Ultra-low NO₂ detection by gamma WO₃ synthesized by Reactive Spray Deposition Technology

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Abstract:

A porous tungsten oxide (WO₃) NO₂ sensor was developed by a one-step flame based process called Reactive Spray Deposition Technology (RSDT). This nano-crystalline WO₃ film was deposited directly on gold interdigitated electrodes. The sensing characteristics of this NO₂ sensor was measured at the parts per million (ppm) level, (0.17-5 ppm in air) at 300°C. The sensors

showed a relatively fast response time (~ 7 s) and recovery time (~ 5 min), respectively. The stability of the sensor was evaluated for 300 h in 0.5 ppm NO₂ at 300°C in (2000 response-recovery cycles). The sensor was stable up to 6 days (~ 150 h) of continuous operation and degraded between 150 to 300 h. The morphology and surface properties of the WO₃ film were investigated with XRD, Raman spectroscopy, BET, SEM, TEM, and HRTEM.

Keywords: Gas sensor; Combustion; NO₂ sensing; Flame spray pyrolysis; Tungsten oxide nanoparticles; Reactive Spray Deposition Technology

Abbreviations:

RSDT: Reactive Spray Deposition Technology

COPD: Chronic Obstructive Pulmonary Disease

SIDS: Sudden Infant Death Syndrome

OSHA: Occupational Safety and Health Administration

DOAS: differential optical absorption spectroscopy

CRDS: cavity ring down spectroscopy

REMPI: resonance enhanced multi photon ionization

YSZ: yttria stabilized zirconia

NASICON: sodium superionic conductor

PECVD: plasma-enhanced chemical vapor deposition

PEL: permissible exposure limit

THF: tetrahydrofuran

ICDD: International Centre for Diffraction Data

1. Introduction:

NO_x (NO_2 , NO) is a toxic air pollutant which is produced as a byproduct of gasoline combustion in an internal combustion engine [1]. Exposure to unsafe levels of NO_2 (>10 ppm) causes irritation in eyes, nose and throat, while higher exposure (>25 ppm) can cause severe reactions for people with underlying pulmonary diseases like Chronic Obstructive Pulmonary Disease (COPD) or asthma. NO_2 reacts with water droplets in the trachea and lungs and forms droplets of nitric acid. These tiny droplets of nitric acid penetrate deeply into the lungs and causes various respiratory diseases. NO_2 exposure has also being associated with Sudden Infant Death Syndrome (SIDS) [2]. A detailed report of the actual accidental release of NO_2 and its subsequent health effect on the population is provided by Bauer et al [3]. The United States Occupational Safety and Health Administration (OSHA) has set a 5 ppm workplace permissible exposure limit for NO_2 , time averaged over an 8 h work shift. NO_2 also leads to the formation of ozone which is hazardous to both aquatic and terrestrial ecosystems. Current methods of quantification of NO_2 in the air includes gas chromatography equipped with mass spectroscopy (GC-MS) [4], chemiluminescence [5], differential optical absorption spectroscopy (DOAS) [6], laser induced fluorescence (LIF) [7], cavity ring down spectroscopy (CRDS) [8] and resonance enhanced multi photon ionization (REMPI) [9]. However, these analyses can be very expensive, requiring trained experts, and having complex, bulky and non-portable instrumentation. Metal-oxide semiconductor based gas sensors could be an effective solution to the underlying limitations faced by currently used methods for measuring NO_2 . Metal oxide materials, such as yttria stabilized zirconia (YSZ) [10], sodium superionic conductor (NASICON) [11], In_2O_3 [12], and

WO₃ [13], have been used for NO₂ gas sensing. Among metal oxides, WO₃ is considered to be a good candidate for low concentration NO₂ sensing.

WO₃ is an n-type semiconductor with a band gap of 2.75 eV which is known to exist in multiple polymorphs such as tetragonal (α) [14], orthorhombic (β) [15], monoclinic (ϵ and γ) [16], and triclinic (δ) [17]. Each of these forms exhibits different electrical, optical and magnetic behaviors which are favorable for particular applications. Gas sensing property of WO₃ was discovered for the first time by Shaver, in 1967 when he observed a change in conductivity of WO₃ thin film in presence of low concentration of H₂. Since then n-type WO₃ has been extensively used for sensing H₂ [18], H₂S [19], NO_x [13, 20], NH₃ [21], O₃ [22], CO [23], and acetone [24-25].

