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Research paper

Preparation and characterization of Ag-doped In_2O_3 nanoparticles gas sensor

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ABSTRACT

Pure and Ag-doped In_2O_3 nanoparticles are synthesized by the co-precipitation method and are characterized by X-ray diffraction, transmission electron microscopy and photoluminescence spectroscopy. Gas sensing properties of the sensors has been investigated towards methanol, ethanol, acetone and LPG at different operating temperatures. It is found that the sensor response magnitude of the 3% Ag-doped In_2O_3 nanoparticles sensors is higher to 50 ppm of ethanol at 300 °C, to acetone at 350 °C and to LPG at 400 °C. This is mainly attributed to the large number of oxygen vacancies and defects in doped sensors as corroborated by the photoluminescence studies.

1. Introduction

Semiconductor metal oxide (SMO) based gas sensors have been applied widely in public safety and environmental monitoring because of their remarkable gas sensing properties [1,2]. The change in the conductivity of the sensor because of the surface chemical reaction between the surface of sensor and the exposed reducing or oxidizing target gases, forms the basis of sensing mechanism [3]. It is widely agreed in the literature that various parameters like size, morphology, and surface defects influences the interaction between the SMO surface and target gas and hence, can greatly affect their gas sensing properties [4–6]. So many researchers have attempted different ways to alter one or more of the above mentioned parameters of semiconductor metal oxide by different methods like doping of metal oxide with different metals, decoration with metal nanoparticles, structure control and defects control synthesis to improve the sensing properties of SMO [7–10].

Doping creates defects and provides preferential sites for the adsorption of gas molecules and dopant act as catalysts that promotes the adsorption and surface reactions and hence enhances the sensor performance by increasing the sensor response, by reducing response and recovery time, by reducing the operating temperature and, by increasing selectivity [7,11,12]. Hence, doping is deemed as one of the effective method to tune the sensitivity and selectivity of semiconducting oxides gas sensor. It is well-known that noble metals, like Ag [13–15], Pd [16,17], Pt [18], and Au [19–21] are often used in gas sensing materials. Among them, the dopant Ag noble metal is comparatively cheap and an active catalyst that helps to accelerate the chemisorption process of SMO and enhance the gas sensing performance of SMO gas sensors. To the best of our knowledge, relatively little work has been carried out on Ag-doped In_2O_3 nanoparticles as a gas sensor. So in this, we report the synthesis, characterization and gas sensing properties of (0%, 1%, 3% and 5%) Ag-doped In_2O_3 nanoparticles gas sensors towards methanol, ethanol, acetone and LPG at different operating temperature. The results show that 3% Ag-doped In_2O_3 sensor have enhanced sensor response as compared to other and this is mainly attributed to the large amount of defect/vacancies and high catalytic effect of Ag in Ag-doped In_2O_3 sensor.

2. Experimental results

2.1. Synthesis of nanoparticles

Pure indium oxide and (1%, 3% and 5%) silver doped indium oxide nanoparticles were synthesized by using a co-precipitation method. In this method, 0.2 M aqueous solution of ($In(NO_3)_3$) was prepared using distilled water and then NH_4OH was added drop wise till the pH = 9 of the solution. The white colored In$(OH)_3$ precipitates were then separated by filtration, washed with ethanol, and dried at 80 °C for 5 h. After that precipitates were calcined at 500 °C for 3 h to get In_2O_3 nanoparticles. Similarly, (1%, 3% and 5%) Ag-doped In_2O_3 nanoparticles were prepared by adding the appropriate amount of silver nitrate into the aqueous solution of $In(NO_3)_3$.

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2.2. Characterization

The X-ray powder diffraction (XRD) patterns of prepared nanoparticles were recorded on a D8 Focus, Bruker, Germany diffractometer with Cu Ka radiation, wavelength 1.54056 Å. The TEM (transmission electron microscopy) images, HRTEM (high-resolution TEM) images were obtained on a JEOL TEM-2100. Photoluminescence spectra were recorded using Perkin Elmer fluorescence spectrometer, Lambda 45 at the excitation wavelength of 310 nm.

