

Study of the Optical Characteristics of Aluminum Doped ZnO Thin Film

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ABSTRACT

In this work, the study on the influence of the aluminum on the optical properties of ZnO thin film was carried out with a focus on the influence of variation of aluminum ions on the optical behavior of the ZnO thin film. The film was deposited on the glass substrates by chemical bath deposition technique and aluminum was used in the following varied quantities, 0.1, 0.2, and 0.3M, to dope the thin films, respectively. The solutions were prepared using zinc sulphate, ammonia and Hexamine with aluminum nitrate. The optical characteristics of the film such as the spectral absorbance, reflectance and transmittance within the ultraviolet and near infra red region of electromagnetic wave spectra were investigated using UV-VIS spectroscopy with the energy band gap found to be in the range of 3.5eV to 3.9eV

(Keywords: zinc oxide, ZnO, aluminum, Al, influence, doping, thin film, chemical bath deposition, optical properties, band gap, semiconductors)

INTRODUCTION

Lately, ZnO thin films have become a major focus among all the oxide based thin films and as a result has attracted attention of nanoscientists with a lot of ongoing work on ZnO thin film including review and analysis of functionalities (19) and applications of the film in both microelectronics and photovoltaic cells (1) and as a filter to electromagnetic radiations coupled with the fact that its properties could easily be improved upon by doping and annealing which also results in tailoring the film to another area of application such as Sensors. This thin film material is a II-VI compound semiconductor with a hexagonal wurtzite crystal lattice structure (16).

ZnO is also seen as a better replacement for Indium tin oxide widely used as a transparent

conducting oxides TCO (2) because it is more abundant and nontoxic. Zinc Oxide thin film is found to have a large band gap of about 3.33-3.37eV, It is one of the potential materials for being used as a TCO due to its good optical and electrical properties Zinc Oxide (ZnO) thin films is an inexpensive n-type semiconductor having large and direct band gap of about 3.3 eV and is one of the most potential materials for used as a TCO because of its good electrical and optical properties, abundance in nature, [3, 4] and the ability to deposit these films at relatively low substrate temperatures [5]

Pure ZnO thin films are not stable against corrosive environments as adsorption of dioxygen in the films decreases the electrical conductivity and also modifies the surface morphology (6). These films become more stable by doping them with trivalent metal cations [7-10] especially with aluminum (11).

Al doped ZnO is cheap, more abundant, non-toxic, and has good stability in hydrogen plasma and above all its optical and electrical property can be improved or modified by controlling their doping concentrations [12], which is critical to achieving optimal functionalities and applicability of TCO-based devices. Therefore, it is useful to investigate the correlation between the optical properties of Al-doped ZnO films and the concentration of Al doping.

Numerous techniques have already been used to deposit both doped and undoped ZnO thin films on different substrate including spray pyrolysis [6], organ metallic chemical vapor deposition [13], pulsed laser deposition [14], sputtering [15], and sol-gel process [4]. Among these, Chemical Bath Deposition, (CBD) is relatively new and a less investigated process credited with several advantages, such as deposition of high purity, homogeneous, cheaper, large-area films at relatively low temperatures.

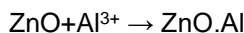
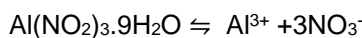
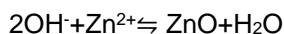
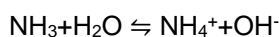
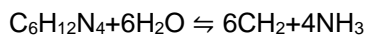
Having discovered from the ongoing study that pure ZnO thin films are not stable against the corrosive environment because of adsorption of dioxygen in the film, the film is found to be more stable by doping them especially with aluminum (18) which has been achieved using spray pyrolytic technique that has been claimed by some researchers to be more proficient deposition technique to achieve in that as it is simple and reproducible (17). In view of this, we intend to use chemical bath deposition technique which is simpler, cheaper, and more reproducible than spray pyrolytic method and some other methods that have been hitherto used to dope ZnO thin films with aluminum to deposit AlZnO thin film and to analyze the influence of the variation of aluminum as a dopant on the optical properties of the thin film.

EXPERIMENTAL PROCEDURE

ZnO thin films prepared by CBD method is based on the heating of alkaline bath of zinc salt containing the substrates immersed in it. 0.1M of zinc sulphate was used as a source of zinc, to make the solution alkaline, aqueous ammonia solution was added with constant stirring. Firstly, the solution became milky-turbid due to the formation of zinc hydroxide $Zn(OH)_2$. Further addition of excess ammonia dissolved the turbidity and made the solution clear and transparent. The pH value of the resultant solution was ~11.0. The substrates were immersed in the bath at room temperature and the bath was heated at a temperature of 343K for 2 hours, heterogeneous reaction occurred and the deposition of ZnO took place on the substrates.

