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STRUCTURAL AND ELECTRICAL PROPERTIES OF ZnO EMBEDDED IN PANI SOLVENT

Khalaf AL Abdullah[1],Tarik Zarwri[2],Wafaa Hajismail[2]

[1]Dept. of Electrical & Electronics Engineering, Aleppo University, Aleppo-SYRIA
[2]Dep of physics, Aleppo University, Aleppo-SYRIA
faceeealepuniv@gmail.com

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ABSTRACT

Zinc oxide/polyaniline (ZnO/PANI) hybrid structures have been investigated for their structural and electrical properties. ZnO nanoparticles had prepared by sol-gel method, then pressed in the form of pellets were used for this purpose. The hybrid ZnO/PANI structure was obtained by the addition of PANI on the surface of ZnO. The XRD-pattern of the ZnO modified pellets show shift of peak toward smaller angles so thecrystallitesize decrease, AC and DC measurements where carried out. The results reveal that the hybrid structures have lower potential barrier height and higher donor density.

Keyword: ZnO, electricalproperties, XRD

I. INTRODUCTION

In recent years the manufacture of devices using inorganic/organic hybrid materials has attracted much interest from both the scientific and the technological pointsof view, improvements in the electronic and the optical properties of these devices are closely related to surface effects. The grain boundaries (a double Schottky barrier could be formed at the grain boundaries) of polycrystalline materials play a significant role in their electrical properties and interfaces, which usually play important roles in device characteristics [1]. Zinc oxide, which is *n*-type semiconductor, with 3.36 eV energy band gap [2], ZnO nanostructures such as nanofibres and nanorods, and nanowire have attracted the attention of several researchers for their potential applications as solar cells, gas sensors, and biosensors. Polyaniline (PANI) is a promising conducting polymer due to ease polymerization environmental stability [3]. PANI is usually considered as a *p*-type semiconductor [4], presence of reactive –NH– groups in the polymer chain which in parts chemical flexibility to the system and improves the processcibility to a large extent [5]. Electrical and optical properties can be changed by oxidation and/or by protonation [1].

Several reports are dealing with the preparation of hybrid materials such as TiO_2/polyaniline [6], Fe_2O_3/polyaniline [7], SnO_2/polyaniline [8] and ZnO/Polyaniline [9]. PANI is widely used in the area of electrochemical materials, light-emitting diodes, biosensors, chemical sensors, and battery electrodes. In this work ZnO nanoparticales and ZnO-PANI structures where synthesized. Electrical and structural properties were studied. AC and DC measurements were carried out.

II. EXPERIMENTAL

II. 1 Zinc oxide nanoparticles synthesis:

ZnO nanoparticles were synthesized using sol–gel Technique [10]. Zinc acetate hydrate $[(CH_3COO)_2Zn{\cdot}2H_2O]$ as precursor and methanol as a solvent were used in the preparation. 0.6 M solution was mixed thoroughly using a magnetic stirrer at temperature at 60◦C for 2 h. The clear transparent solution thus obtained was heated at 80◦C (higher than the boiling point of methanol) to evaporate the remnant methanol till a white powder (precursor complex) it can be further heat-treated to obtain zinc oxide powder. ZnO was heated at 600◦C for 1 h to get ZnO nanoparticles .(600 mg) of ZnO powder was compressed in the form of pellets with 1.2 cm in diameter and 1.6 mm in thickness by applying a pressure of (300 Kg/Cm^2) this sample labeled by Z_0.

II. 2 PANI Synthesis

Polyaniline was synthesized by oxidative polymerization of aniline in the presence of hydrochloric acid using ammonium persulfate (1mol/aqueous hydrochloric acid solution ammonium persulfate as oxidant with an oxidant/aniline molar ratio ≤1.15 in order to obtain high electrical conductivity yield). The monomer concentration was $1mol.l^{-1}$. The solution

temperature was between 0 and 2◦C. The reaction was done in 2h.The experimental part consists of adding slowly (even drop by drop) the aqueous ammonium persulfate solution to the aniline/HCl solution, both solutions being pre-cooled to 0◦C. The mixture is stirred for about 1 h. Then the formed precipitate filtred and washed many times then it dried [10]. The final obtained material is a polyemeraldine salt.

II. 3 Preparation of ZnO/PANI interfaces

In order to form an interfaceZnO/PANI, PANI was dissolved in *N*,ND imethylFormamide (DMF) which was stirred to obtain a uniform solution.600mg of ZnO powder was taken and pressed in the form of pellet by applying the previous pressure, then the pellets was obtained at 600°C for 2h. Then pellet was dipping in PANI solution for 24h .and dried at atmospheric condition (sample labeled by Z_1).

