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Repeatability of indium oxide gas sensors for detecting methane at low temperature

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ABSTRACT

A simple method for fabricating methane gas sensor of indium oxide (In_2O_3) transparent film was presented. Indium of 3 mg as a raw material was used to direct deposition of In_2O_3 film through a simplified thermal evaporation method. X-ray diffraction confirmed the cubic polycrystalline structure of the as prepared In_2O_3 film. The transmittance (T) of the film was recorded as high as 96%. The optical band gap (E_g) of the deposited film was found of 3.68 eV. The sensing properties of In_2O_3 film toward methane gas (CH_4) were investigated at various operating temperatures and various gas concentrations. The prepared film highly detected CH_4 gas at concentrations much lower than the explosive limit. Good performance (sensor response and stability) of the film for CH_4 gas was exhibited. The film exhibited a good repeatability with repeating the gas sensing measurements towards CH_4.

1. Introduction

In_2O_3 thin films are important wide band gap of semiconductor materials, chemically stable, and transparent to visible light. Several of deposition techniques have been used for the preparation of In_2O_3 thin film; such as electron beam evaporation [1], spray pyrolysis [2], ultrasonic spray CVD [3], sol-gel [4], and sputtering technique [5]. The thermal evaporation is a method used to synthesis of indium oxide film [6]. Although it is a simple method, a lot of raw indium material is wasted out during the deposition. Moreover, after deposition, the film is followed by annealing in oxygen environment in order to form In_2O_3.

Up to date, In_2O_3 films have been applied for many applications, such as solar cell [7], transparent conducting oxide [8], and optoelectronic devices [9]. Although there are many papers on indium oxide as a gas sensor application are reported. However, few of them seem to give satisfactory performance of doped- In_2O_3 in detecting to CH_4 at high temperatures [10–13]. CH_4 gas enhances the global warming, and its consequent reactions can cause respiratory ailments. The explosive limit of CH_4 gas concentration is 5% [10]. However, detection of CH_4 gas at lower concentrations is essential for preventing and warning purposes for leaking gas systems.

We have paid attention to synthesis highly sensitive In_2O_3 film toward CH_4 gas, aiming to develop semiconductor devices applicable to the safety control. The film is fabricated by available and low cost one-step thermal evaporation method [14], reducing the wasted indium and the dissipated power. The film structure and morphology are characterized by x-ray diffractometer, scanning electron microscope, and spectrophotometer techniques. Methane sensing properties of In_2O_3 thin film, where few papers have been reported, are presented at a low operating temperature as well as a low gas concentration. The sensor stability and repeatability of In_2O_3 film is investigated.

2. Experimental procedures

The experiment was carried out in an evaporation set consisted of a small crucible covered by the glass substrate and surrounded by a heating element. This evaporation set was placed in a vacuum stainless steel chamber of 34 cm in a diameter and 40 cm in a height. The deposited area of thin film was about πr^2 (r=1 cm). For preparation of In_2O_3, indium pieces of 3 mg with a purity of 99.99% were used as a raw material. The pressure was kept at 7×10^{-2} mbar, allowing the air flow during the deposition process, where the rotary pump is kept connected. Then the crucible was heated up to 900 °C within 2 min and maintained at this temperature for 30 min. Afterward the crucible was cooled down to room temperature. The substrate surface found to be coated with a transparent layer of In_2O_3 thin film with a strong adhesion with the substrate.

The crystal structure of deposited film was investigated by X-ray diffractometer (Philips Type PW 1710) with *CuK*α radiation. The morphology was observed by a scanning electron microscope (SEM)

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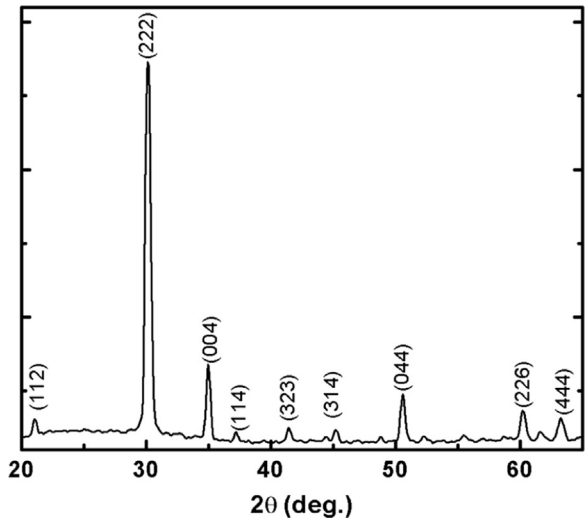

Fig. 1. XRD patterns of In_2O_3 thin film.

(JEOL JSM-5400LV). The optical transmittance (T) and reflectance (R) of the film were recorded by Shimadzu UV–vis–2101 PC dual beam scanning spectrophotometer with monochromatic light in the wavelength range of 200–900 nm. The surrounding medium was air. The measurements were carried out at room temperature.

