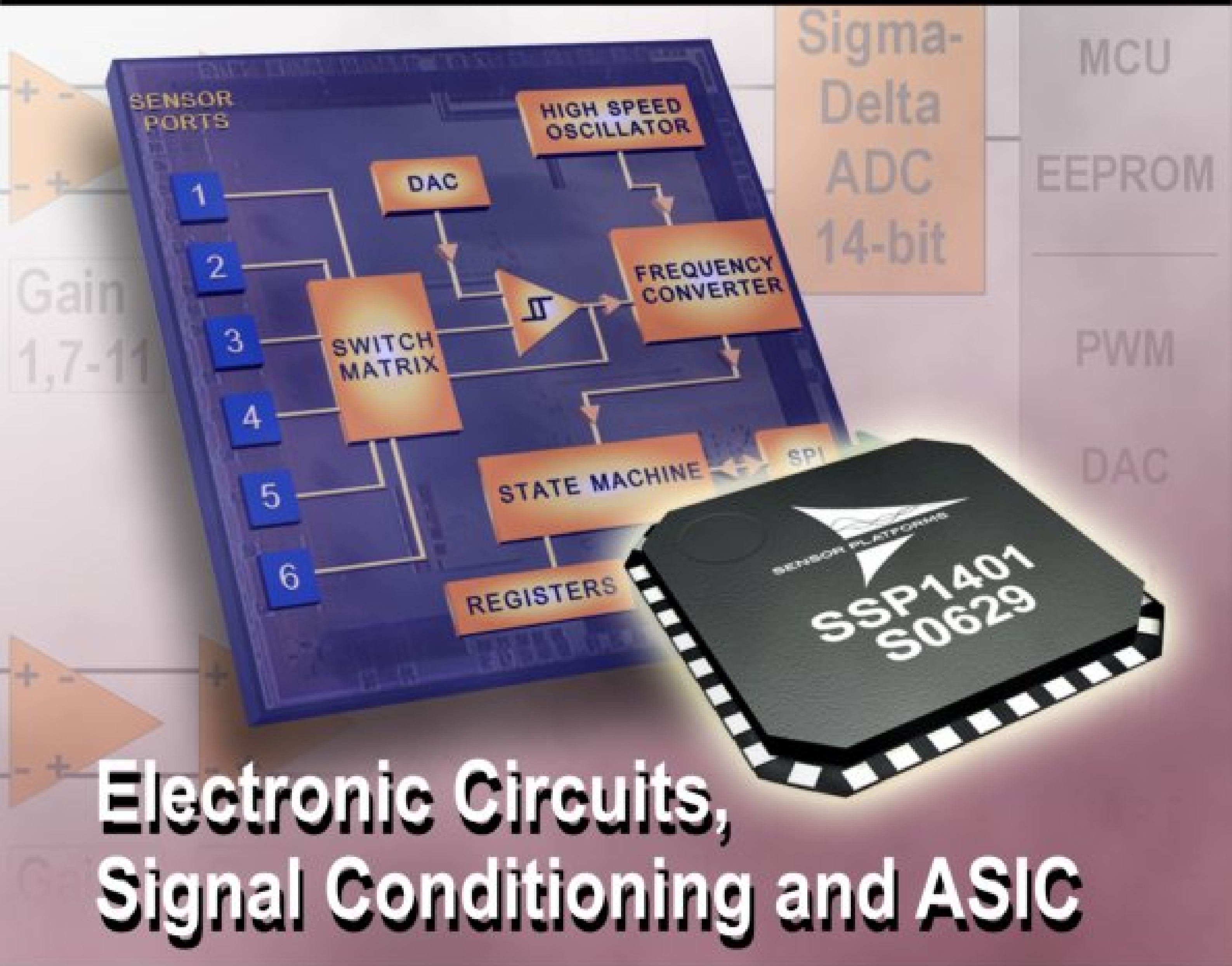
ISSN 1726-5479

SENSORS & TRANSDUCERS

vol. 117
6/10



Electronic Circuits, Signal Conditioning and ASIC

International Frequency Sensor Association Publishing

IFSA

Sensors & Transducers

Volume 117, Issue 6,
June 2010

www.sensorsportal.com

ISSN 1726-5479

Sensors & Transducers Journal (ISSN 1726-5479) is a peer review international journal published monthly online by International Frequency Sensor Association (IFSA).
Available in electronic and on CD.

