Structural, Optical and Sensing Properties of ZnO:Cu Films Prepared by Pulsed Laser Deposition

Saleem A Hussain¹, Awatif J Radi¹², Firas A Najim¹, Mohamed A Shaheed¹

Saleem.hussain@qu.edu.iq

¹Department of Physics, College of Education, University of Al-Qadisiyah, Diwaniyah, Iraq
²Babylon Education Directorate, Babylon, Iraq.

Abstract. This research aims to study the effect of deformation on the structural, optical and allergic properties of ZnO films prepared by pulsed laser deposition technique were deposited on glass substrate. ZnO were deformed with a copper element in different ratios (3%, 7%, 9%) due to changing the environment temperature at 275°C and annealed to 400°C. The X-ray diffraction shows that all films have polycrystalline structure with hexagonal shape due to annealing process, and they have a high permeability of 80% with energy gap 3.35eV. The best sensitivity was clear at (7%) ratio.

Key words: Zinc oxide, Pulse laser deposition, X-ray diffraction, Optical properties, Electrical resistance, gas sensing

1. Introduction

Zinc oxide is a semiconductor of the second-hexagonal group (II-IV) with a polycrystalline hexagonal structure [1]. It has large exciting binding energy and wide direct band gap of (3.3eV), so that excitonic emission processes can persist at or even above room temperature [2-3]. Pure zinc oxide is a white solid, nontoxic, not soluble in water or alcohol. Zinc oxide is an amphoteric substance because it dissolves in acids such as acetic acid, mineral acids, ammonia, ammonium carbonate and alkaline hydroxides [4]. The crystal structure of zinc oxide including three types as shown in fig. 1. The crystal structure is more stable. It has a unit cell with constants (a = 3.24 Å) and ((c = 5.19 Å), cubic crystal structure which is divided into: a- Rock salt cube, b- Zinc blende and c- Wurtzite. The ZnO crystallizes in the wurtzite structure [5]. Zinc oxide is utilized in many applications including transistors, transparent electrodes for laser diodes, solar cell aggregates, radiation shielding, microwave applications, dilute magnetic semiconductor and it is suitable for optoelectronic applications [7]. Copper is one of the most important substances in semiconductor and used for doping the elements of the group (II-VI), when exposed to a thermal effect that will increases propagation inside the material to increase resistance of material [8,9]. The copper element depends on the location it occupies in the host material, either as an impurity donor (or as an acceptor), so that it is either in interfacial sites or in compensatory sites within the crystal structure of the added material depending on the diameters between the copper and the material.
2. Experimental Work.

The pulse laser deposition (PLD) technique is similar to the mechanism of growth of thin films, in this way with other methods of techniques for the preparation of thin films in terms of the formation of the substances, the formation of multiple layers will increasing the cohesion and coherence of layers. The formation of layer will change, as the power density of pulse laser increasing it will lead to changing the thickness of the layer, that mean the particles with high-energy will hit surface target of material. The multiplicity of the particles at the collision area will growth the thickness area of the sample. The collision area is a source of all of kinds particle condensation. The thermal equilibrium is obtained when the particle condensation ratio is greater than the particle precipitation on the collision area, and the film grows on the surface of the substances. Thin films of pure ZnO and ZnO:Cu were prepared at different doping ratios (3%, 7%, 9%) when the substrate temperature (Ts= 275°C) and the number of pulses (300) pulses where all films have thickness approximately (125nm).

3. Result & Discussion:

3.1 X-Ray diffraction

Copper doping ZnO prepared with ratios (3%, 7%, 9%) with substrate Temperature 275°C and annealed to 400°C. The X-ray diffraction showed a hexagonal structure. Polycrystalline structure, the reflections magnitude showed at (100) (002) (101) (102) (110) accompanying with the angles (31.68 °) (34.34 °) (36.16 °) (47.46 °) (56.52 °). These results showed a good matching with ICDD card as in figure (2).
3.2 Atomic Force Microscope:

Atomic force microscopy (AFM) diagnosis of ZnO:Cu doping with different ratio (3%, 7%, 9%). The results showed that the pure and doping films were homogeneous through 2D and 3D diagnostics with no grouping observed. Irregular material or voids on the surface of the films are homogeneous and vertical heights of the peaks of the material as shown in the images of the atomic force microscope in Figure (3).

