www.amlett.org, www.amlett.com, DOI: 10.5185/amlett.2012.6364 Published online by the VBRI press in 2012

The influence of substrate temperature on the structure, morphology, and optical properties of ZrO_2 thin films prepared by e-beam evaporation

K. J. Patel, M. S. Desai and C. J. Panchal*

Applied Physics Department, Faculty of Technology and Engineering, M. S. University of Baroda, Vadodara, 390001, India

*Corresponding author. E-mail cjpanchal_msu@yahoo.com

Received: 11 June 2011, Revised: 26 June 2012 and Accepted: 28 June 2012

ABSTRACT

Zirconium dioxide thin films were prepared by e-beam evaporation method to study the effect of substrate temperature on the structural, surface morphology, compositional, and optical properties. X-ray diffraction measurement shows that the films grown at 400 °C substrate temperature have monoclinic crystal structure. The root mean square surface roughness of the film increases with increase in the substrate temperature. The optical transmittance spectra indicate an average 80% transmittance in the visible region of light. The optical energy band gap of ZrO_2 thin film decreases from 5.68 to 5.63 eV as the substrate temperature increases from room temperature to 400 °C, respectively. Copyright © 2012 VBRI press.

Keywords: Zirconium dioxide thin film; e-beam evaporation method; substrate temperature; X-ray diffraction; atomic force microscope, optical properties.

Keyur J. Patel received his M.Sc. degree in applied physics from M.S. University of Baroda, Vadodara, India, in 2006. Since then, he has been working for his PhD at the M.S. University of Baroda, Vadodara, India. His area of interest is electrochromic thin film devices and semiconductor metal oxide gas sensors.

M. S. Desai received his M.Sc. degree in nuclear physics in 1977 from University of Bombay, Mumbai, Maharashtra, M.S in physics and Ph.D. degree in particle physics in 1990 and 1991 respectively from University of California, USA. He is presently working as an Associate professor in the Applied Physics Department of M.S. University of Baroda, Vadodara. He worked extensively in the areas of semiconductor thin film active and passive devices. His current areas of research include semiconducting thin film hetero-structures, sensors and development of high power diode lasers.

C. J. Panchal received his M.Sc. degree in applied physics in 1990 from M.S. University of Baroda, Vadodara, Gujarat and Ph.D. degree in electronics in 1995 from Sardar Patel University, Vallabh Vidyanagar, Gujarat. He is presently working as an Associate Professor in the Applied Physics Department of M.S. University of Baroda, Vadodara. He worked extensively in the areas of semiconductor thin film active and passive devices. His current areas of research include semiconducting thin film hetero-structures, sensors and development of high power diode lasers.

Introduction

Zirconium dioxide is being investigated for its future potential applications as an insulator in transistors in nano-electronic devices [**1, 2**]. It is also used to replace SiO_2 as the gate dielectric material in metal-oxide-semiconductor devices because of its high dielectric constant (~25), good thermal stability on silicon, and large band gap (5.6 eV) [**3**]. Zirconia-based ceramics are often used as thermal insulators because of their low thermal conductivity (2.2 W/mK) over temperatures ranging from cryogenic to >1200 °C, e.g., for thermal barrier coating (TBC) [**4**]. Zirconium dioxide is the most popular electrolyte material for solid oxide fuel cells and electrochromic devices due to its high ionic conductivity [**5**]. Zirconium dioxide is used as a thin film coating on the facets of high-power laser diode in order to protect the laser facets from degradation and to ensure long-term reliable operation [**6**].

The performance of the ZrO_2- based devices considerably depends on the crystal structure of ZrO_2. Pure ZrO_2 exists in three crystal phases at different temperatures: For very high temperature ranges (> 2370 °C) it has a cubic structure, whereas at intermediate temperature ranges (1170 to 2370 °C) it has a tetragonal structure, and for low temperature ranges (below 1170 °C) the material has a

 Copyright © 2012 VBRI press

monoclinic structure [**7**].

Zirconium dioxide thin films can be prepared by a wide variety of techniques including sputtering [**8**], chemical vapor deposition [**9**], sol-gel process [**10**], spray deposition [**11**] and e-beam evaporation [**12**]. In any deposition technique, the growth conditions strongly affect the microstructure and the chemical compositions of the thin films, which directly affect its optical properties. From the point of view of application, ZrO_2 thin film should be non-porous and homogeneous. The e-beam deposited ZrO_2 thin films have a relatively higher density and uniformity compared to the chemical vapor deposition technique (CVD) [**13**]. In this study, we have investigated the effect of the substrate temperature on the structural, surface morphological, compositional, and optical properties of e-beam evaporated ZrO_2 thin films.

