

# Liquid petroleum gas sensing performance enhanced by CuO modification of nanocrystalline ZnO–TiO<sub>2</sub>

R.B. PEDHEKAR<sup>1,\*</sup>, F.C. RAGHUWANSHI<sup>2</sup>, V.D. KAPSE<sup>3</sup>

<sup>1</sup>G.H. Raisoni College of Engineering & Management, Amravati 444701, India

<sup>2</sup>Vidya Bharati Mahavidyalaya, Amravati 444602, India

<sup>3</sup>Arts, Science & Commerce College, Chikhaldara 444807, India

Nanocrystalline ZnO–TiO<sub>2</sub> (with molar ratios 9:1, 7:3, 1:1, 3:7 and 1:9) were successfully synthesized by hydrothermal method. Synthesized materials were examined with the help of X-ray diffraction and transmission electron microscope. Liquid petroleum gas sensing characteristics of the ZnO–TiO<sub>2</sub> films were investigated at different operating temperatures. The ZnO–TiO<sub>2</sub> thick film (with 1:1 molar ratio) exhibited good response toward liquid petroleum gas as compared to other investigated compositions. Further, liquid petroleum gas sensing characteristics of CuO modified ZnO–TiO<sub>2</sub> thick films were investigated. 0.2 M CuO modified ZnO–TiO<sub>2</sub> thick film exhibited excellent liquid petroleum gas sensing characteristics such as higher response (~1637.49 at 185 °C) with quick response time (~30 s), low recovery time (~70 s), excellent repeatability and stability at low operating temperature.

Keywords: ZnO–TiO<sub>2</sub>; nanocrystalline material; gas sensor; CuO

© Wrocław University of Technology.

## 1. Introduction

Liquid petroleum gas (LPG) is highly inflammable as it mainly consists of butane mixed with compounds of sulfur (methyl mercaptan and ethyl mercaptan) which have foul smell. It is hazardous because an explosion might be caused when it leaks accidentally. It has been reported that the concentration level of LPG noticeable by smell is higher than the lowest explosive limit of the gas in air. As it is used for both domestic and industrial purposes there is a great rise in demand for gas sensors to monitor the concentration level of LPG.

There are many parameters of materials for gas sensor applications such as adsorption ability, catalytic activity, sensor response, stability, etc. There are a number of research publications reporting the application of metal oxides in gas sensors [1–7]. In metal oxide based gas sensors, gas-sensing mechanism is a surface-controlled phenomenon. It is a well-known fact that sensor response depends upon the grain size, surface state and oxygen adsorption.

Larger surface to volume ratio offers more adsorption and increases sensor response [8, 9]. Physical and chemical properties of materials depend on synthesis methods, synthesizing conditions, etc. In the literature, several methods are described for synthesis of nanomaterials such as chemical, mechanical, gas phase and molten salt synthesis [10]. Hydrothermal technique is a chemical synthesis method which allows fabrication of shaped, size-oriented materials without involving any melting steps. There are a number of advantages of this method, such as the short duration of experiments as compared to the classical procedures of synthesis, more control over crystal size and level of agglomeration, low cost instruments and less consumption of energy as compared to other synthesis routes. Also, it is an eco-friendly method [11, 12].

Semiconductor metal oxides like ZnO, SnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub> etc. have been investigated for the detection of gases [13–15]. However, very few of them are suitable to fulfil all the requirements. To overcome these limitations, researchers have recently been focused on composite materials like SnO<sub>2</sub>–ZnO [16], Fe<sub>2</sub>O<sub>3</sub>–ZnO [17], ZnO–CuO [18],

\*E-mail: rajeshpedhekar@gmail.com

etc., because it has been recognized that sensors developed by mixing two components together are more sensitive than those made of individual component. This is due to a synergistic effect between two metal oxides [17]. Preparation of mixed oxides leads to alteration of the electronic structure of the system which causes changes in the bulk as well as in the surface properties [19]. Surface properties are expected to be affected by new boundaries between grains of different chemical compositions. It is anticipated that all these phenomena will contribute favorably to the gas-sensing mechanism [20]. Furthermore, it was reported that adequate and specific selection of impurities is connected with an optimum response of materials for a specific gas. Materials like CuO, Fe<sub>2</sub>O<sub>3</sub>, etc., when dispersed onto semiconductor oxide films, enhance the sensor response to the reducing gas [21, 22]. This paper reports the effect of CuO modification of ZnO–TiO<sub>2</sub> thick film on LPG sensing properties. The experimental results show that the CuO modification of ZnO–TiO<sub>2</sub> thick film greatly improves the sensing response toward LPG selectively against CO<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>S with good repeatability and stability at low operating temperature. In addition, variation of gas response with operating temperature and amount of CuO in a film is presented graphically. The results are interpreted on the basis of surface morphology of the film and conclusions are summarized.

## 2. Materials and method

### 2.1. Synthesis of nanocrystalline ZnO–TiO<sub>2</sub>

For obtaining nanocrystalline ZnO–TiO<sub>2</sub> (sample A) with a molar ratio 9:1, analytical grade ZnO and TiO<sub>2</sub> were dispersed in aqueous NaOH solution followed by hydrothermal treatment at 180 °C for 24 h in a Teflon-lined autoclave. Then, it was allowed to cool naturally and the obtained precipitate was isolated from the solution by centrifugation at 5000 rpm for 30 min and subsequently washed with distilled water and ethanol and then dried at 120 °C for 12 h. The same procedure was followed for the synthesis of ZnO–TiO<sub>2</sub> with molar

ratios 7:3 (sample B), 1:1 (sample C), 3:7 (sample D) and 1:9 (sample E). The synthesized materials were examined by X-ray diffraction (XRD, X'Pert PRO) and transmission electron microscope (TEM, Techai G2 20).

### 2.2. Fabrication of sensor element and gas-sensing measurements

A thixotropic paste was formulated by mixing the synthesized nanocrystalline ZnO–TiO<sub>2</sub> powder sample with ethyl cellulose and a mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and terpeneol. Then the prepared paste was screen printed on a glass substrate. The same procedure was followed for fabrication of thick films of other synthesized material samples. Furthermore, the thick film of ZnO–TiO<sub>2</sub> (with a molar ratio 1:1) was modified by dipping it into 0.1 M, 0.2 M and 0.3 M aqueous solutions of copper chloride (CuCl<sub>2</sub>) for 30 min. The films were dried in air and fired in a heating furnace at 450 °C for 24 h. They were termed as CuO modified ZnO–TiO<sub>2</sub> thick films. For the measurements of gas sensing properties of all the films, silver electrodes were used for electrical contacts.