III. RESULTS AND DISCUSSION

III. 1.Structural properties

X-ray diffraction (XRD) analysis was carring out using XRDLEYBOLD-TYPE1.03 diffractometer with CuKα radiation of wavelength, λ= 1,5148 µA Figure (1) shows XRD patterns of samples Z_0, Z_1. The presence of prominent peaks shows that the film is polycrystalline in nature.the lattice constant a=3.0031Å for Z_0 and a=2.9941 Å for Z_1.crystallite size of the ZnO was calculated by using Scherrer'sFormula [11]

$$D = \frac{0.94\lambda}{\beta cos\square} \quad (1)$$

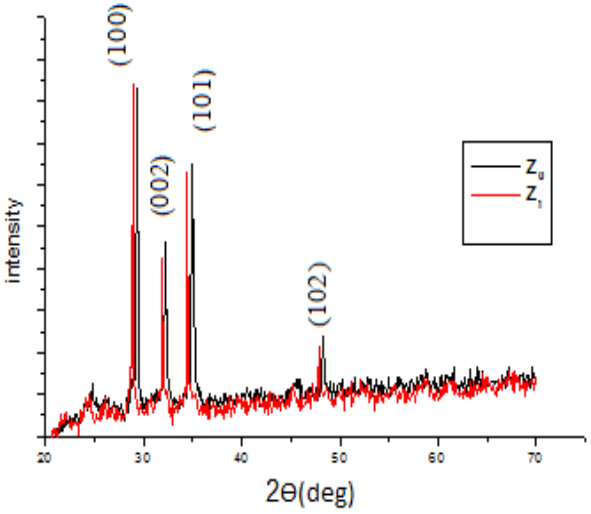

Fig. 1: XRD patterns of Z_0 and Z_1

where *D* is the crystallite, λ is wavelength of the X-ray used, β is full width at half maximum intensity (fwhm) in radians and θ is the angle of diffraction.

Table (1**)** crystallite size along prominent diffraction planes.

Table 1: crystallite size

	Crystallite Size (nm) along diffraction plane		
	(100)	(002)	(101)
Z_0	16.831	16.829	9.706
Z_1	10.527	9.4302	10.678

III. 2 DC-measurements

III. 2 1 I-V Characteristics

I-V characteristics were recorded using high resistance meter typeMEGOHMETER (M1500P). figure (2) shows *I*-V characteristics for Z_0, .Z_1 samples which reveal that sample Z_1 have the higher current than the current's Z_0 (pure ZnO).

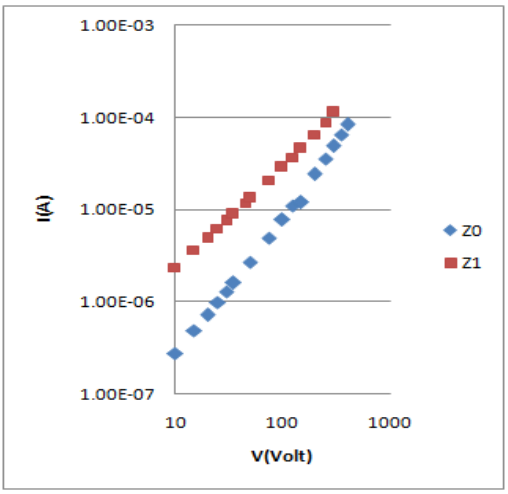

Fig. 2: I-V characteristics of samples

III .2.2 Barrier height determination:

Figure (3) and figure (4) show I-V curves measured at different temperatures (333, 348, 363)K.

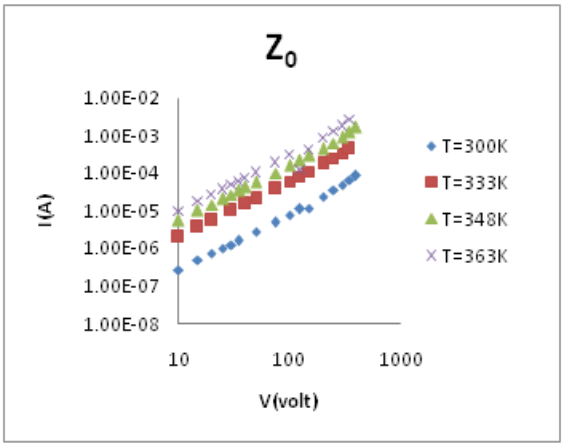

Fig. 3: I-V curves of Z_0 with different temperatures

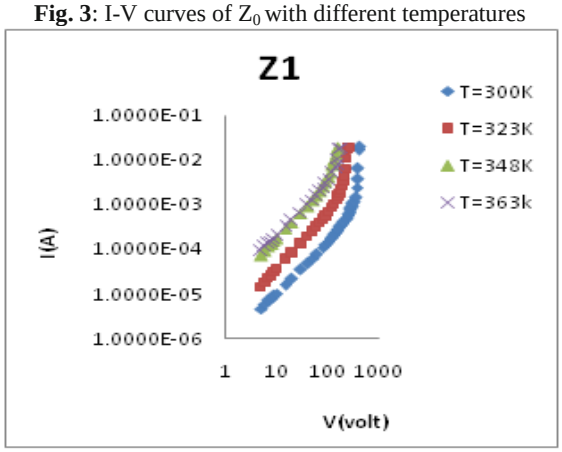

Fig. 4: I-V characteristics of Z_1 for different temperatures

Potential barrier height □ can be calculated by using Arhenius relationship [12]

