www.amlett.org, www.amlett.com, DOI: 10.5185/amlett.2012.5350 Published online by the VBRI press in 2012

Fabrication of ultra-sensitive optical fiber based humidity sensor using TiO_2 thin film

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Received: 12 May 2012, Revised: 14 July 2012, Accepted: 17 July 2012

ABSTRACT

Thin films of titanium dioxide in anatase form have been prepared using isobutyl titanate as precursor. The resulting TiO_2 was coated on an U-shaped pyrex glass rod to sense the humidity of a controlled humid environment using optical fiber approach. The humidity sensing characteristics and the sensing mechanism have been investigated by measuring the output power of the sensor at different humidity. The developed humidity sensor was responded in the humidity ranging from 10 to 95% of relative humidity and exhibited the sensitivity of 0.78, response time 36s and recovery time 73s. Copyright © 2012 VBRI Press.

Keywords: Humidity sensor; titanium oxide; sensing mechanism; optical fiber.

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Introduction

Titanium oxide (TiO_2) is an interesting n-type semiconducting material due to fundamental properties. It has wide range industrial applications such as chemical sensor, catalyst, paint, and medicine and antireflection coatings on solar cells [**1-3**]. Further, advent of nanotechnology increases its applications many fold and different nanostructures of TiO_2 have been used for different types of sensing applications [**4-6**]. TiO_2 can be prepared using techniques like sputtering, vacuum evaporation, pulse laser deposition, molecular beam epitaxial, sol-gel, chemical bath deposition etc. [**7-9**]. However, sol–gel methodology is relatively cheap, convenient and produces good quality materials which can be used in the different form of films and coatings [**10**].

These days, demand of humidity sensors has been exponentially increased in industrial process control, manufacturing of sophisticated integrated circuits, intelligent control of living environment, cooking control of microwave oven, sterilizers, incubators and pharmaceutical process [**11-12**]. The humidity sensors are developed by using wide range of materials including TiO_2 [**13-14**]. However, most of humidity sensors are insensitive at low humidity level and provides limited detection range as listed in **Table 1**. Further, the anatase form of titania has high water adsorption capacity and better photocatalytic activity [**22**]. Further, TiO_2 film prepared by sol-gel method with sintering for few minutes at temperatures below 500 ^{0}C is more suitable for humidity sensing purposes [**23-24**]. Therefore, it is essential to develop a reliable, portable, sensitive and economical humidity sensor.

In this communication we report the development of thin film of TiO_2 on glass substrate employing dip → dry → fire technique at 450 ^{0}C with related characterization through different analytical techniques including TG-DTA, FTIR XRD and SEM. The efforts have also been made to use one of the TiO_2 coated on U- shaped substrate for wide range humidity sensing of a controlled humid environment using optical fiber approach.

Experimental

Materials

Isobutyl titanate (99.9%, Aldrich, USA) and butyl alcohol (99.8%, E. Merck, Germany) have been used without further purifications. All supplementary chemicals were of analytical grade.

Preparation of TiO_2 film using precursor solution

The precursor solution was prepared by diluting isobutyl titanate by butyl alcohol in v/v ratio of 1:100 under the anhydrous condition. The solution was then stored in anhydrous condition and used to cast the film on U-shaped pyrex glass rod (length: 2.5 cm and diameter: 1 cm) by dip-dry technique. Later, the film was annealed to ~ 450 ^{0}C in order to decompose into TiO_2 after removing organic components from precursor solution. The titanium oxide film was also casted on glass substrate using the spin coating technique at 2000 rpm to perform physico-chemical and spectroscopic characterization.

Characterization

Chemical characterization was done using Perkin-Elmer (RK-1310) FTIR spectrometer whereas TG-DTA was studied with Rigaku Thermoflex PTC-10A thermal analyser at 10 ^{0}C per min heating rate. The structure and morphology was observed by Rigaku Rotaflex (RAD/ Max-200B), Rigaku Corporation, Japan X-ray diffractometer at 1^0 per minute scanning speed and JEOL-840, JEOL Corporation Japan, scanning electron microscope (SEM) after sputtering a gold film. The moisture adsorption behavior was studied by ESCA -750, Shimadzu Corporation Japan X- ray photoelectron spectrometer.

