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IMPROVEMENT OF PROMISING GAS SENSOR SYNTHESIZED BY TRANSPARENT In_2O_3 FILM USING FURTHER THERMAL TREATMENT

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Transparent In_2O_3 film has been synthesized by one-step thermal evaporation for CH_4 gas sensor. X-ray diffraction pattern confirmed the polycrystalline cubic bixbyite-type structure of indium oxide film. The transmittance of the film was recorded of 71%, where the optical band gap was found to be 3.68 eV. A gas sensor was fabricated by In_2O_3 film, and the sensor was calcined at 350^{o}C before the gas sensing investigation. The gas sensing performance of the film toward CH_4 gas was measured at various operating temperatures. At low temperature the sensor exhibited a good performance, while at high temperature of 250 and 350^{o}C the sensor exhibited an undesirable behavior. Afterward, the sensor undergoes thermal treatment at 450^{o}C once again before the applying for the sensing measurement. It was observed that the gas sensing performance was dramatically improved, showing a good repeatability and stability.

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1. Introduction

Up to date, In2O3 has been frequently used for various applications, such as solar cell, transparent conducting oxide, and optoelectronic devices [1-3]. Conversely, there are a number of reports on indium oxide as a gas sensor application, although it is one of the promising materials for gas sensing. The most studies of In_2O_3 focused on various gases [4-7], however, few of them seem to give satisfactory performance of indium oxide in detection of CH_4 at high temperatures [8, 9]. CH_4 is the most important component of natural gas, enhances global warming, combine with nitrogen oxides to form ground-level ozone, which can cause respiratory ailments such as asthma and decreased lung function, and it is extremely flammable and may form explosive mixtures with air at 5% concentration [10].

Several deposition techniques have been used for the preparation of indium oxide thin film; such as electron beam evaporation [11], spray pyrolysis [12], ultrasonic spray CVD [13], sol-gel [14], and sputtering technique [15]. Among these methods, thermal evaporation technique is used to synthesis of indium oxide film [16]. Although it is a simple method, a lot of raw indium is wasted during the deposition as well as In_2O_3 films have been fabricated in two steps. First step is to deposit the indium film, and is then followed by an oxidation process of heat treatment.

We have paid attention to synthesis a low cost thin film of In_2O_3 by a plain method in order to develop CH_4 gas sensing device operating at low temperatures, and applicable to the safety control. The structure and morphology of In_2O_3 by using x-ray diffractometer (XRD) and scanning electron microscope (SEM) are studied. The gas sensing performance of indium oxide

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thin film toward CH_4 at various operating temperatures and gas concentrations is demonstrated. The effect of further thermal treatment on the sensor response, stability, and repeatability is well proposed.

2. Experimental procedures

In_2O_3 film was prepared by an evaporation set consisted of a small crucible covered by the glass substrate and surrounded by heating element. This evaporation set is located in a vacuum stainless steel chamber of 34.0 cm in diameter and 35.0 cm in height. The deposited area of thin film is about πr^2 (r = 1 cm), and the ambient gas is the surrounding lab air. Indium pieces of 3.0 mg with a purity of 99.99% were used as a raw material. The steel chamber was evacuated to 8 x 10^{-2} mbar, and then the crucible was heated up to 900^{o}C within 2 min and maintained at this temperature for 30 min. Afterward, the crucible was cooled down to RT, resulting in a substrate surface coated by a thin transparent layer of In_2O_3. The crystal structure of deposited films was investigated by X-ray diffraction (XRD) using an X-ray diffractometer (Philips Type PW 1710) with Cu Kα radiation. The morphology was observed by a scanning electron microscope (SEM) (JEOL JSM-5400LV). A Shimadzu UV–Vis-2101 PC dual beam scanning spectrophotometer was used to record the optical transmittance, and reflectance of the films with monochromatic light in the wavelength range of 200–900 nm.

To apply the sensor for gas sensing measurements, the sensors were calcined at 350˚C in ambient air for 1 h. In order to investigate CH_4 sensing properties, sensors were placed in a quartz tube, which was inserted into an electric furnace. The operating temperature varied from 150 up to 300˚C. Dry synthetic air, mixed with different concentrations of CH_4 gas, was passed at a rate of 200 ml/min through the quartz tube. The gas flow was controlled by Horiba mass flow controllers (SEC-N112 MGM). The electrical measurements were carried out using computerized data acquisition instrument (LXI Agilent 34972A), as outlined in Fig.1. The resistance of the sensor was measured by applying a potential difference of 5 V to electrical circuit, which included a standard resistance and the sensor. The sensor response, S, was estimated as the ratio of two electrical resistances as follows:

$$S = \frac{R_a}{R_g} \tag{1}$$

where R_a is the electrical resistance in the absence of CH_4 gas, and R_g is the maximum electrical resistance in the presence of CH_4 gas.