The ZnO coated substrates were removed from the bath washed with distilled water, dried in air and preserved in an air-tight container. These procedure leads to deposition on undoped ZnO on the glass substrate. To deposit aluminum doped ZnO (AlZnO) thin film, three different concentrations of Al dopants ZnO were used a follows; 0.1M, 0.2M, and 0.3M of Al to the starting material. The optical characteristic within the ultraviolet and near infrared region of electromagnetic wave spectra was analyzed using UV-VIS spectroscopy.

Equation of Reaction



RESULT AND DISCUSSION

The results of the work are as presented in the Figure1 and Figure 2 showing the spectral transmittance and reflectance while Figure3 depicts absorbance, while that of Figures 4 and 5 represent the a plot of $(\alpha h\nu)^2$ against photon energy from where the band gaps was deduced considering the extrapolation if the graph to intercept the energy axis at $(\alpha h\nu)^2$ equals zero.

TRANSMITTANCE

Figure 1 shows the of transmittance spectra against wavelength, the films depicts high transmittance at visible region to near infrared region and low transmittance at the ultraviolet region. The transmittance increased with increase in aluminum concentration this is because addition of aluminum improves the crystal structure which results to reduced surface roughness. The value of transmittance for ZnO films is high (20 – 90%) in the spectral region which matches maximum sensitivity for photonic vision. This suggests that the films could be employed as a transparent oxide in solar cells.

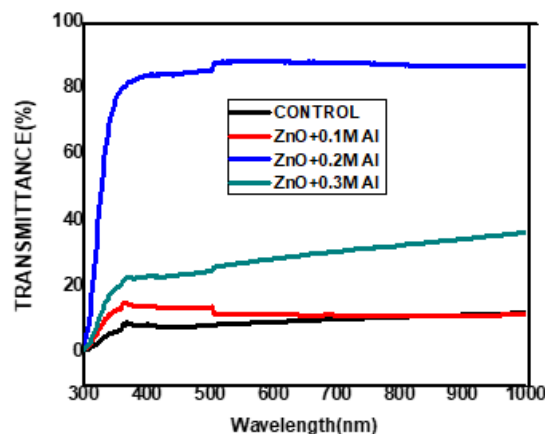


Figure 1: Transmittance Spectra of Undoped ZnO and AlZnO Doped with different Al Concentrations.

REFLECTANCE

Figure 2 shows that for all ZnO thin films, the reflectance is high within the visible region and gradually decreased between 300 to 400nm. The highest value recorded is $> -2\%$ while the lowest value recorded is $< -80\%$. The films reflectance is seen to be decreasing with increase in doping concentration which suggest that this material is good for use as anti-reflectance or in anti-reflection coating.

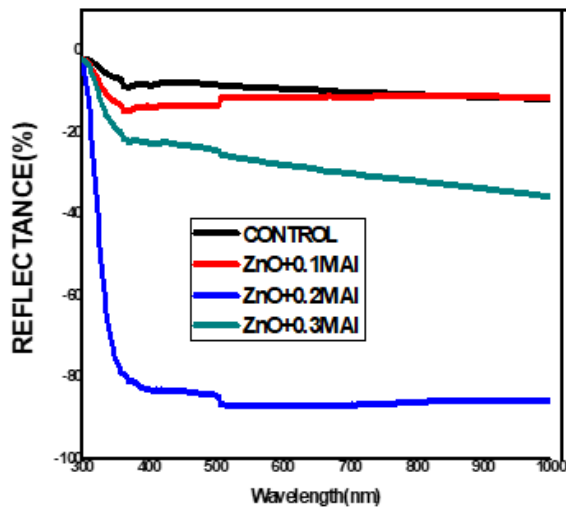


Figure 2: Reflectance against Wavelength of Undoped ZnO and AlZnO with Different Al Concentrations.

ABSORBANCE

Plots of absorbance versus wavelength is as shown in Figure 3. The plot indicates that all the films are absorbing within the visible region of the spectrum, and it also show that the absorbance is lowered with increase in aluminum concentration.

The film exhibited high spectral absorbance at a wavelength 200nm which falls exponentially to 400nm and gradually decrease with increase in wavelength that appears to vary with increase in the increase of the aluminum dopant. This suggests that the doping has significant effect on the material and as such serves as good material for the building of poultry roofs and walls to warm the inside of the poultry house for chicken brooder

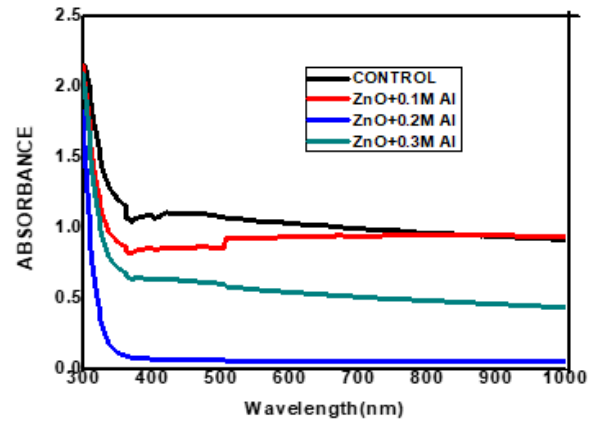


Figure 3: Absorbance against Wavelength of Undoped ZnO and AlZnO at Different Al Concentrations.