For applying the sensor for sensing measurements, it was first calcined at 350 °C for 1 h in the ambient air to avoid the recrystallization during the gas sensing measurements. In order to investigate CH_4 sensing performance the sensor was placed in a quartz tube, which was inserted into an electric furnace. The operating temperature varied from 100 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 is controlled by Horiba mass flow controllers (SEC-N112 MGM). The electrical measurements were carried out using computerized data acquisition instrument (LXI Agilent 34972 A). To measure the resistance of the gas sensor, a potential difference of 5 V was applied to the electrical circuit, which includes a standard resistance and sensor. The sensor response was estimated as the relative resistance, R_a/R_g, where R_a was the electrical resistance before introducing the gas, and R_g was the maximum electrical resistance after introducing the gas.

3. Results and discussions

3.1. Structural characteristics

It is expected that In_2O_3 has been formed due to the reaction between evaporated Indium and Oxygen which flows partially from the ambient air during the deposition. Thus, x-ray chart of the deposited film are depicted in Fig. 1. X-ray data analysis indicated that the deposited film is polycrystalline and indexed on a cubic bixbyite-type structure of In_2O_3. The investigated film showed a preferred orientation of (222). X-ray diffraction 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 (Card No. 04-005-9883). This expand in d-spacing is observed for indium oxide thin films prepared by ultrasonic spray CVD [3]. It was 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 [3,15].

The (hkl) indices are calculated in curriculum of cubic bixbyite-type In_2O_3 structure. The lattice parameters are listed in Table 1. It is clear from the Table 1 that the lattice parameter dimension of the In_2O_3 is greater than the bulk value 10.11 Å [16].

Table 1
d-spacing, difference in d-spacing and miller indices, lattice parameter and volume of deposited film.

d_{exp}	d stand.	diff. ($d_{exp}-d_{sand}$)	h	k	l	a (Å)	volume (A^3)
4.212	4.136	0.076	1	1	2	10.21	1069.22
2.962	2.924	0.038	2	2	2		
2.563	2.532	0.031	0	0	4		
2.414	2.388	0.026	1	1	4		
2.177	2.160	0.017	3	2	3		
2.003	1.987	0.016	3	1	4		
1.803	1.791	0.012	0	4	4		
1.535	1.527	0.008	2	2	6		
1.469	1.462	0.007	4	4	4		

The average crystalline size of the nanocrystals can be estimated using Scherrer formula [17]:

$$D=\frac{K\lambda}{\beta}\cos\theta \tag{1}$$

where the constant K is taken to be 0.94, λ is the wavelength of the x-ray $CuK\alpha$ radiation (λ=1.5418Å) source. β is the full width at half maximum of the diffraction peak corresponding to 2θ. The average crystallite size of 15.2 nm was calculated for most intense diffraction lines of (222), (004), and (044). The strain induced in the obtained film due to crystal imperfection and distortion was calculated using the following formula [16,18]:

$$\varepsilon=\frac{\beta}{4\tan} \tag{2}$$

According to the above formula, plotting the values of β (in rad) versus 4 tan θ should give a straight line, as shown in Fig. 2. From the least square fit to the experimental points, the slope of the straight line gives directly the strain (ε)-value (8.15×10^{-3}) of the In_2O_3 film. According to the previous work [16], the average internal lattice strain value was found to be 1.4×10^{-3} for the In_2O_3 nanoparticles which in the range of the as prepared In_2O_3 film. These strain values confirm the specimen uniformity in all crystallographic directions. Fig. 3 shows a low magnification SEM image of In_2O_3 deposited film. The morphology of the deposited film can be described as a porous, fine particles and rough surface. It is seen that, a bright spots refer to the agglomerated particles on the surface. However, almost are in size comparable to the crystalline size calculated from XRD.

3.2. Optical characteristics

The transmittance (T) and reflectance (R) spectra of In_2O_3 films were measured in the range of 900–200 nm. The absorption coefficient and optical band gap on the absorption edge of In_2O_3 film have been investigated. It is known that In_2O_3 thin films are important semiconductor materials with wide band gap ranged between 3.57 and 3.68 eV [3,19,20]. Fig. 4 shows the transmittance and reflectance as a function of the wavelength. From the plot, it is seen that the film is highly transparent over the visible and infrared region, reaching ~96%. The absorption coefficientα was calculated using the formula [21]:

$$\alpha=\frac{1}{d}ln\left[\frac{(1-R(\lambda))^2}{T(\lambda)}\right] \tag{3}$$

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 $h\nu$ greater than the energy gap E_g, the absorption coefficient can be varied by the empirical relationship to determine the band gap as follow [22]:

$$(\alpha h\nu)^2=A(h\nu-E_g) \tag{4}$$