Device fabrication and humidity sensing measurement

The above titania coated U-shaped pyrex glass rod was fixed on the wall of a glass fitted in a glass chamber (4 cm × 7 cm) via two holes. The both arms of U-shaped glass rod were projected outside and coupled with optical fiber.

Table 1. Comparison of the characteristics humidity sensors.

Sensing Material	Sensor type	Sensing range	Reference
Gallium-doped ZnO	Impedancometric	30–90%	[**15**]
KCl-doped ZnO nano-fibers	Impedancometric	25–95%	[**16**]
ZnO–In_2O_3	Electrical type	11-95%	[**17**]
ZnSnO	Electrical type	11-97%	[**18**]
Chitosan	Optical type	20-95%	[**19**]
Polyaniline nanofiber	Impedance	20-90%	[**20**]
TiO_2	Optical type	-	[**21**]

The unpolarized laser light from He–Ne laser source (2 mW) was passed from one end of the fiber and the output intensity was measured at the other end of the optical fiber using by optical power meter.

A reference hygrometer and thermometer was also kept inside chamber to monitor absolute humidity and temperature. The used experimental setup is shown in **Fig. 1** [**25-26**]. During experimental observations setup, the relative humidity inside the sensing chamber was variably controlled up to 90% using saturated solution of potassium hydroxide. All experiments were conducted at room temperature (~25 ◦C) maintained by air conditioner using identical setup of measurements. However, prior to each measurement the sensor element was heated in vacuum at 100 ◦C for 60 min to completely remove the adsorbed moisture.

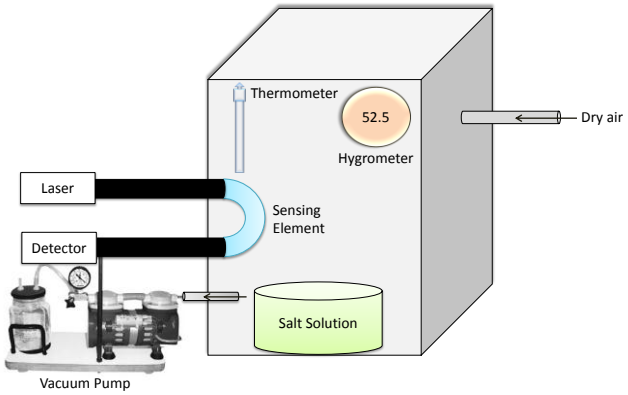

Fig. 1. Experimental setup for humidity sensing measurement.

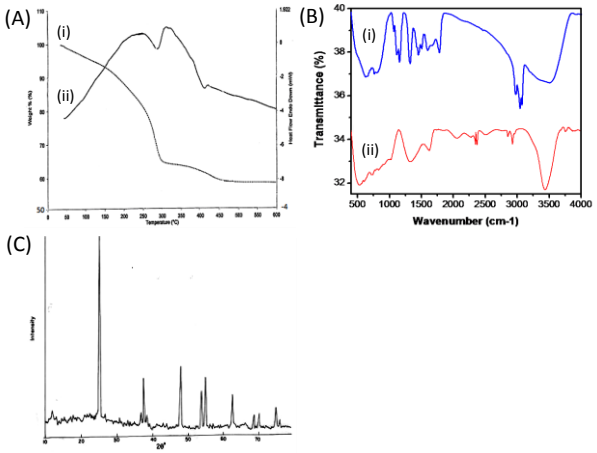

Fig. 2. (A) Curve of precursor film (i) TG and (ii) DTA; (B) FTIR spectra of (i) precursor material (ii) TiO_2; and (C) XRD of TiO_2 thin film.