Gas-sensing measurements were carried out on a computer-controlled static gas-sensing system. Ni–Cr alloy coil was used for heating and a chromel–alumel thermocouple was used to monitor temperature. Picometer cum voltage source (Keithley 6487) was used to measure the sensor resistance. Test gas was injected into the chamber through an inlet port. The concentration of gas was kept at 286 ppm and a well dried gas with relative humidity 20 % was used to avoid the moisture effect on the sensor response. The sensor response (*S*) was defined as the ratio of resistance in air (*R<sub>a</sub>*) to that in target gas (*R<sub>g</sub>*) [23]:

$$S = R_a/R_g \quad (1)$$

## 3. Results and discussion

### 3.1. Materials characterization

Fig. 1 shows X-ray diffraction (XRD) patterns of synthesized ZnO–TiO<sub>2</sub> powder samples. From

the XRD patterns, it is seen that the materials are polycrystalline in nature with mixed hexagonal and tetragonal phases. The characteristic peak in the XRD pattern matches the hexagonal ZnO (JCPDS Card No. 00-036-1451) and tetragonal TiO<sub>2</sub> (JCPDS Card No. 01-071-1166). Also, the peaks which appeared at  $2\theta = 29.95^\circ$ ,  $36.83^\circ$ ,  $56.74^\circ$ ,  $62.18^\circ$  and  $70.41^\circ$  correspond to Zn<sub>2</sub>TiO<sub>4</sub> (JCPDS Card No. 01-073-0578). The extra peak that appeared at  $2\theta = 44.8^\circ$  is related to surface hydroxyl groups on the ZnO–TiO<sub>2</sub> surface [24]. The average crystallite size (D) was determined by using Debye-Scherrer formula [25]:

$$D = 0.9\lambda / \beta \cos \theta \quad (2)$$

where  $\lambda$  is the wavelength of incident beam (1.5406 Å),  $\beta$  is the full width at half maximum (FWHM) of the peak in radian and  $\theta$  is the diffraction angle. The average crystallite size of samples A to E was calculated from bordering of the diffraction line and found to be in the range of 49 nm to 68 nm.

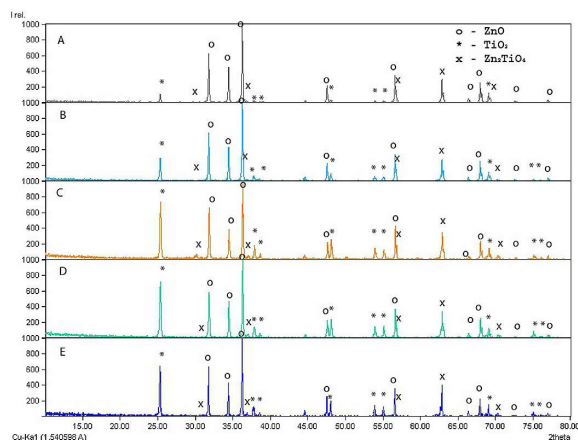


Fig. 1. XRD patterns of synthesized ZnO–TiO<sub>2</sub> powder samples with molar ratios (A) 9:1, (B) 7:3, (C) 1:1, (D) 3:7 and (E) 1:9.

The morphology of the synthesized material samples was further investigated by transmission electron microscope (TEM). Fig. 2 illustrates TEM images of synthesized ZnO–TiO<sub>2</sub> powder samples with molar ratios (A) 9:1, (B) 7:3, (C) 1:1, (D) 3:7 and (E) 1:9. The small amount of agglomerations can be seen in the micrographs. TEM images

confirm that the average crystallite size of the synthesized material is in nanometer range.

The surface morphology and nature of ZnO–TiO<sub>2</sub> thick films with molar ratios (A) 9:1, (B) 7:3, (C) 1:1, (D) 3:7 and (E) 1:9 were analyzed by using scanning electron microscope (SEM, JEOL JSM 6380A). SEM images of ZnO–TiO<sub>2</sub> thick films with molar ratios (A) 9:1, (B) 7:3, (C) 1:1, (D) 3:7 and (E) 1:9 are shown in Fig. 3. From the SEM images it can be seen that the ZnO–TiO<sub>2</sub> thick film (molar ratio 1:1) has a large number of pores which account for maximum porosity and high surface roughness which results in large surface to volume ratio. Moreover, it appears that the film surface is almost crack free. This improves the LPG sensing response of the film.

The elemental composition of 0.1 M, 0.2 M and 0.3 M CuO modified and unmodified ZnO–TiO<sub>2</sub> thick films (molar ratio 1:1) were analyzed by using an energy dispersive X-ray spectrometer (EDS). From the spectra, it can be seen that major constituent elements of ZnO–TiO<sub>2</sub> thick film are O, Ti, Zn and the major constituent elements of CuO modified ZnO–TiO<sub>2</sub> thick films (molar ratio 1:1) are Cu, O, Ti, Zn. The elemental composition of 0.1 M, 0.2 M and 0.3 M CuO modified and unmodified ZnO–TiO<sub>2</sub> thick films (molar ratio 1:1) is shown in Table 1.

Fig. 4 shows the SEM images of 0.1 M, 0.2 M and 0.3 M CuO modified ZnO–TiO<sub>2</sub> (with a molar ratio 1:1) thick films. CuO dispersion on the surface of the ZnO–TiO<sub>2</sub> thick film is confirmed by comparing the SEM image of ZnO–TiO<sub>2</sub> (with a molar ratio 1:1) thick film with SEM images of 0.1 M, 0.2 M and 0.3 M CuO modified ZnO–TiO<sub>2</sub> (with a molar ratio 1:1) thick films. It indicates that the microstructure of 0.2 M CuO modified film is uniform with an adequate dispersion of CuO.

