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Correlation Of The Optical Properties Of Thin Films Of Zinc Oxide With The Molar Concentration Value Of Spraying Zinc Nitrate Solution

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Abstract. *Zinc oxide (ZnO) is classified as a transparent conductive oxides (TCO) with important physical properties [1], which makes it the most widely used material in various field. In this work we deposited thin films of Zinc oxide by dissolving Zinc nitrate in methanol with different concentrations (0.05mol/l, 0.1mol/l,0.16mol/l, and 0.22mol/l) by spray pyrolysis at a temperature 370°celcus to study the impact of molar concentration of used Zinc nitrate sprayed solution on the optical proprieties of thin films .The measurement of visible and Ultra Violet ray through the transmittance spectrum of the wavelengths range (300-800nm), showed that transmittance decreases with increasing concentration, the absorption increase with increasing concentration, energy gap increase in the range (3.14eV-3.26eV) and Urbach energy decrease in the range (0.35-0.30eV) as inversely proportional to the energy gap, all that means there is the sensitivity of optical proprieties of ZnO thin film to the concentration of their spraying Zinc nitrate solution .*

Key words: *transparent conductive oxide, Zinc oxide, spray paralysis, molar concentration spectroscopy, UV-visible*

1. Introduction

Conductive transparent oxides(TCO) are among the basic materials used in the fabrication of thin layers, characterized by two important properties: the high transparency in the visible light region and the good electrical conductivity, because they have aroused the interest of many researchers through their contribution to the development of many industrial and research fields, in particular the field of optoelectronics, field of batteries, gas sensors, reagents and photo catalysts using in solar cell [2‹1]. Among the TCO, we are interested in Zinc oxide (ZnO) because it has many application in several areas [3]. It is known as Zincate in the natural state, can exist in the powder forma or as a massive crystal, it comes In three crystalline form depending there production conduction: hexagonal würtzite type appear in normal condition, CFC sphalerite structure under the high pressure and the Rock–salt structure under very high pressure, in general it is a transparent material in the bulk case with a refractive index value is equal to 2, while it is between 1.37 and 2.20 in the case of thin films, it is an n-type semiconductor with medium direct optical band gap of 3.3eV[4,5] but this value is varied allowing their preparation method. The choice of ZnO based on its richly available on the crust Earth, no-toxic or polluting the environment, and it is easy to prepare, such as it can be obtained from many resources, and this is what qualified it to be an effective component in many applications, the most important of which are: the manufacture of solar cells [6-8], Gas sensors and emitting diode and it is frequently used for photovoltaic field [9]. Therefore conferring of its infinite physical properties, its production coast and the probability of depositing it into varied substrates, our choice referenced on the glass one because of it is no expensive and the value of their thermal expansion coefficient is too equal of zinc oxide lead to a better adhesion and a homogenous ZnO thin layer. The quality of Zinc oxide thin film is no based only on the type of used substrate but also on the prepared condition for example the kind of prepared technique physical or chemical one, the prepared temperature, the speed of preparation and the resource of ZnO or the concentration of the resource solution, …… etc. this paper come under this field of research while it is a presentation of our results about the elaboration of zinc oxide and the effect of the value of the molar concentration of spraying zinc nitrate solution on the optical properties of thin film of prepared zinc oxide thin film.

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2. Materials and experimental

It is worth noting that there is no reference method for depositing thin layers, as different methods can be used, but the process of preparing the substrate is a basic and important step to obtain good samples, or in other words, thin films with good adhesion to the substrate, and as we know, several techniques and methods are used to achieve these purposes [10].

The process of preparing thin films varies between physical and chemical methods [11-13] , and each method is branched into several secondary methods. Despite this, the deposition process, although its nature differs, is generally subject to three basic steps, which are [14]:

1. Production of precipitating materials (ions, molecules, atoms).
2. Transfer of deposited materials from the source to the substrate.
3. Condensation of deposited materials on the substrate either directly or by chemical reaction.

In this work, we used the simplest chemical method, which is the method of chemical spraying by thermal evaporation under atmospheric pressure and at room temperature.

The sample preparation process was carried out in stages: starting from the substrate preparation stage, which is considered the most important stage because the condition of the substrate has a significant impact on the nature of the resulting sample. That is why we showed great interest in this stage, as we were keen to remove any impurities from the surface of the substrates by placing them in an acetone solution for 5 minutes, then in a methanol solution for a sufficient period, then washing them well with distilled water, and then we dried them well to remove any remaining traces on the surface of the substrates.

Then, we prepare an initial solution using zinc nitrate (Zn $(NO_3)2.6\ H_2O$) as a source of zinc. We dissolve a mass of m of zinc nitrate in a volume V = 12mL of methanol. The mass required to be dissolved is calculated to obtain solutions with different concentrations. (C =0.1mol/L, 0.16mol/L, and 0.22mol/L) using the following relationship: m = M.C.V. Where: M: molar mass of zinc nitrate (mol), C: Solution concentration (mol/L) and V: Volume of solution (L).To ensure that the solution dissolves well and obtain a transparent and homogeneous solution, we mix it with a magnetic effect for a period of time (15-20 minutes).