Results and discussion

Characterization of TiO_2 film

The TG-DTA curve of precursor film is shown in **Fig. 2a**. The TG curve shows weight loss in three steps: i) RT - 150 ^{0}C, ii) 150 - 345 ^{0}C and iii) 350 – 440 ^{0}C, **Fig. 2a(i)**. The mass loss in first is due to desolvation, while in second and third steps are because of decomposition and formation of titanium oxide. The DTA curve shows two endothermic peaks at 287 ^{0}C and at 406.29 ^{0}C, **Fig. 2a(ii)**. However, in the initial step of weight loss (between RT -150 ^{0}C), DTA does not show any sharp peak. This is because of the discrete weight loss (like evaporation) from the surface and decomposition is completed up to 450 ^{0}C.

The FTIR spectrum of the precursor film (isobutyl titanate) and TiO_2 is shown in **Fig. 2b** (i) and (ii), respectively. The major absorption bands of -CH_3 and -CH_2 corresponding to butyl titanate is not present in the spectrum of the TiO_2 deposit. This means that the organic butyl titanate was completely decomposed without organic remains in the deposit.

The XRD spectrum of synthesized titanium oxide is shown in **Fig. 2c**. The spectrum matches well with reported pattern of anatase form of titania [**27**]. The absence of any other peak in the XRD spectrum confirms the purity of prepared film. Moreover, SEM photographs of synthesized titanium oxide are shown in **Fig. 3**. The thin film of precursor changed morphology with respect to temperature curing up to 450 ^{0}C in **Fig. 3(a-c)**. The bigger particles appeared like cluster of particles or the association of some particles because of symmetric nature of TiO_2 particles refractive index of cladding changes due to adsorption of water vapors and subsequently transmitted output power trough optical fiber also changes. This change in output power is used to estimate the humidity inside chamber [**30**]. The trend of recorded output power against the humidity after heat curing at 200 ^{0}C is shown in **Fig. 3b**. After 450 ^{0}C temperature treatment, precursor film attained uniformly distributed TiO_2 cubes of ~ 80-25 nm size (**Fig. 3c**).

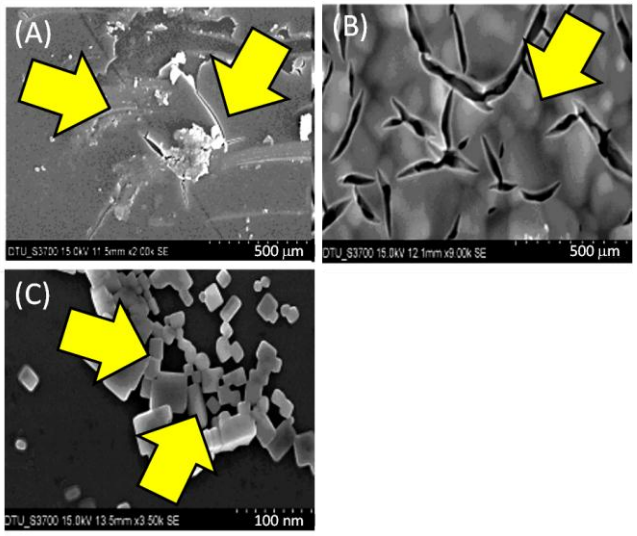

Fig. 3. SEM images of (A) precursor film, (B) precursor film heated at 200 ^{0}C, and (C) precursor film heated at 450 ^{0}C.

Sensing behavior

Most of the TiO_2 based humidity sensors are electrical type; however limited reports are available using optical transducer. In general, optical method has advantages like free external (electric and magnetic) interference, low cast, high sensitivity, and miniaturization. The small size of

optical sensor and the possibility of multiplexing the information make it useful for industrial and domestic applications [**28-29**].

