

# Selectivity of Ti-doped $\text{In}_2\text{O}_3$ ceramics as an ammonia sensor

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## Abstract

Nanoscale  $\text{In}_2\text{O}_3$  powders doped with titanium were prepared by using  $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$  as a source matter. The materials doped with  $\text{Ti}^{4+}$  ions obviously showed the enhanced selectivity to ammonia sensor, compared with two reducing gases of  $\text{H}_2$  and  $\text{CO}$ , in the concentration range of 5–1000 ppm at a low operating current (165 mA, equal to 145 °C). Characterization of the materials was performed by thermal analysis, XRD, BET, FTIR, and magnetic susceptibility measurement. The mechanism of the selective gas sensing is proposed on the basis of the differences in gas molecular structure for adsorption and activation.

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**Keywords:**  $\text{In}_2\text{O}_3$ ; Ammonia sensor; Selectivity; Sensing mechanism

## 1. Introduction

An efficient gas sensor must have high sensitivity and good selectivity at low operating temperature. Because of the complexity of gas sensing mechanism, the main method of giving suitable selectivity is implemented generally by altering the operating temperature, using effective gas filters, and adding catalytically active dopants at present [1,2].

Ammonia ( $\text{NH}_3$ ) is a colorless gas with a special odour and is very harmful to the human body. It is not only used largely to synthesize various materials in chemical industries, but also may exist in agricultural production and our dwelling place. Therefore, it is necessary to monitor the concentration of ammonia for atmospheric environment measurement and control.  $\text{In}_2\text{O}_3$  can be used as a material of ammonia sensors, but the major problem associated with  $\text{In}_2\text{O}_3$  is its cross-sensitivity, as encountered with most oxide semiconductor sensors. As  $\text{NH}_3$ ,  $\text{H}_2$  and  $\text{CO}$  are all reducing gases, conventional ammonia sensors are invariably more sensitive to  $\text{H}_2$

and  $\text{CO}$  than to  $\text{NH}_3$  [3]. The literature reported that the main cause of the low sensitivity to  $\text{NH}_3$  is the competitive occurrence of two reactions during the  $\text{NH}_3$  oxidation on the sensor surface; consumption of chemisorbed oxygen and chemisorption of negatively charged  $\text{NO}_x$  species (especially  $\text{NO}_2$ ) as the oxidation products of  $\text{NH}_3$  [4]. A sensitization mechanism has been proposed which explains the sensitivity of  $\text{NH}_3$ ,  $\text{H}_2$  and  $\text{CO}$  of metal oxide sensors, and it is known that a Pt-catalyst can greatly increase the sensor response [5–7]. With respect to the oxidation reactions, the adsorbed  $\text{O}_{2\text{ads}}^-$  and  $\text{O}_{\text{ads}}^-$  species and also the exposed oxygen atoms on step sites are classified as reactants [8,9]. The details are well described by Yamazoe et al. [10] and Kohl [11] about the surface reactions between metal oxides and oxygen adsorbates. Romanovskaya [12] reported that Pt-loaded  $\text{In}_2\text{O}_3$  ceramics can increase the sensitivity to  $\text{NH}_3$ . However, there is little related description about how to decrease the sensitivity to  $\text{H}_2$  and  $\text{CO}$  for this kind of materials. In this paper, therefore,  $\text{Ti}^{4+}$ -doped  $\text{In}_2\text{O}_3$  materials are examined for detecting  $\text{NH}_3$ , and it is found that the materials exhibit significantly larger responses to  $\text{NH}_3$  than to  $\text{H}_2$  and  $\text{CO}$ . The mechanism for the selective  $\text{NH}_3$  detection is also explained on the basis of the differences in molecular structure for adsorption and activation.

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## 2. Experimental

### 2.1. Preparation of specimens

Pure and  $\text{Ti}^{4+}$ -doped  $\text{In}_2\text{O}_3$  nano-particles were obtained by using indium chloride ( $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ ) and tetrabutyl titanate ( $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ ) as starting materials and polyethylene glycol 2000 as a dispersant, and an ammonia water solution was joined for preparing the indium hydroxide sol. The amount of the doped  $\text{Ti}^{4+}$  was 0.5, 1.0 or 5.0 mol%. To achieve the homogeneous sol, the sol was stabilized with nitric acid and mixed around for several days. After vacuum-drying at  $80^\circ\text{C}$ , the powder obtained (precursor) was made into thick films.

The measurement electrode was composed of a pair of four-fingered gold electrodes of  $120\ \mu\text{m}$  width and  $40\ \mu\text{m}$  spacing between fingers on an alumina substrate. The overlap distance of the fingers was  $400\ \mu\text{m}$ , and a Ni–Cr heater ( $37\ \Omega$ ) was made on the opposing face of the substrate. The thick film was coated with a layer of sensor materials of  $\sim 10\ \mu\text{m}$  thick mixed with terpineol (chemical pure grade), followed by vacuum-drying at  $80^\circ\text{C}$ . Then, the thick films were annealed at different temperatures for 1 h under ambient pressure. Finally the sensors were subjected to measurement of sensor responses to  $\text{NH}_3$ ,  $\text{H}_2$  and  $\text{CO}$ .