2.3. Fabrication of sensors and measurement of gas sensor response

For the fabrication of In_2O_3 nanoparticles gas sensor, a suitable amount of In_2O_3 nanoparticles were milled for 5 min in an agate mortar pestle into fine powder and paste were made using few microlitres of deionized water. Then, this paste was coated onto an alumina substrate (12 mm × 5 mm size) to make thick film (~25 μm) between pre-printed two gold electrodes (electrode distance 2 mm). After that, the film was sintered in air at 400 °C for 1 h. (For the photo of sensing device with gold electrodes see the supplementary files). In a similar manner, (1%, 3% and 5%) Ag–doped In_2O_3 sensors were also fabricated and their gas sensing performances towards various volatile organic compounds (VOC) (like ethanol, methanol, acetone) and LPG gas at operating temperature range of 250–450 °C were investigated. The sensor performance of sensors was tested in in an indigenously built apparatus (see the photograph in the supplementary files) consists of 40L test chamber includes sample holder, mixing fan and oven. The sensor was placed in the chamber oven and a volume of test VOC/gas was injected into the chamber using syringe. By using conventional circuit [22], computer and Keithley Data Acquisition Module KUSB-3100, the variation of voltage signal with time across the resistance R in series with the sensor resistance (R_S) was measured at input circuit voltage (V_I) of 12V. The sensor response has been measured as R_a/R_g ratio, where R_a and R_g are the resistances of sensor in air and air-target gas mixture respectively.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1(a) shows the XRD patterns of the pure In_2O_3 and Ag-doped In_2O_3 nanoparticles. The XRD pattern illustrates that all the diffraction features can be indexed to cubic bixbyte phase (JCPDS card no. 06-0416) and no other undesired phases are present. Also, from Fig. 1(b) it is clear that there is a shift of the maximum intensity (222) peak towards higher angle in Ag-doped In_2O_3 samples. This anomalous shift in the peak position suggests that the Ag ion has occupied the interstitial sites of In_2O_3. Also, from the previous study [23], it is generally observed that if the dopant ion has higher ionic radii than host ions and there is a shifting of peak towards relatively lower 2θ values, then the dopant ions substitutes the host ions [23]. On the other hand, if shifting is towards relatively higher 2θ values then suggesting interstitial occupancy [23]. In our case, the dopant Ag ions (1.22 Å) has higher ionic radius as compared to Indium ions (1.06 Å) [24], hence suggests that Ag incorporated in In_2O_3 by interstitial doping [25]. The lattice constant (a) and crystalline size (D) has been calculated by using Bragg's law and Scherrer's formula [26] respectively and listed in Table 1. It is observed that the lattice constant decreases and the crystalline size increases as the amount of dopant Ag increases in In_2O_3.

Table 1
Structural parameters of pure In_2O_3 and Ag-doped In_2O_3 nanoparticles.

Sample	$a = b = c$ (Å) ±0.002	Crystallite size D_S (nm) ±0.3	Particle size (D_{TEM}) (nm)
In_2O_3	10.109	11.59	11.1 ± 0.2
In_2O_3:1% Ag	10.083	12.21	12.2 ± 0.1
In_2O_3:3% Ag	10.077	13.35	12.4 ± 0.2
In_2O_3:5% Ag	10.048	14.07	16.3 ± 0.3

3.2. TEM study

The low resolution and high resolution TEM images of In_2O_3 and Ag-doped In_2O_3 nanoparticles are shown in Fig. 2(a–d) and (e–l) respectively. Nearly spherical shape with some agglomeration and their sizes distributed over the nanometer range for pure and Ag-doped In_2O_3 nanoparticles has been observed. The rings in SAED pattern (Fig. 2(m–p) correspond to (211), (222), (400), (444), and (622) planes of cubic bixbyte phase of In_2O_3 [27]. Further, from the HRTEM image (Fig. 2(i)), the interplanar spacing (d) has been calculated using IMAGE J software and illustrates that d is 0.29 nm for pure In_2O_3, which is consistent with the (222) plane of bcc In_2O_3 [28]. For 5% Ag-doped In_2O_3 (Fig. 2(l)), the interplanar spacing 0.28 nm corresponds to (222) plane of In_2O_3 and

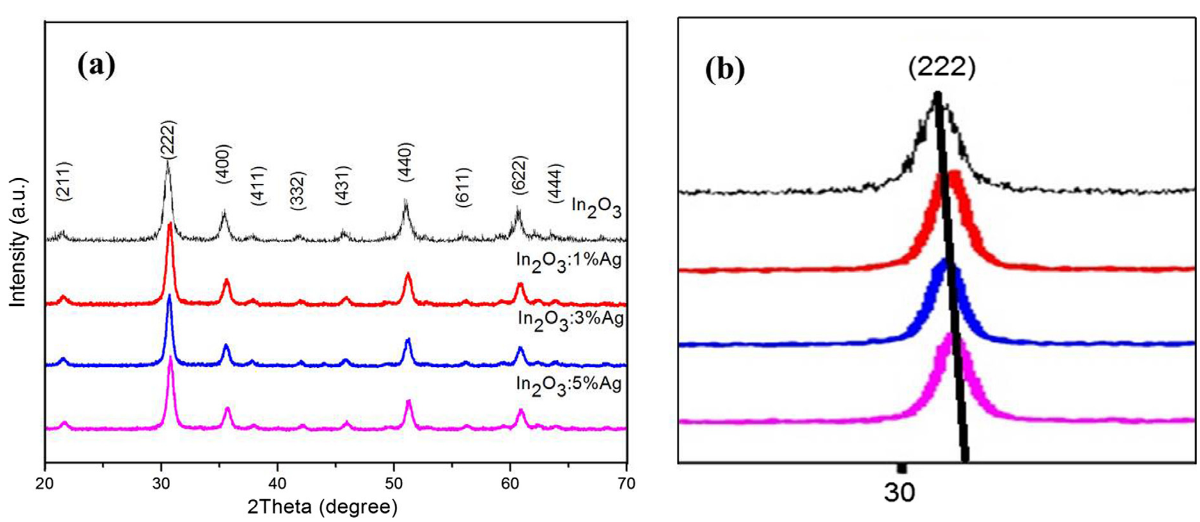

Fig. 1. (a) XRD patterns In_2O_3 and Ag-doped In_2O_3 nanoparticles and (b) magnified image of maximum intensity peak (222) of In_2O_3 and Ag-doped In_2O_3 nanoparticles.