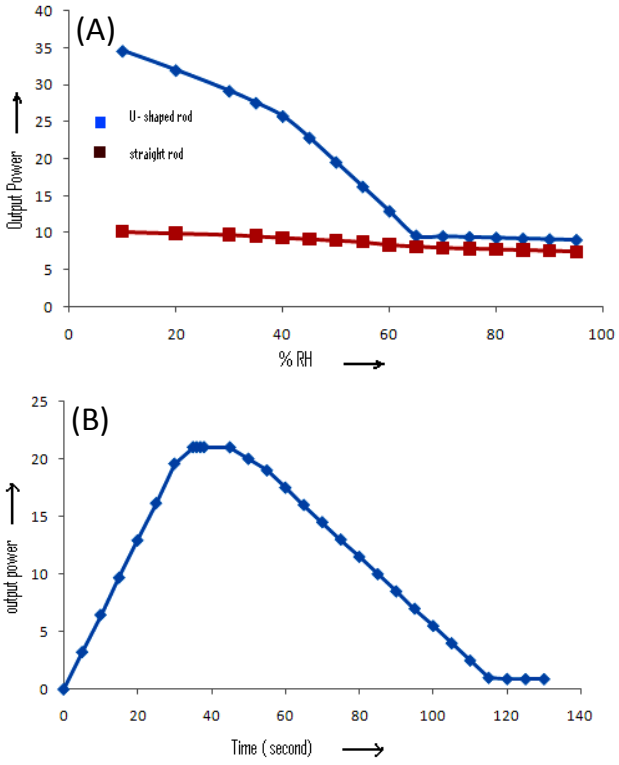

Fig. 4. (A) Variation of light output power in different humidity environment and (B) Response time curve of TiO_2 coated on U-tube.

The surface sensitive property of the optical fiber coated with TiO_2 as cladding (i.e., after the removal of the original cladding from the optical fiber) was used for humidity sensing purposes in the present study. The through optical fiber coated with TiO_2 is shown in **Fig. 4a**. The output power decreases with the increase in humidity. The change in output power is may be due to decreases the refractive index of TiO_2 by adsorption of water vapor molecule. Since, the refractive index of titania varies from 1.8 to 2.7, i.e., depending upon film preparation techniques and refractive index of H_2O is 1.33. Thus, composite layer (optical fiber coated with TiO_2) shows lower refractive index than TiO_2, which results in the decrease of output power based on Snell equation.

The lowering of output power can also be explained by change in density of composite layer after absorption of water molecules. The reported density of TiO_2 is 3.84 and of H_2O is 1.004 g per cc. Thus, the density of titania may alter after adsorption of H_2O and which may cause change in transmittance of light, and resulted decrease in output power with particular adsorption characteristics. **Fig. 4a** shows the two curves for U- shaped rod and straight rod. It was observed that U- shaped rod is highly sensitive as compared to straight glass rod. Since, in straight glass rod the interaction of light in the cladding of TiO_2 and water molecules is less as the light transmits through the fiber including the glass rod, whereas U-shaped rod provides ample scope for light interaction with so called cladding of TiO_2 and water molecules. Therefore, sensing element coated on U- shaped rod is shown highly sensitive. The sensitivity of sensor element towards humidity was calculated as per reported method [**31**]. The sensitivity was found the best in 10-62% RH, i.e., 0.78 after that the value decreases to 0.11. It may be because after 62% RH the TiO_2 layer may get saturated with H_2O and reduces the H_2O adsorption. The change in output power with time at fixed humidity is shown in **Fig. 4b.** The graph infers the response time 36s (i.e., time of 90% change in output power), recovery time of 73s (i.e., time to recover the original output power). The sensing behavior was found stable up to 60 day.

