International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.2, pp 878-883, 2014-2015

ICONN 2015 [4th -6th Feb 2015]
International Conference on Nanoscience and Nanotechnology-2015
SRM University, Chennai, India

Influence of Annealing on Optical Fiber Gas Sensing Properties of TiO_2 Nanomaterial

B. Renganathan*, A.R. Ganesan

Applied Optics Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India

Abstract : A fiber optic toxic gas sensor with modified cladding region coated with a sensing material of TiO_2nonmaterial has been proposed in this work. The change in refractive index of the cladding and the phenomenon of evanescent wave absorption are used in the sensing principle here, to study the sensitivity towards toxic gases(acetone, isopropyl alcohol and benzene). The intensity variation is maximum at the wavelengths of 641.42 nm and 756.76 nm for and hence shows good sensitivity towards toxic gases. The sensor has been used for detection of toxic gases such as acetone. As-prepared and annealed(500 ºC,1200 ºC)samples were used as gas sensing media.The average particle size characterized from powder X-ray diffraction (XRD) was found to be around 13,16 &21 nm for as-prepared and annealed TiO_2nanomaterials respectively. The spectral characteristics of the fiber optic gas sensorare studied for various concentrations of toxic gases (0–500 ppmin steps of 50 ppm). The sensor exhibits linear variation in the spectral peak intensity with the acetone concentration. The characteristics of the sensor with benzene and isopropyl alcohol gases are also studied for gas selectivity. The time response characteristics of the sensor are reported.

Keywords: Fiber-optic sensor, Refractive index, Toxic gases, TiO_2, Room temperature, cladding modification, acetone gas.

Introduction:

The plastic optical fiber with cladding modification is very attractive for gas sensing because of its large dynamic range and high sensitivity. Optical modes propagating through the fiber interact with core and cladding interface and therefore are more sensitive to the changes in the cladding material, for gas sensing, Gas sensor at ambient temperature, is proposed based on cladding modification method in metal oxide, the advantages of the optical fiber sensor over conventional sensors are immune to electromagnetic radiation, low cost[1,2] TiO_2 is considered as one of the most interesting materials in the field of gas sensor, TiO2 is widely used as a gas sensing medium in electrical resistive type sensors because of its high gas Sensitivity& thermal stability [3,4,5]. Recently, the development of fiber optic chemical sensor, for the detection of toxic chemical gases such as acetone, isopropyl alcohol and benzene are studied and experimented. The gas sensor shows a linear variation in the output light intensity with the concentration. The light intensity as a function of concentration exhibits a linear increase for all gases as-prepared and annealed,1200 ºC in isopropyl alcohol and benzene gases only) whereas it decreases for all gases in 500 ºC. The cladding modified fiber sensor allows one to easily modify the cladding with different types of sensing materials in order to improve the gas sensing properties. In this paper, the gas sensing properties of TiO_2 nanoparticles using cladding modification technique is presented.

Experiment:

The fiber optic sensor uses a white light source (Halogen light source HL-2000) with wavelength ranging from 360 to 2000 nm and a miniature fiber optic spectrometer (Ocean optics USB4000) having spectral range of 200 to 850 nm. The heart of the sensor is the multimode step index optical fiber having length 42 cm and diameter 750 µm with the sensing region of about 3 cm at the center of the fiber. This fiber made up of poly (methyl methacrylate) (PMMA) is cleaved at both ends to have flat edges and is then integrated with the light source and the spectrometer. The refractive index of the core is 1.492 and cladding is 1.402. The gas sensing region is obtained by completely removing the clad part with the careful use of a razor without affecting the core of the fiber. This sensing region should be smooth and hence its uniformity was monitored by an optical microscope. Finally, the samples were mixed with isopropyl alcohol to form a paste and coated on the sensing region by dip coating method. After the coated fiber was dried at room temperature, the optical fiber was inserted into the gas chamber. Toxic gases prepared in different ppm levels (0-500 ppm) of acetone, isopropyl alcohol and benzene solutions were prepared separately and taken in a circular bottom flask for the study. Vapors produced from the flask were directly passed into the gas chamber through the gas inlet without any carrier gas. The outlet of the gas chamber was exposed to the atmosphere. The spectral response of the sensor was recorded for each concentration after 10 min by allowing the solutions to produce sufficient toxic vapors. Experiments were done in a dark room at room temperature and normal atmospheric pressure conditions. The level of relative humidity in the experimental atmosphere was around 71%.Were passed into the chamber and the intensity variations were recorded using the spectrometer interfaced with a personal computer. The response time required for the sensor to stabilize to its final value is fixed as 10 min for the accurate assessment of the change in the concentration of toxic gases. The experimental set up of the optical fiber sensor is given in the work of [1]