Sensors & Transducers Journal

Contents

Volume 117
Issue 6
June 2010

www.sensorsportal.com

ISSN 1726-5479

Research Articles

Authors are encouraged to submit article in MS Word (doc) and Acrobat (pdf) formats by e-mail: editor@sensorsportal.com
Please visit journal's webpage with preparation instructions: http://www.sensorsportal.com/HTML/DIGEST/Submition.htm

International Frequency Sensor Association (IFSA).

Sensors & Transducers Journal, Vol. 117, Issue 6, June 2010, pp. 92-98

Sensors & Transducers

ISSN 1726-5479

Effect of Different Post Deposition Annealing Treatments on Properties of Zinc Oxide Thin Films

Arti Arora, Anil Arora, P. J. George, [1]V. K. Dwivedi, [1]Vinay Gupta
Kurukshetra Institute of Technology & Management, Kurukshetra, India
Department of Physics and Astrophysics, South Campus, New Delhi, India
E-mail: aarti25nov@gmail.com

Received: 30 March 2010 /Accepted: 21 June 2010 /Published: 25 June 2010

Abstract: Two different post deposition annealing atmospheres of oxygen and forming gas have been investigated for the improvement of rf sputtered zinc oxide thin films. The results show that type of atmosphere (oxidant o reduction) plays an important role in the changes observed in structural, electrical and optical properties. It has been found that the structural properties of rf sputtered zinc oxide films improve in all the annealing environments. The intensity and grain size increases as the annealing temperature increases. It has been found that films become stress free at lowest temperature in oxygen as compare to forming gas annealing. The zinc oxide films annealed in oxygen shows sufficient resistivity associated to high transmittance (83 %) characteristics required for MEMS based acoustic devices. *Copyright © 2010 IFSA.*

Keywords: Annealing, rf sputtering, Zinc oxide thin films

1. Introduction

ZnO belongs to a member of hexagonal wurtizite class with 6 mm symmetry. It is a semiconducting, piezoelectric and optical waveguide material and has variety of potential applications. For the application of zinc oxide thin films in acoustic sensors, surface acoustic wave devices and bulk acoustic wave devices. For the low frequency applications of ZnO, high resistivity [1] of the order of 10^6 to 10^8 Ω-cm is of great concern. ZnO films have small oxygen deficiency under ordinary circumstances. For piezoelectric and acoustic applications, it is very important to raise the resistivity of ZnO film. Other required characteristics are good orientation, smooth surface, stress relief and high packing density. The as deposited films require an annealing treatment to improve stability and reduce possible undesired influence of the substrate. The present paper describes the influence of two different atmospheres on structural, electrical and optical properties of ZnO thin films. Many reports are available in literature on post deposition annealing in air [2-5] and oxygen atmosphere [6-8]. Here the effect of oxygen and forming gas (N_2H_2) has been studied on the structural, electrical and optical properties such as orientation, grain size, FWHM, stress, refractive index and packing density etc.

2. Experimental

Sputtering of ZnO films at room temperature (RT) on oxidized silicon substrates was performed using 6” diameter metallic zinc target (Cerac, Inc. USA, 99.999 % pure) in O_2+Ar sputtering ambient. The deposition parameters are described elsewhere [9]. The thickness of the film was about 2.7 µm. The as deposited sample was separated into small samples with each 1.0x1.0 cm^2. These samples were annealed into a quartz furnace at three different temperatures of 500, 600 and 700 °C. The samples were held at each temperature for 1 hour in oxygen and forming gas environments, and then the furnace is cooled at room temperature. The slow cooling rate of 2° C/min was maintained to avoid the possibility of any type of stress and strain in the film as expected in rapid cooling of the furnace. The electrical properties were studied at a maximum temperature of 350°C due to presence of aluminium as bottom and top electrode.

3. Results and Discussions

3.1. Structural Properties

Fig. 1 shows the X-ray line profile of as deposited ZnO thin film. The crystal structure and orientation of the films were investigated by x-ray diffraction using XRD instrument Philips PW3710 x-ray diffractometer (λ=1.5406Å). From the X-Ray analysis, it has been found that crystallinity of ZnO film increases independent of the environment used for annealing. The X-ray peak increases with annealing treatment, which means that treatment leads to the improvement in crystallinity of the films. The increase in intensity of (002) orientation may be due to energy provided by high annealing temperature to the film atoms to enhance the mobility that could decrease the defects in ZnO films. The grain size of the ZnO films annealed in oxygen and forming gas is calculated using Scherer’s relation [10].