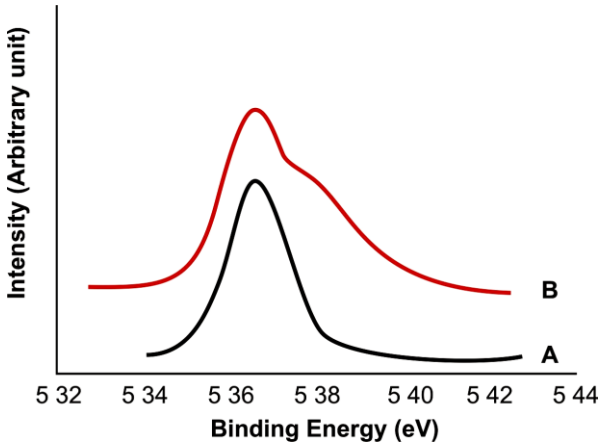

Fig. 5. XPS study of (A) TiO_2 film and (B) TiO_2 film after exposed to humidity.

Further, water adsorption behavior on TiO_2 surface was studied using XPS spectra of TiO_2 before and after exposure to humidity (~65% RH). The spectra are shown in **Fig. 5**. There is a clear shift in O ($2p_{3/2}$) peak after exposing the film due moisture with 0.95 eV. The small value in shift indicates the weak type physiosorption. It supports the reversibility quality of film as sensing surface easily after dehumidifying. The reaction may be represented similar to equation (1).

$$TiO_2 + H_2O \leftrightarrow TiO_2.xH_2O \qquad (1)$$

Sensing mechanism

The earlier proposed optochemical sensing mechanism was based on adsorption and capillary condensation depends on surface morphology. Typically, the adsorption behaviour at diffuse (gaseous phase) concentration can be expressed as equation (2) [**32-34**].

$$\text{(Sensing platform)} + \text{(Water vapor)} \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} \text{(Sensing platform)} - \text{(Water vapor)} \qquad (2)$$

where K_1 and K_2 are adsorption and desorption rate constants. The amount of water molecule (Δm) adsorbed on

sensing layer at particular time. %RH value is given by Langmuir adsorption isotherm condition [**33-34**].

$$\Delta m_t = [(\text{Sensing platform}) - (\text{Water vapor})]_t \quad (3)$$

$$= \Delta m_\infty [1-\exp(- t / \tau)] \quad (4)$$

$$\tau^{-1} = K^1[\text{Water vapor molecules}] + K^{-1} \quad (5)$$

where Δm_∞ is the maximum molecules adsorbed on the sensing film at $t \to \infty$ and τ is the relaxation time. The adsorption time courses at various concentrations were determined using above equations. The linear correlation can be achieved between inverse of relaxation time ($1/\tau$) of adsorption and relative humidity (concentration) of water molecules on sensing film. This yields the adsorption rate constant K^1, desorption rate constant K^{-1} and association constant $K = \frac{K^1}{K^{-1}}$ for water molecules on the sensing film. The obtained values of τ^{-1} are shown in **Fig. 6**. The straight line confirms the validity of Langmuir model up to 60% RH. The Langmuir model proposes the presence of entire homogeneous adsorption sites, which is perhaps not present in the present humidity sensitive surface. The complete solution is beyond the scope of present study.

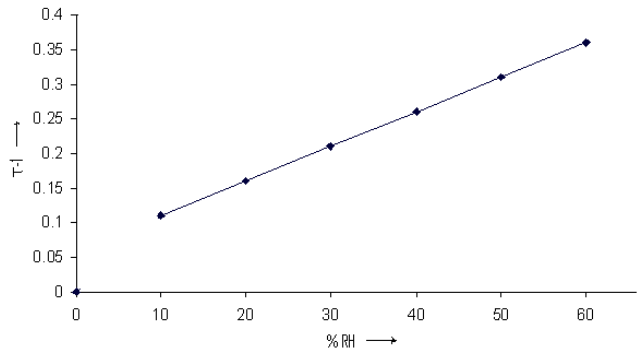

Fig. 6. Plot of reciprocal of relaxation time (τ^{-1}) against percent relative humidity (%RH).

Table 2. Amount adsorption and desorption temperature on TiO_2 surface at different %RH.

