

Influence of Sol Composition on Microstructural, Optical and Photocatalytic Properties of Zinc Tin Oxide Thin Film

Moumita Pal, Susanta Bera, Saswati Sarkar and Sunirmal Jana *

Sol-Gel Division, CSIR-Central Glass and Ceramic Research Institute (CSIR-CGCRI)
196 Raja S.C. Mullick Road, P.O. Jadavpur University, West Bengal, Kolkata 700032, India

*Corresponding author: Tel.: +91 33 23223303, fax: +91 33 2473 0957

E-mail address: sjana@cgcri.res.in, janasunirmal@hotmail.com (S. Jana)

Abstract. We report the deposition of vacuum annealed (450°C) zinc tin oxide thin films (thickness, 26 – 43 nm) on glass by dipping technique from precursor solutions of varying Sn to Zn content ($R = 0.43$ to 0.54) in 2-methoxy ethanol with acetylacetone. Grazing incidence XRD patterns confirm the formation of hexagonal ZnO at lower R values. However, the film crystallinity is found to diminish on increasing R and reaches to an amorphous system when R is 0.54. An influence of Sn content on ZnO morphology is also observed from FESEM and TEM measurements. The films have also been characterized by UV-Vis transmission and FTIR spectral analyses. Photocatalytic activity of the films towards degradation of Rhodamine-6G dye under UV (254 nm) has been tested. A linear relationship of decomposition rate constant with film crystallinity is noticed. This study can be useful for tailoring the dye decomposition activity in other sol-gel thin films.

Key words: Sol-gel thin film, Semiconductor oxide, Surface morphology, Crystallinity, Ultraviolet visible spectra, Photocatalyst

I. INTRODUCTION

Thin films of zinc tin oxide (ZTO) are attractive for their novel optical, electrical and electronic properties [1], [2] and enormous applications [3], [4] including photocatalyst for degradation of organic pollutants (e.g. dyes, volatile organic compounds, detergents, pesticides), transparent conducting oxide (TCO) material. Many film deposition techniques [1]-[3], [5] are presently known among which the sol-gel is a facile and cost effective one. In sol-gel process, the optical and microstructural properties [6], [7] of materials primarily depend upon sol chemistry, annealing condition, etc. Moreover, the sol composition can greatly influence [6], [8] upon the properties of the thin films. Annealing treatment in different conditions such as vacuum annealing, controlled-atmosphere annealing can also play an important role [9], [10] to change the film properties.

This is because various chemisorptions and desorption processes along with oxygen diffusion mechanisms are highly involved during the annealing process. It is also reported that to obtain relatively high quality film,

Vacuum annealing would sometimes advantageous over the others. Some researchers [11], [12] studied the tetravalent metal ions incorporated ZnO thin films to tailor/advance the property of the materials. In this respect, the works on sol-gel ZTO films had already been done by many researchers [2], [6], [10]-[12]. Among them, Kurtz and Aegerter [2] had been prepared the films on glass in air using different sources of zinc and tin in the precursor sols by varying tin contents from 25 to 60 % with respect to Zn.

Now-days, environmental problems due to the growth of dye industries are increasing day-by-day. In this respect, the semiconductor oxide as photocatalyst may solve the problems economically. In semiconductor oxide, a number of physical characters such as crystallinity, particle size, surface area etc. can control the photocatalytic activity (PA) [13] towards decomposition of dyes. Previously, we reported [10] the PA of vacuum annealed zinc tin oxide thin films derived from the precursor sol containing Sn/Zn (atomic ratio), 0.49 by varying the pH of precursor sol. To the best of our knowledge, the PA of sol-gel ZTO thin films deposited by varying Sn/Zn (sol composition) has yet been performed.

Thus, the present work is basically devoted to observe the effect of sol composition by changing tin to zinc ($R = 0.43, 0.49$ and 0.54) on microstructure, crystallinity and optical property of zinc tin oxide thin films deposited on soda lime silica glass and annealed under vacuum condition at 450°C. Moreover, the photocatalytic activity (PA) of the films towards degradation of Rhodamine 6G dye on exposure of UV light (254 nm) has also been checked and the change of PA has been explained on the basis of the experimental results.