The essential components of a gas sensing device are: a metal-oxide sensing layer deposited on gold or platinum interdigitated electrodes which are attached to, an alumina or silicon substrate with a heater and a temperature probe to increase and control the temperature of the sensing layer. WO₃ film deposited interdigitated electrodes possesses both receptor and transducer functions, where the reaction of the NO₂ species takes place on the WO₃ film (receptor function) and the adsorbed NO₂ changes the resistance (transducer function) of the sensing film. This change in resistance can be correlated with the concentration of NO₂. The response (S) for NO₂ is calculated as the ratio of the resistance of the WO₃ film on gold interdigitated electrodes at different gas concentration and is given by the following equation [26]:

$$S = \frac{R_g}{R_a}$$

where, R_g is the resistance of the film in presence of NO₂ and R_a is the resistance of the film in air. Metal-oxide gas sensors based on this principle are one of the most studied gas

sensor types because of its low cost of production, miniature size, low power consumption, and large number of applications [27].

The detailed mechanism of a n-type semiconductor thin film sensor is explained by Franke et al. [28] which can be used as a model to define the interaction between n-type WO₃ and NO₂. Fig. 1 depicts the mechanism. At elevated temperature, oxygen from the air is adsorbed on the WO₃ surface. Since a constant voltage is applied externally on the WO₃ film, the electrons are exchanged from the conduction band of WO₃ to the adsorbed oxygen causing them to convert to ionosorbed species. NO₂ is a strong oxidizer, because of the presence of an unpaired electron in its outermost shell, which supports the formation of ionosorbed oxygen [20] according to the following equations:

This causes the formation of an electron depletion region around the individual WO₃ particle, also known as space-charge layer, Λ_{gas} [30]. At the junction of two particles a larger electron depletion layer ($2 * \Lambda_{\text{gas}}$) is formed causing conduction band bending of WO₃ and the generation of a surface potential barrier (height of band bending qV_s). Since the electronic conduction occurs along a percolation path via particle to particle contact, presence of the large electron depletion region hampers the electron path causing an increase in overall WO₃ film resistance.

“PLEASE INSERT FIGURE 1”

The gas sensing property of WO_3 films strongly depends on the preparation method and the growing conditions of the film itself. Many synthesis procedures have been proposed for producing the WO_3 films for NO and NO_2 sensors. These include spray pyrolysis [31], drop coating [32], co-precipitation [33], sol-gel synthesis [20], plasma-enhance chemical vapor deposition (PECVD) [34], thermal evaporation [13, 35], and glancing angle DC magnetron sputtering [36]. In order to have a high productivity, low resistance, and a low power consumption sensor, the current trend is to construct all sensing elements on a chip [37].

Here we have proposed an open atmosphere flame based process also known as Reactive Spray Deposition Technology (RSDT) for the synthesis of $\gamma\text{-WO}_3$ films directly on gold interdigitated electrodes. The RSDT process allows the flexibility to create $\gamma\text{-WO}_3$ with control of the particle size, porosity and thickness of the film. The sensitivity of porous WO_3 increases when the particle size is below its Debye length (L_D) which is 25 nm [38]. RSDT is a subset of flame spray pyrolysis which was developed by Maric et al. [39] for the synthesis of nanoparticles. This process can employ a broad selection of precursors [40-46] compared to conventional vapor-fed flame reactors. In RSDT, nanoparticles are generated in the flame, and then are either directly deposited on the substrate as a film or collected as a nanopowder. This eliminates the intermediate steps of filtration, drying, and calcination. By incorporating a secondary spray system, nanoparticles can also be deposited on various supports such as carbon [47], magneli phase titania [48] and ceria [41-42]. RSDT provides complete control of the nanoparticle size, crystallinity [49], porosity, film thickness, and support concentration [47]. Ability to control the substrate temperature from 20-1000°C enables the use of a wide array of substrates [39]. We have successfully used RSDT for the synthesis of various nanomaterials [41, 43, 46, 48-51]. In our previous work, it had been shown that RSDT can be employed for the synthesis of WO_3 films with

