap (2.5eV) within the visible spectrum range [14]. CuO is a p-type semiconductor, narrow band gap. It has a monoclinic structure and many features: super thermal conductivity, photovoltaic properties, and durability. CuO can be used many fields of science [15]. CuO has a favored monoclinic structure and ranges its band gap within (1.2 - 1.9) eV [16].

The purpose of this work was to study the effect of metal oxide, such as (MnO_2, Fe_2O_3 and CuO) doping and annealing temperature on the electrical properties of (ZnO-TiO_2) films prepared by PLD techniques.

Experimental work

(ZnO-TiO_2) powder (85:15 wt. %) doped with nano transition metal oxides such as (MnO_2, Fe_2O_3 and CuO) at x = 0.9 wt. were prepared. The powder were mixed together for 10 minutes using a gate mortar. Pellets of 1 cm diameter and 0.2 cm thickness under pressure of 5 tons for 10 minutes were prepared using hydraulic piston form (SPECAC). The pellets were sintered for 1 hour in air at temperature 673°K, and then cooled to room temperature. The glass substrates (2.5×2.5) cm, were washed with distilled water for 15 min and then with alcohol for 15 min using an ultrasound path. The distance between objective and laser beam was set to 10 cm and between target and substrate was 1.5 cm and the target makes angles to 45°. The films were prepared using Nd: YAG with (λ = 1064 nm), energy (800 mJ) and frequency (6Hz) and number of shots 400.The thickness of the film was 200 nm. The DC conductivity was measured according to the temperature function for pure (ZnO-TiO_2) and doped with transition metal oxides (MnO_2, Fe_2O_3 and CuO) in the temperature range of (303-423) K using (Keithly Sensitive Digital Scale 616) and electric oven. (Memmert U10 oven made in Germany).

Results and discussion
DC Conductivity

The effect of the dopant transition metal oxides (MnO_2, Fe_2O_3 and CuO) on the electrical conductivity of the ZnO-TiO_2 thin films deposited by pulse laser on glass substrates at RT with annealing to temperature 573 K is presented in Figs.1 and 2. It is observed from these figures the electrical conductivity of ZnO-TiO_2 films depends on the dopant metal oxide. The electrical conductivity has been measured as a function of temperature for films in the range (303-423) K. The change of electrical conductivity with temperature for most cases of intrinsic semiconductors is given by the following equation [17]:

$$\sigma = \sigma_o \exp(-E_a/k_B T) \tag{1}$$

where σ_o is the minimum electrical conductivity at 0 K, k_B is the Boltzmann constant, E_a is the thermal activation energy and T is the absolute temperature.

From Figs.1 and 2, It is observed that the conductivity of the samples increases when ZnO-TiO_2 was doped with the metal oxides at RT while decreases when the films were annealed to 573 K. This increase in conductivity with adding metal oxides is due to the increase the number of charge carriers (electrons or holes) from donors (Cu, Fe) and acceptors Mn ions incorporated in the interstitial or substitutional sites of Zn^{2+} cations [18]. Also, these figures show that all films have two activation energies E_{a1} and E_{a2}. This means that there are two mechanisms for conductivity. The activation energy in the low temperature depends on the ionization impurity and at high temperature depends on the generation of electron-hole pairs [19]. The activation energy (E_a) was calculated from the slope of $\ln_\sigma$ vs. 1000/T according to equation:

$$\ln\sigma_{DC} = \ln\sigma_o - \Delta E_a/k_B T \tag{2}$$

Table 1 shows that the value of E_{a1} is smaller than values of E_{a2}. This indicates that conductivity depends on temperature. These activation energies decrease when adding metal oxides. It is noticed that the highest activation energy was found at pure (ZT).