RH %	Quantity of H_2O adsorbed (%)	Desorption temperature (^{0}C)
20	0.78	105.0
40	0.85	107.5
60	0.96	109.0
80	1.01	112.5
95	1.07	125.0

Further, a close study of the sensing mechanism [**35-36**] needs to be categorized either a) surface reaction b) external diffusion c) mass transport or d) fractal reaction. The type of reaction decides the time dependent rate coefficient as well as sensor efficiency. In present case the efforts have been made to explain this by measuring the extent of water adsorption at different RH values on TiO_2 surface and the desorption temperature (**Table 2**). The values reveal that increase in desorption temperature at higher RH values and lowering in extent of adsorption. It may be conclude that in the present case the limited external diffusion type reaction is taking place. Since, the extent of adsorption becomes quite reduced after 62 % RH. Which is may be due to low diffusion potential of H_2O molecule in gaseous form after a define relative humidity of environment.

Conclusion

In this study, we have fabricated and characterized of titanium oxide films. The optical permeability of the films was strongly affected by the presence of H_2O even at very low amount and can be highly applicable as ultra-sensitive humidity sensing probe for range of applications. The response of sensing element to other interfering chemical species (such as ethanol, methanol, and ammonia) was found be very low. The obtained system could be used as active element in solid-state moisture sensors. The attempt has been made to explain suitable sensing mechanism along with other sensing parameters.

Acknowledgements

Authors thank to University Grant Commission (UGC), Government of India for financial support (MRP. 8-3(47)/2011) and Principal, Bhaskaracharya College Applied Sciences, University of Delhi, India for permission to use laboratory.

Reference

1. Fujishima, A., Honda, K. Nature 1972, 238, 37. **DOI:**10.1038/238037a0
2. Chen X., Mao S. S., Chem. Rev. 2007, 107, 2891. **DOI:** 10.1021/cr0500535
3. Dubey G. C., Solar Cell, 1985, 15, 1.
4. Gu, L., Wang, J., Cheng, H., Du, Y., Han, X., Chem. Commun. 2012, 48, 6978. **DOI:** 1039/c2cc33163B
5. Zhu, Y., Shi, J., Zhang, Z., Zhang, C., Zhang, X., Anal. Chem. 2002, 74, 120. **DOI:** 10.1021/ac010450p
6. Kim I. D., Rothschild A., Lee B., Dong H., Kim Y, Jo S. M., Tuller H. L., Nano Lett., 2006, 6, 2009. **DOI:** 10.1021/nl061197h
7. Imhof A., Pine D.J., Nature, 1997, 389, 948. **DOI:** 10.1038/40105
8. Liu H. , Wang W. , Ma Y., Cao Y. and Cao J. , New J. Chem, 2002, 26, 975. **DOI:** 10.1039/B202102C.
9. Murugan A. V. , Samuel V., Ravi V., Mater. Lett, 2006, 60, 479. **DOI:** 10.1016/j.matlet.2005.09.017
10. Han D., Li Y., Jia W., Adv. Mat. Lett. 2010, 1, 188. **DOI:** 10.5185/amlett.2010.7137
11. Chen Z., Lu C., Sensor Letters, 2005, 3, 274. **DOI:** 10.1166/sl.2005.045
12. Yamazoe N., Shimizu Y., Sens. and Actuators 1986, 10, 379. **DOI:** 10.1016/0250-6874(86)80055-5
13. Srivastava R. and Yadav B. C., Adv. Mat. Lett. 2012, 3(3), 197. **DOI:** 10.5185/amlett.2012.4330
14. Shukla S.K., Bharadvaja A., Tiwari A., Pilla S., Parashar G.K., and Dubey G.C., Adv. Mater. Lett. 2010, 1, 129. **DOI:** 10.5185/amlett.2010.3105
15. Su P.G., Tseng J.Y., Huang Y.C., Pan H. H., Li P. C., Sens. Actuators B 2009, 137, 496. **DOI:** 10.1016/j.snb.2009.01.026
16. Qi Q., Zhang T., Wang S., Zheng X., Sens. Actuators B 2009, 137, 649.

