

Optical Absorption Measurement of Synthesized ZnO using Ultra Violet-Visible Spectrophotometer

Nagla El Badri Mohammed Saeed El Badri¹, Kamal Mahir Sulieman²

¹Physics Department, College of Applied and Industrial, Sciences, University of Bahri, Sudan

²Physics Department, Faculty of Education, AL-Zeem Al-Azhari University

Abstract: Zinc oxide (ZnO) is characterized by its unique electrical and optical properties. It is a future substance and promising compound which can be applied in different structures and used to fabricate different devices. The main objective of this work is to investigate the optical properties of ZnO annealed at 1000°C in muffle furnace for 3, 6 and 9 hours. The annealed samples were Zinc, Zinc sulphide and zinc sulphate, where commercial zinc oxide was used as a control sample. The oxidized ZnO samples were dispersed in an absolute ethyl alcohol with ultrasonic wave. The excitonic peaks of the prepared ZnO samples appeared at 229.99 and 207.51 nm. The excitonic absorption of Zn samples annealed at 1000°C for 3, 6, and 9 h represented the strongest and sharp peaks around 229.99 nm. The absorbance values spectra of ZnSO₄ samples annealed at 1000°C for 3 h represented a higher value of 0.89 au as compared with the control and other samples. These results indicated that high temperature for a long time will improve the electrical and optical properties of ZnO samples obtained from different sources.

Keywords: Absorbivity of ZnO, UV-Vis spectrophotometer, absorbance value, ultrasonic wave, Optical absorbance.

1. Introduction

Semiconductors materials are characterized by the small band group ranging from 0.2 to 2.5eV, which is quite small as compared to that of insulators (6.0eV). This character determine the wavelength of radiation which can be emitted or absorbed by the semiconductors and hence help in application in different devices such as light emitting diodes (LEDs) and laser. ZnO exhibits semiconducting, piezoelectric or pyroelectric properties. Due to this, ZnO can be used in many devices, electrochemical applications.....etc [1]. It is characterized by strong luminescence in the green-white region of the spectrum, therefore it can be used as suitable material for phosphor application. The emission spectrum have a peak at 495nm and a very broad half-width of 0.4eV. Also it is a bio-friendly oxide semiconductor and an inexpensive luminescent material. It plays a role in photo-decompose harmful bacteria [2] and protects skin and eyes from UV radiation without causing irradiation [3]. There is no any evidence that ZnO is carcinogenic or genotoxic or produce toxins in humans [4]. Due to all these properties, ZnO is a promising material in the future to be used in different fields.

The UV-VIS uses two light sources, deuterium lamp for ultraviolet light, and tungsten light which is designed to verify the ultraviolet and visible light protection level accurately and consistently. As reported by [5] ZnO absorbed only in the UV region because of its large bandwidth of 3.2eV ($\lambda = 380$ nm). ZnO exhibited two emission bands, ultraviolet (UV) emission band and another in the green region[6]. Also they found that the intensity of the UV peak remained the same, while the intensity of the visible peak increase with the increase in the annealing temperature. The nano-linear absorption coefficient increased from 2.9×10^{-6} to 1.1×10^{-4} m/W when the annealing temperature increased from 300 to 1050°C.

However the presence of defects (vacancies, interstitial, and antisites) and impurities will play an important role in improvement of electrical and optical properties of ZnO [7]. Zinc interstitial has a high formation energies and low diffusion barriers [8]. They are thus unlikely to be incorporated into stability of ZnO structure. Oxygen vacancies lowest the formation energies and its vacancy is deep rather than shallow donor in the ZnO structure.

Today improving of ZnO properties can be achieved by using different methods such as doping and exposing of Zn and its compounds to heat treatment at different temperatures. The main objective of this work is the investigation of the optical absorption and absorbance value of synthesized ZnO samples after annealing at 1000°C for different time intervals using Ultra Violet-Visible Spectrophotometer.

2. Material and Methods

2.1 Collection of Samples

The samples used were Zn (65.38) powder material, zinc sulphate (ZnSO₄), zinc sulphide (ZnS) and commercial zinc oxide (ZnO) M.W. 81.38, all are manufactured by British Drug Houses LTD. All samples were obtained from Food Science and Technology and Soil Departments, Faculty of Agriculture, University of Khartoum, and Chemistry Department, Collage of Science and Technology, Sudan University.

2.2. Samples Preparation

Firstly, 3 grams of each investigated ZnO samples were put in a crucible and annealed at 1000°C in a muffle furnace (England, Maximum Temperature 1200°C) for 3, 6 and 9 hours to obtain the oxidized form of ZnO compounds, while the commercial ZnO sample is not subjected to heat treatment and used as a control.