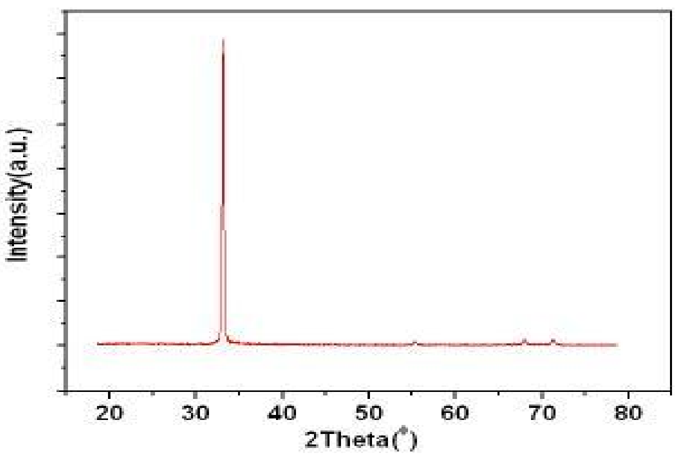


Fig. 1. XRD scans of as deposited ZnO sample.

$$D = 0.94\lambda/(\beta cos\theta)\text{,} \quad (1)$$

where D is the grain size, λ is the wavelength having value of 1.5406 Å for Cu K_α radiation, β is the full width half maximum (in radians) of XRD peak. Here using 2θ= 33.76°, β=0.352, λ= 1.5406Å for CuKα, value of D using equation 2.7 is 25 nm.

The grain size is found to increase continuously in O_2 atmosphere annealing while in case of forming treatment at higher temperature grain size is found to be decreased due to oxygen outdiffusion and insertion of hydrogen atom at such high temperature. A comparison table for structural properties stress value is shown in Table 1.

Table 1. Comparison of structural properties of oxygen and forming gas annealed samples at different temperature.

Annealing temperature(°C)	**As Deposited**	**Oxygen Annealed**			**Forming gas Annealed**			**Bulk ZnO**
		500°C	**600°C**	**700°C**	**500°C**	**600°C**	**700°C**	**34.43**
2 θ (deg)	33.76	34.38	34.57	34.58	34	34.32	34.57	-
FWHM (deg)	0.352	0.22	0.20	0.18	0.167	0.22	0.3620	-
Grain size (nm)	25	40	44	50	53	40	24	-
C-axis (Å)	5.3056	5.210	5.184	5.182	5.2392	5.2212	5.1842	5.206
Stress (GPa)	-8.55	-0.34	1.90	2.07	-5.44	-1.20	1.901	0

The stress is calculated from the XRD data [11-12] using following formula

$$\sigma = 450\left(\frac{C_o - C}{Co}\right)GPa\text{,} \quad (2)$$

where C_o is the strain free lattice constant. The as deposited films have a stress value of -8.55 GPa. The negative sign here indicates that as deposited zinc oxide film is in state of compressive stress [13]. In both annealing atmospheres stress in the ZnO thin film is found to be varied from compressive to tensile. At some suitable temperature, the stress present in the film becomes zero, i.e., stress relief temperature is found to be different for O_2 and N_2H_2 gas environment. It has been found that the films annealed in an O_2 environment becomes stress free at lower temperature (530 °C) as compare to the films annealed in forming gas (640 °C). The comparison of lowest stress values of the two environments is shown in Fig. 2.

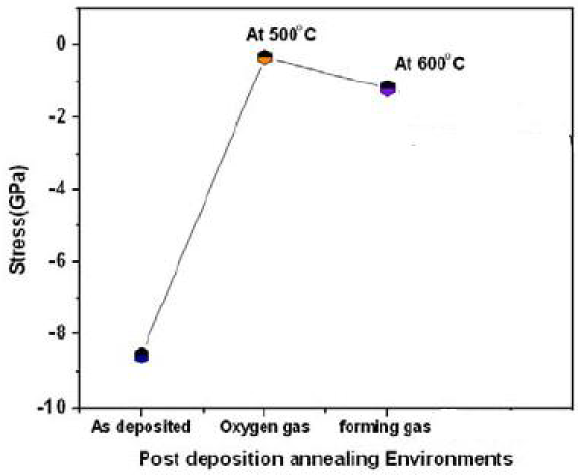


Fig. 2. Lowest stress temperature for two environments.