While, when the films were annealed to temperature 573K, it was noticed that the activation energy E_{a1} and E_{a2} were higher increased than their values at room temperature (RT) for all doping metal oxide, as show in Figs.3 and 4. The variation of (E_{a1} and E_{a2}) as a function of doping metal oxides for both room and annealing temperature. It was also found that the best result was obtained when (ZnO-TiO_2) was doped with Fe_2O_3 films because oxygen defects induces the hydrophilic surface of the particles and their cluster to form larger secondary particles .Therefore, its electrical properties are improved. These results matched the four point probe results. Also, this increase in the conductivity when doped with Fe_2O_3 can be attributed to the increase in the carrier concentration in the layers.
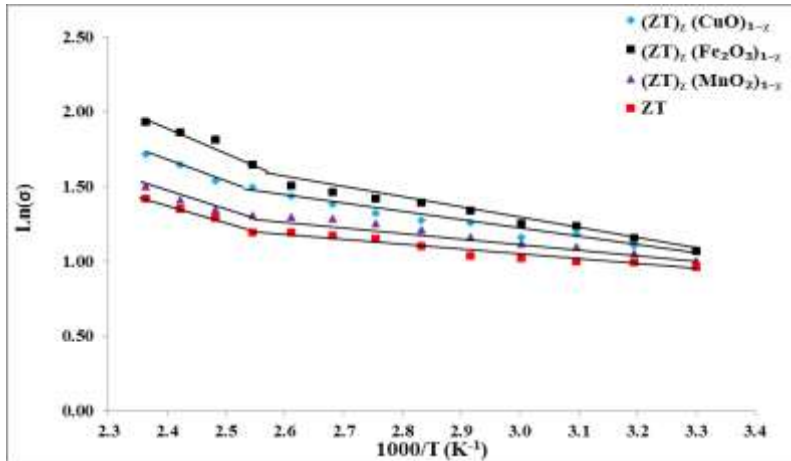
***Fig.1: Ln σ versus 1000/T of ZnO-TiO₂thinfilm at room temperature and doped
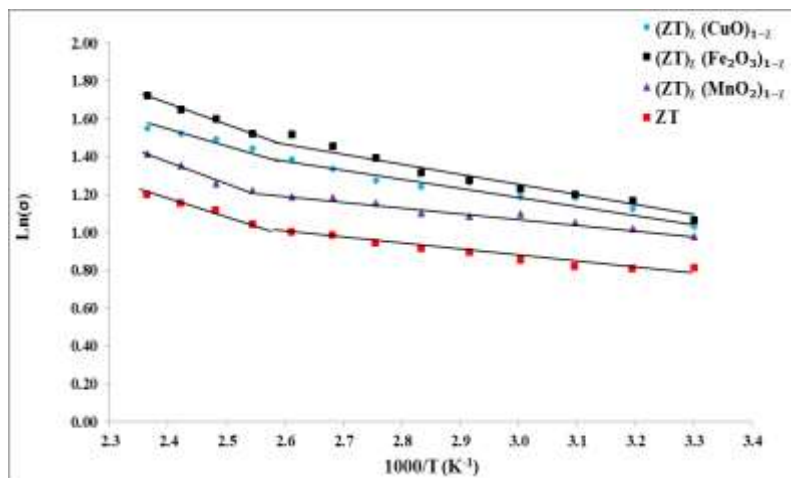with (MnO₂, Fe₂O₃, CuO).***

***Fig.2: Ln σ versus 1000/T of ZnO-TiO₂thin film at annealing temperature (573 K)
and doped with (MnO₂, Fe₂O₃, CuO).***

***Table 1: DC activation energy and conductivity for thin ZnO-TiO₂ films doped with (MnO₂
Fe₂O₃, CuO), at room temperature and annealed at (573 K).***