X-Ray diffraction analysis:

The powder X-ray diffraction studies were performed with a Rigaku diffractrometer using Cu K_α (0.15406 nm) radiation. A beam voltage of 40 kV and a 30 mA beam current were used. The data were collected in the 2θrange 20-80 ° with a continuous scan rate of 0.2 deg/min. Fig 1(a,b,c) shows the XRD pattern of TiO_2sample, indicating it was aanatase phase.X-ray line broadening analysis provides a method of finding bulk average size of coherently diffracting domains. The average crystallite size (D_v) from X-ray line broadening has been calculated using the Scherrer equation. $D_v = \frac{k\lambda}{\beta_{hkl}\cos\theta}$ where, D_v= volume weighted crystallite size, k= a constant usually taken to be unity, λ= wavelength of Cu $k\alpha$ radiation (1.5406 A°), β_{hkl} = integral breadth of reflection (in radians) located at 2θ and θ= angle of reflection (in degrees) was utilized for relating the crystallite size to the line broadening. XRD study reveals that the obtained TiO_2 products are anatase structure having nano sized particles with no impurity peaks. The values in the parenthesis indicate respective miller indices. The average crystallite sizes of as-prepared, annealed (500°C, 1200°C) TiO_2nanoparticles were found to be 13, 16 and 21nm, respectively. (fig:1(a,b,c).

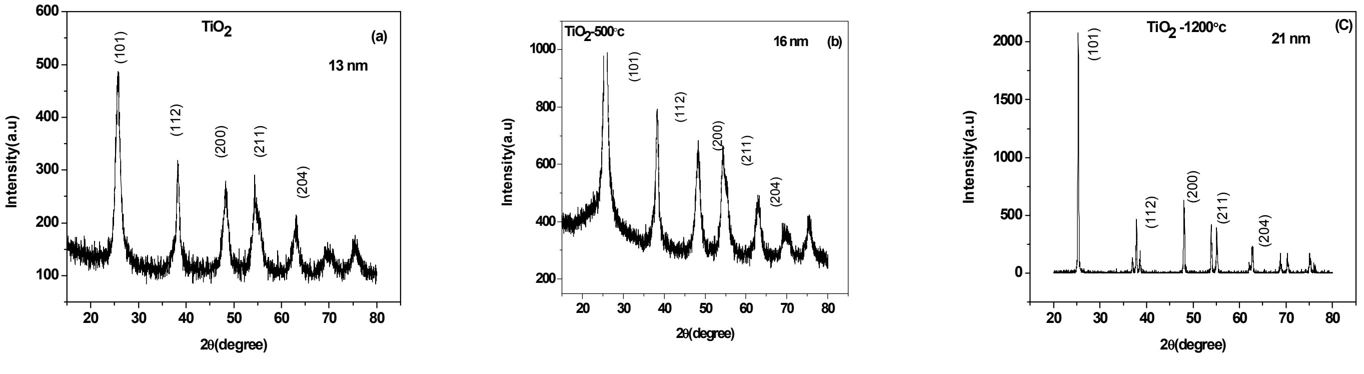


Fig.1 (a,b,c) Powder XRD pattern of nanocrystallineTiO$_2$ as prepared and TiO$_2$annealed(500˚c,1200˚c)

SEM and EDS analysis:

Figs.2(a,b,c,) show the SEM micrographs of the as-prepared and annealed (500^{o} $1200^{o}C$) samples of TiO_2nanoparticles. The different size and shape of the nanoparticles are observed in SEM micrographs of the as-prepared and annealed samples. All the SEM micrographs show the aggregation of many particles which are composed of many primary particles

The EDS spectrum of TiO_2 shown in Figs. 2(d.e,f)reveals the presence of Ti and O elements alone in the sample TiO_2 and TiO_2(500^{o},1200^{o})) shows the presence of Ti, and O elements, confirming the absence of any other impurities. The atomic percentage of the elements, Ti and O in$TiO_2$are 58.15 and 41.85 %, TiO_2 (500^{o}) 66.73 and33.27 and TiO_2(1200^{o}) 65.35 and 34.65 respectively, which shows oxygen deficiency in the sample.