precise control of particle size, film morphology, and crystal structure [40]. In this study, we have employed RSDT for the deposition of nano crystalline WO_3 thin films directly on a gold interdigitated electrode which is to be assembled into an NO_2 sensing device. Here we provide a brief description of the synthesis, fabrication and testing procedure of the NO_2 sensor. The microstructure of the tungsten oxide films, and the effect of the film structure, grain size, and the sensor response to the ppm level concentration of NO_2 will be described. NO_2 response behavior on the tungsten oxide surface at various operating temperatures will also be presented.

The properties of the WO_3 film was investigated by X-ray diffraction (XRD), Raman spectroscopy, the Brunauer-Emmett-Teller (BET) method, high resolution transmission electron microscopy (HRTEM), and scanning electron microscopy (SEM). The sensor response was tested from 0.17-5 ppm at different operating temperatures (250-350°C) to determine the optimum working temperature. The sensor film was ultimately performance tested for NO_2 response in the 0.17-5 ppm range at 300°C. The sensor was further tested for stability for 300 h in 0.5 ppm NO_2 in the air which is 10 times lower than the workplace permissible exposure limit (PEL) as per the Occupational Safety and Health Administration (OSHA) specification. The sensor was tested below the PEL because it is desirable for the workplace atmosphere to remain below the PEL of NO_2 . In order to check the selectivity, the sensor was also tested for 10 ppm acetone, 100 ppm ethanol, 10-100 ppm H_2 , and 10 ppm isoprene. We have also compared the test data of WO_3 based NO_2 sensors prepared by RSDT with the results reported in the literature.

2. Experimental:

2.1 Synthesis of WO_3 :

An explanation of the RSDT equipment and process has been described in detail by Jain and Roller et al. [41, 44]. Fig. 2 shows the schematic of RSDT along

with the cross sectional view of the combustion nozzle. Tungsten hexacarbonyl $[\text{W}(\text{CO})_6]$ was obtained from Sigma Aldrich (Catalogue #AC221040100) and was dissolved in a tetrahydrofuran (THF) (enthalpy of combustion: 2501 kJ/mol) (Fisher Scientific # SHBD3901V). The precursor was chosen based on its low decomposition temperature of 170°C. 20 wt% sulfur free liquefied propane (Airgas catalogue # PRCP350S) was added to the above to form a precursor solution resulting in a final concentration of 5 mM/L $\text{W}(\text{CO})_6$, and 18 wt% propane. THF has a dual role of an inexpensive solvent and fuel for the combustion of the $[\text{W}(\text{CO})_6]$. The precursor solution was filled in a syringe pump (Teledyne Isco 500D) and after heating to 50-60°C it was directed through a 4 mL/min stainless steel capillary tube of 100 μm inner diameter to the combustion nozzle. Six methane-oxygen flamelets (methane and oxygen at 0.5 L/min each) surround the capillary end, which ignites the combustible precursor mist. The precursor solution was atomized by oxygen (5 L/min) and a pressure drop of 125 psi was maintained at the exit point of the nozzle. At 10 cm from the combustion nozzle, an circular air quench ring (Exair, Super Air Wipe[®]) with a compressed air flow rate of 70 L/min was positioned. The distance between the combustion nozzle and the air quench is considered the reaction zone and the length of the reaction zone is proportional to the residence time of the nano-particles in that zone. Adjusting the length of the reaction zone and the flow rate of compressed air gives unique conditions to obtain an assortment of crystalline structures and phases of the material [52]. This also enables “nano quenching” thereby limiting the particle size growth in the flame. Two silicon plates (Nova electronic materials item#8289) and two gold interdigitated electrodes on alumina base (Electronic design center-Case Western Reserve University item#102) were used as substrates. Silicon plates were used only to evaluate the film thickness since they can be easily fractured and can be mounted at 90° on a SEM stub. Gold interdigitated electrodes on alumina base (Electronic design center-Case Western