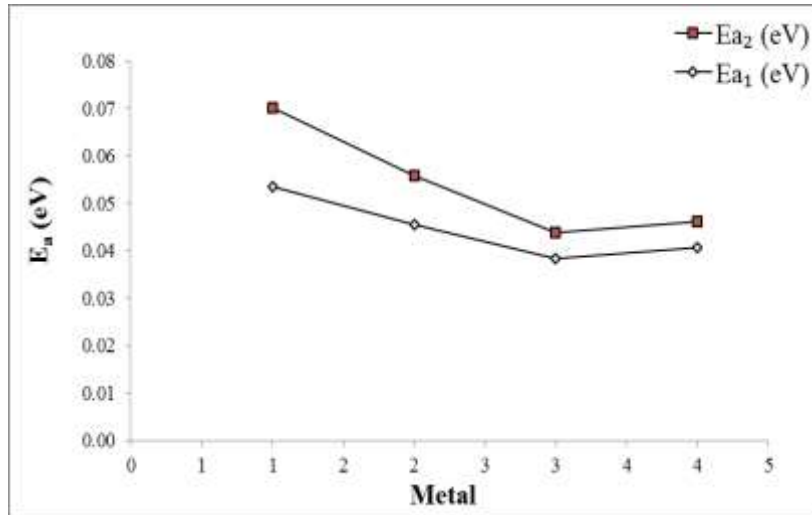| Metal	E_{a1} (eV)	Range (K)	E_{a2} (eV)	Range (K)	σ_{RT} ($\Omega^{-1}.cm^{-1}$)
ZT pure	0.054	303-423	0.070	303-423	2.608
(ZT)$_\chi$(MnO$_2$)$_{1-\chi}$	0.046	303-423	0.055	303-423	2.723
(ZT)$_\chi$(CuO)$_{1-\chi}$	0.041	303-423	0.046	303-423	2.940
(ZT)$_\chi$(Fe$_2$O$_3$)$_{1-\chi}$	0.038	303-423	0.043	303-423	2.913
T=573K					
ZT pure	0.062	303-423	0.071	303-423	2.256
(ZT)$_\chi$(MnO$_2$)$_{1-\chi}$	0.052	303-423	0.064	303-423	2.657
(ZT)$_\chi$(CuO)$_{1-\chi}$	0.048	303-423	0.056	303-423	2.805
(ZT)$_\chi$(Fe$_2$O$_3$)$_{1-\chi}$	0.046	303-423	0.051	303-423	2.904

Fig.3: Variation of DC activation energies for ZnO-TiO₂ films at room temperature and doped with (MnO₂, Fe₂O₃, CuO).
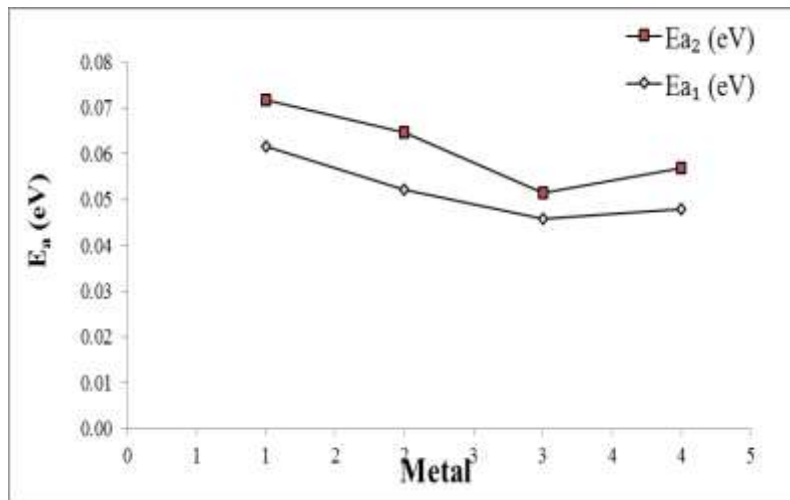

Fig.4: Variation of DC activation energies for ZnO-TiO₂ films annealed at 573K and doped with (MnO₂, Fe₂O₃, CuO).

Hall Effect

The Hall measurements of the deposited samples were done to determine the   type of charge carriers, concentration (n_H), Hall mobility (μ_H), conductivity (σ) and resistivity (ρ) for pure (ZnO-TiO₂) and doped with MnO₂, Fe₂O₃ and CuO metal oxides at room and annealing temperature (573K).

