Characterizations study ZnO-TiO_2 nano rods thick films as Photo detector

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Abstract

First, ZnO nanorods were successfully synthesized by simple evaporation method, using single stage controllable horizontal tube furnace and quartz tube without catalyst. The ZnO nano powder was mixed with (10 and 20%) of TiO_2 powder (weight ratio), then ZnO-TiO_2 thick films were synthesized using simple, low-cost efficient screen print technique. The thick films were heated at 500 C° for one hour to remove the organic binder and any impurities. The prepared thick films were examined with X-Ray, and FESEM to study the structural and morphology of the films, the X-ray results show that the films are polycrystalline with sharp and high intensity peaks indicating high crystalinity of the product. The FESEM pictures show nanorods with diameters less than 100 nm and several micrometers in length of ZnO with TiO_2 nanoparticles. ZnO-TiO_2 device was built up by electroding the thick films. The I-V characterization of the films were studied in dark and light, then photo detection parameters were estimated and it was found to be efficient and high response in UV range detection.

Keywords: nanostructures, ZnO, simple evaporation.

دراسة خصائص الاغشية السميكة ZnO-TiO_2 النانوية التركيب ك كاشف ضوئي

الخلاصة

في البداية تم تحضير اوكسيد الخارصين بتراكيب نانوية (nanorods) باستخدام تقنية التبخير البسيط باستخدام فرن انبوبي وانبوبة كوارتز بدون عامل مساعد حيث تم تبخير معدن الخارصين عند درجة حرارة 700 م وبوجود غاز الاركون والاوكسجين وبنسبة خلط 90-10 على التوالي. واستمرت العملية مدة تم تصنيع اغشية سميكة من الخليط باستخدام تقنية الطباعة على الشبكة وهي بسيطة وذات كلفة واطئة وفعالة، ان هذه الطريقة تعطينا اي تصميم او ابعاد للغشاء وبالتصاقية جيدة بين الغشاء والقاعدة. بعد ذلك تم تسخين الاغشية المحضرة لمدة ساعة وعند درجة حرارة 500 م للتخلص من الرابط العضوي واي شوائب اخرى. تم دراسة الخصائص التركيبية و دراسة السطح للاغشية المحضرة بفحصها ب باجهزة ال X-ray, FESEM حيث اظهرت فحوصات الحيود بالاشعة السينية ان الاغشية ذات تركيب متعدد التبلور مع قمم حادة ذات شدة عالية مما يدل على تبلور جيد للمادة، واظهرت صور المجهر الالكتروني الماسح nano rods وباقطار اقل من 100 نانومتر وباطول مختلفة تصل بضعة مايكومترات ل اوكسيد الزنك ان اهذه التراكيب النانوية تعزز وتحسن من اداء الكاشف. تم بناء الكاشف الضوئي بعد تقطيب الاغشية وبنفس تقنية الطباعة على الشبكة وتم دراسة الخصائص الكهربائية في الظلام والاضاءة وحساب العوامل الكشفية للجهز حيث اظهر الكاشف استجابة عالية كفاءة جيدة في منطقة الاشعة فوق البنفسجية.

الكلمات المرشدة: تراكيب نانوية، ZnO، تبخير بسيط.

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INTRODUCTION

The nano sized ZnO with the features of large volume to area ratio high ultraviolet (UV) absorption, and long life-span has been widely used as catalyst gas sensor ,active filler for rubber and plastic, UV absorber in cosmetics and anti-virus agent in coating [1], ZnO nanoparticles can be synthesized by various approaches including sol–gel processing homogeneous precipitation mechanical milling, microwave method, spray pyrolysis, thermal evaporation [2] and chemical synthesis [3]. However, ZnO nanoparticles are prone to aggregate due to the large surface area and high surface energy. In order to improve the dispersion, it is necessary to modify the surface of ZnO nanoparticles. Some researchers have revealed several physical and chemical methods for modifying the surface of ZnO nanoparticles. The chemical surface modification, which can be classified as surface grafting and esterification, is the most promising method because of the strong covalent bond between the surface modified particles and polymer chains [4]. During the last two decades, metal-oxide semiconductors (MOS) had a great amount of attention for their applications in several areas such as medical diagnosis, toxic gases sensors and opto-electronic industries [5]. Recently the Nano-structured materials appeared to show higher efficiency due to gain in the ratio of the surface to volume ratio and their single crystalline Nanostructure and other physical properties [6]. ZnO is one of the (MOS) materials that played a good role in different applications in electronic sensors and opto-electronic devices in respect of having many advantages such as low cost, having a good electronic mobility, and showing a good thermal and Chemical stability [7]. ZnO is one of the II-VI semi-conductors, it has a direct wide band gap–(3.37 eV) and excitation energy (60 meV) [8], has great attention for researchers because of its optical properties which make it important material.