3.2 Electrical Properties

For acoustic device applications highly resistive zinc oxide films are required. In the present work the effect on the dielectric constant and ac conductivity of zinc oxide thin films annealed in oxygen and forming gas is being studied. The dielectric constant of as deposited film is found to be about 10.9. It increases to 11.8 after annealing in oxygen environment and 12.5 after forming gas annealing. Hence an increase in capacitance of the MIM capacitor has been observed for both cases and the values of dielectric constant is found to be with in the reported values [14]. The ac conductivity σ_{ac} of zinc oxide thin films has been estimated using metal insulator metal configuration shown in Fig. 3 from the capacitance frequency characteristics with sweep frequency 20 Hz to 20 kHz at room temperature using following formula [15-16].

$$\sigma_{ac} = \omega\varepsilon_o\varepsilon'' , \quad (3)$$

where ω is the angular frequency, ε_o is permittivity of the free space, ε'' is the dielectric loss. The value of ac conductivity at 350ºC for oxygen annealing at 10 KHz is found to be decreased from 4.4 $\times10^{-11}$ Ω^{-1}cm^{-1} to 2.5 x 10^{-13} Ω^{-1}cm^{-1}, i.e., the resistivity increases by three orders of magnitudes after

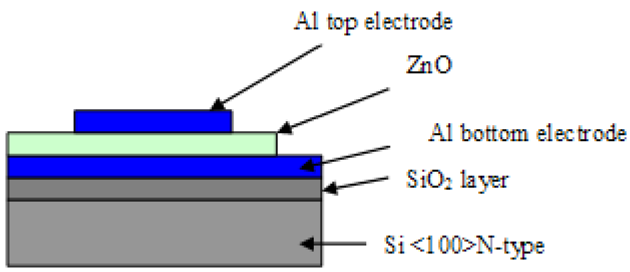


Fig. 3. Schematic of MIM Capacitor for electrical characterization.

oxygen annealing. Where as the ac conductivity for forming gas annealing is found to be shifting from 4.4x10^{-11} to 1.94x10^{-9} Ω^{-1}cm^{-1}. This means that the films have low order of resistivity due to desorption of oxygen atoms from grain boundaries reducing the number of oxygen states, which acts as traps for electrons [17]. The comparison of ac conductivity of zinc oxide films annealed in two atmospheres is shown in Fig. 4.

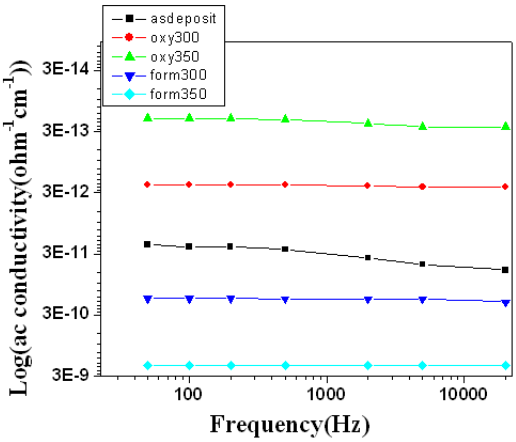


Fig. 4. Comparison of zinc oxide annealed films in two atmospheres.

3.3. Optical Properties

The transparency of as deposited zinc oxide film is found to be high (≈67.99 %) at 800 nm in the ultraviolet- visible region which is sufficient to determine the band gap and refractive index of the thin zinc oxide film. The transmission spectra of as deposited and annealed films are shown in Fig. 5. The transmittance increases to 80.53 % as the annealing temperature increases to 350 ºC for oxygen annealing. This shows that the film has good optical properties and low absorption losses. The increase in transmittance is due to reduction in scattering centers or defects after annealing in oxygen. The same result is reported by other workers [18] as well. They reported that stoichiometric ZnO films with large grain size should have higher transmission than as grown films. Another feature, observed during optical studies is a shift in the interference fringes with respect to annealing temperature. The transmittance increases to 88% as the annealing temperature increases to 350 ºC in forming gas. The increase in transmittance may be due to effect of nitrogen and hydrogen atoms present in forming gas and their insertion into the voids of as deposited zinc oxide films. The transmittance of forming gas annealed films is larger than the transmittance of films annealed in oxygen environments.