Experimental

Thin films of ZrO_2 were deposited on organically cleaned glass and sapphire substrates using the e-beam evaporation technique. Zirconium dioxide powder (Sigma Aldrich, <5 micron, 99%) placed in a graphite crucible is used as the source material. The films were grown, at a base pressure of 10^{-5} mbar, at different substrate temperatures ranging from room temperature (RT) to 400 °C. The substrate is heated using infrared (IR) heater, and its temperature is measured by a Chromel-Alumel thermocouple. ZrO_2 thin films of thickness 3000 Å are grown at a rate of 5 Å/s. The thickness measurement involves piezoelectric quartz crystal placed inside the vacuum chamber. The rate of deposition is controlled and monitored with the help of the quartz-crystal-based thin film deposition controller (Sigma Instruments, SQC 122c).

The microstructure of the ZrO_2 thin films is determined by the glancing incident X-ray diffraction (GIXRD) method using Cu Kα radiation at an incident angle of 0.5° (Bruker-AXS D8 Advance) in 2θ range from 20° to 60°. The surface morphology of the films is determined using atomic force microscope (AFM) (Nanosurf easy Scan 2) in contact mode and the root mean square (rms) surface roughness is calculated using the instrument's software. The surface composition of these thin films is determined using X-ray photoemission spectroscopy (XPS). The XPS measurement is carried out using VSW ESCA instrument, with Al-Kα (1486.6 eV) X-ray source at a base vacuum of 8.0×10^{-10} Torr. The optical transmittance is measured using ultraviolet visible (UV-Vis) spectrophotometer (Shimadzu UV-2450) in the wavelength range 150 - 900 nm.

Results and discussion

X-ray diffraction measurement

X-ray diffraction measurement is carried out in order to examine the crystallization behaviour of ZrO_2 thin films as a function of substrate temperature. **Fig. 1** shows the XRD patterns of ZrO_2 thin films prepared at different substrate temperatures ranging from RT to 400 °C.

From the XRD patterns as shown in **Fig. 1**, it is observed that the films grown at RT to 100 °C show the amorphous nature with hump at the 2θ range of 30 to 32°. While films grown at 200 °C show small peaks, which appear at 24.6°, 28.25°, 31.55°, 34.5°, and 50.4° corresponding to (110), ($\bar{1}$11), (111), (002), and (220), respectively. As the substrate temperature increases up to 400 °C the intensity of ($\bar{1}$11) and (111) increases and the other peaks almost disappear, which indicates the monoclinic structure (JCPDS-83 0940) of the film. The transition of ZrO_2 thin film from amorphous to monoclinic occurred at ~300 °C substrate temperature. The transition temperature is lower than the reported value using sol-gel dip coating technique [**14**] and spray deposition technique [**11**], which can be attributed to the high ion energy in the e-beam evaporation. The average crystallite size, determined using the Scherrer equation for ($\bar{1}$11) plane is found to be 8.55 nm and 15.0 nm for 300 °C and 400 °C substrate temperatures, respectively. At higher substrate temperatures, the mobility of the condensing particles on the substrate surface is more, which favors the crystallization and the growth of large crystallites.

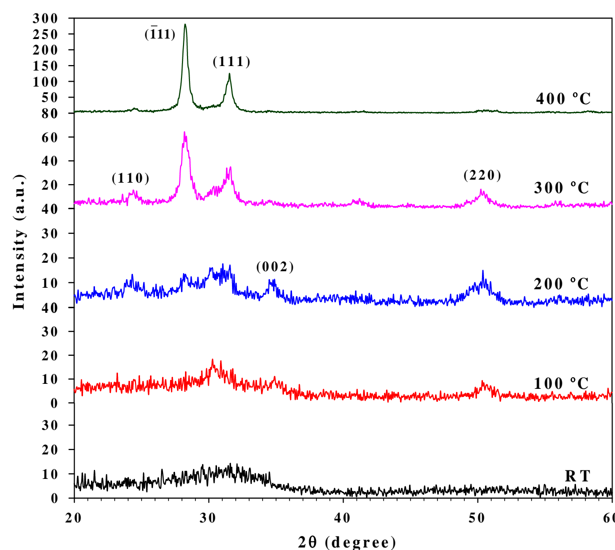


Fig. 1. XRD spectra of ZrO_2 thin films deposited at different substrate temperatures.