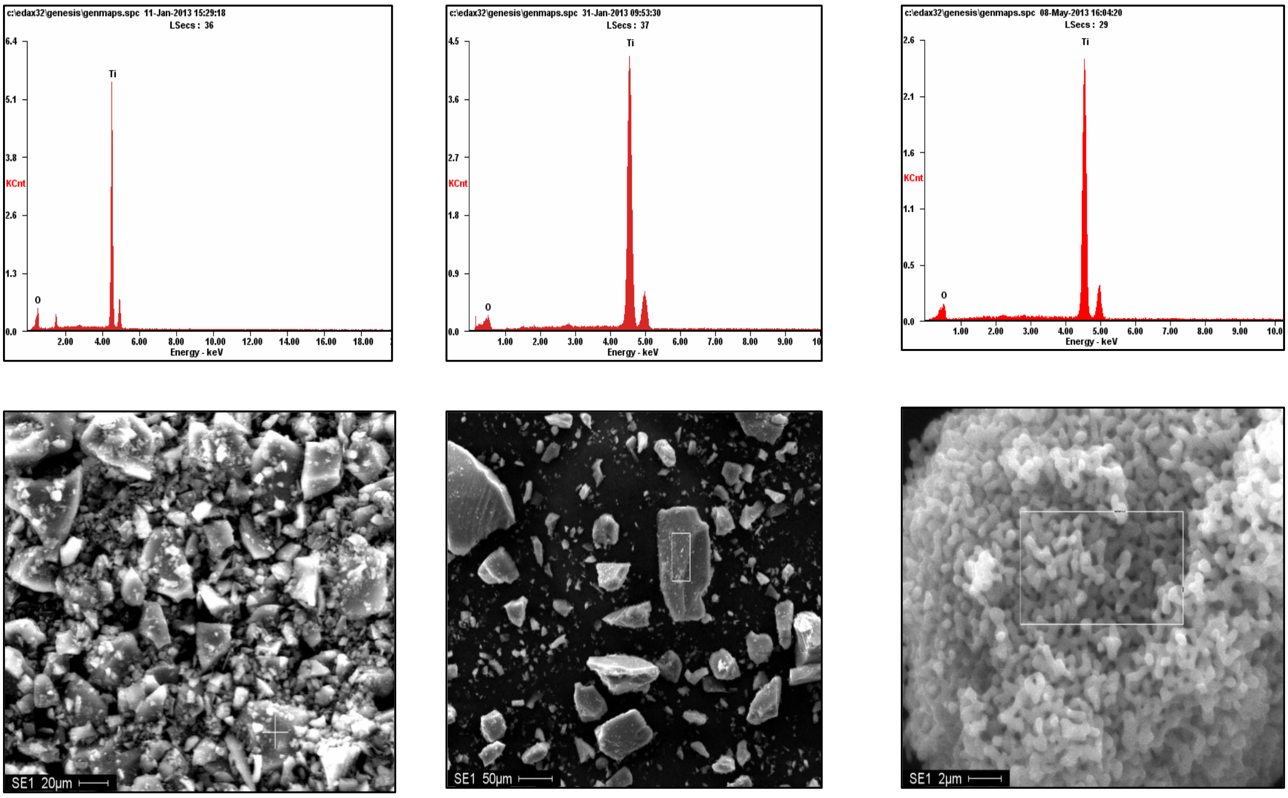


Fig.2 SEM micrographs and EDS of as prepared TiO_2(a,b,c) and TiO_2annealed($500^{\circ}c$,$1200^{\circ}c$) (d,e,f)

Results and discussion:

Basic operation of fiber optic gas sensor

Exposure of sensors to chemical or physical stimulus will vary the intensity of the light signal traveling through an optical fiber. The attractive feature of the fiber optic sensor using cladding modification is its large dynamic range and high sensitivity. Optical modes such as total internal reflection or partial reflection modes which propagating through the fiber interact with the core/cladding interface which are more sensitive to the refractive index changes in the coated cladding material[1].