A certain weight (0.1g) of oxidized samples (Zn, ZnS, and ZnSO₄) and commercial zinc oxide (ZnO) as a control were dissolved in an absolute ethyl alcohol (Media Laboratories, India) by using ultrasonic apparatus (BANDELIN, SONOREX, NO, 301, 0003321, 012, Germany, 2007). The optical absorption spectra of synthesized ZnO samples was measured by UV-VIS spectrophotometer in the range of 190-1100 nm. Then each sample solution (dissolved ZnO) was held in cuvette quartz with optically flat faces held perpendicular to the radiation beam. The control cell was calibrated at range of absorptivity from 0 to 10⁶. Values above 10⁶ are termed high-intensity absorption, while the values below 10³ are low-intensity absorption. Transitions have absorptivities in the range from 0 to 1000 are neglected. The results were recorded as a plot of absorbance versus wavelength.

3. Results and Dissections

The results of the ZnO samples obtained from Zn annealed at 1000°C for 3, 6, 9 hours were showed in Fig. 1, 2, and 3, while for the samples obtained from ZnS were showed in Fig. 4, 5, and 6. As for the samples obtained from ZnSO₄ were presented in Fig. 7, 8, 9, and for the commercial ZnO showed in Fig. 10. It can be seen that the excitonic peaks of the prepared ZnO samples appeared at 229.99 and 207.51 nm. The excitonic absorption of oxidized Zn samples annealed at 1000°C for 3, 6, and 9 h represented the strongest and sharp peaks around 229.99 nm followed by control sample (commercial ZnO sample) around 227.54 nm, and then followed by oxidized samples of ZnS around 225.10 nm and ZnSO₄ around 224.61nm. Similar results were obtained by [9] who stated that thin films deposited at and below 300°C did not absorb light in the 300-1100 nm with only slight absorption between 200 and 300 nm. The absorption between or at shorter wavelength was somewhat improved for film deposited at 350°C and above as well as for films annealed at 600°C-1000°C. Also the stated that the suspension of the ZnO nanoparticles showed excellent UV-absorption capacity and high transparency in visible light. This result suggest that ZnO particles are well-dispersed maintaining high stability with less agglomeration, which in turn can reduce of visible light since ZnO has band-gap energy of ~ 3.3eV. The absorption behavior of ZnO suspension is predominate on the valence band to conduction band transition. ZnO has good absorption for light in the wavelength in the range of 220-350 nm [10]. The absorption of synthesis ZnO was at 373 and 379 nm as the annealing temperature increased from 300°C to 500°C [11].

Another study revealed that the absorption ranges of ZnO nanorods obtained from a low power DC thermal plasma reactor were about 300nm and 340nm as the peak at 311nm, which was classified as short UV. Also they claimed that the prepared ZnO nano-rods exhibited high UV-blocking capacity which is useful to be applied in cosmetic field as sun block [12]. The absorption spectrum at shorter wavelength in this study may attributed to the formation of small particles size of ZnO samples. The absorption spectra at wavelength < 370 nm indicated the smaller size of ZnO formed [13]. Another study was carried out by [14] who reported that the particles size will affect the absorption of spectra gradually shifted from 370 to 380 due to the increase

of the size of particles from 20 to 40 nm, and the shift absorption edge with the decreasing of crystallite particles was attributed to the light quantum confinement. As pointed by [15], the sharp excitonic peak in the absorption spectra at 300°C