![Atomic force microscopy images](image)

**Figure 3.** Atomic force microscopy images of ZnO:Cu thin films doped with (a: 3%, b: 7%, c: 9%)

3.3 Optical absorption spectrum

Optical absorbance defined as the ratio of the intensity of light falling upon a material and the intensity transmitted. The figure (4) shows the optical absorption spectrum of copper doping ZnO films in different ratios and with substrate temperature (R.T. and Ts=275°C). The results show that the absorption decreases for all films with increasing wavelength and increasing due to increasing the deformation.

![Optical absorption spectrum](image)

**Figure 4.** shows an Optical absorption spectrum for ZnO:Cu thin films doped with (3%, 7%, 9%) prepared at R.T. and at Ts=275°C and annealed at (400°C).
3.4 Optical transmittance spectrum.
Optical transmittance is the ratio between the intensity of the incident radiation from the material to the initial intensity of the radiation falling on the material. The transmittance spectrum depends on the thickness. Surface imperfections and surface roughness also affect the amount of permeability as they work to disperse the incident beam and thus reduce the permeability of the prepared films. Wavelength will decreases with increasing deformation ratio as shown in figure (5).

![Figure 5](image)

Figure 5. Optical transmittance spectrum of ZnO:Cu thin films doped with (3%, 7%, 9%) prepared at R.T. and at $T_s=275^\circ$C and annealed at 400$^\circ$C.

3.5 Optical Energy Gap.
The energy gap was calculated in the allowable direct electronic transfer at (400$^\circ$C). The plot shows relationship between $(\alpha h\nu)^2$ and the energy of the incident photon $(h\nu)$as in figure (6). The straight line of the curve and intersect it with the photon energy axis at point $(\alpha h\nu)^2=0$ where the intersection point shows the energy gap value is given for the allowed direct transitions of doping films, and the amount of the energy gap ranges between (2.95-3.26 eV). These results are consistent with [11] and [12].
ZnO:Cu 3%  
R.T. (°C)  
\( \alpha \) vs. \( \gamma \) 
\( Eg = 3.26 \, \text{eV} \)  

ZnO:Cu 7%  
R.T. (°C)  
\( \alpha \) vs. \( \gamma \) 
\( Eg = 2.95 \, \text{eV} \)  

ZnO:Cu 9%  
R.T. (°C)  
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\( \alpha \) vs. \( \gamma \) 
\( Eg = 3.26 \, \text{eV} \)
3.6 Sensing properties

3.6.1 Electrical resistance of ZnO:Cu films

The electrical resistance (R) of pure ZnO and ZnO:Cu films doping with different ratio (3%, 7%, 9%) was measured as a function of time with constant temperature and then the resistance was measured at different operating temperatures (35°C (R.T), 100°C, 200°C, 300°C). Sensing reactions appeared at all these degrees except 35°C (R.T), there was no response to the films at this temperature. The film prepared from pure ZnO observed that the resistance increases with increasing temperature. The figure (7) shows the relation between time in minute and the electrical resistance and as we seen that the prepared films moved from the n-type to p-type because of annealing operation.
Figure 7. Resistance as a function of time at different operating temperatures for pure ZnO and doped ZnO:Cu films with (3%, 7%, 9%) ratio at (100°C, 200°C, 300°C).

3.6.2 Operating temperature and latency response.

The response time ($T_{res}$) is defined as the time at which the gas response occurs and returns to the initial state. Figure (8) shows the response and recovery time of pure ZnO and ZnO:Cu films with different ratios (3%, 7%, 9%).
Figure 8. Response and recovery time as a function of the operating temperature of the prepared films for pure ZnO and ZnO:Cu doping with (3%, 7%, 9%) ratio.

