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High sensing response of β-Ga_2O_3 thin film towards ammonia vapours: Influencing factors at room temperature

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ABSTRACT

The gallium oxide (β-Ga_2O_3) thin films were deposited onto a quartz substrate using spray pyrolysis technique with gallium acetylacetonate as precursor salt. The X-ray diffraction pattern of the annealed film at 900 °C indicated the formation of monoclinic β-Ga_2O_3 phase with polycrystalline nature. Field emission scanning electron micrograph showed nanocrystallites over the film surface. The ammonia sensing property of the film at room temperature (~30 °C) was studied by chemiresistive method. Influencing factors such as vapour concentration, relative humidity and film thickness in ammonia sensing performance were studied and reported.

1. Introduction

Ammonia (NH_3) finds diversified applications in the field of agriculture, automobiles and food industry in the form of a fertiliser, fuel and antimicrobial agent respectively [1]. The detection of ammonia is important owing to its toxic and strong reducing nature. The Occupational Safety and Health Administration (OSHA) established the maximum recommended exposure level of ammonia to be 25 ppm [2]. Several analytical techniques to detect ammonia in a gas/vapour stream include the electrochemical method [3], laser technology [4], mass spectrometry [5] and optical method [3]. These techniques were found to be time consuming and require sophisticated instruments. Hence a cost effective and real-time ammonia sensor would be preferable to suit the scenario. Thin film based semiconductor metal oxides are capable as chemical sensing element because of its strong atmosphere dependent electrical conduction.

Gallium Oxide (Ga_2O_3) exhibits five-polymorphic phases and the monoclinic β-Ga_2O_3 is chemically and thermodynamically stable [6] when compared to the other phases. It also stands as a promising candidate for sensing various gases and vapours in low and high temperature range [7–10]. Lin et al. [8] reported the use of DC-sputtered β-Ga_2O_3 nanobelt as a NO_2 sensor at room temperature. Schwebel et al. [9] investigated the use of Ga_2O_3 thin film with Au cluster on the surface for CO sensing at 600 °C and Baban [10] reported the RF sputtered Ga_2O_3 thin film for oxygen sensor at 900 °C. Different organic and inorganic materials [11–15] were reported for the sensing of ammonia vapour at low temperature by chemiresistive method. Lauque et al. [16,17] reported the ammonia sensing properties of ionic conductor of CuBr with good reproducibility. Yet, the response and recovery time were in the order of minutes because of slow ionic conducting nature of copper.

Factors such as vapour concentration, relative humidity (RH) and film thickness influencing the ammonia sensing performance of the material at room temperature were found less significant reporting. The present work highlights the influence of relative humidity and film thickness in the ammonia sensing performance of β-Ga_2O_3 thin film. Different techniques, such as spray pyrolysis [18], sol–gel [19], sputtering [8], pulsed laser deposition [20], chemical vapour deposition [21] and thermal evaporation [22] have been presented for deposition of β-Ga_2O_3 films. In the present work, spray pyrolysis technique was chosen due to its simple film preparation as well as various nanostructured films can be obtained by optimising precursor salt concentration, carrier gas pressure, solution flow rate and substrate temperature.

2. Materials and methods

2.1. Sensing element preparation

Gallium oxide thin films were deposited onto a quartz substrate by a home-built spray pyrolysis system [23]. Gallium

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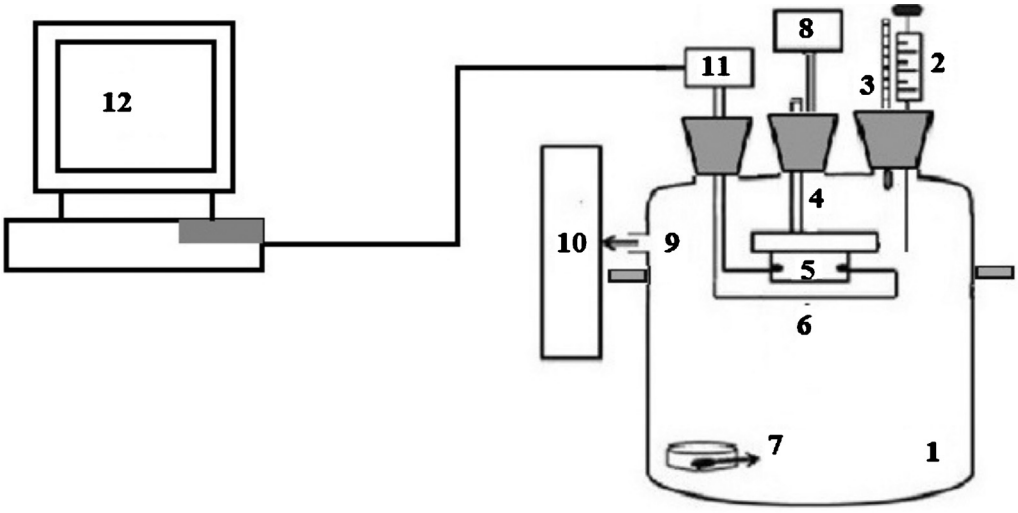