II. EXPERIMENTAL

In the precursor sols, Sn to Zn (atomic ratio, R (0.43, 0.49 and 0.54) has been varied using requisite amount of zinc (II) acetate dihydrate (ZA) and tin (IV) chloride pentahydrate in a polar solvent (2-methoxy ethanol) with a sol stabilizer (acetylacetone, acac; ZA : acac = 1 : 1.4,

mol ratio). Equivalent oxide content is kept fixed at 4 wt% in all the sols. Adherence of as-prepared precursor sols onto the cleaned soda-lime silica glass substrate (microscopic glass slide, Rivera, India, dimensions, 76.2 x 25.4 x ~1 mm) is found to be poor but after ageing the sols for about 48 h, we obtained homogenous films by dipping technique (Dip Master 200, Chemat Technology Inc., USA). The cured films under vacuum (-1 mBar) have been designated as ZSF1, ZSF2 and ZSF3 using the precursor sols having $R = 0.43, 0.49$ and 0.54 , respectively. The details regarding the sol preparation to film deposition are given elsewhere [10]. However, a flow diagram showing the preparative aspects is displayed in Figure 1.

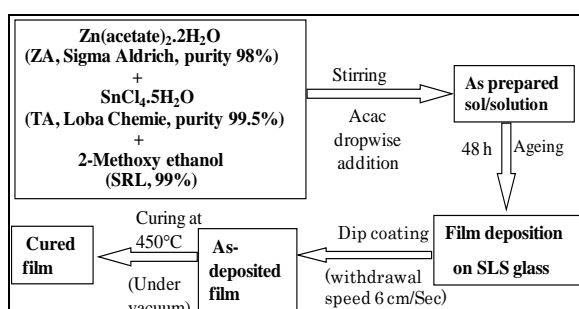


Fig. 1: Flow diagram showing the preparative aspects of precursor sol to film deposition

III. CHARACTERIZATIONS

Film physical thickness (T) has been measured by adopting an Auto Gain Ellipsometer (Gartner, model: L116B) at 632.8 nm He-Ne red laser source. It is found that on increasing Sn content, the thickness is increased from 26 nm to 43 nm. This can be due to increase of viscosity of precursor sol [10], [14]. Film crystallinity and crystal phase have been studied by using grazing incidence X-ray diffraction (GIXRD, Rigaku SmartLab) and $\text{CuK}\alpha$ (1.5406 Å) radiation source in the diffraction angle, 2θ to 60° . Transmittance spectra in the ultraviolet and visible regions have been recorded by an UV-Vis spectrophotometer (Shimadzu, Model: 3101PC). Microstructures including clustered shape and size of hexagonal ZnO have been analyzed by field emission electron microscope, FESEM (ZEISS, SUPRATM 35VP) and transmission electron microscope, TEM (G2 30ST, FEI, operating at 300 kV) and their tentative film compositions are found out from the corresponding EDS data. Photocatalytic activity of the films (total area, 19 cm^2) towards degradation of Rhodamine 6G dye (concentration, $1 \times 10^{-5} \text{ M}$) have been studied in a custom built stainless steel UV curing chamber well equipped with a lid and arrangement of three equally spaced UV lamps (wavelength, 254 nm and power, 8 watt each). The details of the measurement set-up have been reported elsewhere [10], [15].