In a Photoconductivity measurements are among the most valuable techniques to explore the optoelectronic properties of photoconductive semiconductors. Photoconductivity is defined as electrical conductivity resulting from photo-induced electron excitations in which light is absorbed. In semiconductors, photoconductivity arises due to photo-generation of electron hole pairs after absorption of photons which increases carrier density and conductivity of material. A photo detector is a device that measures photon flux or optical power by converting the energy of the absorbed photons into a measurable form [9]. Photoconductivity (PC) is an important property of semiconductors by means of which the conductivity of the sample changes due to incident radiation.

Experiments

The preparation of ZnO nanostructure is carried out in a single stage controllable horizontal tube furnace (40 cm) with a quartz tube (50 cm) long and (3cm) in diameter. The quartz tube was cut and the two ends of the tube been altered to be suitable and fitted for entry the gas mixture and exit the gas in the other end. A pure metallic Zinc powder (merick) Germany (99.9%) is used as a raw material. (1 gm) of Zinc powder is placed in ceramic boat (1x1x10 cm). The boat was placed at the center of the tube furnace, and the Si/SiO_2 substrates are positioned down the stream of the gas flow. Before increasing temperature The quartz tube is purified from residual gases using pure Argon for 3 minutes, then we increase the temperature inside the furnace to 700 C$^{\circ}$ with gas mixture ($Ar+O_2$) flowing at a rate of (100, 200 and 300 sccm) with a ratio of (10:1). The flow of gases was controlled by two flow meters. White cotton like powder is deposited on the substrates and the wall of the tube. The furnace left to cool down naturally to collect the product

TiO_2 nanoparticles were synthesized by Sol-gel method in advanced material laboratory in Physics dept., college of science, Al-Mustansiriyah University and examined by X-Ray diffraction. Then different weight ratios were taken for both ZnO-TiO2 (90% - 10%), (80% - 20%). Then these ratios were mixed together inside a test tube and adding a small amount of Ethanol and the mixture was stirred for one hour at room temperature then dried and screen printed at different substrates, the screen printed films were heated in a box furnace at 500C° to remove all organic materials, study the (TiO_2–ZnO) thick films properties. This mechanical mixing not contains melting or phase transformation but affects the properties of ZnO films.
The product is collected carefully. A suitable amount of PVA was added to produce the ZnO- PVA paste. The paste is screen printed in (1 cm) square pattern, the screen print is a simple technique to prepare the thick films This technique gives exact and desire dimensions for the film pattern with a good adhesion between the film and the substrate. And then the thick films are dried in air then, heated in a box furnace to 500 C° with a rate of 8 C°/min for one hour to remove impurities and the organic material. Then the films were examined by different devices to study its structural properties. Ohmic contacts interdigitated electrode IDE metal masks were fabricated by the screen print technique using silver paste as conducting material.

Results and Discussion

The prepared thick films were examined by X-Ray diffractometer (miniflex II Rigaku, Jaban) (Cu, kα), and Field Emission Scanning Electron Microscope (Hitachi S-4160) (FESEM). Comparing with (JCPED) card all the peaks are for ZnO and TiO_2 no other peaks of impurities was appearing. The estimated crystallite size shows that the crystallite size growth in the direction (100) and increased in the direction (101) and not effected in the direction (002) for both mixing ratio. The other structural parameters were calculated and illustrated in table (4-4) also from the XRD pattern it is clear that the dominate growth were in the direction (101) indicating preferring growth along c-axes in that direction. The other peaks indicate the pollycrystallinity nature of ZnO. The crystallite size is calculated [10, 11] by the relation:

$$D = 0.9\gamma/\beta COS\theta \qquad \dots (1)$$

While cell parameters (a and c) were estimated using equation (2)

$$d_{hk} = \mathrm{a} \Big/ \sqrt{4/3(\mathrm{h}^2 + \mathrm{k}^2 + \mathrm{hk} + \mathrm{i}^2\mathrm{a}^2/\mathrm{c}^2} \qquad \dots (2)$$

Because of the heat treatment and preparation conditions the films undergoes strain and dislocation in its structure these parameters were calculated [12] by equations (3) and (4) respectively.