### 3.2. I-V characteristics of nanocrystalline ZnO–TiO<sub>2</sub> thick films

Fig. 5 shows I-V characteristics of ZnO–TiO<sub>2</sub> thick films with molar ratios (A) 9:1, (B) 7:3, (C) 1:1, (D) 3:7 and (E) 1:9 in air ambient at room temperature. The graphs indicate the ohmic nature of the contact between silver electrodes and the film.

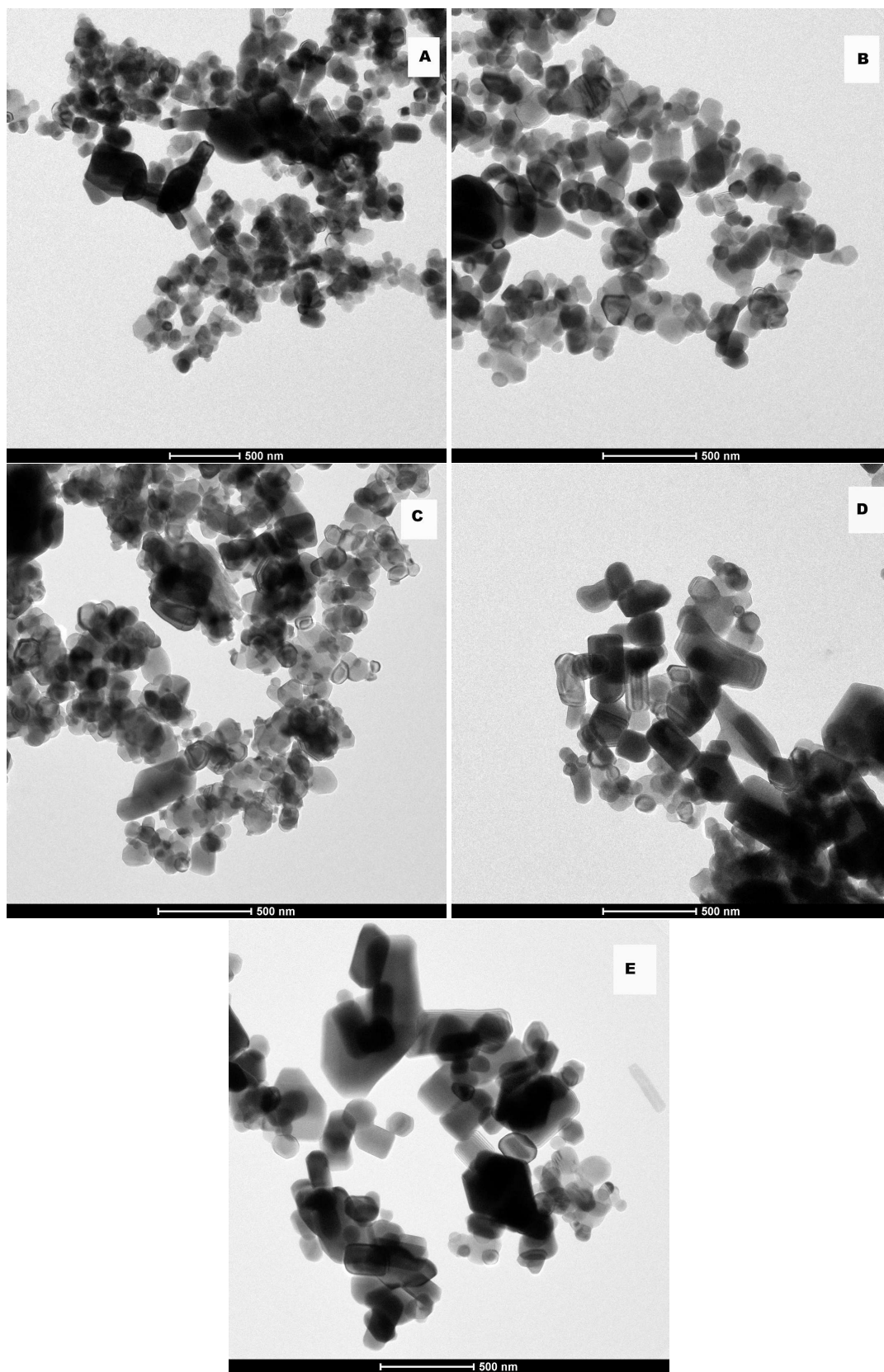


Fig. 2. TEM images of synthesized ZnO-TiO<sub>2</sub> powder samples with molar ratios (A) 9:1, (B) 7:3, (C) 1:1, (D) 3:7 and (E) 1:9.