Atomic force microscopy measurement

Fig. 2 shows the surface morphology of the ZrO_2 thin films deposited at different substrate temperatures as determined from the AFM with a scan area of 1 μm × 1 μm. The rms surface roughness of the films is determined using Nanosurf easy Scan software.

The thin film deposited at RT has a well-defined grain with an rms surface roughness value of 2.92 nm, while at 200 °C, the surface becomes smoother, with rms roughness value of about 2.43 nm. Furthermore, with the increase of the substrate temperature to 400 °C the surfaces get much rougher again with the rms roughness value of 5.46 nm. At the RT, the grain growth is observed but due to the porous structure of the film, the roughness is high compared with that at 200 °C. At 200 °C substrate temperature, the density of the grain increases due to uniform distribution and thereby the rms roughness slightly decreases. Furthermore, with the increase in the substrate temperature to 400 °C some of the grains diffuse and form clusters, which results in an increase of rms roughness of the film's surface.

Copyright © 2012 VBRI press

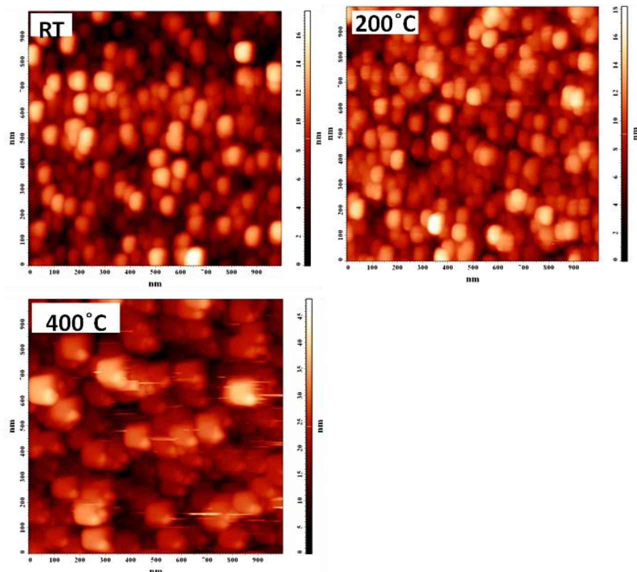


Fig. 2. The AFM image of ZrO_2 thin film deposited on glass substrates at RT, 200, and 400 °C.

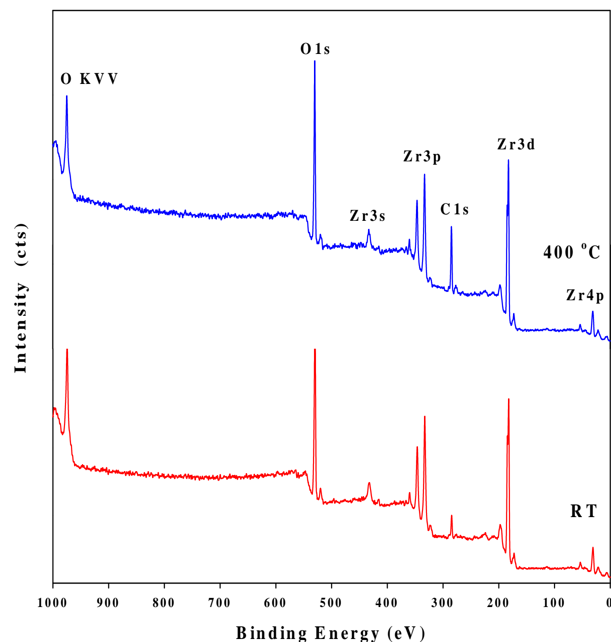


Fig. 3. The XPS survey scan spectra of ZrO_2 thin films grown at RT and 400°C substrate temperatures.

X-ray photo-emission spectroscopy measurement

The chemical composition of the surface of the ZrO_2 thin film is investigated using XPS measurement. **Fig. 3** shows the survey scan XPS spectra of zirconium oxide thin films deposited on glass substrates in the binding energy range of 0 - 1000 eV.