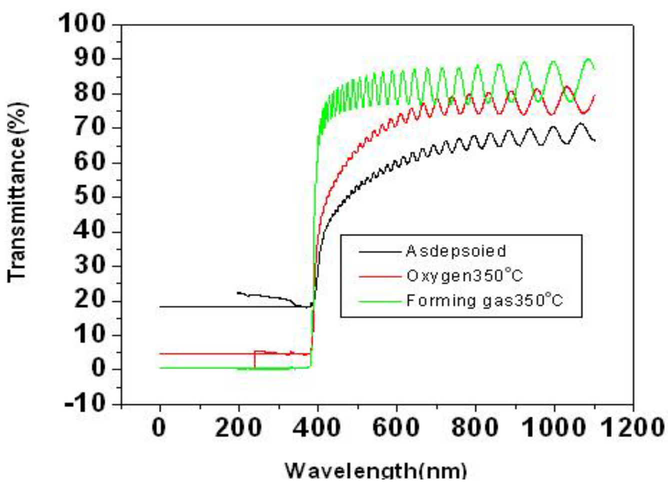


Fig. 5. Transmission spectra of as deposited and annealed films.

Optical band gap of the ZnO thin films has been calculated from the Taue plot of $(\alpha)^2$ *vs* photon energy (*hv*). Intercept on energy axis obtained after extrapolating linear portion of the plot gives the value of band gap (*Eg*) gives the value of band gap. Band gap of stoichiometric films is found to be 3.2 eV by other workers, which is close to the value 3.18, obtained for zinc oxide annealed at 350 ºC after oxygen annealing. This indicates that the film after annealing at 350 ºC is of good quality having higher transmission. The refractive index of thin film was determined from transmission spectra using the envelope method as described by Manifacier et. al [19]. In the region of low absorption, the refractive index (n) has been obtained from the interference maxima (T_{max}) and minima (T_{min}) using the relation

$$n = \left[N_o + (N_o^2 - n_0^2 n_1^2)^{1/2} \right]^{1/2} \quad (4)$$

where

$$N_o = \frac{n_0^2 + n_1^2}{2} + 2 n_o n_1 \left(\frac{T_{max} - T_{min}}{T_{max} T_{min}} \right) \quad (5)$$

here n_0 and n_1 are refractive indices of two transparent media (air and substrate). The refractive index may be a good parameter to detect the packing density. The packing density (p) of ZnO thin films [20] can be calculated by following formula

$$p = \frac{5 n_f^2 - 1}{3 n_f^2 + 1} \quad (6)$$

The comparison of the optical properties has been given in Table 2.

Table 2. Comparison of optical properties.

Environments	Temperature (°C)	Transmittance (%) (λ= 800nm)	Band gap(Eg)(eV)	Refractive index(n)	Packing Density(p)
As deposited	RT	67.99	3.07	1.76	1.405
Oxygen gas	350ºC, one hour	80.53	3.18	1.94	1.925
Forming gas	350ºC, one hour	88.10	3.20	1.9	1.441

4. Conclusion

From the present studies it has been found that the grain size is has been increased much in the case of oxygen as compared to the forming gas. In forming gas, grain size increases but at high temperature of 700 ºC it decreases abruptly. The film is shifting from compressive to tensile stress in oxygen and forming gas. At some suitable temperature, the stress present in the film becomes zero, i.e., stress relief temperature is obtained for oxygen and forming gas. After annealing in oxygen environment, the films are becoming stress free at lower temperature as compared to forming gas. The resistivity is found to be more in oxygen atmosphere as compare to forming gas. Thus oxygen annealing is preferable for acoustic devices. The optical properties are also found to be better in oxygen with good packing density.

References

[1]. Sheng-Yuan Chu, Walter Water, Jih-Tsang Liaw, Influence of post deposition annealing on the properties of ZnO films prepared by RF magnetron sputtering, J*ournal of the European Ceramic Society*, Vol. 23, 2003, pp. 1593–1598.

[2]. Z. B. Fang, Z. J. Yana, Y. S. Tana, X. Q. Liua, Y. Y. Wang, Influence of postannealing treatment on the structure properties of ZnO films, *Applied Surface Science*, Vol. 241, 2005, pp. 303–308.

[3]. R. J. Lad, P. D. Funkenbusch, C. R. Aita, Post deposition annealing of RF sputtered ZnO films, *J. Vacuum Science Vacuum*, Vol. 17, 4, 1980, pp. 808-811.

[4]. Vinay Gupta, Abhai Mansigh, Effect of post deposition on sputtered zinc oxide film, *IEEE*, 1995, 57, pp. 508-511.