Sensing property of proposed sensor

The phenomenon of total internal reflection (TIR) occurs in any optical waveguide such as planar waveguide or an optical fiber for the guidance of light. To satisfy the TIR, the guiding region i.e. core, has to have a refractive index larger than the surrounding regions, i.e. cladding. In leaky waveguides, the cladding region with low refractive index will have a finite thickness comparable to the penetration depth of the guided light field [2]. The refractive index of core (n_c = 1.49) lower than modified cladding (n_{mc}=2.4). When the incident light is reflected from an interface at an angle greater than the critical angle, the total internal reflection occurs. However, its intensity does not abruptly decay to zero at the interface and a small portion of light penetrates into the reflecting medium. This penetrated electromagnetic field is called the evanescent wave [2].

Fig 3 (a-c) shows the output spectral characteristics of as-prepared and annealed TiO_2samples exposed to acetone, isopropyl alcohol and benzene for various concentrations. The spectra exhibit two peaks around 642.41and 756.76 nm. The spectral intensity increases with the increase in the concentration of three gases for as prepared, annealed at 1200^{o}C) It is seen that the spectral intensity decreases with the increase in the concentration of three gases with concentration of acetone, isopropyl alcohol and benzene in annealed 500^{o}C.

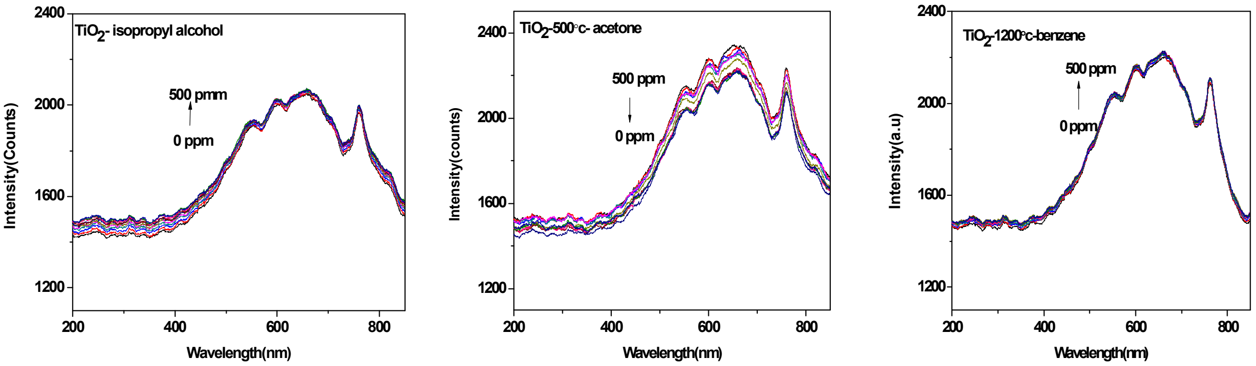
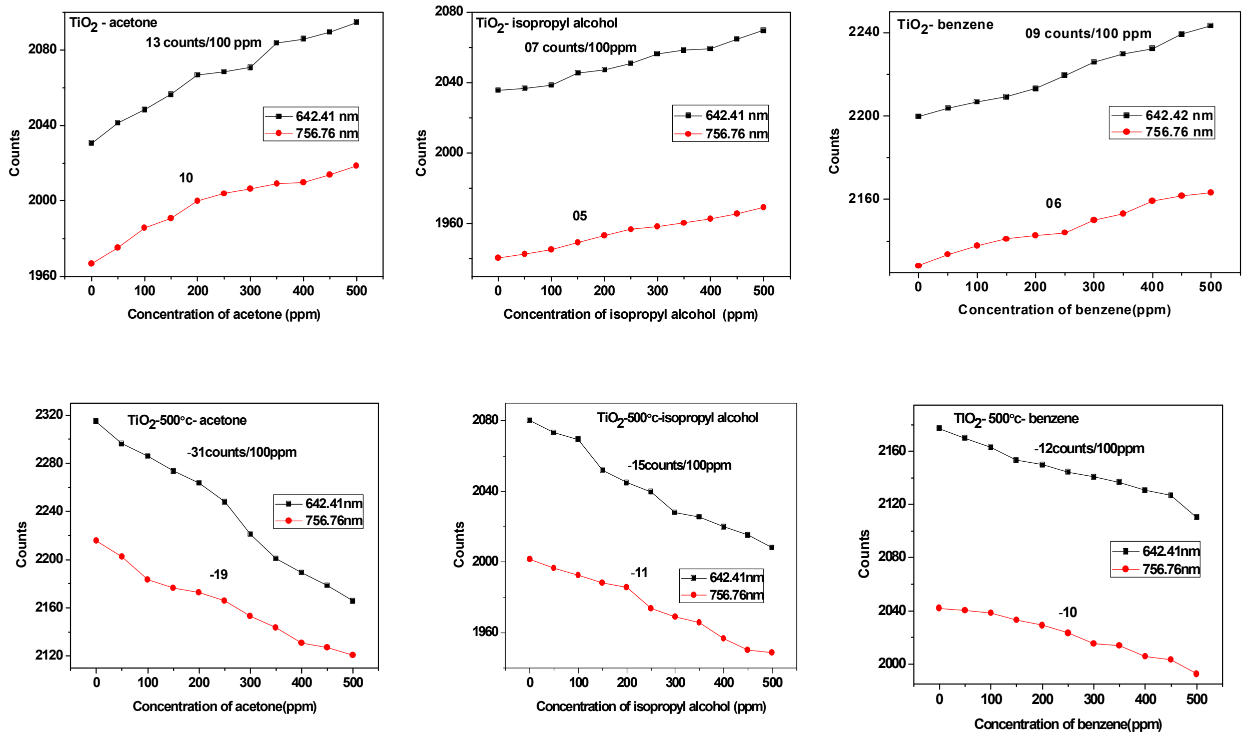