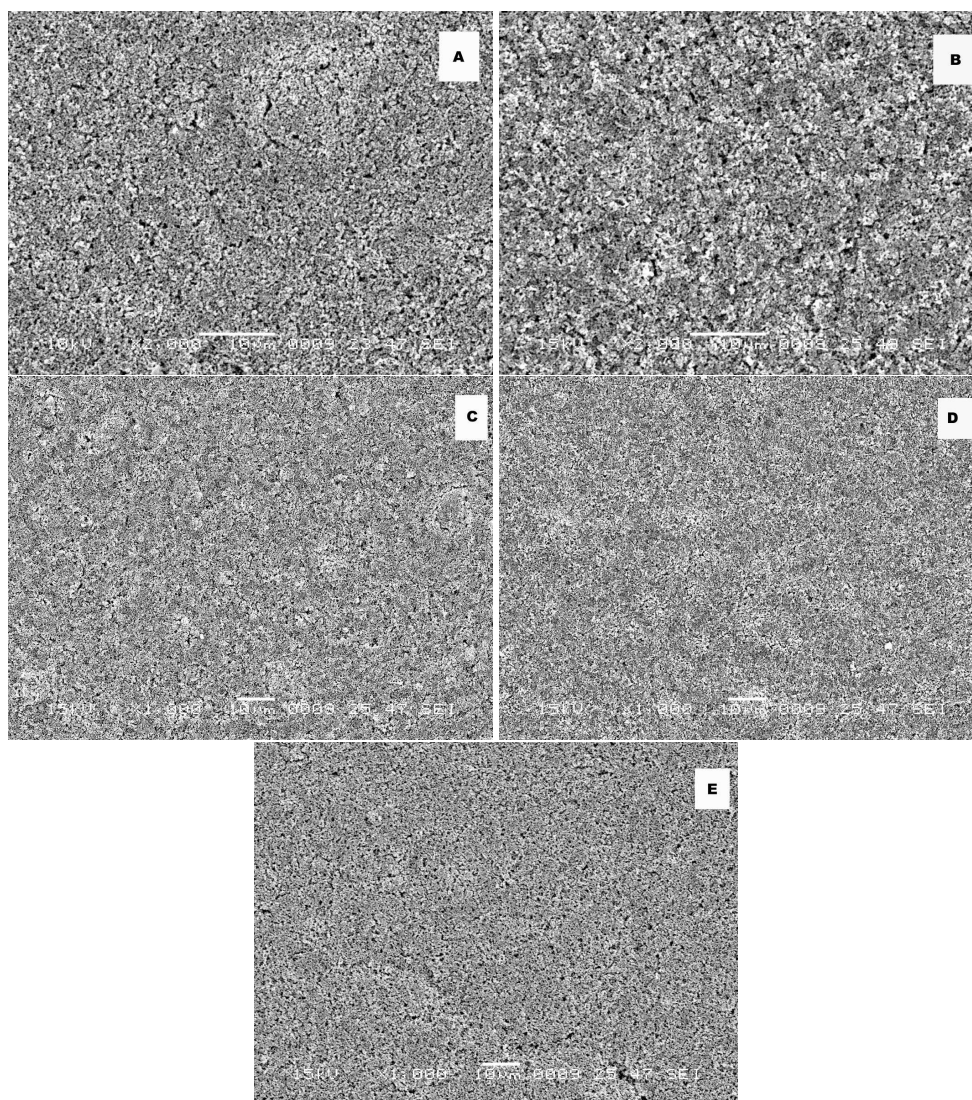


Fig. 3. SEM images of ZnO–TiO<sub>2</sub> thick film with molar ratios (A) 9:1, (B) 7:3, (C) 1:1, (D) 3:7 and (E) 1:9.

Table 1. Composition of 0.1 M, 0.2 M and 0.3 M CuO modified and unmodified ZnO–TiO<sub>2</sub> thick film (molar ratio 1:1).

Element wt.%	0.1 M CuO		0.2 M CuO		0.3 M CuO		ZnO–TiO <sub>2</sub> (molar ratio 1:1)	
	Norm. wt.%	Atom. at.%	Norm. wt.%	Atom. at.%	Norm. wt.%	Atom. at.%	Norm. wt.%	Atom. at.%
O	29.62	60.61	24.53	54.17	21.81	50.57	32.58	63.30
Zn	1.09	0.54	1.24	0.67	1.05	0.60	40.66	19.33
Ti	21.67	14.74	21.31	15.73	19.92	15.43	26.76	17.37
Cu	47.62	24.41	52.92	29.43	57.22	33.40	Nil	Nil

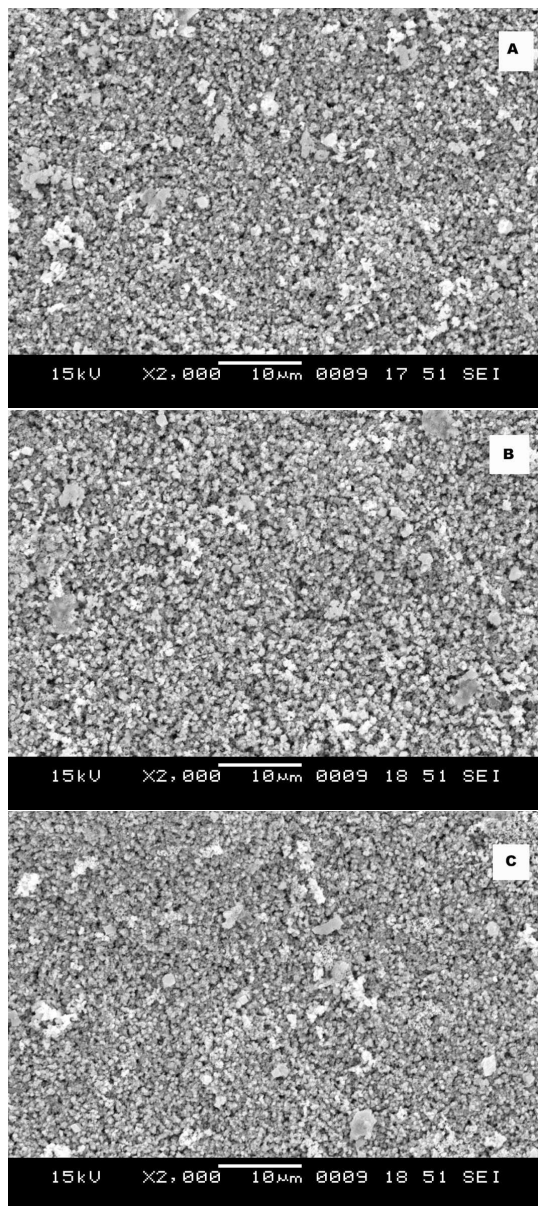


Fig. 4. SEM images of ZnO-TiO<sub>2</sub> thick films (with molar ratio 1:1), modified with (A) 0.1 M CuO, (B) 0.2 M CuO, (C) 0.3 M CuO.

### 3.3. Gas sensing characteristics

Fig. 6 illustrates the response of ZnO-TiO<sub>2</sub> based thick films with molar ratios (A) 9:1, (B) 7:3, (C) 1:1, (D) 3:7 and (E) 1:9 towards 286 ppm LPG. The films were maintained at different operating temperatures in the range of 30 °C to 225 °C and tested for 286 ppm LPG. From the figure, it can be seen that within the studied temperature range and

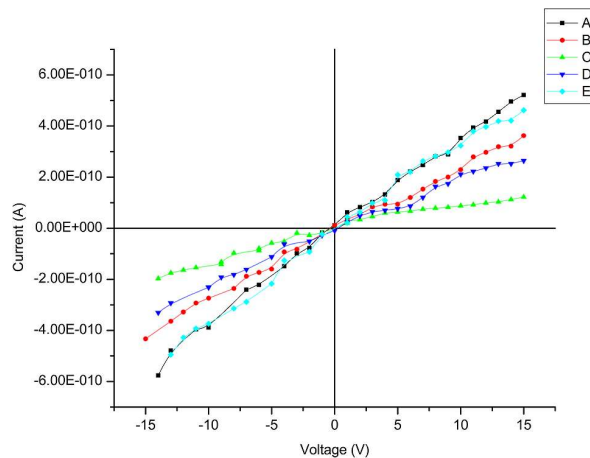


Fig. 5. I-V characteristics of nanocrystalline ZnO-TiO<sub>2</sub> thick films with molar ratios (A) 9:1, (B) 7:3, (C) 1:1, (D) 3:7 and (E) 1:9 at room temperature.

among the tested compositions, ZnO-TiO<sub>2</sub> based thick film (with a molar ratio 1:1) exhibited maximum response of 498.24 at 185 °C.