IV. RESULTS AND DISCUSSION

The GIXRD patterns of films are displayed in Figure 2. As can be seen in the figure, from the intensity of appeared XRD peaks, the film crystallinity abruptly deteriorates on increasing Sn content of precursor sols and the ZSF3 film ($\text{Sn}/\text{Zn} = 0.54$) is found fully XRD amorphous. The crystalline films are found to enrich with hexagonal ZnO (h-ZnO) because the diffraction peaks with 2θ appears at $31.9^\circ, 34.5^\circ, 36.3^\circ, 47.6^\circ, 56.7^\circ, 63^\circ$ and 68° are matched [h-ZnO, JCPDS card 36-1451] [10] with the h-ZnO crystal phase. Interestingly, the h-ZnO is slightly orientated along (002) plane in ZSF2 ($\text{Sn}/\text{Zn} = 0.49$) film indicating the crystal growth occurs along c-axis which may result in rod-like ZnO structure (discussed later) formation. However, no crystalline phase or phases of SnO_2 and / or any compound of ZnO and SnO_2 are found from the XRD patterns. Hence, the oxide of tin may remain as amorphous phase in the film network. The decrease of crystallinity of the films with increasing Sn content may emphasize the increase of M-OH ($M = \text{Zn}, \text{Sn}$) [10] moiety which can lead to form three dimensional M-O-M network. This is because the Sn(IV) chloride pentahydrate may readily hydrolyze [16] in the sol. In this respect, it should mention that the zinc acetate dihydrate may also form Zn-OH by its own water of crystallization. Thus, the M-O-M network may prevent the film crystallization at the experimental annealing temperature of 450°C . On the other hand, the crystallite size of ZnO has been calculated along (002) plane using Scherer's equation [17]. We observe the crystallite size slightly decreases from $21.4 \pm 1.5 \text{ nm}$ to $19.4 \pm 1.3 \text{ nm}$ in ZSF1 and ZSF2 respectively. The M-O-M network formation may consider as one of the reason (discussed later) for the decrease of crystallite size. Surface morphology (Fig. 3a, b) of zinc tin oxide films is found to depend upon Sn content of precursor solutions. As seen from

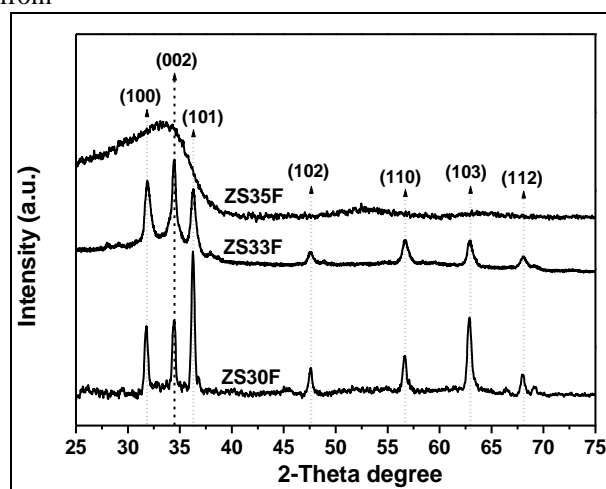


Fig. 2: GIXRD patterns of zinc tin oxide films. The XRD peaks are indexed to hexagonal ZnO (h-ZnO).

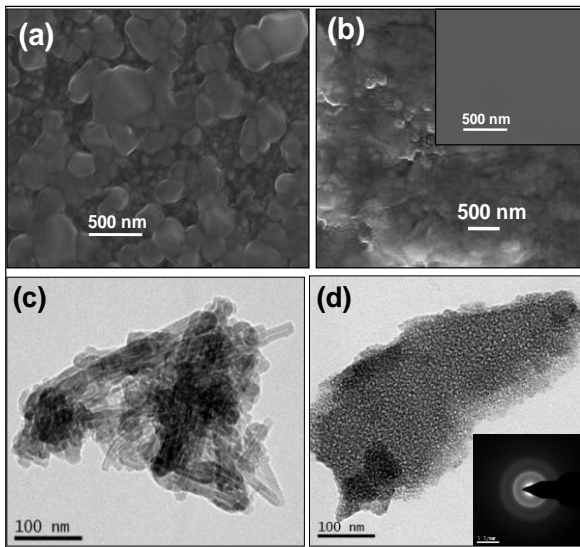


Fig. 3: (a), (b) Show FESEM images of ZSF1 and ZSF2, respectively. Inset of (b) is the FESEM image of ZSF3. (c) and (d) are the TEM bright field images of ZSF2 and ZSF3, respectively. Inset of (c) represents the selected area electron diffraction pattern (SAED), taken on the image of (d) of ZSF3 film. The diffused pattern indicates that the film is amorphous.

Figure 3a for ZSF1 film, the large quasi-spherical particles (size range, 250-570 nm) are randomly spread over relatively small particles (size range, 50-90 nm). This special surface feature may indicate relatively high crystallinity in ZSF1 film and also supports the XRD result (Fig. 2).

However, the surface feature (Fig. 3b) is seen to further change in ZSF2 film derived from the precursor sol of relatively higher Sn concentration. The film shows mostly agglomerated feature with some spherical particles (size ~165 nm) of clear grain boundaries. From the XRD results, the particles as observed from the FESEM images can be h-ZnO. Interestingly, from FESEM image of ZSF3 film which is XRD amorphous shows (inset, Fig. 3b) fully particle free smooth surface.