From **Fig. 3**, one can reckon the presence of zirconium (Zr), oxygen (O) and carbon (C) atoms on the surface of the films. **Fig. 4 (a)** and **(b)** show the XPS core level spectra for zirconium Zr3d, and oxygen O1s at the surface of the ZrO_2 thin film, respectively. In **Fig. 4 (a)** the doublet peaks centered at 182.1 eV and 184.5 eV, correspond to $Zr3d_{5/2}$ and $Zr3d_{3/2}$, respectively. The binding energy of $Zr3d_{5/2}$ is expected to be observed at 179 eV, and in our case, the $Zr3d_{5/2}$ peak is located at 182.1 eV, which shows the formation of zirconium oxide in its +4 state [**15**]. The XPS spectra of the ZrO_2 thin film reveal that the binding energy of the O1s peak is 529.8 eV. The higher energy shoulder observed at 531.6 eV is perhaps due to the surface oxidation. The peak intensity is nearly same for both the cases, which indicates that the RT to 400 °C substrate temperature does not affect much the chemical composition of the film.

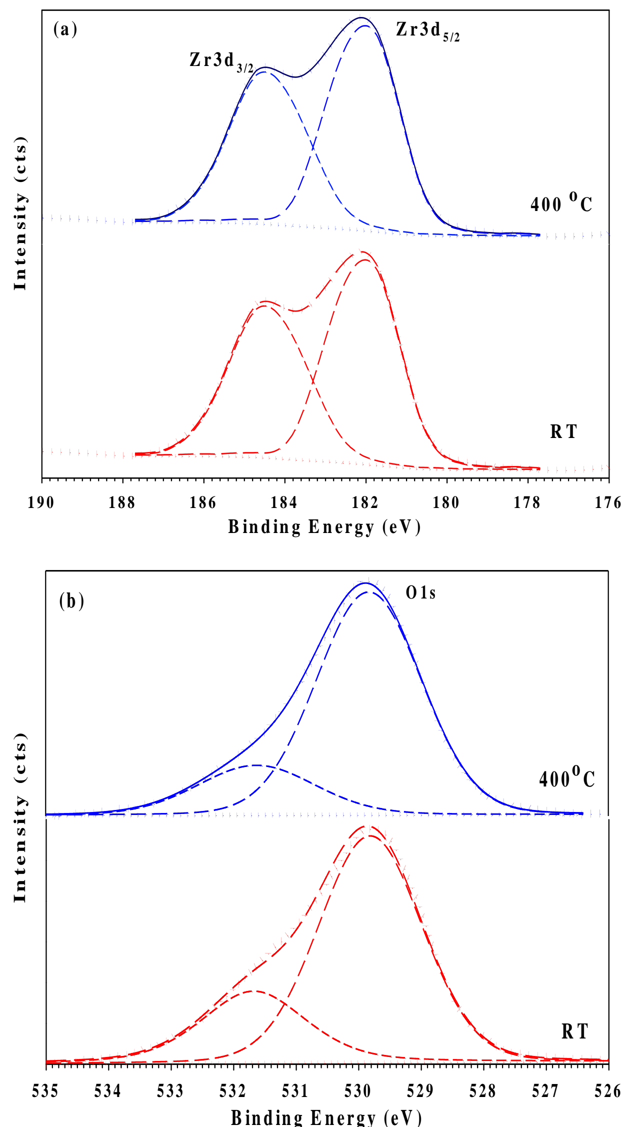


Fig. 4. The XPS spectra of (a) Zr3d and (b) O1s for ZrO_2 thin films grown at RT and 400 °C substrate temperature, respectively.

Optical measurement

The optical transmittance of the ZrO_2 thin films is measured in the range of 200 – 900 nm using UV-Vis spectrophotometer. The sapphire substrate is used for the optical measurement, which is nearly transparent from 200 – 900 nm wavelengths. The transmittance spectra of the sapphire substrate and the ZrO_2 thin film grown on sapphire substrate at different substrate temperatures are shown in **Fig. 5**.

Copyright © 2012 VBRI press

The plot of the optical transmittance spectra of the ZrO_2 thin films show an average 80% transmittance in the visible region of light. The interference fringes in transmittance spectra of **Fig. 5** indicate that the ZrO_2 films are homogeneous and of uniform thickness. These fringes arise from the constructive and destructive interference of the light beams generated from partial reflection of the incident light beam at the first and second surfaces of a ZrO_2 thin film.