$$\beta COS\theta/4 \qquad \dots (3)$$

$$\delta = 1/D^2 \qquad \dots (4)$$

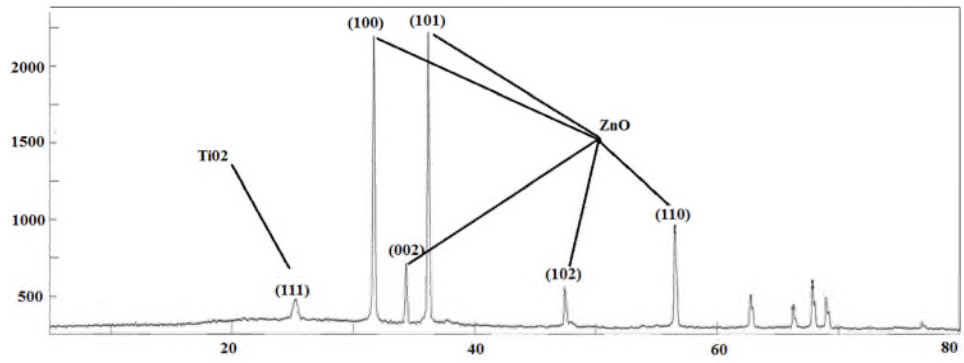

Figure (1) XRD pattern for ZnO-TiO_2 thick film.

Table (1) structural parameters for pure and mixed ZnO thick films.

Plain no.	**D(crystallite size) nm**	**Lattice parameter a(A°), c(A°)**	**Dislocation Density δ x 10^{15} ($line^2/m^2$)**	**Micro strain ξ x 10^{-3}**
		ZnO		
(100)	29.3	3.229-5.270	2.36	1.69
(002)	29.3		1.83	1.465
(101)	27.28		2.031	1.58
		ZnO:10%TiO_2		
(100)	28.3	3.229-5.270	1.71	2.29
(002)	30.7		1.53	1.89
(101)	30.9		1.52	1.96
		ZnO:20%TiO_2		
(100)	21.4	3.229-5.270	2.29	1.71
(002)	24.1		1.89	1.53
(101)	29.1		1.96	1.52

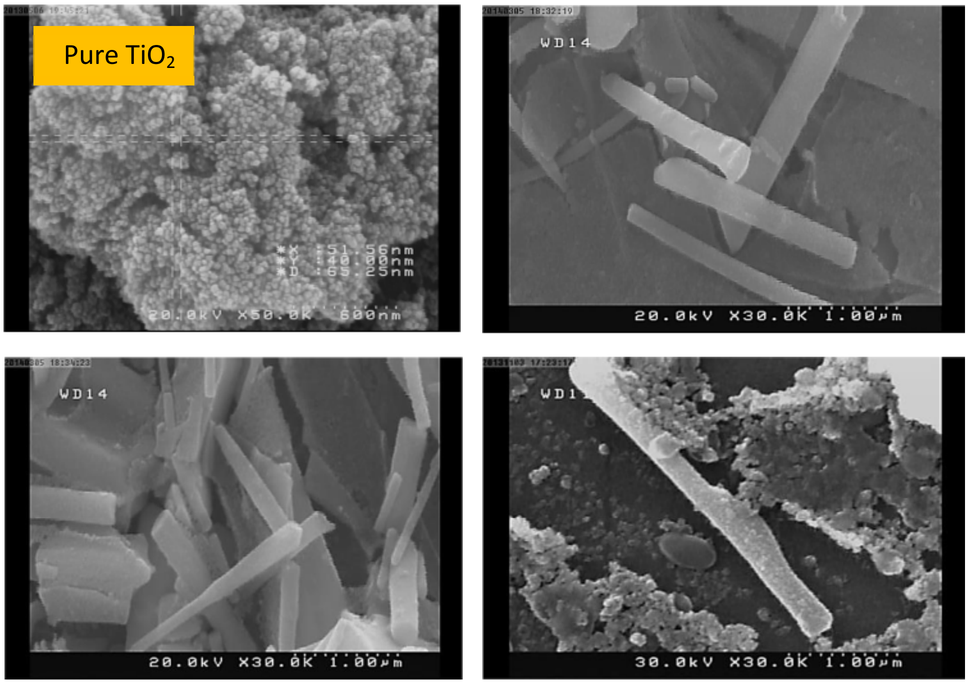

Figure (2) FESEM pictures for ZnO-TiO$_2$ thick films.