Reserve University item#102) were used as substrates for the gas sensing. This thick film printed electrode consists of interdigitated gold deposits on a 0.6 mm thick alumina substrate. The dimensions of the alumina base is 15 mm by 15 mm. The gold thick film screen printed electrode digits are 250 μm wide with 250 μm spacing between them. The gold digits are connected with a pair of gold bonding pads which allow wires to be threaded through them as an aid for electrical connection. Prior to WO_3 deposition, the electrode was cleaned with acetone, methanol and deionized water, in order and dried in an air oven operating at 80°C for 1 h. The four substrates were mounted on a stainless steel substrate holder, which was placed on an x-y-z platform. This enabled the substrates to move along a serpentine path in front of the flame to ensure even coating of WO_3 on the substrates. The total deposition area was 25 cm^2 . All the samples were annealed in the air at 500°C for 5 h in an oven to stabilize the WO_3 film. The characterization and gas sensing measurements were performed on the post annealed samples.

“PLEASE INSERT FIGURE 2”

2.2 Characterization:

XRD patterns of WO_3 films directly deposited on gold interdigitated electrodes were recorded in the air at 25°C on a Bruker D8 advanced powder diffractometer using the source: $\text{CuK}\alpha_1$ radiation (wavelength: 1.54058 Å), operating at 40 kV and 40 mA and the detector: LynxEye, super speed detector. The scans were taken in the 2θ range of 20-55° with a step size of 0.02° and time per step of 5 s. Raman spectra were obtained in air at 25°C in the spectral range between 100 and 1200 cm^{-1} with a Renishaw Ramascope micro-Raman spectrometer fitted with a reflected light microscope using a 50 mW laser (514.5 nm) and exposure time of 10 s. Laser power delivered to the sample was set at 20% (10 mW) to avoid sample damage. Instrument alignment was optimized using a 521 cm^{-1} signal of a silicon wafer.

Raman measurements for WO_3 is well known to provide structural and phase information of WO_3 material [53]. The surface area of WO_3 particles was calculated by the Brunauer-Emmett-Teller (BET) method using N_2 sorption experiments on a Micromeritics ASAP 2020 BET system. Samples were degassed for 12 h prior to N_2 sorption measurements. For obtaining the samples for BET, a separate experiment was performed in which, WO_3 nanoparticles powder was directly collected on a stainless steel substrate holder. The deposit was scrapped off using a plastic spatula and analyzed for N_2 sorption experiments. SEM micrographs were collected on an FEI ESEM Quanta 250 with a field emission gun at 5 kV accelerating voltage and 8 mm working distance. For determining the cross sectional thickness of the film, the silicon substrate with WO_3 film was fractured, and mounted on a 90° aluminum stub. The sample was gold sputter coated prior to imaging under SEM. TEM micrographs and selected area diffraction pattern (SADP) of WO_3 particles were obtained on a 120 kV FEI Tecnai T12 S/TEM with a LaB_6 source. HRTEM micrographs were obtained on a 200 kV FEI Metrios TEM with an X-FEG source. 300 mesh Cu grids coated with holey/thin carbon films (Pacific Grid Tech Cu-300HD) were used. A small portion of the film was scraped off from the gold interdigitated electrodes and was sonicated with ethanol. Few drops of the resulting solution were dropped on the grids and air dried before they were placed in the ultra-high vacuum (UHV) chamber of the TEM.

2.3 *Gas sensing test:*

Gas sensing tests were performed in a dynamic flow system, implemented in the laboratory as shown in Fig. 3. Prior to gas sensing, the electrode was annealed in the air at 500°C for 5 h in an electric oven to stabilize the WO_3 film. A WO_3 coated gold interdigitated electrode was introduced in a quartz cylindrical test chamber (10 cm length and 3.2 cm inner diameter) which was wrapped by a high temperature nozzle band heater (McMaster