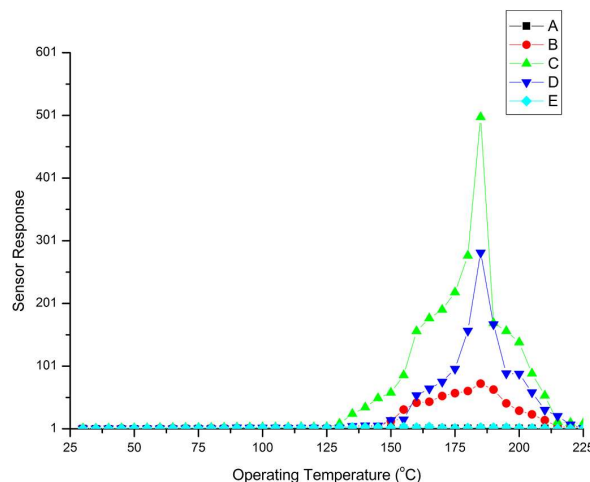


Fig. 6. Response of ZnO-TiO<sub>2</sub> thick films with molar ratios (A) 9:1, (B) 7:3, (C) 1:1, (D) 3:7 and (E) 1:9 toward 286 ppm LPG.

Fig. 7A shows the resistance of ZnO-TiO<sub>2</sub> based thick film (with molar ratio 1:1) at different operating temperatures in air ambient. From the figure it can be seen that the resistance of the film decreases with an increase in operating temperature, indicating a negative temperature coefficient of resistance.

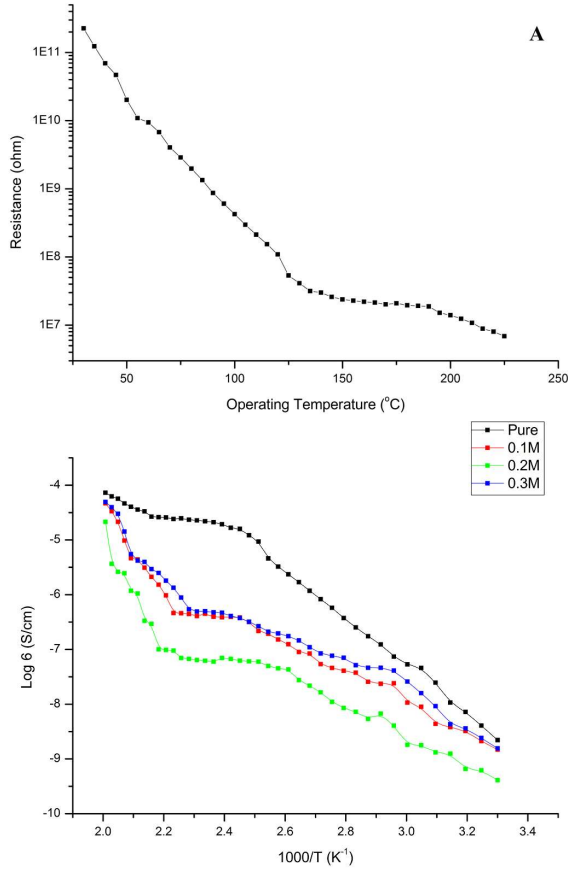
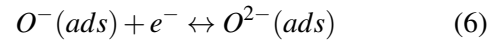
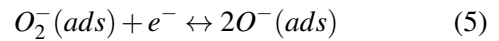
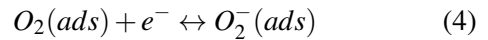
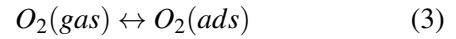


Fig. 7. (A) Resistance of ZnO–TiO<sub>2</sub> thick film (1:1 molar ratio) vs. operating temperature. (B) Arrhenius plot for 0.1 M, 0.2 M, 0.3 M CuO modified and unmodified ZnO–TiO<sub>2</sub> thick films (1:1 molar ratio) in air ambient.

The Arrhenius plots of 0.1 M, 0.2 M, 0.3 M CuO modified and unmodified ZnO–TiO<sub>2</sub> thick films (with molar ratio 1:1) is shown in Fig. 7B. It is observed that in air ambient, the conductivity of the film goes on increasing with an increase of temperature, showing the semiconducting nature of the film [1]. The activation energy  $E_a$  (I) and (II) of 0.1 M, 0.2 M, 0.3 M CuO modified and unmodified ZnO–TiO<sub>2</sub> thick film (with molar ratio 1:1) in air ambient have been calculated by measuring the slope of the best fit straight line of the plot in the temperature range of 30 °C to 130 °C and 175 °C to 225 °C, respectively, and presented in Table 2. The activation energy of CuO modified films is different from that of the unmodified ZnO–TiO<sub>2</sub> thick film.

This may due to different adsorption chemistry of CuO modified thick films. The CuO modified film surface adsorbs more oxygen species than unmodified film surface and the number of adsorbed oxygen species would depend on the amount of CuO dispersion on the film surface [21].