Fig. 3(a to c) Spectral response of TiO_2 as prepared and annealed at (500˚c, 1200˚c) in Isopropyl alcohol, acetone and benzene

Figs4(a-i) give the plot between the spectral peak intensity (642.41 nm) and vapour pressure of acetone, isopropyl alcohol and benzene gases for as-prepared and annealed. The as prepared sample exhibits highest gas sensitivity for acetone (13counts/100ppm). Annealed sample at 500^{o}C exhibits highest gas sensitivity for acetone gas (-31counts/100ppm). And annealed TiO_2 1200^{o}C exhibits highest gas sensitivity for isopropyl alcohol(21 counts/100ppm) In the case of as-prepared sample, it is about 13, 07 and 09 (counts/100ppm) for acetone, isopropyl alcohol and benzene, respectively. It is -31, -15 and -12(counts/100ppm) in the case of annealed sample at 500^{o}C, and (-20,21and 07(counts/100ppm) in the case of annealed (1200^{o}C) Tio2. Another peak intensity (wavelength) 756.76nm of as-prepared sample, it is about 10, 05 and 06 (counts/100ppm) for acetone, isopropyl alcohol and benzene, respectively. It is -19, -11 and -10(counts/100ppm) in the case of annealed sample at 500^{o}C, and (-16,19and 06(counts/100ppm) in the case of annealed (1200^{o}C) Tio2.



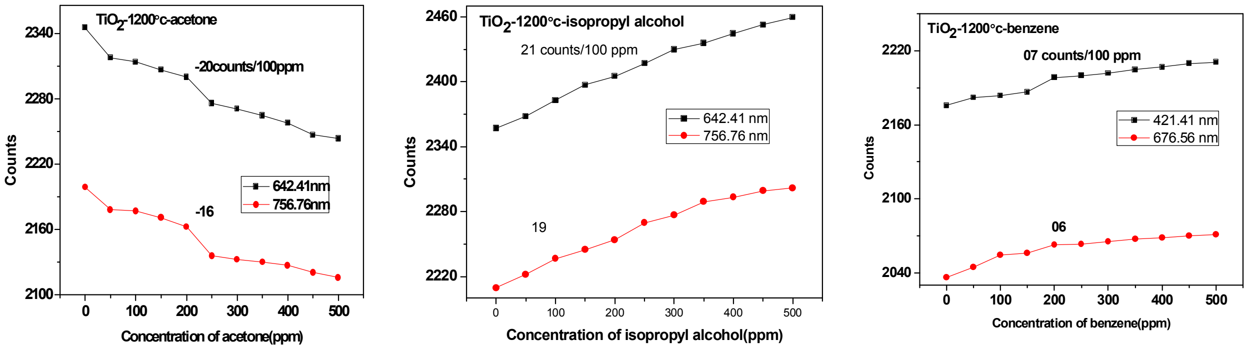


Fig. 4 Plot of obtained peak intensity for different concentrations of as prepared TiO_2 (a-c) and annealedTiO_2 (500˚c(d-f),1200˚c(g-i)) for acetone, isopropyl alcohol and benzene