BAND GAP

Figure 4 shows the plot of $(ahv)^2$ vs $h\nu$ which reveals that the electronic energy band gap of ZnO is dependent on concentration of its constituent elements. The optical band gap increased in accord with an increase in concentration of aluminum dopant and the value is within the range of (3.5-3.8eV). The observed band gaps are within the range of values reported by (20).

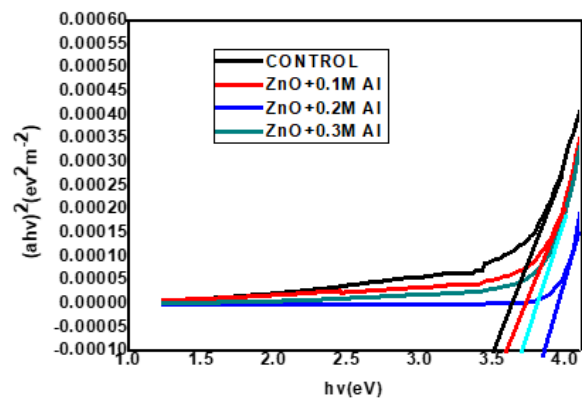


Figure 4: Plot of $(ahv)^2$ against Photon Energy of Undoped ZnO and AlZnO with Different Al Concentrations.

EXTINCTION COEFFICIENT

It is observed from Figure 5 that extinction coefficient, k decreased up to the region of the fundamental absorption that is the range of photon energies at which the energy band gap occurred and then increased afterward. However, the values of k for undoped sample is higher compared to that of doped which means that aluminum dopant decreases the extinction coefficient of ZnO. Also seen is a gradual increase in of k values after band gap value towards the higher photon energy value and the positive value shows that the material is strongly absorbing which will be ascribed to the surface smoothness of the sample and uniformity of the solution.

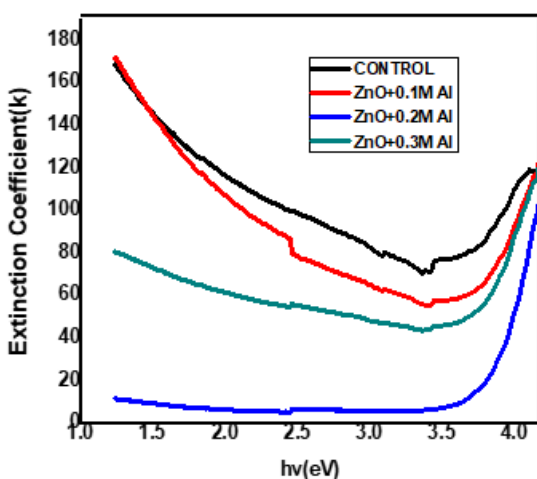


Figure 5: Extinction Coefficient versus Photon Energy of Undoped ZnO and AlZnO with Different Al Concentrations.

CONCLUSION

Transparent ZnO thin films doped with aluminum were prepared by Chemical Bath Deposition techniques and the effect of aluminium concentrations on the optical properties were studied. The absorbance plot reveals that all the deposited ZnO thin films are absorbing in the visible region of the spectrum at different maxima wavelength between 300nm – 450nm and that increase in Al concentrations causes decrease in absorbance value of the film is a proof that Al dopant have a profound effect on the optical properties of the films.

High absorbance in the UV region also makes the films better material for the building of poultry roofs and walls to warm the inside of the poultry house and the high absorbance of the deposited ZnO thin films suggests that they can also be used in solar cell fabrication as an absorber.

From the transmittance plots, the deposited ZnO films have relative high transmittance at the visible to infra-red region and the transmittance increases with increase in Al concentrations. High transmittance in the visible region and wide energy band gap shown by these films, suggest that these films could be employed in solar cell architecture as window layer.

The energy band gaps of these films fall within the range of (3.5-3.9eV). This increase in band gap as doping concentration increases shows that aluminum dopant enhances the band gap and the wide band gap exhibited by these films, suggest that these films are good materials for application in laser diode and photovoltaic applications. In general, the deposited film is a possible material that can be used for solar application.