The results in figure (3), (4), gives the I-V characteristics behavior of the (n-ZnO/p-Si) device in the forward and revers bias. Two regions are recognized; the first one represents recombination current, the first current established when the concentration of the generated carrier is larger than the intrinsic carrier concentration (n_i), i.e. ($n*p>n_i^2$), which lead to recombination process for mass low applicable. The second region at high voltage represented the diffusion or bending region which depending on serried resistance and in (MOS) case represented the tunneling region. From the comparison between the results obtained for all devices prepared at different methods condition, it is recognized the values of the current improved for simple evaporation method due to decrease in the resistivity for n-type ZnO film results in an increase in the electron concentration. This causes a decrease in the hole concentration and thus a reduction in I_s. The ideality factor all devices were estimated at the optimum conditions and it has been found to be ranging between (1.97-3.6).

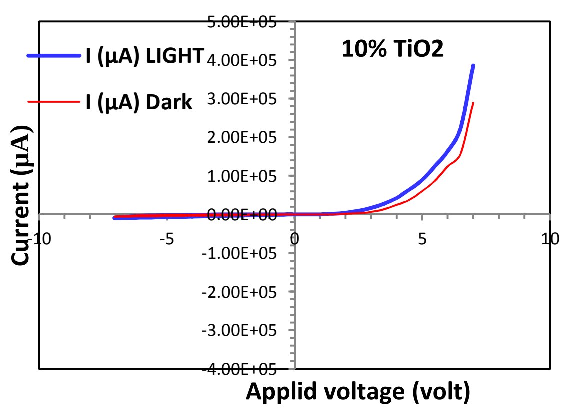

Figure (3) I-V characteristic for 10%TiO$_2$.

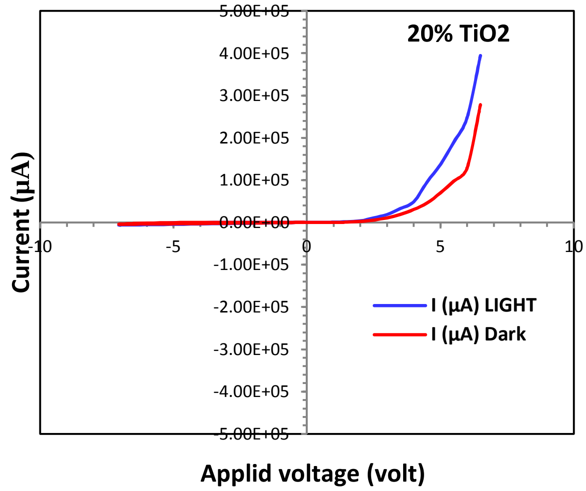

Figure (4) I-V characteristic for 20%TiO$_2$.

Figure (5) explain the change of resistance after illumination to 370 nm light from Xe lamp for 60 second and then the light was shut down to study the recovery for the films prepared by mixing method with different TiO$_2$ ratios and hydrothermal method. The resistance decreases after illumination by 48%, 56% for mixing ratio 10% and 20% indicating that increasing TiO$_2$ ratio enhance the response for UV light this is due to the roughness increase causing increasing in absorption portion.

The responsivity, detectivity and the quantum efficiency for all condition were calculated [13,14] according to equations (5, 6, 7) respectively and illustrated in table (2)

$$R_\lambda = \frac{I_{ph}}{P_i} \quad \dots (5)$$

$$D^*_\lambda = \frac{R_\lambda}{I_n}\sqrt{A\Delta f} \quad \dots (6)$$

$$\eta = 1.24\,\frac{R_\lambda}{\lambda} \quad \dots (7)$$

Table (2) The Responsivity, Detectivity and Efficiency estimated at wavelength (370 nm) for different preparation conditions.

Preparation Condition	Responsivity $R_{\lambda\,(A/W)}$	Detectivity $D^*(cm.Hz^{1/2}/W)\ x10^{12}$	Efficiency η
10%TiO$_2$	0.52	6.9	0.00174
20%TiO$_2$	0.48	6.7	0.00160

Conclusion

ZnO Nanorods and tetrapod were successfully synthesized by simple evaporation method. The structure of ZnO is found to be wurtzite hexagonal compared with (JCPD) card. The micro strain and dislocation density were estimated and found varied with preparation conditions. The cell parameters were calculated and found much closed with the typical results. The ratio of the organic binder to the material affects the adhesive of the film with the substrate. Also, the rate of the heating temperature contributes in improving the adhesion.

The prepared films show high responsivity and detectivity in the UV range as photodetector.

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