Carr item# 3594K981). The ends of the test chamber were sealed by stainless steel fittings. Several ports were introduced in the test chamber for (1) gas inlet, (2) 2 gas outlets, and (3) standard k-type thermocouple to monitor temperature. Gas flow to the furnace was controlled by Environics Series 4040 Computerized Gas Dilution System with an option for precise humidification control (0-100% relative humidity at a given temperature). Presence of 2 gas outlets in the test chamber allows a precisely controlled change in the atmosphere of the test chamber, as soon as the gas concentration is changed from NO₂ to pure air and vice versa. Dry synthetic air (Airgas #AI UZ300) was used as a diluent gas and 10 ppm NO₂ in the air (Airgas #X02AI99C15A2520) was used for adjusting the NO₂ concentration. Humidity level of 100% r.h. was maintained throughout the tests at the gas inlet to the test chamber as measured by a calibrated hygrometer (Vaisala HMT 337). The water vapor pressure of the test gas at the inlet of the heated test chamber was 23.7 torr. Flow rate of 1.5 L/min was maintained in the test chamber. For the two probe amperimetric measurements, the WO₃ coated electrode was connected with two Pt wires (99.9% metals basis) (0.127 mm diameter) (Alfa Aesar#F20X038) and connected with a CHI instrument's electrochemical analyzer (CHI6116E). Current (I) was measured as a function of time and gas flow concentration at a constant 1 V DC power supply. Resistance (R) was calculated by applying Ohm's law ($R = V/I$). The data was collected every 100 ms.

“PLEASE INSERT FIGURE 3”

3. Results:

3.1 Structural properties

3.1.1 X-ray diffraction (XRD):

Fig. 4 (a) shows the XRD pattern of the WO₃ film coated on gold interdigitated electrodes pre and post NO₂ tests. The WO₃ film showed the monoclinic structure and was indexed to ICDD#01-043-1035. The characteristic main peaks for γ -WO₃ were seen at the 2θ value of 23.2°, 23.6° and 24.4° and can be associated with the (002), (020) and (200) reflections respectively. Average crystallite size of WO₃ was calculated from X-ray line broadening by Debye Scherrer's method and was 21 nm on the as prepared sample, and 27 nm on the post NO₂ test samples. As seen from the XRD pattern, there was an increase in the intensity of the WO₃ film post NO₂ tests. This could be due to the increase in crystallinity of the WO₃ particles under the high temperature of testing. However no change in the overall structure of the film was observed verifying that the film was stable under the NO₂ test conditions.

“PLEASE INSERT FIGURE 4”

3.1.2 Raman spectroscopy:

Raman spectroscopy technique was used for identifying the phases in the WO₃ film since this technique is well known to give the “fingerprint” of WO₃ material [53]. Fig. 4 (b) shows the Raman spectroscopy results of the WO₃ film directly deposited on gold interdigitated electrodes, both pre and post NO₂ tests. The strongest peaks were seen at 808 and 715 cm⁻¹ which are similar to those of the monoclinic γ -WO₃. A relatively strong peak was observed below 150 cm⁻¹ for all the samples which indicates the O-O deformation mode [54]. Intensity of the WO₃ film after NO₂ sensing has increased, consistent with the XRD results. On the basis of XRD and Raman spectroscopy results, it can be safely concluded that the structure of the WO₃ film in this study is monoclinic γ phase.

3.1.4 Electron microscopy (SEM and TEM):

Fig. 5 (a), (b) and (c) shows the SEM micrographs of the WO₃ film as deposited on a Si wafer and gold electrode. The Si wafer was the chosen as a substrate because it can be easily fractured which enables the examination of the WO₃ film cross section. From Fig. 5 (a) the film thickness was measured to be 2.5 μm . Fig. 5 (b) shows the WO₃ film directly deposited on the gold interdigitated electrode. Uniformly coated gold lines with WO₃ can be seen and it can be inferred that the film formation is conformal in nature. From Fig. 5 (c) it can be inferred that the WO₃ film surface is rough and porous with the formation of some agglomerates around 5-10 μm wide. Various open pores could be seen which is advantageous for the diffusion of gases in the bulk of the film [55]. The total WO₃ deposition area on the gold electrodes was 97.5 mm². The surface to volume ratio of the WO₃ film was 400 mm⁻¹. The images indicate high quality porous WO₃ films deposited by RSDT without any cracks, voids, dense regions or surface abnormalities.