TEM measurements have been carried out for two representative films, ZSF2 and ZSF3. The bright field TEM images are shown in Fig. 3c and 3d for ZSF2 and ZSF3, respectively. In Fig. 3c, rod-shaped particles of wide sized length (80 – 275 nm) with diameter ~15 nm are found along with spherical shaped nano particles (size, 25-30 nm). These crystalline particles are ZnO as evidenced from its TEM-EDS (not shown here) analysis on the image (Fig. 3c). The EDS analysis shows that approximately 87 Zn and rest is Sn (considering only Zn and Sn) is present in the rods. The spherical particles can believe to be the primary ZnO particles which may self-organize [15] along c-axis of hexagonal ZnO to form the rod-shaped particles. Therefore, the TEM result also supports the XRD (Fig. 2) as the later shows the peak orientation along the (002) plane of h-ZnO. However, the amorphous character of ZSF3 (Fig. 3c) as observed from

the XRD pattern also is proved by TEM analysis. As seen in Fig. 3c, a continuous phase in TEM image of the film is observed and its diffused SAED confirms the amorphous character.

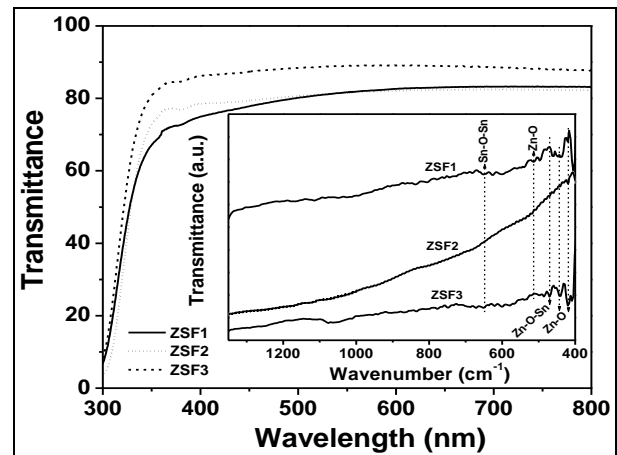


Fig.4: UV-Vis transmittance and substrate corrected FTIR (inset) spectra of zinc tin oxide films.

The percent (%) transmission (Fig. 4) of the films, both UV and visible regions are observed to differ on increasing Sn content of the precursor sols. However, the films show the %transmission roughly over 78 to 89% in the visible region. In the UV portion, there is a gradual increase of transmission from ZSF1 to ZSF3 films. The lower value %transmission can enhance the relative increase of absorption which may be useful for enhancing the photocatalytic efficiency of the films (discussed later). On the other hand, the enhancement of %transmission especially on increasing Sn content may be inversely related to the film crystallinity as evidenced from the XRD patterns (Fig. 2). The FTIR spectra (inset, Fig. 4) of substrate corrected films approximately show the vibrational peaks located at (i) ~420, ~440 and ~515; (ii) ~470 and (iii) ~645 cm^{-1} (very clear in ZSF3 film), attributed to [6], [10], [15], [18] Zn-O, Zn-O-Sn and Sn-O-Sn, respectively. The presence of Zn-O-Sn and Sn-O-Sn may support three dimensional network formations especially in the higher Sn content of the films. This result may also be a support for the change of crystallinity of the films as observed from the XRD measurement (Fig. 2). Photo catalytic activity (Fig. 5, Table 1) of the films towards decomposition of Rhodamine 6G dye under UV light (wavelength, 254 nm) irradiation is measured at room temperature. The dye decomposition rate constant, k (considering first order chemical kinetics) are 3.8×10^{-3} , 3.1×10^{-3} and $2.1 \times 10^{-3} \text{ min}^{-1}$ for the films ZSF1, ZSF2 and ZSF3, respectively. This indicates that the k value is decreasing on increasing Sn content of the precursor sols. It is known [10], [13] that a number of physical characters such as crystallinity, surface area (inversely related to particle size), etc. can control the photo catalytic activity (PA) of