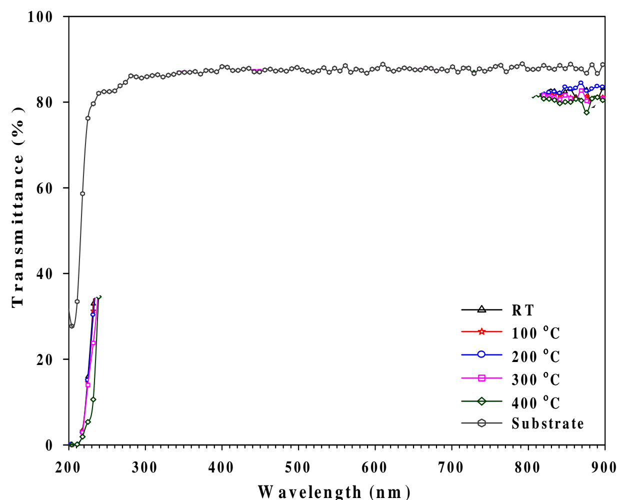


Fig. 5. Transmission spectra of ZrO_2 thin films deposited at different substrate temperatures on the sapphire substrate.

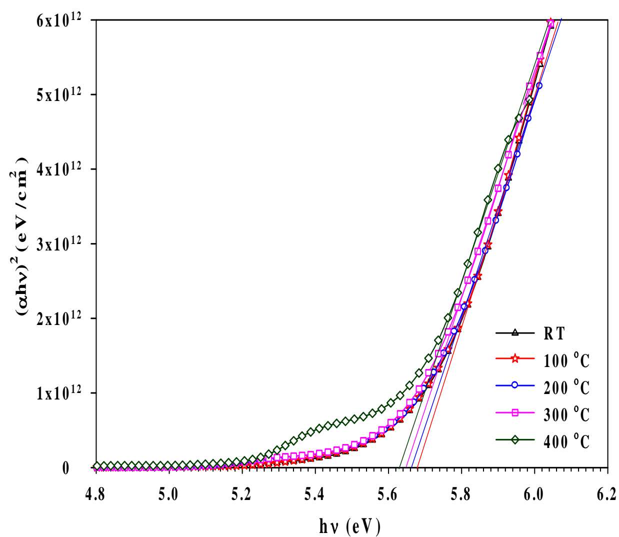


Fig. 6. $(\alpha h\nu)^2$ vs. $(h\nu)$ plot for the optical energy band gap of ZrO_2 thin films.

There is a small variation observed in the energy band gap with substrate temperature from RT to 400 °C; this is because the substrate temperature is low compared to the high melting point (2715 °C) of ZrO_2. The XPS data also indicates that there is not any major change in the composition of the ZrO_2 thin film observed with substrate temperature. Thus, the small variation in the band gap, from 5.68 to 5.63 eV, with increase in substrate temperature, from RT to 400 °C, is due to the improvement in the crystallization of the film. The optical energy band gap is almost same as obtained by other methods as reported by H. Nohira et al. [**17**]. The values of energy band gap for different substrate temperatures are presented in **Table 1**.

Table 1. The energy band gap values and the corresponding substrate temperatures for ZrO_2 thin films.

Substrate temperature (°C)	RT	100	200	300	400
Energy band gap (eV)	5.68	5.68	5.66	5.65	5.63

Conclusion

Zirconium dioxide thin films were deposited on different substrates and at different temperatures using the e-beam evaporation method. The XRD measurement shows that the crystallization improves with increase in the substrate temperature and also the surface roughness increases as observed by AFM measurement. The optical properties of the thin films show that there is a small variation in the transmittance observed and the band gap varies from 5.68 to 5.63 eV with increase in substrate temperature from RT to 400 °C, respectively, due to the improvement in the crystallization of the film.

Acknowledgement
A part of this work was performed at UGC-DAE Consortium for Scientific Research, Indore, India.