“PLEASE INSERT FIGURE 5”

Fig. 5 (d) and (e) shows the bright field TEM and HRTEM micrographs of the WO₃ particles. Various oval shaped particles can be seen. From TEM point analysis, a particle size (d_{TEM}) distribution ranging between 20-30 nm was observed. No evidence of sintering of the nanoparticles was found which is attributed to the use of air quench in RSDT. The selected area diffraction patterns (SADP) of WO₃ is shown in the inset of Fig. 5 (d). The brightest diffraction ring corresponds to the (002), (220) and (114) planes. Fig. 5 (e) shows the HRTEM micrograph of one of the particle with the lattice fringes clearly visible. The lattice fringe spacing corresponds to the (002) plane of γ -WO₃.

3.1.5 BET surface area:

N₂ sorption measurements were performed for the WO₃ powder and the surface area was calculated by the BET method. The BET surface area was calculated as 46 m²/g. An average particle diameter was estimated using the BET surface area and the density of WO₃ (7.16 g/cc) by making the assumption that the particles are uniformly sized spheres. Particle diameter (d_{BET}) was calculated to be 18 nm.

3.2 Response dependence on temperature:

The WO₃ film was tested for NO₂ response in the range of 0.17 ppm to 5 ppm between 275-350°C to establish the relationship between NO₂ concentration and temperature, and to determine the working temperature at which the best response can be obtained. Fig. 6 (a) shows this relationship. It can be seen that as the temperature is increased, the response increases till it reaches the maximum value at 300°C. If the temperature is further increased, the response is reduced. This could be due to increased desorption of NO₂ at high temperature which reduces the concentration of ionosorbed oxygen at the WO₃ surface.

“PLEASE INSERT FIGURE 6”

3.4 Gas sensing results:

Fig. 6 (b) shows the normalized response-recovery curve vs time for the NO₂ concentration ranging from 0.17-5 ppm in the air at 100% at 300°C. The measurable limit for our tests was 0.17 ppm. The response increases as the concentration of NO₂ is increased. This is because of the increased adsorption of NO₂ molecules at higher NO₂ concentration. The adsorption and desorption of the NO₂ molecules on the WO₃ film takes place simultaneously and is a reversible process. During the response stage, adsorption is higher than desorption and the resistance of the film increases. This is because NO₂ diffuses through the porous WO₃ film and

oxidizes the WO_3 surface thereby increasing the ionosorbed oxygen concentration of the film. This causes an increase in electron scattering sites. NO_2 also captures electrons from the conduction band of WO_3 causing the formation of an electron depletion region, triggering an increase in its resistance. It was seen that the sensor response was spontaneous as the gas concentration in the test chamber was changed from pure air to NO_2 in the air. The response time was calculated to be 7.2 s. The sensor stabilized at the maximum value of resistance, very quickly. At this point, the adsorption rate is equal to the desorption rate. Maximum adsorption had taken place at that particular analyte concentration and the WO_3 film was in equilibrium with the NO_2 molecules. Recovery of the sensor started when pure air was switched back to the test chamber. At this point, adsorption was nil and desorption was the only process which was taking place. Presence of two vents in the test chamber expedited the exchange of the gas atmosphere. However it was seen that desorption was still slower than adsorption. A drift can be seen when the resistance of the film is measured in air after exposure to NO_2 at different concentrations. This is caused because of incomplete recovery during the 5 minute of recovery phase.

3.5 Stability tests:

Stability tests of the WO_3 films were conducted for 300 h at 0.5 ppm NO_2 in the air which was maintained at 100% relative humidity at 25°C prior to being sent to the test chamber. This concentration of NO_2 is 10 times lower than the workplace permissible exposure limit (PEL) as per the Occupational Safety and Health Administration (OSHA) specification. The sensor was tested below the PEL because it is desirable for the workplace atmosphere to remain below the PEL of NO_2 . 0.5 ppm NO_2 was switched on every 5 minutes (response) followed by 5 minutes of pure air (recovery). Resistance of the film was measured every 100 ms to record the response and recovery cycle (response + recovery time = 10 min). A total of

2000 response-recovery cycles were recorded. Fig. 7 shows the resistance over time for WO_3 film in pure air (R_a) and 0.5 ppm NO_2 in air (R_g) respectively. The resistance is calculated as the moving average for the data collected every 24 h. It can be seen that the sensor is stable till day 6 (~150 h). From day 6-14 (150-300 h) the sensor began to degrade possibly due to the growth of the WO_3 nanoparticles. This shows that maximum degradation of the sensor occurred after day 8 (~200 h) as evident from the fluctuation of resistance.

