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Room Temperature NH3 – Sensing Properties of WO3 thin films Synthesized by Microprocessor Controlled Spray Pyrolysis

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Abstract: *Tungsten trioxide thin films were deposited on glass substrates by microprocessor controlled spray pyrolysis method. The characterization and gas sensitivity of WO3 thin film sensor were investigated. The WO3 thin films were observed to be sensitive for NH3 vapor at different concentrations (5-200ppm) at room temperature. The maximum sensitivity for NH3 vapor by WO3 sensor was found at 200ppm concentration. The response (~ 50s) and recovery (~30s) were the main features of these sensors. The high sensitivity, quick response and fast recovery indicated that WO3 thin film sensors are selective for NH3 vapor when compared with ethanol, acetone and toluene vapors.*

Keywords: *Microprocessor controlled spray pyrolysis, NH3 sensor, Room temperature, WO3 thin film, XRD.*

I. Introduction

Metal oxide semiconductor thin films have been widely used in gas sensors towards a wide range of gases like NH3, NO2, CH4 and H2S [1, 2]. Commercial SnO2 gas sensors have been extensively used to detect many gases in ppm levels. The lack of selectivity in SnO2 thin film gas sensors led researchers to investigate other MOS such as WO3. The sensing principle in the detection of gases is that there will be a change in electrical resistance [3]. Sensing mechanism depends highly on the operating temperature [3]. Sensing of gases like NH3, NO2, CH4 and H2S using WO3 thin film sensors have been reported at higher operating temperature (200o C) [4]. The reduction of operating temperature is an important factor in the manufacturing of MOS gas sensors.

Ammonia, a natural reductive gas is highly toxic with a limiting value of 25ppm for the exposure of 8 hrs [5]. Previously some of the researchers reported the use of WO3 thin film sensors for the detection of NH3 gas/vapor. Aravind Reghu et.al [6] reported the properties of WO3 sensors for detecting NH3 in the ppb range at the operating temp 450˚ C. The gas sensing properties of nanocrystalline WO3 with platinum doping was investigated by Senguttuvan et.al [7].

Most of the MOS gas sensors operate at elevated operating temperature. This will increase the power consumption, reduce sensor life and complexity in designing gas sensor unit [8]. In the present study, WO3 thin film sensors have been prepared by advanced microprocessor controlled spray pyrolysis method [9]. To our knowledge, this is a novel attempt in studying the gas sensing properties of WO3 thin film sensor for detection of NH3 vapor at room temperature.

II. Experimental Details

Precursor solution of 0.05 M was prepared by dissolving appropriate quantity of pure AR grade WO3 powder in 50 ml hot ammonia solution by continuous stirring using magnetic stirrer and then diluted with de-ionized water to desired volume.

The cleaned substrates were then placed on the substrate heater of the spray equipment to provide proper heating with uniformity to films. The temperature controller was set to 300˚ C. The ammonium metatungstate precursor solution was sprayed on the preheated glass substrates heated at a temperature 300˚ C. The substrate temperature was controlled by microprocessor. Preparative parameters were optimized for the best quality WO3 thin film. Some of the samples were annealed at 500˚ C for 1hr and cooled down to room temperature naturally.

The gas sensing unit comprised Chromel-Alumel thermo couple, digital temperature indicator, heating plate and gas chamber. Two probe dc measurement technique was used to measure the electrical resistance in the presence of the test gas and air.

A constant voltage of 20 Volt is applied and the current passing through the sensor film was monitored in digital picoammeter. The Cr-Al thermocouple was used to sense the operating temperature of the sensor. The output of the thermocouple was connected to a digital temperature indicator. The sensor response was measured at room temperature. The required concentration of the target gas/vapor inside the chamber was achieved by injecting a known volume of test gas / vapor using a micro pipette.

After completing the measurement in target gas/vapor, air was allowed to enter into the chamber and the sample's resistance was measured in air. The sensor resistance was measured for different concentration of the target gas by successive exposure to test gas and air.