$$I = I_0 e^{-\Psi/KT} \qquad (2)$$

K is Boltzman Constant and T is temperature.

By plotting ln(I) in function of 1/T, Ψ. can be determinate from the slope of the resulting line. Figure (5) and figure (6) show potential barrier height as function of potential.

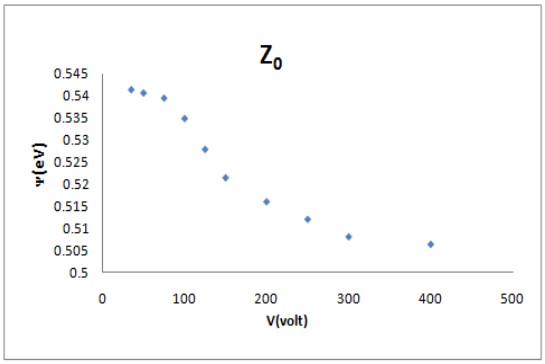

Fig. 5: barrier values for different potentials for Z_0

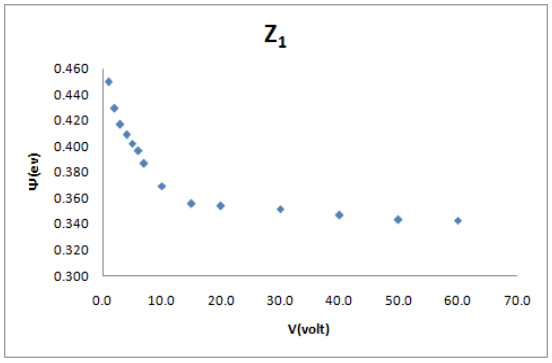

Fig. 6: barrier values for different potentials for Z_1

The barrier height decreases in Z_1 and the value of barrier height is lower than that of Z_0. This might be due to polyaniline affects the ZnO. Interfacial interactions occurring between ZnO and PANI resulted in decrease of the potential barrier height between ZnO grains .

III. 3 Ac-measurements:

Ac-measurements were carried out with a LCR meter and figure (7) shows the resistances of Z_0, Z_1 as functions of log(ω).

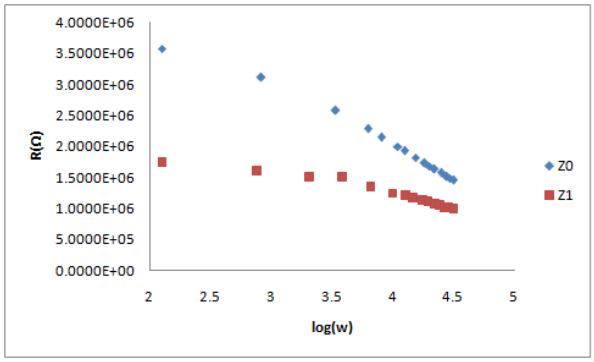

Fig. 7: Z_0, Z_1 resistances as function of log(ω)

Capacitance Cp as function of AC frequency signal *log*(ω) was carried out and seen in figure (8) and figure (9) [13] The trapped electric charge follows the applied voltage oscillations and contributes to the total capacitance only if their frequency does not exceed the characteristic trap frequency ω_t. Therefore, in the case of low frequencies $\omega << \omega_t$, the trap related capacitance Ct is equal to the low frequency capacitance where the deep and shallow trap contributes to capacitance. In high frequency ($\omega >> \omega_t$) measurements the junction capacitance Cs is the high frequency capacitance where the shallow trap contributes to capacitance. Table (2) shows the Ct and Cs values of Z_1 and Z_0.

