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# Vacuum deposited $WO_3$ thin films based sub-ppm $H_2S$ sensor

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ABSTRACT

A simple method of vacuum deposition using W foils has been utilized to fabricate Au-incorporated $WO_3$ thin film sensors. Incorporation of Au has been demonstrated to improve both the sensitivity and the selectivity of the sensor films towards $H_2S$. The effect of operating temperature, Au loading and gas concentrations have been investigated and correlated with the observed sensitivity values to determine the optimum conditions for realizing $H_2S$ sensor with better sensing properties. The sensor film containing 2.32 at.% Au detected $H_2S$ selectively with an enhanced sensitivity of $S = 16$ (1 ppm) at an operating temperature of 250 °C. The enhanced response kinetics has been confirmed further using Raman and work function measurements.



## 1. Introduction

$WO_3$, an n-type wide band gap material, has demonstrated its potential for realizing highly sensitive and selective sensors towards different gases [1,2]. Similar to other semiconducting oxides like $SnO_2$ and ZnO, its surface is characterized by the presence of oxygen vacancies. These oxygen vacancies act as donor levels and contribute in the governing sensing mechanism [3]. Various sensors including $C_2H_5OH$, $O_3$, $NH_3$, $NO_x$, $H_2S$, have been attempted and realized using $WO_3$ in conventional thin films as well as nanoforms [4–7]. Thin film based sensors have been commonly deposited using techniques like micromachining, sputtering, thermal evaporation and sol–gel [8]. To improve sensitivity and selectivity, the host matrix is generally modified with various sensitizers including Pd, Pt, Ag, Au, and often a bimetallic sensitizer is also considered [9–12]. In particular, Au incorporation resulted in improved sensing characteristics like faster response time and increased sensitivity values and accordingly, has been found to be a promising sensitizer [13]. Modulation of sensing properties based on Au has been mainly ascribed to the electronic sensitization mechanism. Use of Au has been demonstrated to improve the sensing performance towards different gases like $NO_2$, $NO_x$ $H_2S$, $H_2$, and $NH_3$ [14–18]. Of these hydrogen sulfide ($H_2S$) is one of the highly toxic and flammable gases that is being employed extensively in various industrial applications. In particular, its exposure affects human's nervous system and could cause loss of consciousness at a very low concentration. Its threshold limit value has been set to 10 ppm and hence detection at low or sub-ppm concentrations has become the focus of research. Besides, as the catalytic decomposition of $H_2S$ is known to occur between 300 and 400 °C [19], the $H_2S$ sensors must be operated below 300 °C. Ionescu et al. have reported the sub-ppm detection of $H_2S$ upto 20 ppb with a sensitivity value of ~1.1 ($S = 1.25$ towards 50 ppb) at an operating temperature of 250 °C. Although the sensors responses were good, nanoparticles formation via advanced gas deposition unit is tedious [2]. Tao et al. have investigated the effect of different doping element on $H_2S$ sensing properties of $WO_3$ films deposited by RF plasma sputtering [10]. There report lacks the systematic investigation of doping element and its concentration in the host matrix to realize a better sensing material. Hence to know and understand under what conditions sensitizers imparts sensitivity towards a particular gas demands a detailed investigation.

In the present work we report a systematic investigation of the gas sensing properties of pure and Au-incorporated $WO_3$ sensor thin films towards $H_2S$. The sensor films have been realized using a simple method of vacuum deposition. We have investigated the effect of sensor operating temperature, Au loading, and gas concentration on sensing properties to determine the optimum conditions for the detection of $H_2S$ gas. Additionally, Raman and work function measurements both with and without the test gases

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have been performed to elucidate the nature of interaction with the sensor film. Our studies indicates that Au-incorporated $WO_3$ sensor films could detect sub-ppm (50 ppb, $S = 2.7$) $H_2S$ selectively at an operating temperature of 250 °C.

## 2. Experimental section

### 2.1. Sensor fabrication

The steps involved in the fabrication of sensor films are illustrated schematically in Fig. 1. In brief, $Al_2O_3$ substrates were first cleaned by ultrasonicating in solvents namely trilene, acetone and methanol. Contact electrodes were then predefined on these substrates using Pt-wire and a high temperature drying Au paste followed by curing at 850 °C for 10 min. The predefined electrodes were protected by masking with molybdenum foils. W films (~600 nm thick) were then vacuum deposited using W-foil (purity: 99.99%, dimensions 1 × 4 cm) under application of a very high current (~80 A) in a base vacuum of $2 \times 10^{-4}$ mbar. In order to prepare Au-incorporated $WO_3$ films a sandwich layer of W(300 nm)/Au ($t$ nm)/W (300 nm) ($t$ taking values 1.86, 3.3, 7.4 and 13.3 nm corresponding to 0.55, 1.23, 2.32 and 3.95 at.%, as measured using energy dispersive X-ray analysis (EDAX)) were deposited onto alumina substrates. The resulting films were then subjected to post deposition annealing at 600 °C for 1 h in quartz tubular furnace under constant oxygen ($O_2$) flow of 100 sccm. In order to make electrical contacts 120 nm thick Au layer was deposited using a mask having 400 μm spacing.