III. Characterization Techniques

The structural characterization of WO3 films were carried out using PAN alytical make, Model X'pert PRO X-ray diffractometer with CuKα $(\lambda = 1.5406\ A^0)$radiation in 2θ $20^0 - 80^0$ range . The optical transmittance spectra of the films were recorded on PG-T90$^+$ $UV - VIS - IR$ double beam spectrophotometer in the wave length range 300 – 900 nm. The surface morphological study of WO3 thin films were carried out by Scanning Electron Microscope (SEM) using JSM-6390. The gas sensing properties of WO3 thin films were performed using gas sensing measurement unit available at Multifunctional Materials and Devices Lab, SASTRA University, Thanjavur.

IV. Results and Discussion

4.1 Structural Analysis

Fig.1 shows the XRD pattern of the annealed WO3 thin film. The triplet peak observed at 2θ values 23.1°, 23.5° and 24.4° were related to monoclinic WO3 thin films with (002), (020), (200) planes (JCPDS: 83-0951). The average crystallite size was estimated to be 49.94 nm using the Debye-Scherrer formula.

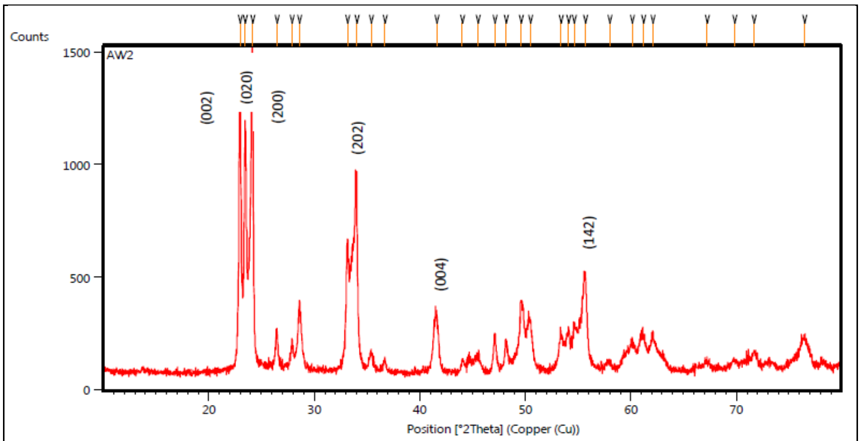

Fig.1. XRD pattern for WO_3 thin film deposited at 300° C and annealed at 500° C for 1 hr

4.2. Optical Properties

The optical properties of WO3 thin films are determined from the transmittance spectra in the wavelength range of 300-900 nm. The optical band gap for direct transition of as deposited WO3 thin film was obtained from Tauc plot (αhν)2 vs hν by extrapolating the linear portion to hν axis. The optical band gap of as deposited WO3 thin film was 3.7 eV, which is in good agreement with the literature [10, 11, 12].

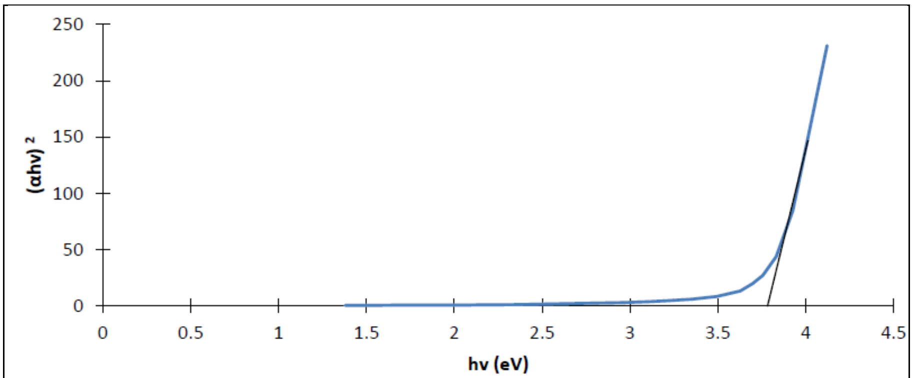

Fig.2. Plot of $(h\nu\alpha)^2$ vs hν of WO_3 thin film deposited at 300° C substrate temperature

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4.3. Surface Morphology

Scanning Electron Microscopy (SEM) was used for studying the surface morphology of WO3 thin films. Fig.3 exhibited the SEM image of WO3 thin film with spherical shaped grains of 380-500 nm diameter.