The sensing mechanism and the change in electrical transport properties of semiconductor oxide based materials generally involve the adsorption and desorption of oxygen molecules on the surface of the materials and/or the direct reaction of lattice oxygen or interstitial oxygen with test gases [26–31]. When ZnO–TiO<sub>2</sub> thick films are exposed to air, oxygen molecules interact with the film surface to form adsorbed oxygen ions like  $O_2^-$  or  $O^-$  or  $O^{2-}$  by capturing electrons from the conduction band and this interaction decreases the concentration of electrons in the conduction band. The processes are as follows [32]:



When the film is exposed to LPG, the LPG molecules interact with the adsorbed oxygen and hydroxyl species present on the film surface. The hydrocarbons, namely butane (C<sub>4</sub>H<sub>10</sub>) and propane (C<sub>3</sub>H<sub>8</sub>) present in LPG would be converted to CO<sub>2</sub> and H<sub>2</sub>O due to their interaction with oxygen ions and oxygen is evolved in electrically neutral state. The energy released in the decomposition of the molecules would be sufficient to shift the electrons into the conduction band of activated ZnO and TiO<sub>2</sub> and this causes a decrease in resistance of the film. The reaction of LPG with adsorbed oxygen can be explained as [33]:

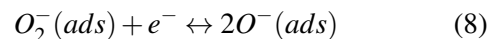
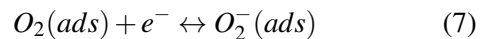


Table 2. Activation energy of 0.1 M, 0.2 M, 0.3 M CuO modified and unmodified ZnO–TiO<sub>2</sub> thick film (molar ratio 1:1) in air ambient.

ZnO–TiO <sub>2</sub> thick film (molar ratio 1:1)	Activation energy E <sub>a</sub> (eV)	
	E <sub>a</sub> (I) 30 °C – 130 °C	E <sub>a</sub> (II) 175 °C – 225 °C
Unmodified	0.378	0.201
0.1 M CuO modified	0.237	0.737
0.2 M CuO modified	0.240	0.861
0.3 M CuO modified	0.234	0.625

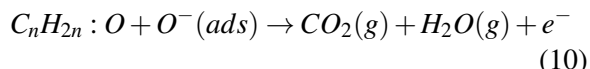
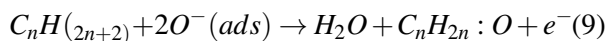


Fig. 6 indicates that the ZnO–TiO<sub>2</sub> thick film (with molar ratio 1:1) exhibits the highest response to LPG at 185 °C among all the investigated compositions. The highest sensing response of the film can be attributed to the crack free surface, optimum porosity and the largest surface area available to react with LPG. Also the optimum amount of TiO<sub>2</sub> in the film can account for maximum response, which indicates that there was an increase in the amount of chemisorbed oxygen ions. This is due to the fact that electron induced by Ti<sup>4+</sup> entering into ZnO lattice can form more chemisorbed oxygen on the surface of the film [22]. The amount of TiO<sub>2</sub> in the film was optimum; hence, it had high initial resistance in air ambient. When the film is exposed to LPG, LPG molecules interact with the oxygen species available at the film surface. In this interaction, the adsorption of LPG molecules accounts for the consumption of oxygen and this reaction leads to an increase in the sensor response. At temperature 185 °C, the reaction product may get desorbed immediately after its formation providing the opportunity for new LPG species to react effectively with the oxygen chemisorbed at the film surface. Due to this, there would be a significant decrease in resistance and hence, the film shows the highest sensing response to LPG. Above the optimum operating temperature (>185 °C), the amount of oxygen would be less. Therefore, in presence of LPG, the probability of reduction reaction of gas with chemisorbed oxygen would be less which results in the decrease of sensing response of the film.

Moreover, the decrease in the response of sample D and sample E to LPG may be attributed to an inhibitory effect of Zn<sub>2</sub>TiO<sub>4</sub> particles: an increase in the proportion of Zn<sub>2</sub>TiO<sub>4</sub>, with the increase in the content of TiO<sub>2</sub> might have resulted in the formation of an insensitive Zn<sub>2</sub>TiO<sub>4</sub>–ZnO grain boundary and subsequently reduce the number of sensitive ZnO–ZnO and ZnO–TiO<sub>2</sub> grain boundaries.

Fig. 8 illustrates the sensing response of 0.1 M, 0.2 M and 0.3 M CuO modified ZnO–TiO<sub>2</sub> thick films (with molar ratio 1:1) towards 286 ppm of LPG at different operating temperatures. The figure illustrates that the sensing response of the film is a function of CuO content. This would be attributed to the number of CuO dispersed on the surface of the film, forming a number of p-n heterojunctions [21]. The resistance of CuO modified films would be very high in air. When these films are exposed to LPG, LPG molecules interact with the film surface, causing disruption of p-type CuO and n-type ZnO–TiO<sub>2</sub> heterojunctions. The distortion of p-n heterojunctions leads to the decrease in resistance of the film. This would cause an easy flow of electrons [34].

The 0.2 M CuO modified ZnO–TiO<sub>2</sub> thick film (with molar ratio 1:1) was observed to be the most sensitive among the investigated compositions. This could be attributed to the adequate dispersion of CuO on the surface of the film and optimum number of p-n heterojunctions formed on the surface of the film. In air ambient, the film resistance R<sub>a</sub> was observed to be very high (4.99 × 10<sup>9</sup> Ω) at 185 °C. On exposure to LPG, the p-n heterojunctions would be disrupted and the film resistance R<sub>g</sub> would be observed to decrease by three orders of magnitude (3.05 × 10<sup>6</sup> Ω) at 185 °C.



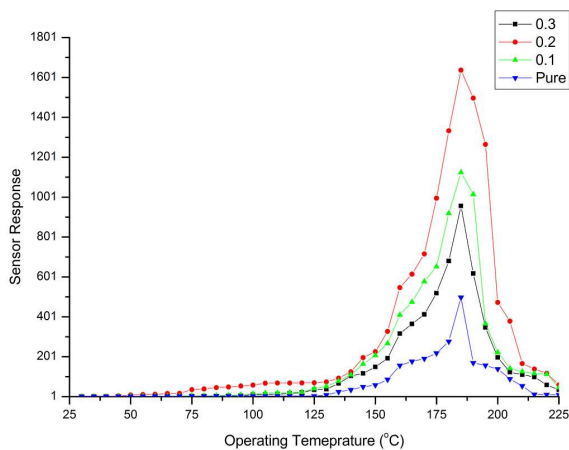


Fig. 8. Response of 0.1 M, 0.2 M and 0.3 M CuO modified ZnO–TiO<sub>2</sub> thick films (with molar ratio 1:1) towards 286 ppm LPG.