semiconductors. The higher crystallinity [19] can minimize the recombination of photo-excited electron-hole pair while the lower particle size (higher surface area) may result in formation of the charge pair with stronger reductive/oxidative ability [10]. In the present work, we have already confirmed that the highest film crystallinity is attained by ZF1 film. However, the crystallinity is decreased rapidly with increasing Sn content. Moreover, the ZSF3 film confirms to be fully amorphous as evidenced from XRD and TEM results (Fig. 2 and Fig. 3). As the ZSF2 film is relatively lower crystalline in nature than the ZS1 film, a relatively lower k value can be expected in ZSF2 film compare to ZSF1 film. On the other hand, the amorphous character of ZSF3 film may be responsible for generating the lowest k value. This is because; the trapping and recombination sites of photo generated charges may be possible [20] by the physical defects which may present in amorphous semiconductors.

On the other hand, the crystallite size of ZnO which is found slightly lower in ZSF2 compare to ZSF1. However, the crystallinity factor is predominating over the particle size but lower %transmission particularly in the UV region (Fig. 4) may be a positive factor towards the dye decomposition in the present work. However, the film surface micro structural changes may definitively be playing a significant role towards the photo catalytic activity.

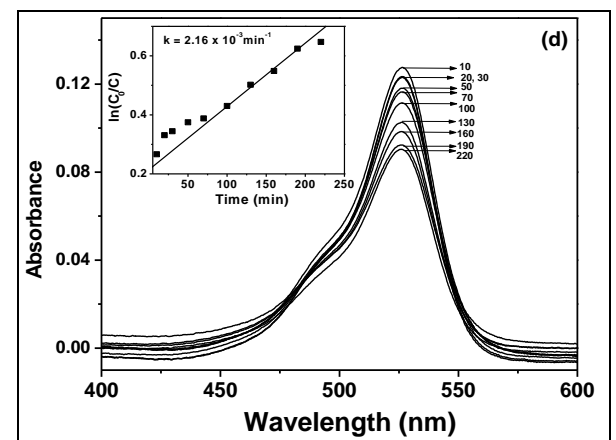
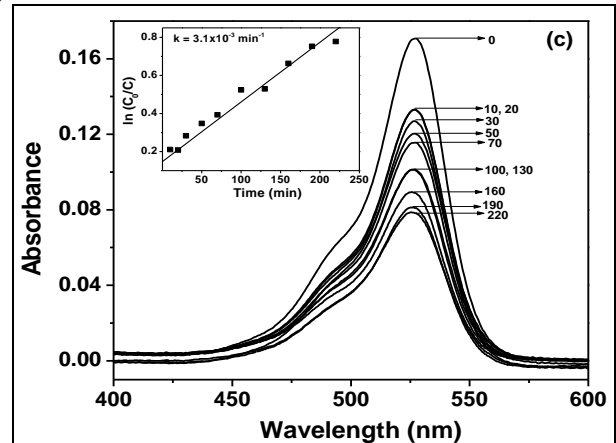
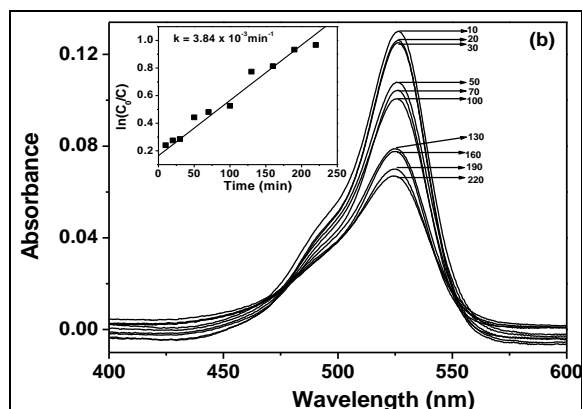
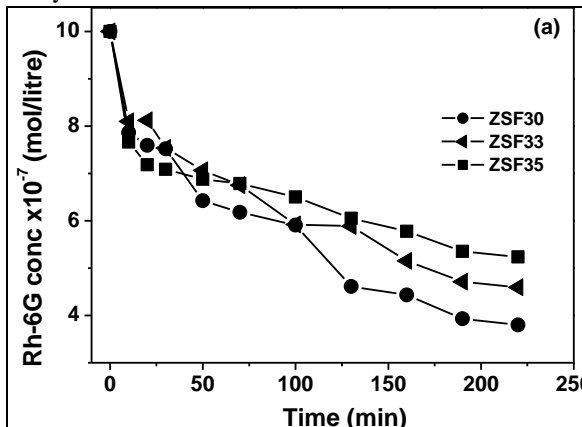