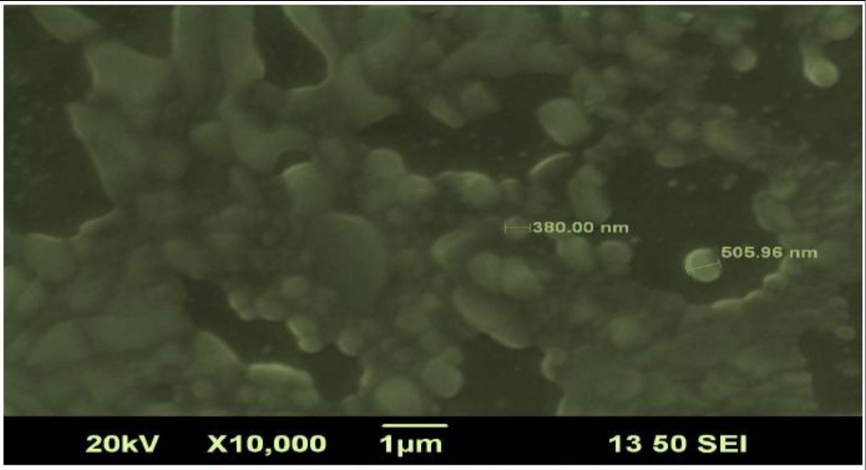

Fig.3.SEM image of WO_3 thin film deposited at 300° C

4.4. Gas sensing properties

The annealed WO3 thin film sensor was kept in the gas chamber to sense NH3 vapor at room temperature. The sensor element was exposed to 5, 10, 20, 50, 100 & 200 ppm levels of NH3 vapor. Once the exposure was completed, the sensor was allowed to recover in the flow of air. The change in current in picoammeter was measured and the corresponding change in resistance of WO3 thin film sensor was estimated.

4.4.1. Sensitivity

Since WO3 is a n-type semiconductor, the resistance of WO3 thin films decreased on the exposure of NH3 [6]. For reducing gas, the sensitivity of the film was calculated using the relation:

$$S = Ra / Rg$$

Where, S is the Sensitivity, Ra is the resistance of the film in air and Rg is the resistance in test gas NH3. The sensor response curve of WO3 thin film was shown in Fig.4. The maximum sensitivity was achieved to 200 ppm concentration of NH3. The Sensitivity of the film as a function of NH3 concentration obtained at room temperature was shown in Fig.5. Response of the film was found to be linear as the concentration increased (5 – 200 ppm).

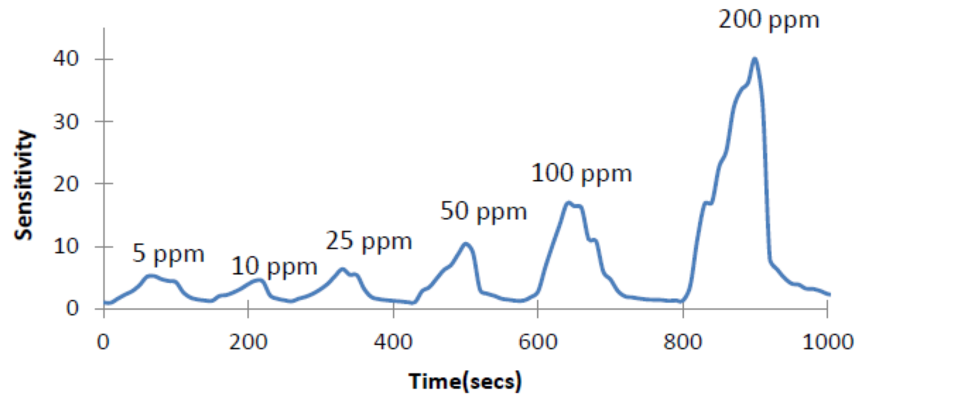

Fig.4. Response of WO_3 thin film sensor for detection of NH_3 vapor at room temperature

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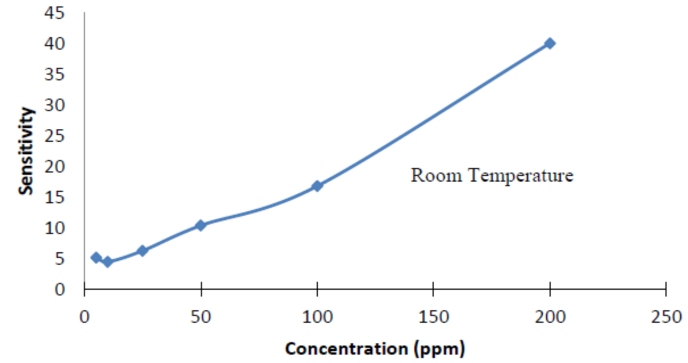

