

MODIFICATION IN OPTICAL PROPERTIES OF ZNO THIN FILM BY ANNEALING

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Abstract: In this work, we have synthesized ZnO thin film on quartz substrate by RF magnetron sputtering method. We annealed these films at three different temperatures of 200°C, 400°C and 600°C. The absorption spectra showed that the band gap of the deposited film was about 3.29 eV. So it confirmed that the film was of ZnO. As temperature increased the band gap of the film decreased. Transmittance spectra revealed that the transparency of the film increased with rise in temperature. Different optical constants such as refractive index, film thickness, band gap, transmittance, extinction coefficient and so on were investigated and compared at different temperatures. Ellipsometry revealed that the thickness of the film was 125 nm.

Keywords: Thin film, sputtering, spectroscopy, ZnO.

I. INTRODUCTION

ZnO is a unique semiconductor material with a wide band gap of about 3.3 eV. It has generated enormous research interest because of its stand out optical properties that are useful for nanolasers [1],piezoelectric nanogenerators [2], dye sensitized solar cells [3], gas sensors [4,5], photocatalyst [6,7], and so on. Many different deposition methods, such as metal organic chemical vapor deposition (MOCVD) [8], molecular beam epitaxy (MBE) [9], sputtering [10], chemical vapor deposition (CVD) [11, 12], pulsed laser deposition (PLD) [13, 14], spray pyrolysis [15] and the sol–gel technique [16], have been utilized for the growth of ZnO films on distinct substrates. Among these techniques, rf magnetron sputtering is considered to be the most common technique because of economic uniform film deposition. The fundamental optical property is refractive index as it gives the idea of electronic polarizability of ions and the local field inside the material [17]. The applications such as switches, modulator and filters, etc have refractive index as their key element for fabrication.

In this context, ZnO thin films were prepared on quartz substrates by the RF magnetron sputtering method and annealed at 200°C, 400°C and 600°C, respectively. Optical constants of the films were explored using method suggested by R Swanepoel [18] and the effect of post-annealing on constants was also investigated.

II. EXPERIMENTAL

The ZnO film was grown on quartz substrate by rf magnetron sputtering method. Prior to the deposition, the substrates were cleaned using acetone and the chamber was evacuated. Base pressure was maintained as 10^{-5} mbar. The distance between substrate to source was fixed at ~10 cm. After that High purity Ar gas was passed through the chamber. The Ar gas pressure was maintained at its optimum value of 10^{-2} mbar. The total pressure is stabilized at 0.015 mbar during the deposition process. Deposition was performed for two hours. Thermal annealing was performed at 200°, 400° and 600° C in air for an hour.

The Zinc Oxide (ZnO) thin film samples were grown on quartz substrates. Absorption and transmittance spectra of the thin film deposited on quartz substrate were obtained by Hitachi 2900 UV spectrophotometer.



III. RESULTS AND DISCUSSION

The optical characterization of ZnO samples were carried out by using dual beam spectrophotometer in the wavelength range from 200 - 800nm. Figure 1 shows the variation of absorption edge of ZnO thin film grown on quartz substrate with wavelength at different annealing temperatures. The absorption edge is obtained from the tauc plot method. [18],

The band gap is determined by drawing tangents on these curves and it shows the decreases in the band gap on different annealing temperature as shown in figure 3.

Figure 2 shows the transmittance spectra of the ZnO thin film deposited at different annealing temperature. Optical constant were calculated from transmittance and compare at different annealing temperature. It can be concluding from the spectra that the optical transmittance increases in the visible region while decreases in ultraviolet region as increase in temperature.

3.1 OPTICAL CONSTANTS

The absorption coefficient can be determined from the transmittance spectra by the following relation [17] and calculated result is shown in figure 1.