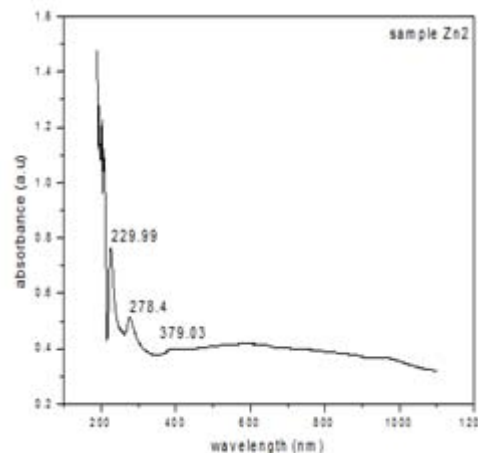


Figure 1: UV analysis of ZnO obtained from Zn annealed at 1000°C for 3 hours

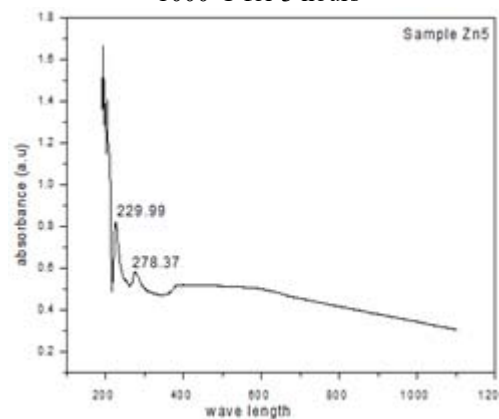


Figure 2: UV analysis of ZnO obtained from Zn annealed at 1000°C for 6 hours

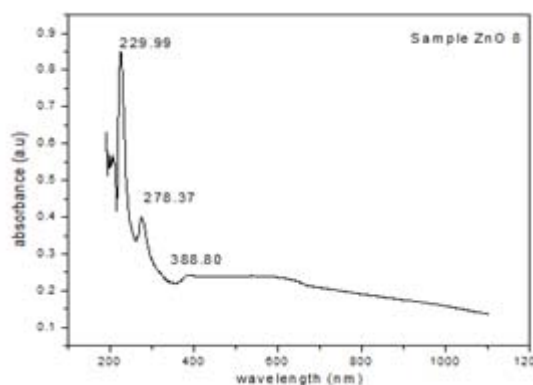


Figure 3: UV analysis of ZnO obtained from Zn annealed at 1000°C for 9 hours

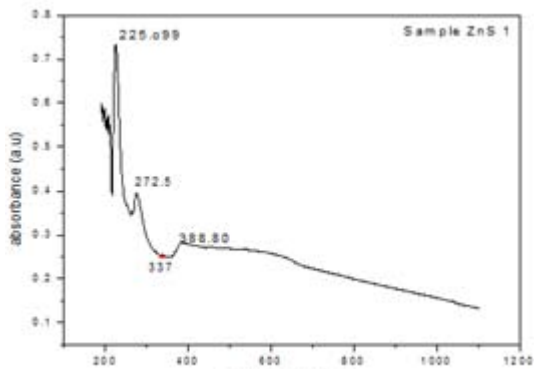


Figure 4: UV analysis of ZnO obtained from ZnS annealed at 1000°C for 3 hours

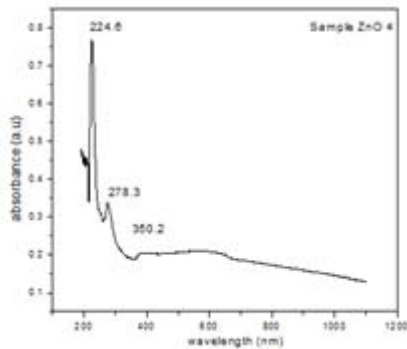


Figure 5: UV analysis of ZnO obtained from ZnS annealed at 1000°C for 6 hours

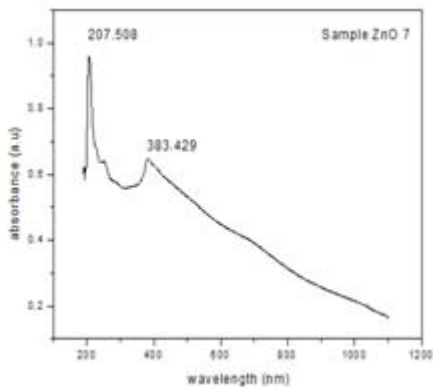


Figure 6: UV analysis of ZnO obtained from ZnS annealed at 1000°C for 9 hours

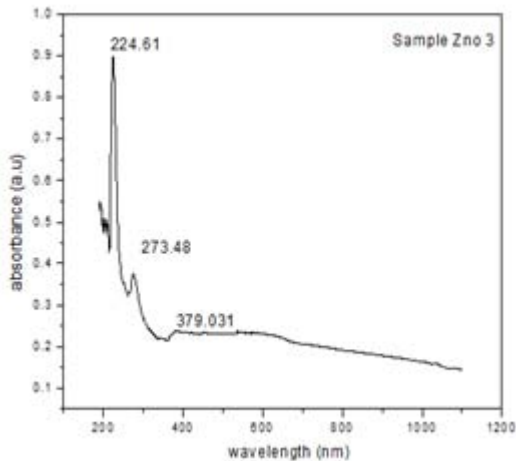


Figure 7: UV analysis of ZnO obtained from ZnSO₄ annealed at 1000°C for 3 hours

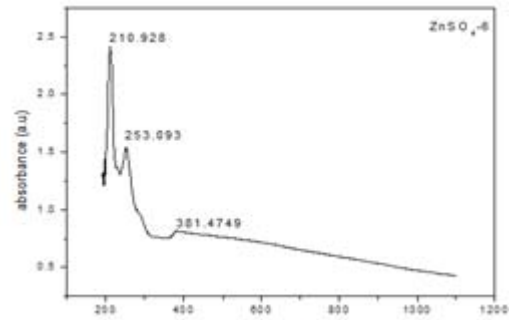


Figure 8: UV analysis of ZnO obtained from ZnSO₄ annealed at 1000°C for 6 hours

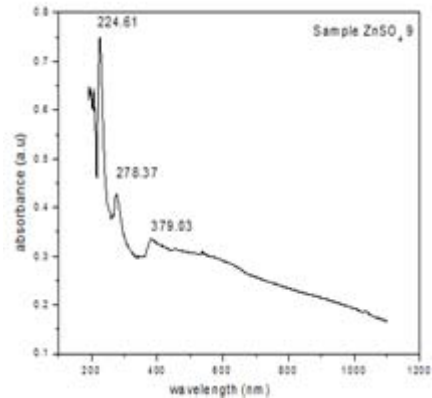


Figure 9: UV analysis of ZnO obtained from ZnSO₄ annealed at 1000°C for 9 hours

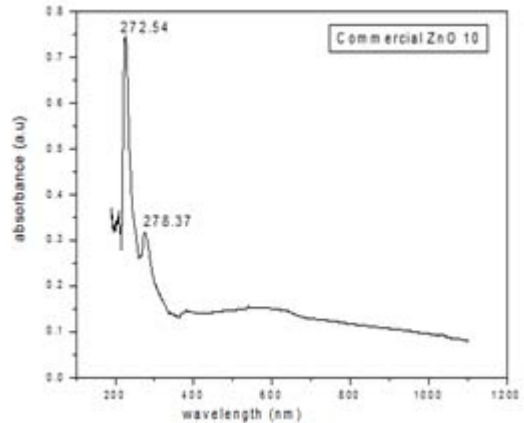


Figure 10: UV analysis of commercial ZnO sample

indicative of small size distribution of nanocrystals in the sample and a broadening of peaks at higher temperature clearly indicates the increase in size nanocrystals with increases of temperature. The absorbance values spectra of ZnSO₄ samples annealed at 1000°C for 3 h represented a higher value of 0.89 a.u. than that of commercial ZnO (0.76 a.u.), followed by Zn sample (0.77 a.u.) and then ZnS (0.73 a.u.) as presented in Figs. 7, 10, 1 and 4. Similar trend was observed for the samples annealed at 1000°C for 6 h, whereas ZnSO₄ showed a high of 2.40 a.u. followed by Zn with value of 0.80 a.u. and ZnS of 0.76 a.u. when compared to the commercial ZnO sample (Figs. 8, 2, 5 and 10).

As for the samples annealed at 1000°C for 9 hours, ZnS sample showed a high value of 0.96 a.u. followed by Zn with value of 0.86 a.u. and ZnSO₄ with a value of 0.76 a.u. as compared to the commercial ZnO (Figs. 6, 3, 9 and 10). The high value of absorbance obtained in this study may be