“PLEASE INSERT FIGURE 7”

3.5 Selectivity:

The response of 1 ppm NO_2 was compared with 10 ppm acetone, 100 ppm ethanol, 10-100 ppm H_2 and 10 ppm isoprene at 0.5 ppm NO_2 in air. This is shown in Fig. 8. It can be seen that the sensor had negligible response for acetone, ethanol and 10 ppm H_2 . However, the response is significant for 100 ppm H_2 and 10 ppm isoprene. Isoprene and H_2 are some of the major component exhaled from the human breath [56]. Typical values of isoprene in the breath of a healthy human range from 0.012-0.58 ppm [57] while H_2 range from 10-20 ppm [58].

“PLEASE INSERT FIGURE 8”

4. Discussions:

On the basis of the characterization and gas sensing results, we can conclude that RSDT can be used for the synthesis of NO_2 sensing films directly on gold interdigitated electrodes. Based on our previous work on WO_3 [40] and a review of the literature, it can be shown that the characteristics of the sensing device that are most important for good performance are: (1) high porosity of the sensing film, (2) particle size of the sensing film smaller than the Debye length (L_D), a characteristic of the semiconductor material, which is 25 nm for WO_3 , (3) film thickness,

(4) absence of impurities in the test atmosphere, (5) test chamber volume, and (6) time required for the exchange of gases in the test chamber. In this discussion we will identify the importance of these factors and show that the gas sensing test data presented in this work adheres to these requirements. We have also shown the comparison between the RSDT synthesized sensors and the sensors synthesized by other techniques as shown in table 1.

“PLEASE INSERT TABLE 1”

Since the sensing is an adsorption-desorption process, gas diffusion through the film plays a major role in the sensor performance. The sensing film must be porous to effectively allow the diffusion process and extend the reaction between NO₂ and oxygen from the surface to the bulk. By assuming steady state conditions, it can be interpreted that the NO₂ concentration decreases with the film depth which causes the formation of various degree of reactions at different depths of the film. The resistance change data recorded by the electrochemical analyzer averages the resistances by providing the overall resistance change of the film. Ideally it would be beneficial to eliminate this variation. Film porosity, thickness, microstructure, and the electrode pattern are the factors which govern this variation [59-60]. From the SEM micrographs in Fig. 5 (c) it can be seen that the WO₃ film synthesized by RSDT is highly porous and uniform.

Gas sensing response is dependent on the particle size of the sensing film. Smaller particles and increased surface area (higher surface to volume ratio) provides larger number of sites for the surface reaction to occur. At the same time, reducing the particle radius below Λ_{gas} , will converge the electron depletion layer ($2\Lambda_{\text{gas}}$) and the electrical conduction will be dominated by the presence of adsorbed NO₂⁻. Λ_{gas} depends on the Debye length (L_D) of the material which is

25 nm for WO_3 . Sharma et al. has described the relationship between gas sensor response and particle size with respect to the Debye length (L_D). When the particle size is smaller than L_D , the ionosorbed oxygen will extract all the electrons from the WO_3 particle causing an increase in film resistance [30]. It was also shown by Tamaki et al. that the sensor response of WO_3 particles at 10 ppm NO_2 were three fold higher when the particle size was smaller than 25 nm as compared to particles larger than 33 nm [38]. In this work, the WO_3 particle size were in the range 20-30 nm as determined by the TEM point analysis in Fig. 5 (d). BET surface area measurements revealed the average particle diameter (d_{BET}) to be 18 nm.

Working temperature is an important factor responsible for the performance of the sensor since sensing is an adsorption desorption process which is also influenced by kinetics [61]. At low working temperature, the activation barrier for the generation of ionosorbed oxygen is higher, while at high temperature, the desorption of NO_2 exceeds adsorption resulting in lower response. Hence the optimum temperature at which balance kinetics and desorption is essential. In this work, the highest response was obtained at 300°C.