[5]. Navina Mehan, Vinay Gupta, Kondepudy Sreenivas, and Abhai Mansingh, Effect of annealing on refractive indices of radio-frequency magnetron sputtered wave guiding zinc oxide films on glass, *Applied Physics*, Vol. 96, No. 6, 2004.

[6]. Hang-Ju Ko, Myung-Soo Han, Young-Sik Park, Yun-Sik Yu, Byong-In Kim, Sang Sub Kim, Jin-Hyeok Kim, Improvement of the quality of ZnO substrates by annealing, *Crystal Growth*, Vol. 269, 2004, pp. 493–498.

[7]. Erik Bak-Mikkelsen, Roger de Reusy and Siebe Bouwstra, Improved quality of zinc oxide thin films by in situ annealing, *J. Micromech. Microeng.*, Vol. 6, 1996, pp. 63–65.

[8]. Shoubin Xue, Huizhao Zhuang, Chengshan Xue, Shuyun Teng, and Lijun Hu, Effect of annealing temperature on properties of ZnO thin films on Si(111) substrates by magnetron sputtering, *Eur. Phys. J. Appl. Phys*., Vol. 36, 2006, pp. 1–4.

[9]. Arora, A. Arora, V. K. Dwivedi, P. J. George, K. Sreenivas and V. Gupta, *Sens. Actuators A,* 2008, 141A, 256–261.

[10]. W. T. Lim and C. H. Lee, *Thin Solid Films*, 12, 1999, p. 353.

[11]. M. L. Cui, X. M. Wu, L. J. Zhuge, Y. D. Meng, Effects of annealing temperature on the structural and photoluminescence properties of ZnO films, *Vacuum*, 81, 2007, pp. 899-903.

[12]. Vinay Gupta, Abhai Mansingh, Effect of Post Deposition Annealing On Sputtered Zinc Oxide Film*, IEEE*, 1995.

[13]. Vinay Gupta and Abhai Mansingh, Hopping conduction in insulating rf sputtered zinc oxide films, *Phy. Rev. B.* Vol.49, 1994, pp 1989-1995.

[14]. Gupta, V. and Mansingh, A., Influence of postdeposition annealing on the structural and optical properties of sputtered zinc oxide film, *J. Appl. Phys*, Vol. 80, 2, 1996, pp. 1063–1073.

[15]. S. Maniv, W. D. Westwood and E. Colombini, *J. Vac. Sci. Technol.*, 20, 2, 1982, p. 162.

[16]. M. L. Cui, X. M. Wu, L. J. Zhuge and Y. D. Meng, *Vacuum*, 81, 2007, pp. 899–903.

[17]. Omina Hamad, Gabriel Braunstein, Harshad Patil, Neelkanth Dhere, Effect of thermal annealing treatment in oxygen, nitrogen and air atmospheres on electrical transport properties of zinc oxide thin films, *Thin Solid Films*, Vol. 489, 2005, pp. 303-309.

[18]. Jingchang Sun, Tianpeng Yang, Guotong Du, Hongwei Liang, Jiming Bian, Lizhong Hu, Influence of annealing atmosphere on ZnO thin films grown by MOCVD, *Applied Surface Science*, Vol. 253, 4, 2006, pp. 2066-2070.

[19]. Manifacier et. al, A simple method for the determination of the optical constants n, k and the thickness of a weakly absorbing thin film, *Journal of Physics E, Scientific Instruments,* Vol. 9, 1976, pp. 1002 1004.

[20]. Z. B. Fang, Z. J. Yana, Y. S. Tana, X. Q. Liua, Y. Y. Wanga, Influence of post annealing treatment on the structure properties of ZnO films, *Applied Surface Science*, Vol. 241, 2005, pp. 303–308.

Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

Topics Covered

Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

- Physical, chemical and biosensors;
- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
- Frequency (period, duty-cycle)-to-digital converters, ADC;
- Technologies and materials;
- Nanosensors;
- Microsystems;
- Applications.

Submission of papers

Articles should be written in English. Authors are invited to submit by e-mail editor@sensorsportal.com 8-14 pages article (including abstract, illustrations (color or grayscale), photos and references) in both: MS Word (doc) and Acrobat (pdf) formats. Detailed preparation instructions, paper example and template of manuscript are available from the journal's webpage: http://www.sensorsportal.com/HTML/DIGEST/Submition.htm Authors must follow the instructions strictly when submitting their manuscripts.

Advertising Information