The Hall coefficient (R_H) was determined by measuring the Hall Voltage (V_H) generated by the Hall field across the sample of thickness (t), given by [20]:

$$R_H = \frac{VH}{I} \cdot \frac{t}{B} \tag{3}$$

where I is the current passing through the sample, B is the magnetic field Carriers concentration can be determined by using the relation [21]:

$$n_H = \frac{1}{e./RH/} \tag{4}$$

Hall's mobility (μ_H) measured in (cm^2/V.s) and can be written in the form [22]:

$$\mu_H = \frac{\sigma}{n.e} \tag{5}$$

The results obtained from the Hall Effect indicated that the ZT films have negative Hall coefficient (n-type) conductivity i.e Hall Voltage decreases with increasing the current at RT and is converted to p-type conductivity after annealing the films. The effects of adding metal oxides on the ZT films is clear. The ZT films has p-type conductivity when it is doped with MnO_2 metal oxide because the excess MnO2 will act as the acceptor impurities that may occupy shallow acceptor levels up valance band in the film [23], while the excess of CuO and Fe_2O_3 metal oxides will act as the donor impurities and may occupy shallow donor levels in the film, resulting in the reduction of conduction activation energy. From Table 2, the value of R_H was increased with dopant MnO_2 and CuO, but decreased with dopant Fe_2O_3 i.e decreases in the carrier concentration with MnO_2 and CuO but increases with Fe_2O_3 leads to decrease of the conductivity with (MnO_2 and CuO) films, but increase of the conductivity with Fe_2O_3 films.

Table 2: Hall Effect parameters for ZnO-TiO$_2$ films doped with MnO$_2$, CuO and Fe$_2$O$_3$ metal oxides.

Materials	(ρ) [$\Omega\ cm$]	(σ) $(\Omega\ cm)^{-1}$	(R_H) [cm^3/C]	(n_H) [$/cm^3$]	(μ) [cm^2/V_s]	Type
ZT pure	1.825×10^3	5.480×10^{-4}	3.887×10^6	1.606×10^{12}	2.130×10^3	n-Type
$(ZT)_x\ (MnO2)_{1-x}$	2.223×10^3	4.499×10^{-4}	1.500×10^7	4.162×10^{11}	6.746×10^3	p-Type
$(ZT)_x\ (CuO)_{1-x}$	7.406×10^3	1.350×10^{-4}	1.291×10^7	4.836×10^{11}	1.743×10^3	n-Type
$(ZT)_x\ (Fe2O3)_{1-x}$	1.516×10^2	6.595×10^{-3}	2.090×10^6	2.987×10^{12}	1.378×10^4	n-Type
Ta=573K						
Materials	(ρ) [$\Omega\ cm$]	(σ) $(\Omega\ cm)^{-1}$	(RH) [cm^3/C]	(n_H) [$/cm^{-3}$]	(μ) [cm^2/V_s]	Type
ZT pure	2.069×10^3	4.834×10^{-4}	1.785×10^7	3.496×10^{11}	8.631×10^3	p-Type
$(ZT)_x\ (MnO2)_{1-x}$	1.386×10^4	7.214×10^{-5}	3.509×10^6	1.779×10^{12}	2.531×10^2	n-Type
$(ZT)_x\ (CuO)_{1-x}$	9.581×10^3	1.044×10^{-4}	2.583×10^6	2.417×10^{12}	2.695×10^2	p-Type
$(ZT)_x\ (Fe2O3)_{1-x}$	2.007×10^4	4.982×10^{-5}	1.366×10^6	4.669×10^{12}	6.806×10^1	n-Type

Conclusions

Pure and doped ZnO –TiO$_2$ thin films with MnO$_2$, CuO and Fe$_2$O$_3$ thin films have been successfully deposited on glass substrates at RT using PLD technique. The electrical conductivity and Hall Effect were measured for films with average thickness of (200) nm. The analysis of the DC conductivity state that there are two stages of DC conductivity mechanism throughout the temperature range (303 - 423) K by which the conductivity increases when doping with metal oxide and the high conductivity occur when doping the films with Fe$_2$O$_3$. Also, the Hall Effect measurements showed that all films have n and p type charge carriers depending on the type of dopant metal oxides. The carriers concentration increased while the mobility decreased with adding the metal oxides. These results showed that adding different metal oxides plays an important role in the improvement of electrical properties of ZnO-TiO$_2$ thin films.

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