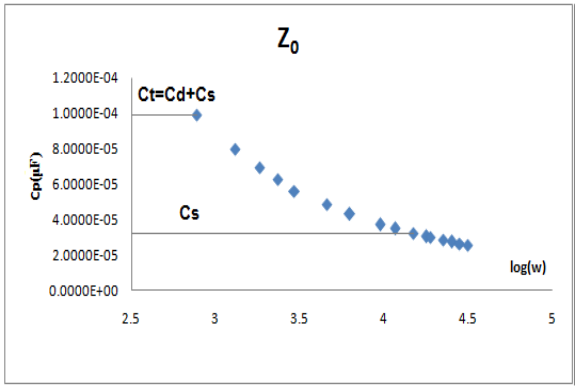

Fig. 8: capacitance Cp as a function of *log*(ω) for Z_0

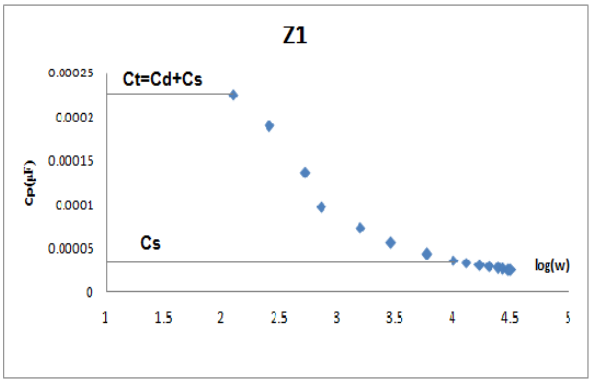

Fig.9: capacitance Cp as a function of *log*(ω) for Z_1

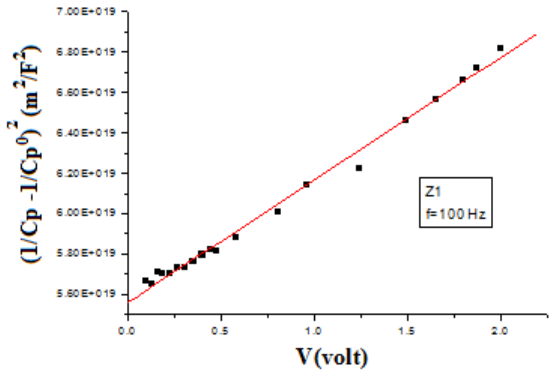

Fig. 10: $(1/C - 1/C_0)^2$ vs V for sample Z_0 at F=100Hz.

Table 2: Ct, Cs value of Z_1,Z_0.

	Ctot=Cs+CD(F)	Cs(F)
Z_0	99.072E-12	31.855E-12
Z_1	22.4E-11	36.256E-12

III. 3.1 *C-V characteristics:*

Mott-Schottky measurements are the common method for studying the capacitive behavior of a double Schottky barrier. It is possible to obtain information about average donor density, based on the following [14] equation

$$\left(\frac{1}{C_p}-\frac{1}{C_p^0}\right)^2=\frac{1}{2q\varepsilon_s(N_{d-}Na)}(V+) \quad (3)$$

where Cp is the capacitance per unit area of a grain boundary, C_p^0 is the capacitance per unit area when V=0, q is the electron charge, ε_s is the dielectric constant of zinc oxide, N_d is the donor density, □ is the barrier height, and V is the applied voltage per grain boundary. By plotting $\left(\frac{1}{C_p}-\frac{1}{C_p^0}\right)^2$ versus the applied voltage figure (10) and figure (11) it is possible to calculate N_d from the slope of the lines and then the traps density N_t .

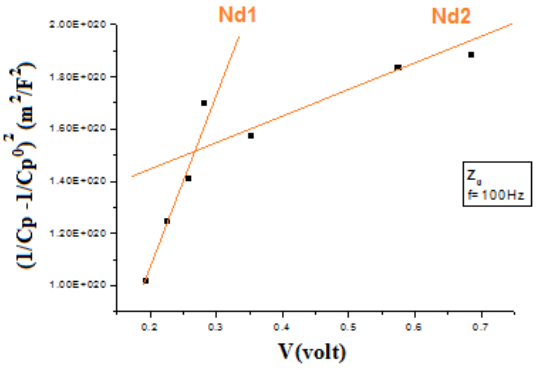

Fig. 11: $(1/C - 1/C_0)^2$ vs V for sample Z_0 at F=100Hz.

From figure (7) Z_0 shows two donor levels so it have two values of donor density N_d and both are lower than that of Z_1 table (3) include donor intensity and trap density of Z_0, Z_1.

Table3: donor intensity and trap density of Z_0 and Z_1

F=100Hz		
	$Nd(cm)^{-3}$	$Nt(Cm)^{-2}$
Z_0	2.226E+08	3.362E+08
Z_0	3.622E+09	1.365E+09
Z_1	2.727E+10	2.952E+10

IV. CONCLUSION

ZnO/PANI hybrid interface was prepared by dipping ZnO pellets in PANI solvent for 24 hours. Observation of this study reveals that the polyaniline affects ZnO. Interfacial interactions occurring between ZnO and PANI resulted in cohesion of PANI molecules with oxide matrix. Organic–inorganic hybrids so formed represent materials which can be used in many applications.

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