Fig. 5: Photocatalytic activity of zinc tin oxide films towards decomposition of Rhodamine 6G dye under UV light ($\lambda = 254$ nm) irradiation. (a) Plot of remnant dye concentration versus UV exposure time. (b), (c) and (d) represent the visible spectra of the dye solution at different exposure time using ZSF1, ZSF2 and ZSF3, respectively as photocatalysts. Insets show the determination of respective dye decomposition rate constants.

In brief, the PA of the vacuum annealed zinc tin oxide films can be tailored by changing the precursor solution composition. This study can be useful for tailoring the dye decomposition activity of other coupled semiconductor oxides thin films deposited by sol-gel technique.

Table 1: Photocatalytic activity of zinc tin oxide films towards dye decomposition under UV irradiation

Film	Percentage dye decomposition with irradiation time (min)										Dye decomposition rate constant ($\times 10^{-3}$ min ⁻¹)
	10	20	30	50	70	100	130	160	190	220	
ZSF1	21.0	24.1	24.8	35.8	38.2	40.9	53.8	55.6	60.7	62.0	3.80
ZSF2	18.8	19.0	24.7	29.4	32.5	40.8	41.2	48.5	52.9	54.1	3.10
ZSF3	23.4	28.1	29.2	31.3	32.2	35.0	39.5	42.2	46.5	47.6	2.10

V. CONCLUSION

Vacuum annealed zinc tin oxide thin films on soda lime silica glass have been deposited by dipping technique from the precursor sols of varying Sn to Zn atomic ratio, R (0.43 to 0.54) in 2-methoxy ethanol with

acetylacetone as sol stabilizer. In the crystalline films, the presence of hexagonal ZnO is observed but the film crystallinity is found to diminish on increasing R value while an amorphous film is obtained when the R is 0.54. An influence of Sn content on the film surface morphology and the percent UV-visible transmission is also observed. Photodecomposition activity of Rhodamine-6G dye under UV (254 nm) is noticed to be decreased with increasing film crystallinity. The film may find application towards decomposition of micro-organisms, and this study may be useful for tailoring the dye decomposition activity in other semiconductor oxides sol-gel based thin films.

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REFERENCES

- [1] C.-Y. Tsay, H.-C. Cheng, Y.-T. Tung, W.-H. Tuan and C.-K. Lin, *Thin Solid Films*, 517, 1032-1036, 2008.
- [2] A. Kurz and M.A. Aegerter, *J. Sol-Gel Sci. Technol.*, 31, 267-271, 2004.
- [3] M.-M. Bagheri-Mohagheghi and M. Shokooh-Saremi, *Thin Solid films*, 441, 238-242, 2003.
- [4] C.C. Li, X.M. Yin, Q.H. Li and T.H. Wang, *Cryst. Eng. Commun.* 13, 1557-1563, 2011.
- [5] S.K. Sinha, T. Rakshit, S.K. Ray and I. Manna, *Appl. Surf. Sci.*, 257, 10551-10556, 2011.
- [6] S. Jana, A.S. Vuk, A. Mallick, B. Orel and P.K. Biswas, *Mater. Res. Bull.*, 46, 2392-2397, 2011.
- [7] N. Samaele, P. Amornpitoksuk and S. Suwanboon, *Powder Technol.*, 203, 243-247, 2010.
- [8] B. Houng, C.-L. Huang and S.-Y. Tsai, *J. Cryst. Growth*, 307, 328-333, 2007.
- [9] M. Zhu, H. Huang, J. Gong, C. Sun and X. Jiang, *J. Appl. Phys.*, 102, 043106-1-043106-6, 2007
- [10] M. Pal, S. Bera and S. Jana, *J. Sol-Gel Sci. Technol.*, 67, 8-17, 2013.
- [11] C. Ge, C. Xie and S. Cai, *Mater. Sci. Eng. B*, 137, 53-58, 2007.
- [12] X.M. Liu, S.L. Wu, P.K. Chu, J. Zhang and S.L. Li, 426, 274-277, 2006.
- [13] J.H. Zeng, B.B. Jin and Y.F. Wang, *Chem. Phys. Letts.*, 472, 90-95, 2009.