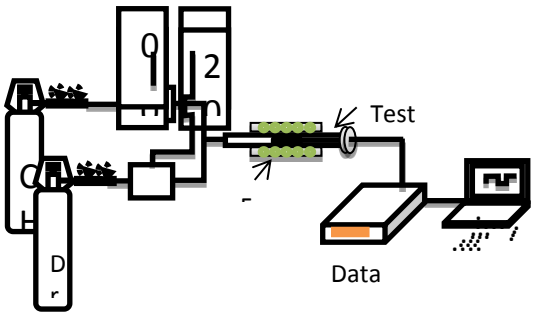

Fig. 1: scheme of gas sensing apparatus.

3. Results and discussions

3.1. Film structure and morphology

X-ray diffraction pattern of the film is shown in Fig. 2. X-ray data analysis indicated that the deposited film had a polycrystalline and indexed on a cubic bixbyite-type structure. The

investigated film showed a preferred orientation of (222) line. X-ray lines were analyzed to determine the structure parameters. From x-ray data shown in Table 1 it can be observed that the d-spacing between the crystalline planes is larger than the respective standard values of the powder diffraction files (card No. 04-005-9883). This increase in d-spacing is observed for indium oxide thin films prepared by an ultrasonic spray CVD [13]. It is ascribed to a compressive stress in the film due to the kinetic growth, which is determined by temperature, pressure, nature and quantities of atoms involved near the surface [13, 17]. Fig. 3 shows a low magnification of SEM image for In_2O_3 film. The morphology of the deposited film can be described as a porous, small particles and rough surface. The size of In_2O_3 particles is about 20-40 nm or less, as indicated the inset figure.

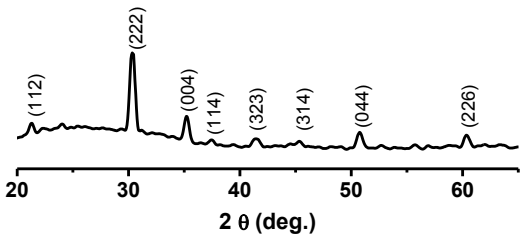

Fig. 2: XRD pattern of In_2O_3 film.

Table1: d-spacing, difference in d-spacing and miller indices of deposited film.

Sample	d_{exp}	$d_{stand.}$	*diff.*$(d_{exp}-d_{sand})$	*h*	*k*	*l*
In_2O_3	4.173	4.136	0.037	1	1	2
	2.942	2.924	0.018	2	2	2
	2.545	2.532	0.013	0	0	4
	2.399	2.388	0.011	1	1	4
	2.176	2.160	0.016	3	2	3
	1.997	1.987	0.010	3	1	4
	1.797	1.791	0.006	0	4	4
	1.532	1.527	0.005	2	2	6

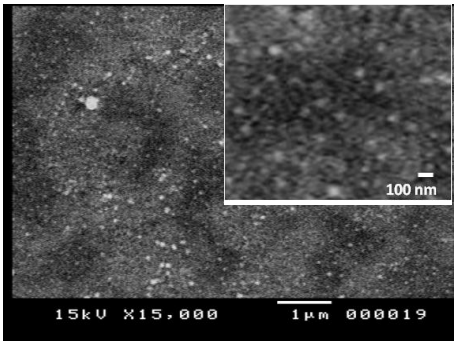

Fig. 3: Low magnification SEM micrograph of In_2O_3 film.

3.2 Optical properties and photocurrent measurements

The transmittance and reflectance spectra of indium oxide film were measured in the range of 900-200 nm, as shown in Fig. 4. One can observe the transparency of the film over the visible and infrared region. The absorption coefficient was calculated using the formula of eq. (2) [18]:

$$\alpha = \frac{1}{d} ln \left[\frac{(1-R(\lambda))^2}{T(\lambda)}\right] \quad (2)$$

where d is the film thickness, R and T are the reflectance and transmittance, respectively. The parabolic density of states is assumed for valence and conduction bands, thus for photon energy hv greater than the energy gap E_g, the absorption coefficient can be varied by the empirical relation derived by Tauc [19] to determine the band gap energy. Here we have considered the direct band gap of indium oxide [20]. The calculated optical band gap energy of the film is ~3.6 eV, which is close to the value reported in literature [13, 21].