DOI: 10.1016/j.snb.2009.01.042
17. Lianga Q., Xu H., Zhao J., Gao S., Sens. Actuators B 2012, 165, 76. **DOI:** 10.1016/j.snb.2012.02.019
18. Bauskar D., Kale B. B., Patil P., Sens. and Actuators B 2012, 161, 396. **DOI:** 10.1016/j.snb.2011.10.050
19. Chen L.H., Li T., Chan C. C., Menon R., Balamurali P., Shaillender M., Neu B., Ang X. M., Zu P., Wong W. C. and Leong K. C., Sensors and Actuators B 2012, 169, 167. **DOI:** 10.1016/j.snb.2012.04.052
20. Lin Q., Li Y., Yang M., Sensors and Actuators B 2012, 161, 967. **DOI:** 10.1016/j.snb.2011.11.074
21. Yadav, B.C., Shukla R.K., Ind. J. Pure. Appl. Phys. 2003, 41, 681.
22. Zheng Z., Wang C.C., Zakaria R., Ying J.Y., J. Phys. Chem B, 1998, 102, 10871. **DOI:** 10.1021/jp982948
23. Chow L.L., Yuen M.M.F., Chan P.C.H., and Cheung A.T., Sens. and Actuators B: Chem., 2001, 76, 310. **DOI:** 10.1016/S0925-4005(01)00602-5
24. Montesperelli G. , Pumo A. , Traversa E., Gusmano G., Bearzotti A. , Montenero A., Gnappi G., Sens. Actuators B 1995, 24-25, 705. **DOI:** 10.1016/0925-4005(95)85156-9
25. Shukla S. K., Parashar G. K., Mishra A. P., Mishra P., Yadav B. C., Shukla R. K., Bali L. M., Dubey G. C. , Sens. and Actuators B: Chem., 2004, 98, 25. **DOI:** 10.1016/j.snb.2003.05.001
26. Shukla S.K., Tiwari A., Parashar G.K, Mishra A.P., Dubey G.C., Talanta, 2009, 80, 565. **DOI:** 10.1016/j.talanta.2009.07.026
27. Shibata R.T., Iric H., Ohmori M. , Nikiyama A., Watanabe T., Hashimoto R., Phys. Chem, Chem. Phys, 2004, 6, 1359. **DOI:** 10.1039/B315777F
28. Brook T.E, Taib M.N., Narayanaswamy R., Sens. and Actuators B, 1997, 38-39, 272. **DOI:** 10.1016/S0925-4005(97)80217-1
29. Wolfbeis O.S., Anal. Chem. 2004, 76, 3269. **DOI:** 10.1021/ac040049d
30. Yadav B.C., Shukla R.K., Bali L.M., Ind. J. Pure Appl. Phys. 2005, 43, 51. **IPC:** G06K 7/10
31. Yadav B.C., Yadav R. C., Dwivedi P. K, Sensors and Actuators B 2010,148, 413. **DOI:** 10.1016/j.snb.2010.05.046
32. Ando M., Trends Anal. Chem. 2006, 25, 937. **DOI:** 10.1016/j.trac.2006.06.009
33. Su P.G., Huang L.N., Sens. Actuator B. 2007, 123, 501. **DOI:** 10.1016/j.snb.2006.09.036
34. Su P-G and Chang Y-P., Sensors and Actuators B: Chemical, 2008, 129, 915. **DOI:** 10.1016/j.snb.2007.10.006
35. Qu W., Meyer J.V, Meas. Sci. Technol., 1997, 8, 593. **DOI:** 10.1088/0957-0233/8/6/002
36. Biju K.P., Jain M.K., Sens. Actuators B, 2008, 128, 407. **DOI:** 10.1016/j.snb.2007.06.029