- [14] S. Sarkar, R.D. Roy, P.K. Biswas, S.K. Bhadra and S. Jana, *IJETIT*, 3, 212-218, 2014.
- [15] M. Pal, S. Bera, S. Sarkar and S. Jana, *RSC Adv.*, 4, 11552-11563, 2014.
- [16] K.-T. Lee and S.-Y. Lu, *J. Mater. Chem.*, 22, 16259-16268, 2012.
- [17] S. Bera, M. Pal, S. Sarkar and S. Jana, *Appl. Surf. Sci.*, 273, 39-48, 2013.
- [18] S.G. Motke, S.P. Yawale and S.S. Yawale, *Mater. Sci. Bull.*, 25, 75-78, 2002.
- [19] Y. Tanaka and M. Suganuma, *J. Sol-Gel Sci. Technol.*, 22, 83-89, 2001.
- [20] R. He and T. Tsuzuki, *Proc., International Conference on Nanoscience and Technology (IOCNN)*, 22-26 February, 2010, Pages 154-157.

AUTHOR'S PROFILE



Moumita Pal is working as Senior Research Fellow (SRF) at CSIR-Central Glass and Ceramic Research Institute, Kolkata, India under the guidance of Dr. Sunirmal Jana, Principal Scientist for her Ph.D. (Science) degree. She received CSIR-UGC NET Fellowship for her Ph.D. dissertation. Ms Pal is working on semiconductor oxide based carbon and nano metal composites by sol-gel processing for photocatalytic activity. Ms Pal completed her M.Sc (Chemistry) from Vidyasagar University, West Bengal, India in the year 2010. Ms. Pal has published 4 research papers in SCI journals and 9 conference articles based on her area of research.



Susanta Bera is working as Senior Research Fellow (SRF) at CSIR-Central Glass and Ceramic Research Institute, Kolkata, India under the guidance of Dr. Sunirmal Jana, Principal Scientist for her Ph.D. (Science) degree. He received CSIR NET Fellowship for his Ph.D. dissertation. Mr. Bera is working on semiconductor oxide (SO) based nano composite materials such as SO-carbon, SO-nano metal; SO-rare earths composites by soft chemical processing. He completed his M.Sc (Chemistry) from Vidyasagar University, West Bengal, India in the year 2011. Mr. Bera has published 6 research papers in SCI journals and 9 conference articles based on his area of research.



Saswati Sarkar is working as Junior Research Fellow (JRF) at CSIR-Central Glass and Ceramic Research Institute, Kolkata, India under the guidance of Dr. Sunirmal Jana, Principal Scientist for her PhD (Sci) degree. Nano metal/alloy coated patterned dielectric thin films for sensor applications is her present field of research. Ms Sarkar completed her M.Sc (Chemistry) from Nagpur University, India. She has published 5 research papers in SCI journals and 6 conference articles based on the fabrication of grating based optical waveguide sol-gel thin films by soft lithography and nanomaterials.



Sunirmal Jana did his M.Sc. (Chemistry) in 1991 from Kalyani University, Nadia, WB, India and obtained his Ph. D. (Sc.) degree in 1998 from Jadavpur University, Kolkata, India. In December 1997, Dr. Jana joined CSIR-Central Glass and Ceramic Research Institute, Kolkata, India as Junior Scientist and presently working as Principal Scientist at the same Institute. His current areas of research are dielectric / semiconductor oxides based sol-gel thin films

and nanomaterials for optics and photonics applications (such as sensor, photocatalytic activity, radar absorbing etc.). Dr Jana has actively involved/coordinated various national and international research projects. At present, he published ~30 research articles in SCI journals, 59 conference articles, 4 Book Chapters and 3 Indian patents. He is the life members of Materials Research Society of India, Indian Ceramic Society, Indian Association for the Cultivation of Science and NCE Bengal & Jadavpur University, Kolkata, India. Dr. Jana availed Brain Pool Fellowship from Korean Federation of Science & Technology Societies (KOFST) at Korea Research Institute of Chemical Technology (KRICT), Daejeon, South Korea. He also worked as visiting scientists with foreign research Institutes (Slovenia and Portugal).