The proportion of p-n heterojunctions in the film is crucial for the resistance of the film and the resistance of p-n heterojunction becomes the key factor to control surface resistance [35].

In 0.1 M CuO modified film, the amount of CuO is less which results in poorer dispersion of CuO than the optimum (0.2 M) on the surface of film. The number of p-n heterojunctions formed on the film surface would be insufficient to drastically change the film resistance and the film would show comparatively lower response.

In 0.3 M CuO modified film, the amount of CuO is higher and thus larger dispersion of CuO on the surface of the film than the optimum (0.2 M). However, only some amount of CuO would be utilized in the formation of p-n heterojunctions and unused CuO would resist the LPG to reach to p-n heterojunction. Due to this, resistance of the film would not change drastically and the film would show comparatively lower response.

In practical applications, response and recovery times of a sensor for a particular gas are important factors. Response and recovery times are defined as the time required for reaching 90 % of the final stable value. Fig. 9 illustrates the response and recovery time of 0.2 M CuO modified ZnO–TiO<sub>2</sub> (with molar ratio 1:1) based thick film to 286 ppm LPG at 185 °C. It indicates that the

response and recovery time of the sensor are 30 s and 70 s, respectively. This result may be recommended for practical application of the sensor for LPG detection.

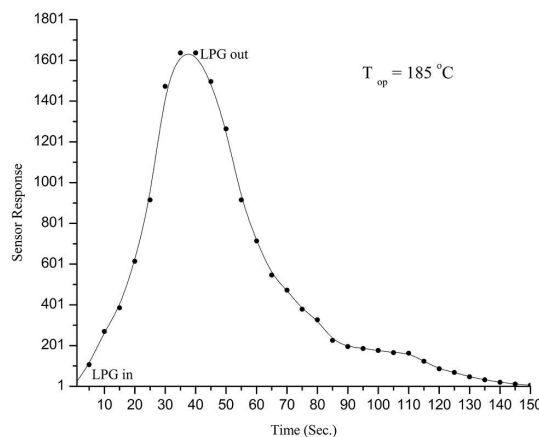


Fig. 9. Response and recovery time of 0.2 M CuO modified ZnO–TiO<sub>2</sub> based thick film (with molar ratio 1:1) towards 286 ppm LPG at 185 °C.

Fig. 10 demonstrates the stability of 0.2 M CuO modified ZnO–TiO<sub>2</sub> (with molar ratio 1:1) thick film sensor towards 286 ppm LPG at 185 °C. Long-term stability test of the sensor element was conducted by maintaining the sensor element at optimum operating temperature of 185 °C and exposure of the sensor element to 286 ppm LPG was performed after every 30 days for six month. It was observed that there was no noticeable deviation in the sensor response. This was due to the presence of TiO<sub>2</sub> in the film [36].

The response of 0.2 M CuO modified ZnO–TiO<sub>2</sub> (with molar ratio 1:1) based thick film toward different gases (286 ppm each) like NH<sub>3</sub>, CO<sub>2</sub>, H<sub>2</sub>S and LPG at optimal operating temperature is shown in Fig. 11. The sensor shows an excellent response at 185 °C towards LPG but a negligible response to CO<sub>2</sub> and poor response toward NH<sub>3</sub> and H<sub>2</sub>S. The excellent sensing response of the sensor element towards LPG resulted from the fact that LPG molecules easily reacted with the sensor element at 185 °C as compared to the other tested gases.

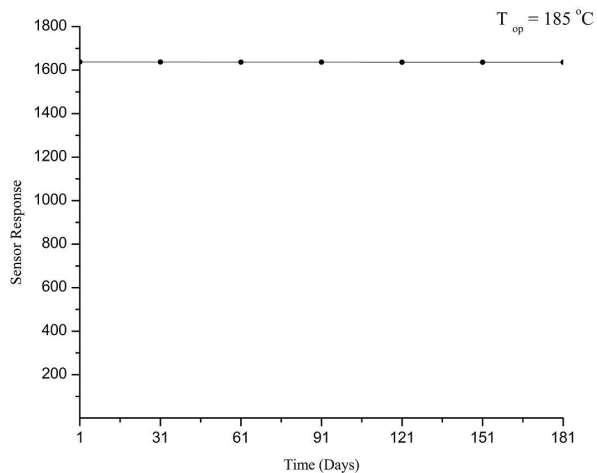


Fig. 10. Stability of 0.2 M CuO modified ZnO-TiO<sub>2</sub> based thick film (with molar ratio 1:1) towards 286 ppm LPG at 185 °C.

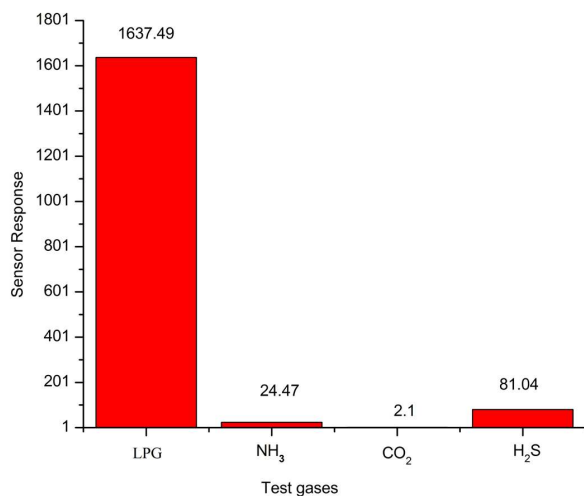


Fig. 11. Response of 0.2 M CuO modified ZnO-TiO<sub>2</sub> (1:1 molar ratio) based thick film towards NH<sub>3</sub>, CO<sub>2</sub>, H<sub>2</sub>S and LPG at 185 °C.

## 4. Conclusions

On the basis of experimental results and the discussion, the following conclusions can be made:

(I) Nanocrystalline ZnO-TiO<sub>2</sub> powders with molar ratios (A) 9:1, (B) 7:3, (C) 1:1, (D) 3:7 and (E) 1:9 were successfully synthesized by hydrothermal method. The crystallite size of the synthesized materials was of the order of 49 nm to 68 nm.

(II) Among the investigated samples ZnO-TiO<sub>2</sub> thick film (with molar ratio 1:1) showed the best response toward 286 ppm LPG.