Though, the annealed (500°C) sample exhibits higher gas sensitivity for acetone, the spectral characteristics are same for all gases (Table 1). Hence, the gas selectivity may be represented in terms of highest gas sensitivity. Thus, TiO_2 is best suitable for acetone gas detection. Fig. 5 shows the time response characteristic for the chamber to reach 500 ppm of acetone after the vapor has been let in, which shows a good reversibility. The response time was calculated by observing the time duration the sensor signal (at 642nm) took for raising from 10% to 90% of the maximum and for recovery time, the intensity fall from 90% to 10% of the maximum. The response time and recovery time were found to be about 17 min. and 15 min.

Table 1 Gas sensitivity of TiO_2 for various gases

Vapours	Gas Sensitivity (Counts/100ppm)					
	TiO_2					
	As prepared		Annealed			
			500°C		1200°C	
Acetone	13	↑	-31	↓	-20	↓
Isopropyl alcohol	07	↑	-15	↓	21	↑
Benzene	09	↑	-12	↓	07	↑

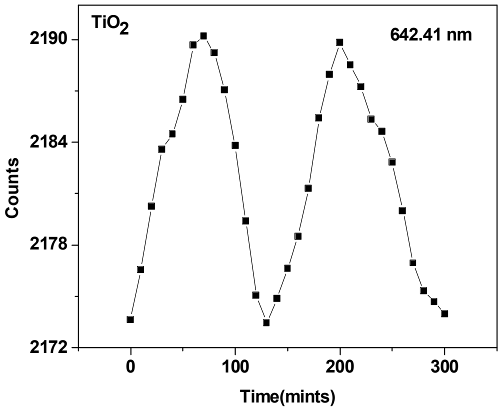


Fig .5 Time response of a sensor forTiO_2

Conclusion:

Fiber optic gas sensor is developed for different concentrations (0-500 ppm) of acetone, isopropyl alcohol and benzene. The TiO_2 and annealed served as a good gas sensor and they exhibited enhanced response for the prepared acetone(annealed 500) emissions as well as for isopropyl alcohol and benzene gas at room temperature. Among the three gas vapors, acetone (500)showed higher sensitivity than isopropyl alcohol and benzene. This phenomenon exhibited acetone selectivity among isopropyl alcohol and benzene.

Acknowledgement

One of the authors (B.R.) acknowledges the DST/SERB, New Delhi, India for financial support by the fast track project for young scientists (Letter No. SB/FTP/ETA-99/2013dated 03.09.2013).

References:

1. Renganathan.B and. Ganesan.A.R., "Fiber optic gas sensor with nanocrystalline ZnO", Optical Fiber Technology, 2014, 20;48-52 .
2. Renganathan .B**,** Sastikumar.D, Gobi.G, Rajeswari Yogamalar.N, and Chandra Bose.A, *Sens. Actuators B*, 2011,156; 263- 270.
3. Karunagaran,B,thirakumar, P.,Chung ,S.J, Velumani,S, and Suh,E-K, "TiO2thin filmgassensor for monitoring ammonia" Mater.Char.2007,58; 680-684.
4. 4.Manera, M.G., Spadavecchia,J., Buso,D.,Fernandez,C. J., Mattei,G.,Martucci, A.,Mulvaney,P., Perez- Juste, J. R., Rella, J., Vasanelli, L.andMazzoldi, P., "Optical gas sensing ofTiO2 andTiO2/Au nanocompositethinfilms", Sens.ActuatorsB,2008,132; 107-115.
5. 5.Ruiz,A.M.,Cornet,A.,Morante,J.R.,"PerformanceofLa-TiO_2 nanoparticiles as gassensingmaterial" Sens.Actuators B,2005,111;7-12.

*****