### 2.2. Characterization

The thermal effects associated with the heat treatment of uncalcined powders were investigated with an instrument of thermogravimetry and differential scanning calorimetry (TG and DSC, NETZSCH STA 449, Germany) at a rate of  $10^\circ\text{C}\ \text{min}^{-1}$  in flowing nitrogen from room temperature to  $1000^\circ\text{C}$ . Specific surface areas were measured by a BET method with a nitrogen adsorption apparatus (Model: ASAP 2000, Micromeritics Instrument Group, USA). Crystalline structure of the samples was analyzed by powder X-ray diffraction (XRD, Model: X'pert, Philips Corp., Holland), and crystallite size was calculated according to the well-known Scherrer's equation.

FTIR spectra of the annealed powders were recorded by a KBr method using a Spectrum-2000 FTIR spectrophotometer (Perkin-Elmer, USA) in the range of  $400\text{--}4000\ \text{cm}^{-1}$ . The surface structure of the thick film sensors was investigated by environmental scanning electron microscopy (ESEM, XL30, Philips Corp.). Magnetic susceptibility ( $\chi$ ) was measured by D-200 Research Magnetic Faraday Balance (Cahn Instrument Ltd., USA) with a sensitivity of  $0.0001\ \text{mg}$  at room temperature ( $25^\circ\text{C}$ ) under high vacuum ( $10^{-6}\ \text{Torr}$ ).

The materials were made into thick films for measuring the sensor responses to  $\text{NH}_3$ ,  $\text{H}_2$  and  $\text{CO}$ . The resistance of a sensitive element was measured in air ( $R_a$ ) and in air-gas mixtures ( $R_g$ ) under the same operating current. The gas response magnitude ( $S$ ) was defined as the ratio of  $R_a$  to  $R_g$  ( $S=R_a/R_g$ ). The concentration of  $\text{NH}_3$ ,  $\text{H}_2$  and  $\text{CO}$  were  $5\text{--}1000\ \text{ppm}$  in air.

## 3. Results and discussion

### 3.1. Analysis and measurement

The TG curve of the precursor (pure  $\text{In}_2\text{O}_3$ ) showed two apparent weight loss stages (Fig. 1). The first weight loss near  $100^\circ\text{C}$  is mainly due to the loss of water, while second at  $100\text{--}320^\circ\text{C}$  is associated with burning of the residual dispersant, removal of  $\text{OH}^-$  group and decomposition of  $\text{HNO}_3$ . The DSC curve indicates two endothermic peaks near  $100$  and  $240^\circ\text{C}$ , and an exothermic peaks at  $310^\circ\text{C}$ . Two weight loss stages are observed corresponding to the two endothermic peaks. The exothermic peak at  $310^\circ\text{C}$  is due to the burning of the residual dipersant. Therefore, the calcination temperatures higher than  $350^\circ\text{C}$  were chosen in present experiments. As the result, the largest response to  $1000\ \text{ppm}\ \text{NH}_3$  of the pure  $\text{In}_2\text{O}_3$  sensor was achieved at  $550^\circ\text{C}$  among the calcination temperatures of  $350\text{--}850^\circ\text{C}$  (Fig. 2). Therefore, the effects of  $\text{Ti}^{4+}$ -doping on the gas-sensing characteristics of  $\text{In}_2\text{O}_3$  sensors were examined at this particular calcination temperature ( $550^\circ\text{C}$ ).

Fig. 3 shows the XRD patterns of pure and  $\text{Ti}^{4+}$ -doped  $\text{In}_2\text{O}_3$  samples calcined at  $550^\circ\text{C}$  for 1 h. The XRD patterns with the largest peak intensity of crystal plane 222 indicate the main crystal phase of bixbyite-type structure (cubic- $\text{In}_2\text{O}_3$ , space group  $\text{Ia}_3$ ; the unit cell contains 16 formulae). No impure phases corresponding to titanium compounds were

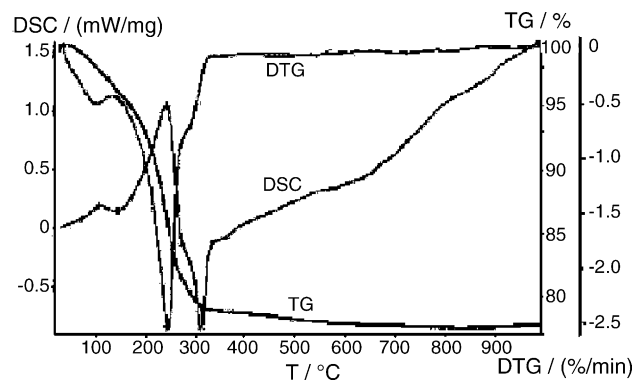


Fig. 1. TG, DTG and DSC curves of pure  $\text{In}_2\text{O}_3$ .

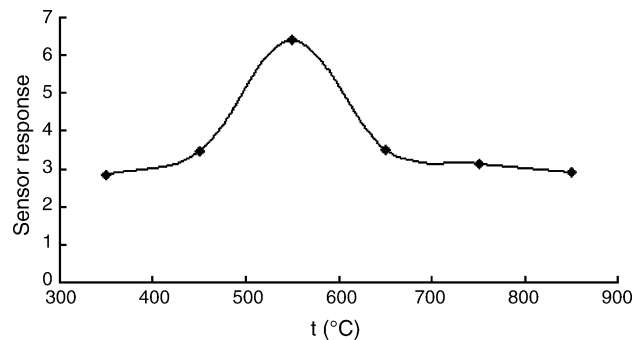


Fig. 2. Annealing temperature dependence of sensor response ( $R_g/R_a$ ) to  $1000\ \text{ppm}\ \text{NH}_3$  of pure  $\text{In}_2\text{O}_3$ .

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