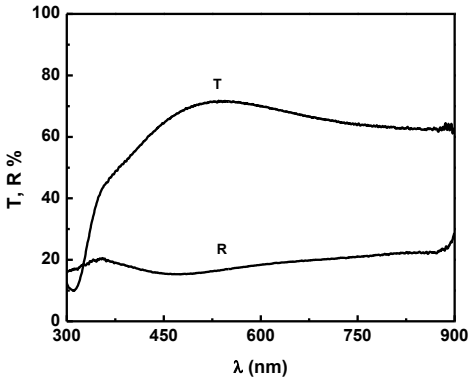

Fig. 4: The photocurrent response of film with UV light turned on/off and by application of a bias voltage of 0.02 V.

3.3 Methane sensing properties

In measuring sensing response, two electrodes of gold were deposited onto the film surface by using DC sputtering, follows by heat treatment at 350^{o}C before undergoing for sensing measurements. The change in the resistance of In_2O_3 film upon exposure to CH_4 gas at different operating temperatures and different concentrations was investigated. Fig. 5 shows a typical gas sensing response measured of In_2O_3 film at operating temperature of 150^{o}C upon exposure to 1% of CH_4 gas. The sensor response was calculated to 1.59 at maximum for this operating temperature.

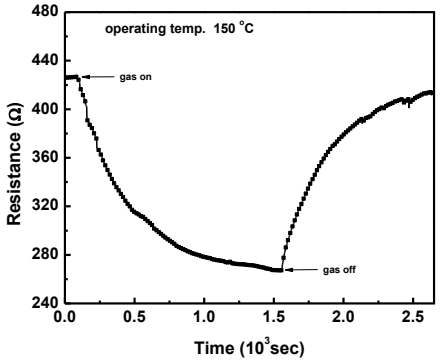

Fig. 5: Gas sensing response of In_2O_3 deposited film up on exposure to 1% CH_4 at operating temperature of 150^{o}C.

More investigations of sensor behavior upon exposure to different concentrations of CH4 have been studied, as shown in Figs. 6-8. Fig. 6 shows the behavior of deposited film exposed to various concentration of 1% – 0 of CH_4 at 200^{o}C of operating temperature. The sensor shows different responses upon exposure to various gas concentrations. However, the sensor is less sensitive to the low concentrations. It may be ascribed to that the surface of film is highly active only at high concentrations. This disadvantage of the sensor gives a doubt about its performance. Thus, we investigated the film response upon exposure to gas concentration starting from low to high one at operating temperature of 250^{o}C, as depicted in Fig. 7. The sensor have a change in the response when the gas concentration changes. However, it still has the high response although its advent of instability.

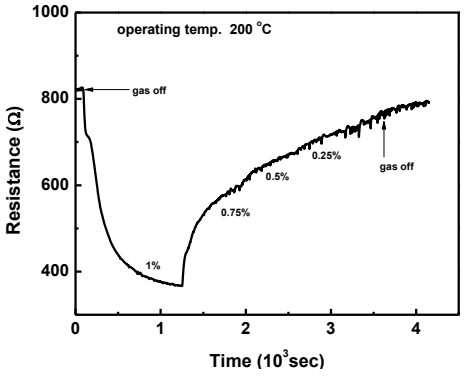

Fig. 6: The sensor signal as function of time exposed to various concentrations at 200^{o}C.

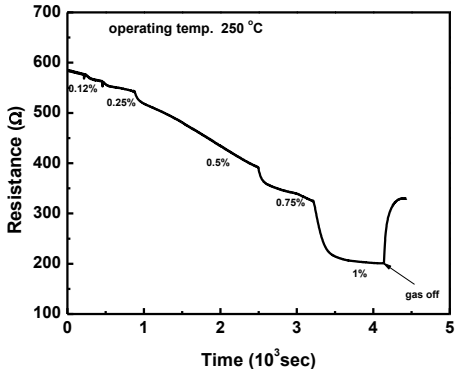

Fig. 7: The sensor siganl as function of gas concentration at operating temperature of 250^{o}C.