After preparing the initial solution of the material to be deposited and cleaning the substrates, we begin the deposition process by following the following steps: We begin by placing the substrate over the electric heater and let it heat from room temperature to the required temperature (370°C) to avoid exposing the glass substrates to thermal shock. Then we spray very fine drops of the solution on the surface of the hot substrate. This allows the chemical reaction between the components of the solution to be activated, so the solution evaporates and a thin layer of zinc oxide is formed.

After the deposition process is completed, we close the electric heater and leave the substrate on top until its temperature drops to room temperature to avoid breaking it and completing the oxidation process of the prepared layer. By repeating the same stages and changing the concentration of the solution, we obtain three samples of zinc oxide, the only difference between them.

Finally, to obtain samples of thin films of zinc oxide, it is sufficient to repeat the same previous stages, but changing each time the concentration of the solution used.

Because the aim of this work is to study the optical properties of zinc oxide thin films, we used spectrophotometry technology in the field of ultraviolet and visible radiation, as this technology allows determining a large number of optical constants characteristic of these films, such as determining the film thickness, energy gap, transparency, and Urbach energy....etc.

3. Results and discussion

3.1. Effect of molar concentration of zinc nitrate solution on the thickness of ZnO thin films

Measuring the thickness of thin layers is used to determine several other necessary constants [15], such as: absorption coefficient, energy interval [16], etc. It is also one of the most important parameters of thin layers, and to calculate it we used the (swanepoel) program. We noticed that changing, or rather increasing, the molar concentration of the thin films from C=0.1mol/L to C=0.22mol/L is accompanied by an increase in the thickness of the resulting zinc oxide films from d=250.99nm to d=450nm, respectively, perhaps as a result of increasing the number of molecules of the substance.

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3.2. Effect of molar concentration of zinc nitrate solution on the optical transmittance of ZnO thin films

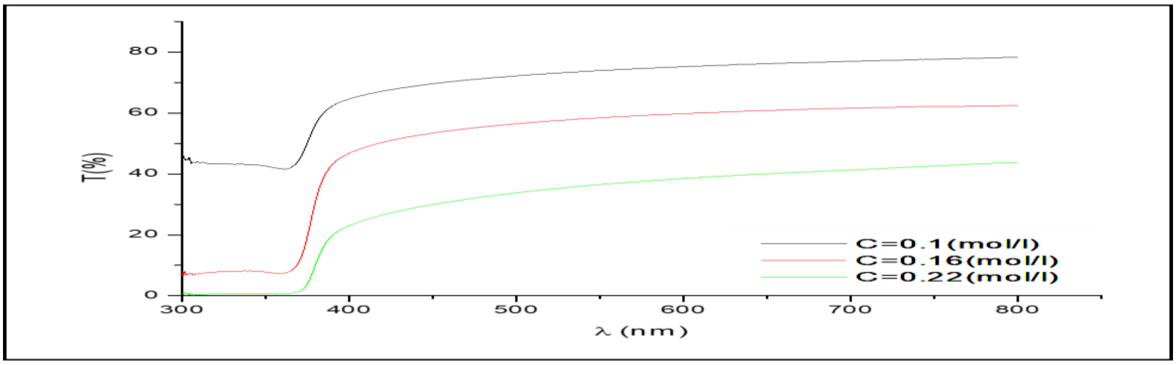
In studying the optical properties of thin layers of zinc oxide with different molar concentrations of the solution used, we relied on spectroscopic analysis of visible and ultraviolet rays within the wavelength range of (300-800 nm). We obtained a curve of changes in the transmittance spectrum as a function of wavelength shown in Figure1. We noticed that the transmittance spectrum of the zinc oxide thin film consists of two basic regions, unrelatedly of the change in molarity value, where we recorded an increase in the transmittance of all ZnO thin films with increasing wavelength, as follows:

• The ultraviolet region <400nm (λ): high absorption as a result of the transfer of electrons from the valence band to the transfer band, while the transmittance is low and increases sharply at the basic absorption edge. This indicates that the material is a semiconductor with a wide energy gap and that the energy of the photons is in the highly transmittance area does not be influenced by absorption.

• The visible region (λ >400nm): We record a change in the behavior of the permeability of the prepared membranes with the change in the molar concentration of zinc nitrate used, as the permeability values decrease from (78%) at the concentration (0.1 mol/L) to the value (43%) at the concentration (0.22 mol/L), and this decrease is due to the increase in the thickness of the layers as the molar concentration increases, which leads to an increase in the absorption of photons and thus the transmittance decreases[17]., and this is consistent with the Beer-Lambert law.

The curve also shows that with the difference in the concentration used in the samples, we obtained thin films of zinc oxide that exhibit similar optical behavior as is the case in the group of transparent conducting oxides (TCO), which indicates that the prepared films belong to this group and their field of application is solar cell windows because the active region is located in the visible range [18].

Fig. 1. Curve of optical transmittance spectra for zinc oxide samples with different molar concentrations



3.3. Effect of molar concentration of zinc nitrate solution on the optical gap of ZnO thin films

The experimental results for the energy separation values of zinc oxide films prepared with different molar concentrations are shown in Table .1. These results prove that the energy interval values decrease with increasing solution concentration and are limited to the range [3.20eV-3.30eV]. This is consistent with the results found in previous studies [19].which proves that the prepared zinc oxide films are a transparent conducting oxide with good physical properties.