Fig.5. Response of WO_3 thin film sensor for different concentrations of NH_3 vapor at room temperature

4.4.2. Selectivity

WO3 thin film sensor had maximum sensitivity in the detection of NH3 vapor when compared with acetone, ethanol and toluene vapors at room temperature. WO3 thin film sensor was highly selective towards NH3. Fig.6 showed the response to NH3, acetone, ethanol and toluene vapors at room temperature.

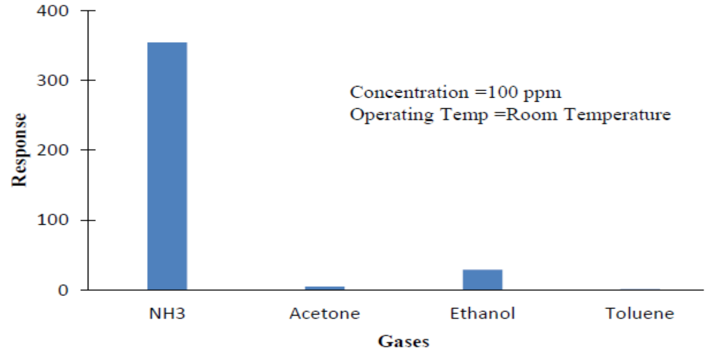

Fig.6. Response of WO_3 thin film sensor to different vapors for 100 ppm concentration at room temperature

4.4.3. Response and Recovery Time

The response time is defined as the time taken by the sensor to achieve 90% of the maximum sensitivity when the sensor is exposed to a test gas[13]. The recovery time is the time period over which the response of the sensor reduces to 10% of the saturation value when the sensor is exposed to air[14]. From Fig.7, we see that when NH3 was injected into the chamber the sensitivity increased and reached a maximum value in 50 sec (response time). On the other hand, on removal of NH3 from the chamber, the response decreased slowly and reached its initial value after 30 sec (recovery time).

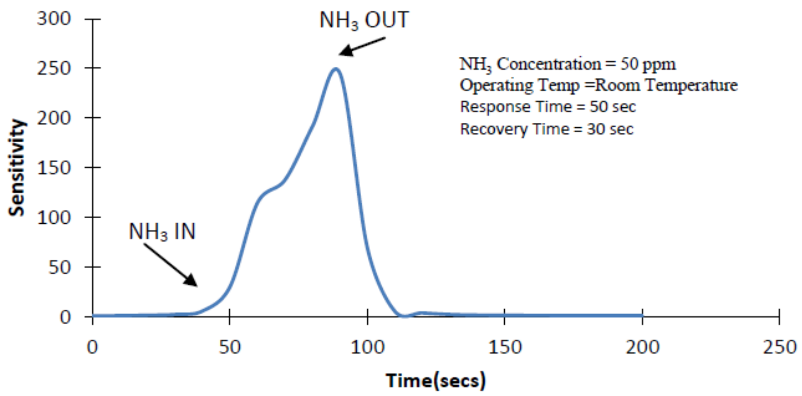

Fig.7. Response and Recovery time of WO_3 thin film sensor for detection of 50 ppm concentration of NH_3 vapor at room temperature

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V. Conclusion

WO3 thin films were prepared by microprocessor controlled spray pyrolysis technique on glass substrates with 0.05 M concentrations at the substrate temperature 300˚ C. From X-ray diffraction spectrum, the WO3 thin films exhibited polycrystalline monoclinic structure. The average crystallite size was found to be 49.94 nm. The direct optical band gap was estimated to be 3.7 eV from the transmittance spectra. The surface morphology consisted of spherical grains of size 300—500 nm.

WO3 thin film sensor was found to be very sensitive to NH3 vapor at room temperature. On the exposure of NH3 vapor, the resistance of WO3 thin film sensor was found to be decreased. The maximum sensitivity to NH3 vapor by WO3 thin film sensor was achieved at 200 ppm concentration. WO3 thin film sensor showed quick response (50s) and fast recovery time (30s) at room temperature for the detection of NH3 vapor indicating that these films can be used as good sensor devices.

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