 $T = \exp[-\alpha(\lambda)d)],$

Where T denotes the transmittance and d is thickness of film. From the absorption spectra it can be concluded that the absorption coefficient decreases with increases in wavelength and it can also be concluded that for a given wavelength, the absorption coefficient decreases in the ultraviolet region while increases in visible region. It is known that the absorption coefficient near the band edge shows an exponential dependence on photon energy: [17]

$$\alpha(\lambda) = \alpha o \exp\left(\frac{hv}{Eo}\right),$$

It is known that extinction coefficient is related to absorption coefficient by the following relation:

$$k(\lambda) = \frac{\alpha(\lambda)\lambda}{4\pi},$$

Where $k(\lambda)$ belong to extinction coefficient and it can be obtained from the absorption spectra of figure 1 over the entire wavelengths. Figure 4 shows the extinction coefficient variation over wavelength at three different annealing temperatures and it can be concluded from figure that there is an increment in the visible region and decrement in the ultraviolet region.

The actual refractive index $n * (\lambda)$ is written as

$$n * (\lambda) = n(\lambda) + ik(\lambda)$$

Where n is the refractive index and k is extinction coefficient. The refractive indices of ZnO film were investigated using interference method as suggested by R Swanepoel [18]. For a given wavelength, the refractive index, of pristine is 1.96, is calculated at different annealing temperature and it is found that the refractive index decreases as the annealing temperature increase as shown in table 1.

IV. CONCLUSION

Absorption spectra were used to obtain extinction coefficient and transmittance spectra were used to calculate optical constants. The effect of annealing temperature on both the spectra was investigated. With increase in temperature the band gap and extinction coefficient show decrement in ultraviolet region and increment in visible region. Refractive spectra also show decrement on increasing temperature at a given wavelength.

References

^[1]Roger Chen, Thai-Truong D. Tran, Kar Wei Ng, Wai Son Ko, Linus C. Chuang, Forrest G. Sedgwick&Connie Chang-Hasnain. Nanolasers grown on silicon, Nature Photonics 5, 170–175 (2011).