The decrease in the value of the energy gap with increasing molar concentration may be explained by the formation of new energy levels in the main band gap near the conduction band [20] and it may also be due to the presence of distortions resulting from the material not being well crystallized or stressed [21].

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Tab.1. Values of the energy gap of zinc oxide films as a function of the molar concentration of the initial solution

Concentration (*mol*/L)	Energy gap values (eV)
0.1	3.30
0.16	3.24
0.22	3.20

3.4. Effect of molar concentration of zinc nitrate solution on the Urbach energy of ZnO thin films

Table .2. Shows the Urbach energy values for zinc oxide films prepared at concentrations (0.1mol/L, 0.16mol/L, and 0.22mol/L). We note that the Urbach energy value increases with increasing molar concentration as a result of increasing the width of the bands of local levels, which resulted in The value of the energy of band gap decreases, as the relationship between them is an inverse relationship, while the Urbach energy represents the tail of the width of transport band and valence band, but the energy of band gap is difference between the tails of the bands [22].

Tab.2. Values of the Urbach energy of zinc oxide films as a function of the molar concentration of the initial solution

Concentration (*mol*/L)	Urbach Energy values (meV)
0.1	322
0.16	324
0.22	333

3.5. Effect of molar concentration of zinc nitrate solution on the extinction factor of ZnO thin films

Figure .2. represents a curve of changes in the annihilation coefficient as a function of wavelength for films prepared with different molar concentrations. The curve shows that no matter how much the concentration changes, the annihilation coefficient (K) changes as a function of wavelength in the same way, as it has a large value in the ultraviolet spectrum region, and this indicates an increase. Absorption in this region, meaning the occurrence of direct electronic transitions, then gradually decreases until it reaches its lowest value at the edge of absorption, and the annihilation coefficient continues to increase at a weak pace in the visible field. We also notice that the annihilation coefficient K increases with increasing molar concentration, which indicates that it is related to thickness. As the thickness of the prepared film increases, the amount of UV attenuation increases.

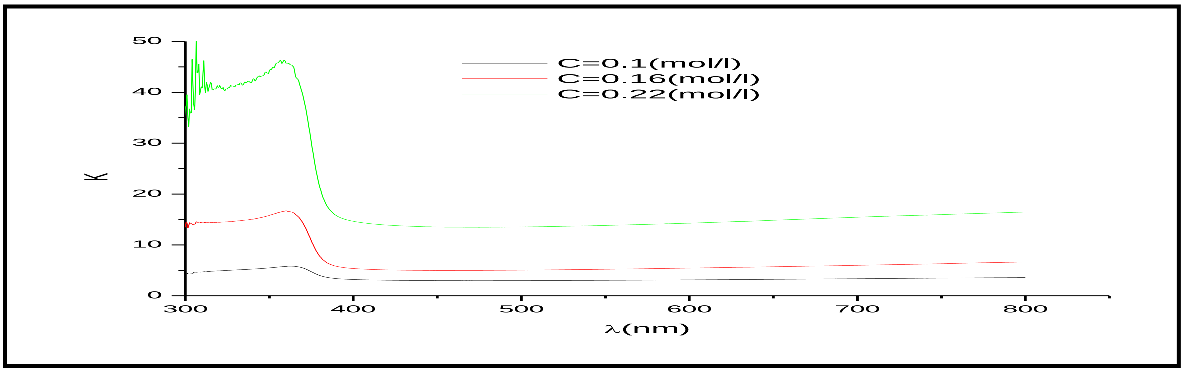

Fig. 2. Variation of annihilation coefficient correlated with wave length obtained for various samples

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4. Conclusion

The optical properties of the prepared ZnO thin films were studied by ultraviolet spectroscopy by recording the transmittance spectrum for the wavelength range (300-800nm). These results showed that the transmittance ranges between (78%-43%) and decreases with increasing molar concentration, this is due to the increase in thickness of layers, which led to an increase in the scattering of photons in the zinc oxide films, as we find that as the thickness increases, the transmittance of zinc oxide decreases.

For the absorbance values, they showed an opposite behavior to the permeability, as they increased with an increase in the molar concentration of the prepared ZnO thin films. This is due to the increase in the number of free electrons that work to absorb the photons, moving them from a lower energy level to a higher energy level.

As for the energy gap values, it witnessed a change depending on the change in molar concentration, as its value ranges between (3.20eV-3.30eV), where it decreases with increasing molar concentration due to the formation of levels in the main energy gap near the conduction band.

As for the Urbach energy, we found that it ranges between (322mev-333meV), as it increases with increasing molar concentration as a result of decreasing the energy interval, as the relationship between them is an inverse relationship, and by calculating the thickness of the thin films, we found that it increases with increasing the molar concentration of the thin films.

We conclude from the above that the optical properties of zinc oxide thin films are very sensitive to changing the molar concentration of the initial solution of zinc nitrate.

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