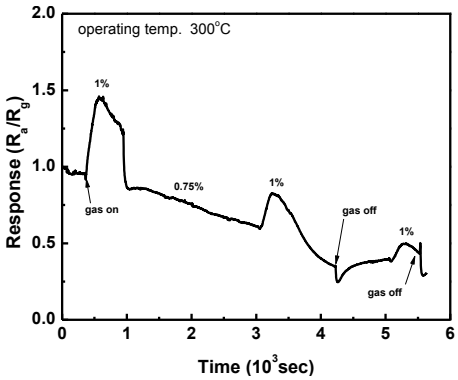

Fig. 8: The sensor output up on repeating the gas dose with time. Note: the sensor is instability with gas repeating dose.

Fig. 8 shows the performance of the sensor against the variation of gas concentration at 300°C. As it is expected the sensor dramatically illustrated instability signal. At high concentration (1%) gives an instable response as it is a n-type material, since this response undergoes by decreasing toward value lower than the baseline. Moreover, with introducing the gas dose once again, the response is lower, repeating the same behavior of the first dose. Instability has been pointed out at the third dose.

This behavior caused a confirmed doubt about the performance of the sensor. Consequently, we have repeated these measurements again two weeks later. The measurements have carried out at 250°C for the same sensor, where the complete doubt about the sensor is confirmed. In the repeated signal, the sensor was exposed to the gas for five times with switching on and off is shown in Fig. 9. In contrary, the sensor showed a totally different behavior where its resistance slightly increased upon exposing to gas, followed by more increase and then decrease when the gas is switched off. This observed behavior of the sensor resistance is repeated with every dose.

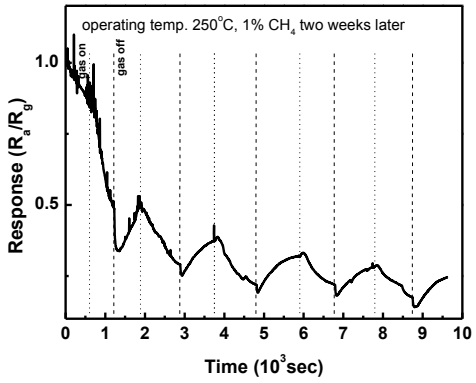

Fig. 9: The sensor output two weeks later upon exposure to 1% of methane gas at operating temperature of 250°C.

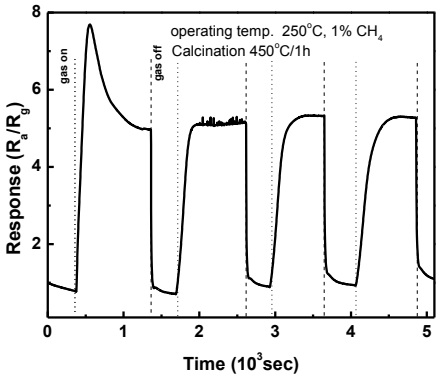

Fig. 10: The sensor signal of sequential exposures after a heating treatment at 450°C for 1h.

Because of the above mentioned outputs, the sensor undergoes a heat treatment at 450°C/1h. Then the gas sensing properties have been investigated once again for 1% CH_4 at 250°C, as shown in Fig. 10. In this case the sensor performs a good signal unless at the first interval. Dramatically change is observed for the sensor, where there is an actual improvement in response and response time of In_2O_3 film deposited at 0.08 mbar. The highest sensor response recorded for the stable signal is 5.0. In order to confirm the stability and repeatability, the sensor was exposed to CH_4 gas for four sequential exposures, as shown in the signal of Fig. 10. It can be seen that the sensors exhibit a high level of stability and repeatability for the sequential exposures of gas, and no variation is estimated compared for the sequential exposure.

4. Conclusions

Polycrystalline indium oxide thin film can be synthesized from one-step modified thermal evaporation-like technique. Structural, optical and gas sensing properties of In_2O_3 film deposited by this method were investigated. The deposited film is identified as a polycrystalline indium oxide with a cubic structure. The transmittance in the visible region exceeded ~71%, and the optical band gap was found 3.60 eV. The gas sensor expressed a quick response and recovery times upon exposure to CH_4 gas. The sensor is performing well at low operating temperature, but is showing undesirable signal at high operating temperatures. On the other words, at low heat treatment of 350^{o}C, the gas sensor made of this film showed an instable signal. However, with further heat treatment of 450^{o}C, a dramatic improvement of senor is observed. The indium oxide film is a candidate for air monitoring applications for CH_4 sensors.

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