attributed to high temperature of annealing for along time which improves the electrical and optical properties [16]-[17] and also may be due to the decrease in crystallinity. Similar study was conducted [18] who reported that the absorption increases as sintering temperature rises from 400°C to 600°C. The rise in absorption observed on increasing sintering temperature may be referred to the decrease in crystallinity, while stoichiometry has seemingly remained unaffected by variations in sintering temperature [19]. It was observed that the absorbance of ZnSO₄ annealed at 1000°C for 6 h in this study was increased to 2.40 a.u and then decreased to 0.76 a.u after 9 h annealing. Similar study revealed that the absorbance of ZnO samples obtained from ZnSO₄.HO₂ increased when the temperature increased from 300°C to 500°C and then decreased at 800°C [15]. The decrease in optical absorption may be due to the improvement in crystallinity and/or stoichiometry [18]. A broadening of ZnO sample peak obtained from ZnS and ZnSO₄ annealed at 1000°C for 9 and 6 h were observed as shown in Fig. 6 and 8 respectively. This result claimed that there is an increase of particles size at high temperature for along time [20]. The broadening of absorption edge at higher sintering temperature (600°C) may be due to the increase of disorder in semiconductor films and leads to the appearance of localized electron or/ hole state [19]. The whole results explain that the synthesized or oxidized ZnO samples from different sources exhibited a good absorbance behavior and ensures the ability of ZnO to absorb short UV and can be used in different application.

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Author Profile

Nagla Nagla El Badri Mohammed Saeed El Badri received the B. Sc degree in Physics/ Mathematics from Upper Nile University-Sudan in 2005 and M.Sc. degree in Solid States from AL-Zeem Al-Azhari University - Sudan in 2014. During 2005-2011, she taught as teaching assistant at Upper Nile University and as a teacher of physics at higher secondary schools at Upper Nile State, South Sudan. Teaching assistant at Bahri University- Department of physics from 2011-2013. Now she is a lecturer in physics department, College of Applied and Industrial Sciences. Bahri University, Sudan.

Kamal Mahir Sulieman Associated professor at physics Department, Faculty of Education, AL-Zeem Al-Azhari University. Now he joined Hael University Saudi Arabia.