REFERENCES

1. He, W.W. and C.H. Ye. 2015. "Flexible Transparent Conductive Films on the Basis of Ag Nanowires: Design and Applications: a review. *J Mater Sci Technol* 31:581–588.
2. Lin, J.J. and Z.Q. Li. 2014. "Electronic Conduction Properties of Indium Tin Oxide: Single-Particle and Many-Body Transport". *J Phys: Condens Matter*. 26:343201.
3. Shan, F.K. and Y.S. Yu. 2005. "Band Gap Energy of Pure and Al Doped ZnO Thin Films". *Journal of the European Ceramic Society*. 24:1869-1872.
4. Kim, Y.S., W.P. Tai, and S.J. Shu. 2005. "Effect of Preheating Temperature on Structural and Optical Properties of ZnO Thin Films by Sol-Gel Process". *Thin Solid Films*. 491:54-60.
5. Pogrebniak, A.D., N.Y. Jamil, and A.K.M. Muhammed. 2011. "Structural and Optical Properties of ZnO Prepared by CVD before and after Annealing". *Metallofiz. Noveishie Tekhnol.* 33: 235-241.
6. Alaeddin, A., I. Rachidi, F. Bahsoun, Y. Mohanna, O. Bazzi, and F.El Haji Hassan. 2009. "Influence of Al Dopant on the Optical and Electrical Properties of ZnO Thin Films Prepared by Spray

- Pyrolysis". *Journal of Applied Sciences*. 9(8): 1588-1592.
7. Leenheer, A, J. Perkins, M. van Hest, J. Berry, R. O'Hayre and D. Ginley. 2008. "General Mobility and Carrier Concentration Relationship in Transparent Amorphous Indium Zinc Oxide Films". *Phys Rev B*. 77:115215.
 8. Bhosle, V., A. Tiwari, and J. Narayan. 2006. "Metallic Conductivity and Metal Semiconductor Transition in Ga-Doped ZnO". *Appl Phys Lett*. 88:032106.
 9. Kim, D., I. Yun, and H. Kim. 2010. "Fabrication of Rough Al doped ZnO Films Deposited by Low Pressure Chemical Vapor Deposition for High Efficiency Thin Film Solar Cells". *Curr Appl Phys*. 10:S459–62.
 10. Steinhauser, J., S. Faÿ, N. Oliveira, E. Vallat-Sauvain, and C. Ballif. 2007. "Transition between Grain Boundary and Intragrain Scattering Transport Mechanisms in Boron-Doped Zinc Oxide Thin Films". *Appl Phys Lett*. 90:142107.
 11. Jimenez-Gonzalez, A.E., J.A. Soto-Ureta, and R. Suarez-Para. 1998. "Optical and Electrical Characteristics of Aluminum Doped ZnO Thin Films Prepared by Sol Gel Techniques". *J. Cryst. Growth*. 192: 430-438.
 12. Benhaoua, B., A. Rahal, and S. Benramache. 2014. "The Structural, Optical and Electrical Properties of Nanocrystalline ZnO:Al Thin Films". *Superlattice Microst*. 68:38–47.
 13. Bandyopadhyay, S., G.K. Paul, and S.K. Sen/ 2002. "Study of Optical Properties of Some Sol–Gel Derived Films of ZnO". *Solar Energy Materials and Solar Cells*. 71:103-113.
 14. Pogrebnyak, A.D., N.Y. Jamil, and A.M. Muhamed. 2011. "Electrical and Optical Properties of ZnO:Al Films Prepared by Chemical Vapour Deposition (CVD)". *Proceedings of 1st International Conference of Nanomaterials: Applications & Properties* (NAP-2011). Crimea, Ukraine. Alushta, September 27-30. 226-232.
 15. Pogrebnyak, A.D. and A.K.M. Muhamed. 2011. "Simulation Study of Effect on Thin Film GIGS Solar Cell Performance". *J. Nano-Electron. Phys*. 3:52-59.
 16. Rozati S.M. and S.A. Akese. 2007. "Influence of Substrate Temperature on the Structure of ZnO:Al Thin Films". *Cryst. Res. Technol*. 43: 273-275.
 17. Krunks, K., O. Bijakina, V. Mikli, T. Varema, and E. Mellikov. 1999. "Zinc Oxide Thin Films by Spray Pyrolysis Method". *Physica Scripta*. (T79): 209.
 18. Anglada, E. and H.L. Gonzalez. 1998.. U.S. Patent No. 5,805,520. U.S. Patent and Trademark Office: Washington, DC.
 19. Ugwu, E.I. 2018. "The Effect of Annealing, Doping on the Properties and Functionality of Zinc Oxide Thin Film; Review". In" *Sol-Gel Method-Design and Synthesis of New Materials with Interesting Physical, Chemical and Biological Properties*. IntechOpen. Chapter 2
 20. Mondal, S. and P. Mitra. 2012. "Preparation of Cadmium-Doped ZnO Thin Films by SILAR and their Characterization". *Bulletin of Materials Science*. 35(5):751-757.

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