(III) Response of CuO modified nanocrystalline ZnO-TiO<sub>2</sub> thick film (with molar ratio 1:1) towards LPG was found to depend on concentration of the dopant.

(IV) 0.2 M CuO modified ZnO-TiO<sub>2</sub> thick film (with molar ratio 1:1) exhibited excellent sensing response of 1637.49 toward 286 ppm LPG at 185 °C with good selectivity, quick response time (30 s), rapid recovery time (70 s) and long term stability.

Hence, 0.2 M CuO modified nanocrystalline ZnO-TiO<sub>2</sub> based thick film (with molar ratio 1:1) fulfils the practical requirements for detecting LPG.

## Acknowledgements

The authors express their gratitude to: the Department of Physics, the RTM Nagpur University, Nagpur, for providing the XRD facility; the Department of Material Technology, VNIT, Nagpur, for SEM and EDS characterization; the Department of Physics, the Pune University, Pune, for TEM characterization.

## References

- [1] WAGH M., JAIN G., PATIL D., PATIL S., PATIL L., *Sensor Actuat. B-Chem.*, 122 (2007), 357.
- [2] MURADE P., SANGAWAR V., CHAUDHARI G., KAPSE V., BAIPEYEE A., *Mater. Sci.-Poland*, 31 (2013), 298.
- [3] KAPSE V., GHOSH S., RAGHUWANSHI F., KAPSE S., *Sensor Actuat. B-Chem.*, 137 (2009), 681.
- [4] YADAV B., YADAV A., SHUKLA T., SINGH S., *B. Mater. Sci.*, 34 (2012), 1639.
- [5] KAPSE V., GHOSH S., CHAUDHARI G., RAGHUWANSHI F., GULWADE D., *Vacuum*, 83 (2008), 346.
- [6] KAPSE S., RAGHUWANSHI F., KAPSE V., PATIL D., *Curr. Appl. Phys.*, 12 (2012), 307.
- [7] ZHANG C., HU Y., LU W., CAO M., ZHOU D., *J. Eur. Ceram. Soc.*, 22 (2002), 61.
- [8] ROTHSCHILD A., KOMEM Y., *J. Appl. Phys.*, 95 (2004), 6374.
- [9] FRANKE M., KOPLIN T., SIMON U., *Small*, 2 (2006), 36.
- [10] LIU X., *Mater. Lett.*, 80 (2012), 69.
- [11] YOSHIMURA M., SUCHANEK W., *Solid State Ionics*, 98 (1997), 197.
- [12] PEDHEKAR R., RAGHUWANSHI F., RAUT G., *IJPRET*, 2 (2014), 127.

- [13] CHUNG W., SHIM C., CHOI S., LEE D., *Sensor Actuat. B-Chem.*, 20 (1994), 139.
- [14] YU-SHENG Y., TIAN-SHU Z., *Sensor Actuat. B-Chem.*, 12 (1993), 5.
- [15] KAPSE V., GHOSH S., CHAUDHARI G., RAGHUWANSHI F., *Talanta*, 76 (2008), 610.
- [16] YU J., CHOI G., *Sensor Actuat. B-Chem.*, 52 (1998), 251.
- [17] ZHU C., CHEN Y., WANG R., WANG L., CAO M., SHI X., *Sensor Actuat. B-Chem.*, 140 (2009), 185.
- [18] YOON D., YU J., CHOI G., *Sensor Actuat. B-Chem.*, 46 (1998), 15.
- [19] PEDHEKAR R., RAGHUWANSHI F., *IJPRET*, 3 (2015), 30.
- [20] SHOULI B., DIANQINGA L., DONGMEI H., RUIXIAN L., AIFAN C., LIU C., *Sensor Actuat. B-Chem.*, 150 (2010), 749.
- [21] PATIL D., PATIL L., *Sensor Actuat. B-Chem.*, 123 (2007), 546.
- [22] PEDHEKAR R., RAGHUWANSHI F., KAPSE V., *IJMSE*, 3 (2015), 219.
- [23] ZHU B., XIE C., WANG W., HUANG K., HU J., *Mater. Lett.*, 58 (2004), 624.
- [24] WONG K., FIELD M., OU J., LATHAM K., SPENCER M., YAROVSKY I., KALANTAR-ZADEH K., *Nanotechnology*, 23 (2012), 015705.
- [25] BADADHA S., MULLA I., *Sensor Actuat. B-Chem.*, 143 (2009), 164.
- [26] YAMAZOE N., *Sensor Actuat. B-Chem.*, 5 (1991), 7.
- [27] GERGINTSCHEW Z., FORSTER H., KOSITZA J., SCHIPANSKI D., *Sensor Actuat. B-Chem.*, 26 (1995), 170.
- [28] YAMAZOE N., SAKAI G., SHIMANO K., *Catal. Surv. Asia*, 7 (2003), 63.
- [29] GAO T., WANG T., *Appl. Phys. A-Mater*, 80 (2005), 1451.
- [30] YAMAZOE N., FUCHIGAMI J., KISHIKAWA M., SEIYAMA T., *Surf. Sci.*, 86 (1979), 335.
- [31] EGASHIRA M., SHIMIZU Y., TAKAO Y., SAKO S., *Sensor Actuat. B-Chem.*, 35 (1996), 62.
- [32] HUANG L., LIU T., ZHANG V., GUO W., ZENG W., *J. Mater. Sci. Mater. Electron.*, 23 (2012), 2024.
- [33] SAHAY P., NATH R., *Sensor Actuat. B-Chem.*, 133 (2008), 222.
- [34] LIU J., HUANG X., YE G., LIU W., JIAO Z., CHAO W., ZHOU Z., YU Z., *Sensors*, 3 (2003), 110.
- [35] HU Y., ZHOU X., HAN Q., CAO Q., HUANG Y., *Mater. Sci. Eng. B-Adv.*, 99 (2003), 41.
- [36] RADECKA M., KUSIOR A., LACZ A., TRENCZEK-ZAJAC A., LYSON-SYPIEN B., ZAKRZEWSKA K., *J. Therm. Anal. Calorim.*, 108 (2012), 1079.

Received 2015-11-17

Accepted 2016-07-03