3.6.3 Sensitivity
The sensitivity of pure and copper doped ZnO films was calculated in different ratios (3%, 7%, 9%) were deposited on glass substrates. After the film resistance was measured with the presence of NO2 gas and its absence as a function of time of the relationship (1). The maximum sensitivity of the films was found in the pure ZnO (98.2456%) with an operating temperature (300°C), which is the suitable operating temperature to sensitize the films. While the operating temperature for the doped thin films decreases and reaches 100°C for the doped films with ratio (3%). The sensitivity calculated from equation (1) to show the relation between an operating temperature and sensitivity as in figure (9) and the table1 shows different values of sensitivity and resistance for pure copper and for different ratios[13].

\[
S = \left| \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \right| \times 100\% \quad (1)
\]

Where : \( R_{\text{air}} \), \( R_{\text{gas}} \): the values of electrical resistance by air and gas, respectively.
Figure 9. Shows the sensitivity as a function of the operating temperature of prepared films.

Table 1. Represents the response and recovery time of pure ZnO and ZnO;Cu films in different ratios, sensitivity and resistance values when R is (On) and R is (off).

| Sample | Tgas °C | t gas | Tgas recover | Response time(s) T<sub>res</sub> | Recovery time(s) T<sub>rec</sub> | R(Ω) | S% |
|--------|---------|-------|--------------|-------------------------------|-------------------------------|------|----|
|        | On      | Off   | On           | off                          |                               |      |    |
|        |         |       |              |                               |                               |      |    |
| Pure   | 35°C    | 0     | 0            | 0                            | 0                             | 0    | 0  |
|        | 100°C   | 23    | 41           | 120                          | 16.2                          | 71.1 | 5.06 | 7.52 | 48.6166 |
|        | 200°C   | 21    | 46           | 100                          | 22.5                          | 48.6 | 3.07 | 4.98 | 62.2149 |
|        | 300°C   | 20    | 34           | 90                           | 12.6                          | 50.4 | 1.71 | 3.39 | 98.2456 |
|        | 35°C    | 0     | 0            | 0                            | 0                             | 0    | 0    | 0    | 0    |
| 3%     | 100°C   | 25    | 81           | 200                          | 50.4                          | 107.1 | 27.1 | 24.6 | 9.2114 |
|        | 200°C   | 22    | 48           | 150                          | 23.4                          | 91.8 | 14.6 | 13.5 | 7.1184 |
|        | 300°C   | 22    | 52           | 100                          | 27                            | 43.2 | 3    | 2.82 | 6     |
|        | 35°C    | 0     | 0            | 0                            | 0                             | 0    | 0    | 0    | 0    |
| 7%     | 100°C   | 23    | 54           | 300                          | 27.9                          | 221.4 | 3.3  | 1.04 | 68.4848 |
|        | 200°C   | 21    | 44           | 150                          | 20.7                          | 95.4 | 66.7 | 22.7 | 65.8620 |
|        | 300°C   | 22    | 36           | 90                           | 12.6                          | 48.6 | 33.1 | 20.3 | 38.6356 |
|        | 35°C    | 0     | 0            | 0                            | 0                             | 0    | 0    | 0    | 0    |
Conclusions.

In this research, the pulsed laser deposition method was successfully used to prepare thin films of pure zinc oxide and copper-induced zinc oxide in three different proportions. It was found that by increasing the deformation ratios, the film crystallization decreased, and the optical measurements showed that the value of the optical energy gap of the prepared films was within (2.95-3.26 eV). Sensitivity measurements of the prepared films showed no response at room temperature, and the increased resistance of the prepared film when increasing the temperature was also shown. The maximum sensitivity of the films was found in the pure ZnO (98.2456%) with an operating temperature (300°C), which is the suitable operating temperature to sensitize the films. While the operating temperature for the doped thin films decreases and reaches 100°C for the doped films with Cu at ratio (3%).

|         | 9%     |
|---------|--------|
| 100°C   | 0 0 0 0 0 0 0 0 0 |
| 200°C   | 21 36 100 13.5 57.6 23.1 20.1 13.2067 |
| 300°C   | 22 32 100 9 61.2 11.6 10.8 6.9349 |

4. Conclusions.

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