### 2.2. Instruments and analysis

Surface morphology of the as-grown films was investigated using scanning electron microscopy, SEM, (TESCAN, model: TS 5130MM) equipped with EDAX unit. X-ray diffraction measurements were performed using Rigaku expert machine with $CuK_\alpha$ radiation having 1.5406 Å wavelength. Raman spectra were recorded on a Labaram-I spectrometer in a backscattering geometry at room temperature. Prior to measurements sensor samples were exposed to $H_2S$ at an elevated temperature of ~100 °C. The change in signal was better observed for higher dose of exposure (100 ppm) and hence was chosen for the experiments. Kelvin probe contact potential difference (CPD) measurements were carried out using SKP Kelvin Probe 4.5 from KP Technology Ltd. UK. All the measurements were performed at room temperature and ambient conditions using Au electrode having tip diameter of 2 mm. For better average value of the work function the electrode tip was scanned across the sample surface (Raster scan) and the relative variation in the CPD was measured. Sensor samples were exposed to 100 ppm of $H_2S$ at an elevated temperature of ~100 °C before measuring the work function [20]. Sensing measurements were performed in a static system as described elsewhere [21]. In brief, sensor films were mounted in a stainless steel test-chamber (volume: 250 $cm^3$) equipped with a temperature control unit. The desired temperature was achieved using a Pt-wire based heater attached to the backside of the sensor film. The desired concentration of the test gas was achieved by injecting the measured quantity of commercial gas inside the chamber. Commercial grade gases having 1000 ppm concentration of desired gas in $N_2$, obtained in half liter cylinders were used to control the final concentration. The resistance of the film was monitored and acquired as a function of time using a personal computer equipped with Labview software. Recovery of the sensors was achieved by opening the housing to the atmosphere.

Sensor response or sensitivity ($S$) was calculated using the relation:

$$S = \frac{R_a}{R_g} \quad (1)$$

for reducing gases namely $H_2S$, $CH_4$ and $NH_3$, and

$$S = \frac{R_g}{R_a} \quad (2)$$

for oxidizing gases namely $Cl_2$, $NO_2$ and NO, where $R_a$ and $R_g$ are resistances in air and test gases, respectively. Response and

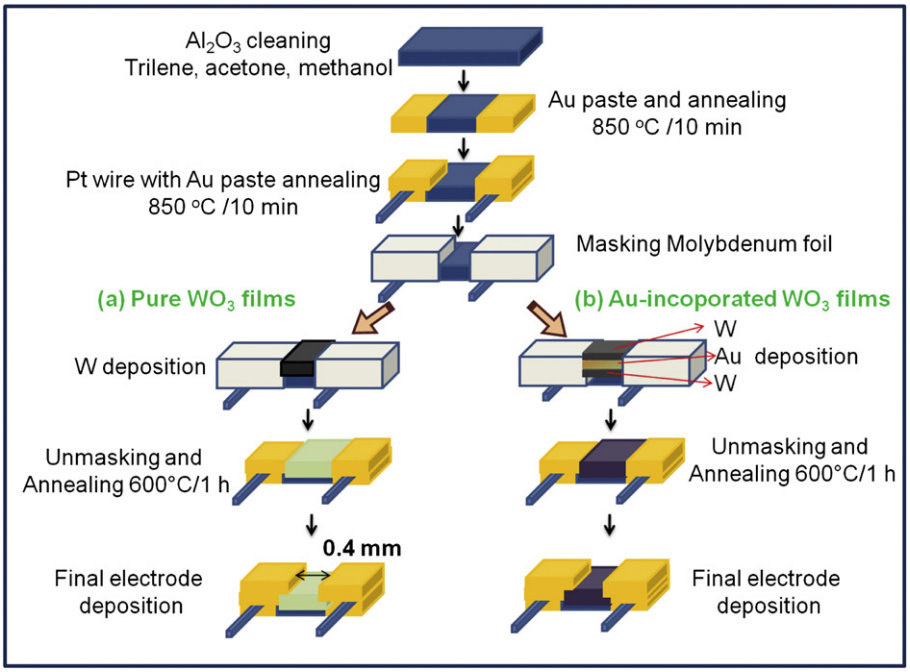


**Fig. 1.** Steps involved in the fabrication of (a) pure $WO_3$ and (b) Au-incorporated $WO_3$ sensor devices.