1. Testing chamber 2. Chromatogrphic syringe 3. Mercury thermometer

4. Sample holder 5. Sensing element 6. Electrical contact

7. Salt solution 8. Humidity meter 9. Vapour outlet port

10. Vacuum pump 11. DAQs board 12. Computer interface

Fig. 1. Schematic diagram of vapour sensing setup.

acetylacetonate ($C_{15}H_{21}GaO_6$, 99.9% purity, Sigma Aldrich) of 0.025 M was used as a precursor salt with a mixture of deionised water (49 mL) and acetic acid (1 mL) as solvent. The precursor solution was atomised as a fine mist by air blast method through a glass nozzle and sprayed at an angle of 45° onto a quartz substrate maintained at a temperature of 350 °C. Large numbers of samples were prepared by varying the substrate temperature to find the optimised condition for obtaining uniform distribution of nanocrystallites over the film surface. It was observed that when the deposition temperature was above 350 °C, the precursor solution vaporises before reaching the substrate thereby forming powdery solid particles which are non adherent [23]. On the other hand, low temperature deposition leads to an incomplete pyrolytic reaction causing partial decomposition of precursor salt [23]. Hence, the substrate temperature was maintained at 350 °C using a micro controller based thermostat fitted with K-type thermocouple. Compressed dry air at a pressure of 2 kg/cm^2 was employed as a carrier gas, and the distance between the substrate and spray nozzle was fixed to 30 cm. To avoid sudden cooling of the substrate, the precursor solution was sprayed onto the substrate for 4 s at an interval of 60 s. The pyrolytic reaction in the formation of gallium oxide is conveyed in Eq. (1)

$$\begin{aligned} &Ga(CH_3COCHCOCH_3)_3 \underset{\Delta 220^\circ C}{\longrightarrow} CH_3COCH_3 + CH_3COCH_2COCH_3 + [Ga(OH)CHOO]^+ \\ &[Ga(OH)CHOO]^+ \underset{\Delta 250^\circ C}{\longrightarrow} Ga + CH_3COOH \\ &Ga \underset{\Delta 350^\circ C}{\longrightarrow} Ga_2O_3 \end{aligned} \quad (1)$$

When the fine mist of gallium acetylacetonate solution reaches the hot substrate, thermal decomposition starts at 220 °C, which can be attributed to a loss of acetone (CH_3COCH_3), and acetylacetone ($CH_3COCH_2COCH_3$) molecules resulting in the formation of non-stoichiometric co-ordinate compound of [Ga(OH) CHOO]$^+$. At 250 °C, the compound decomposes to form gallium (Ga) and acetic acid (CH_3COOH) and, at 350 °C the gallium is readily oxidised to form a gallium oxide as a final solid film.

2.2. Characterisation

Structural studies were carried out using a Bruker – D8 Focus X-Ray Diffraction (XRD) unit with Cu Kα_1 radiation at a generator setting of 30 mA and 40 kV. The surface morphology and elemental identification of the film were obtained from JEOL-6701 Field-Emission Scanning Electron Microscopy (FE-SEM) coupled with Energy Dispersive Spectroscopy (EDS). The film thickness was obtained from a cross sectional SEM (FEI Quanta 300, Icon analytical). The water contact angle over the film surface was obtained using a Goniometer (ramé-hart model 250, Standard Goniometer with DROP image Advance v2.3). For vapour sensing studies, the salts (LiCl (98%), $MgCl_2$ (98%), Mg (NO_3) (98%), NaCl (99%), KNO_3 (98%)) as humidity source and liquid ammonia (25%) as test vapour source were purchased from Merck.

2.3. Chemical sensing setup

The vapour sensing properties of the film have been studied using home-constructed test chamber of 1.5 L capacity as shown in Fig. 1. Before sensing studies, the film was conditioned at 300 °C for 24 h to remove undesirable pre-adsorbed organic and water molecules. Ohmic electrical contacts were made on the film (12 mm × 10 mm) using thin copper wire and silver paste. The change in electrical resistance of the film was recorded using LabVIEW controlled data acquisition system (DAQs), during the process of injection and venting of ammonia vapour. The electrical resistance of the film in dry air atmosphere was found to be 87 GΩ and was taken as a baseline resistance (R_o). For sensing studies, calibrated volume of liquid ammonia (25%) was introduced into the