- [2] Chieh Chang*, Van H. Tran, Junbo Wang, Yiin-Kuen Fuh and Liwei Lin. Direct-Write Piezoelectric Polymeric Nanogenerator with High Energy Conversion Efficiency Nano Lett., 2010, 10 (2), pp 726–731.
- [3] Seung Hwan Ko*, Daeho Lee, Hyun Wook Kang, Koo Hyun Nam, Joon Yeob Yeo, Suk Joon Hong, Costas P. Grigoropoulos, and Hyung Jin Sung, Nanoforest of Hydrothermally Grown Hierarchical ZnO Nanowires for a High Efficiency Dye-Sensitized Solar Cell, Nano Lett., 2011, 11 (2), pp 666–671.
- [4] Jaeseok Yi*, Jung Min Lee, Won II Park, Vertically aligned ZnO nanorods and graphene hybrid architectures for high-sensitive flexible gas sensors, Sensors and Actuators B: Chemical ,Volume 155, Issue 1, 5 July 2011, Pages 264–269.
- [5] Ning Han, Haidi Liu, Xiaofeng Wu, Dongyan Li, Linyu Chai, Yunfa Chen, Pure and Sn-, Ga- and Mn-doped ZnO gas sensors working at different temperatures for formaldehyde, humidity, NH3, toluene and CO, Applied Physics A August 2011, Volume 104, Issue 2, pp 627-633.
- [6] Hongchao Ma, Jihui Han, Yinghuan Fu, Yu Song, Chunling Yu, Xiaoli Dong, Synthesis of visible light responsive ZnO–ZnS/C photocatalyst by simple carbothermal reduction, Applied Catalysis B: EnvironmentalVolume 102, Issues 3–4, 22 February 2011, Pages 417–423.
- [7] Jian-Hui Sun, Shu-Ying Dong, Yong-Kui Wang, Sheng-Peng Sun, Preparation and photocatalytic property of a novel dumbbell-shaped ZnO microcrystal photocatalyst, Journal of Hazardous MaterialsVolume 172, Issues 2–3, 30 December 2009, Pages 1520–1526.
- [8] Jianfeng Su Chunjuan Tang, Qiang Niu, Chunhe Zang, Yongsheng Zhang, Zhuxi Fu, Microstructure, optical and electrical properties of Aldoped ZnO films grown by MOCVD, Applied Surface ScienceVolume 258, Issue 22, 1 September 2012, Pages 8595–8598.
- [9] Han, Seok-Kyu; Oh, Dong-Cheol; Song, Jung-Hoon; Inaba, Katsuhiko; Yao, Takafumi; Hong, Soon-Ku, Lattice Deformation in a-Plane ZnO Films Grown on r-Plane Al₂O₃Substrates Grown by Plasma-Assisted Molecular-Beam Epitaxy, Applied Physics Express, Volume 5, Issue 8, pp. 081101-081101-3 (2012).
- [10] Weifeng Yang, Zhuguang Liu, Dong-Liang Peng, Feng Zhang, Huolin Huang, Yannan Xie, Zhengyun Wu, Room-temperature deposition of transparent conducting Al-doped ZnO films by RF magnetron sputtering method, Applied Surface ScienceVolume 255, Issue 11, 15 March 2009, Pages 5669–5673.
- [11] S.A.C. Carabineiro, B.F. Machado, G. Dražić, R.R. Bacsa, P. Serp, J.L. Figueiredo, J.L. Faria, Studies in Surface Science and CatalysisVolume 175, 2010, Pages 629–633.
- [12] Ning HanPeng Hu, Ahui Zuo, Dangwen Zhang, Yajun Tian, Yunfa Chen, Photoluminescence investigation on the gas sensing property of ZnO nanorods prepared by plasma-enhanced CVD method, Sensors and Actuators B: ChemicalVolume 145, Issue 1, 4 March 2010, Pages 114–119.
- [13] Ling Cao, Liping Zhu, Jie Jiang, Ran Zhao, Zhizhen Ye, Buihui Zhao, Solar Energy Materials and Solar Cells Volume 95, Issue 3, March 2011, Pages 894–898.
- [14] Gareth M. Fuge, Tobias M.S. Holmes, Michael N.R. Ashfold, Ultrathin aligned ZnO nanorod arrays grown by a novel diffusive pulsed laser deposition method, Chemical Physics LettersVolume 479, Issues 1–3, 7 September 2009, Pages 125–127.
- [15] Michael Breedon, Mohammad Bagher Rahmani, Sayyed-Hossein Keshmiri, Wojtek Wlodarski, Kourosh Kalantar-zadeh, Aqueous synthesis of interconnected ZnO nanowires using spray pyrolysis deposited seed layers, Materials LettersVolume 64, Issue 3, 15 February 2010, Pages 291–294.
- [16] T. Ivanova, A. Harizanova, T. Koutzarova, B. Vertruyen, Study of ZnO sol-gel films: Effect of annealing, Materials LettersVolume 64, Issue 10, 31 May 2010, Pages 1147–1149.
- [17] S.W. Xue, X.T. Zu^{*}, W.L. Zhou, H.X. Deng, X. Xiang, L. Zhang, H. Deng, Effects of post-thermal annealing on the optical constants of ZnO thin film, Journal of Alloys and Compounds 448 (2008) 21–26.
- [18]R Swanepoel, Determination of the thickness and optical constants of amorphous silicon, Phys. E: Sci. Instrum. Vol. 16, 1983.

TABLE

1. Refractive Index at three different annealing temperatures.

Annealing Temperature (°C)	Refractive Index
Pristine	1.99
200	1.95
400	1.89
600	1.84

absorbance with



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Figure 1: Variation of wavelength.



Figure 2.Transmission spectra of ZnO thin film annealed at 200°C, 400°Cand600°C.





Figure 3. Band Gap spectra of ZnO thin film annealed at 200°C, 400°Cand600°C.



Figure 4. Extinction Coefficient spectra of ZnO thin film annealed at 200°C, 400°Cand600°C.