Reference

1. Biercuk, M. J., Monsma, D. J., Marcus, C. M., Becker, J. S., Gordon, R. G., Appl. Phys. Lett., **2003**, 83(12), 2405.
DOI: 10.1063/1.1612904
2. Kim, S. J., Yoon, D. H., Rim, Y. S., Kim, H. J., *Electrochem. Solid-State Lett.*, **2011**, 14(11), E35.
DOI: 10.1149/2.006111esl
3. Chang, J. P., Lin, Y. -S., Chu, K., *J. Vac. Sci. Technol. B,* **2001**, 19(5),1782.
DOI: 10.1116/1.1396639
4. Guo, H., Gong, S., Khor, K. A., Xu, H., *Surf. Coat. Technol.,* **2003**, 168(1), 23.
DOI: 10.1016/S0257-8972(02)00925-8
5. Mobius, H.-H., *J. Solid State Electrochem.*, **1997**, 1(1) 2.
DOI: 10.1007/s100080050018
6. Chin, A. K., Satyanarayan, A., Zarrabi, J. H., Vetterling, W., *J. Appl. Phys.*, **1988**, 64(3), 994.
DOI: 10.1063/1.341807
7. French, R. H., Glass, S. J., Ohuchi, F. S., Xu, Y. N., Ching, W. Y., *Phys. Rev. B*, **1994**, 49(8), 5133.
DOI: 10.1103/PhysRevB.49.5133
8. Zhu, L. Q., Fang, Q., He, G., Liu, M., Zhang, L. D., *Nanotechnology*, **2005**,16(12), 2865.
DOI: 10.1088/0957-4484/16/12/022
9. Ben-Dor, L., Elshtein, A., Halabi, S., Pinsky, L., Shappir, J., *J. Electron. Mater.*, **1984**, 13(2), 263.
DOI: 10.1007/BF02656679
10. Liu, W-C., Wu, D., Li, A-D., Ling, H.-Q., Tang, Y.-F., Ming, N.-B, *Appl. Surf. Sci.*, **2002**, 191(1-4), 181.
DOI: 10.1016/S0169-4332(02)00177-0
11. Chun, M. -S, Moon, M. -J, Park, J. -Y, Kang, Y.-C., *Bull. Korean Chem. Soc.*, **2009**, 30(11) 2729.
DOI:10.5012/bkcs.2009.30.11.2729
12. Ochando, I. M., Vila, M., Prieto, C., *Vacuum*, **2007**, 81(11-12)1484.
DOI:10.1016/j.vacuum.2007.04.015
13. Zhang, N.-L., Wan, Q., Song, Z.-T., Shen, Q.-W., Zhu, X.-R., Lin, C.-L., *Chin. Phys. Lett.*, **2002**, 19(3), 395.
DOI:10.1088/0256-307X/19/3/333
14. Joy, K., Berlin, I. J., Nair, P. B., Lakshmi, J. S., Daniel, G. P.,

 Copyright © 2012 VBRI press

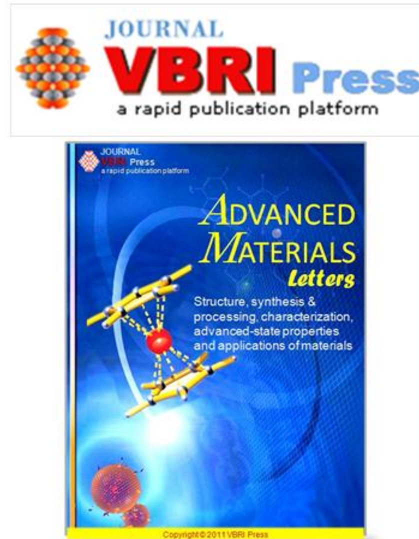
Thomas, P. V., *J. Phys. Chem. Solids*, **2011**, 72(6), 673.
DOI:10.1016/j.jpcs.2011.02.012

15. Ortiz, A., Alonso, J. C., Haro-poniatowski, E., *J. Electron. Mater.*, **2005**, 34(2), 150.
DOI:10.1007/s11664-005-0226-y
16. Tauc, J., *Amorphous and liquid semiconductors,* Chapter 4, ed. by J. Tauc, Plenum, London, **1974**.
17. Nohira, H., Tsai, W., Besling, W., Young, E., Petry, J., Conard, T., Vandervorst, W., Gendt, S. De, Heyns, M., Maes, J., Tuominen, M., *J. Non-Cryst. Solids*, **2002**, 303(2) 83.
DOI:10.1016/S0022-3093(02)00970-5

Advanced Materials Letters

Publish your article in this journal

ADVANCED MATERIALS Letters is an international journal published quarterly. The journal is intended to provide top-quality peer-reviewed research papers in the fascinating field of materials science particularly in the area of structure, synthesis and processing, characterization, advanced-state properties, and applications of materials. All articles are indexed on various databases including DOAJ and are available for download for free. The manuscript management system is completely electronic and has fast and fair peer-review process. The journal includes review articles, research articles, notes, letter to editor and short communications.



 Copyright © 2012 VBRI press