Selectivity with other gases is a major concern for a sensor to be commercially viable, which can lead to false alarm or incorrect gas concentration determination. In this study, it was found that the WO_3 film was responsive towards 10 ppm isoprene and 100 ppm H_2 , while the response towards 10 ppm acetone, 100 ppm ethanol and 10 ppm H_2 was negligible. All the tests were performed in 100% relative humidity of the gas, which was maintained upstream of the test chamber, and cross-sensitivity towards H_2O was not observed. There are various methods suggested in the literature to discriminate the interference towards these gases. The most common approach is to utilize a sensor array described by Albert et al. with various sensor electrodes to filter out the response from the interfering analytes [62]. The other method is to use filters upstream

of the electrode to filter out the gases. One such activated charcoal filter is used by Figaro Inc. in their commercial CO sensor - TGS5042. Since the sensor response is a diffusion driven process, it can be easily applied to improve the selectivity. Porous layers in which gases may have different diffusion coefficient can be directly deposited on the sensing layer. These layers acts as molecular sieves to reject the interfering gases. Description of these porous layer filters have been provided in details in this reference [63].

The long recovery time and the drift of the metal oxides based sensors have been long recognized and various suggestions to counter this limitation have been proposed. From the gas sensing tests in Fig. 6 (b), a drift can be seen when the resistance of the film is measured in the air after exposure to NO_2 at different concentrations. This is caused because of incomplete recovery during the 5 minute of recovery phase. As a gas molecule is chemically adsorbed on the surface of WO_3 , it is in thermal equilibrium and resides at the bottom of the potential well (minimum potential energy). In order to desorb from the surface, the only driving force it experiences is the diffusion caused by the change in the concentration of gases in the test chamber on switching to pure air. However this energy is not sufficient and causes a long delay to achieve complete desorption. Further thermal or electrical energy is required to expedite this adsorption process. Different ways are suggested in literature to eliminate sensor drift. These include, using high-speed gas-switching system and smaller volume test chamber for enabling quicker gas exchange [64] pre exposing the sensing film to the analyte for a set period of time [65], use of mathematical function and modelling [66] to pre-estimate the steady state conditions and remove the time lag [67], use of multiple sensing electrodes in different test chamber to alter between response and recovery [68], use of neural network algorithm for the sensor to “self-learn” [69] use of strong negative field to electro-desorb the residual analyte molecules to “refresh” the sensor

[70] and by illuminating the sensor with ultra-violet (UV) light [71]. Here we have used a two vent test chamber to expedite the atmosphere change. The test chamber volume was 80 cc. We are currently developing a prototype sensing device with a volume of 0.5 cc which will further eliminate this issue.

4. Conclusions

In this study we have evaluated RSDT as a direct deposition technique for the synthesis of γ -WO₃ film for ultra-low NO₂ sensing. Nano quenching was used to optimize the particle size and film morphology to tailor the film towards superior NO₂ sensing performance. Here our main objective was to correlate the influence of the synthesis process, and the resultant structural properties of the γ -WO₃ film with the NO₂ gas sensing performance. We have highlighted these properties and their influence on the NO₂ sensing which will provide a platform for developing better sensors with improved performance compared to the currently used sensors. The reasons for the high response can be attributed to a number of factors, such particle size, porosity and pore size, and film thickness, all precisely controlled by the RSDT. Following conclusions can be made from this work:

1. RSDT synthesized WO₃ film based NO₂ sensor was responsive in the 0.17-5 ppm range, when tested at 300°C.
2. Response time was 7.2 s and recovery time was greater than 5 minutes. The response time was better than the WO₃ sensors synthesized by the traditional wet chemistry processes from literature.
3. The response was highest at the working temperature of 300°C.
4. The NO₂ sensors gave a steady response till 150 h of continuous performance and started to degrade after 200 h possibly due to increase in particle size.

5. Interference was negligible with 10 ppm acetone, 100 ppm ethanol, 10 ppm H₂ and humidity; however, it was significant with 10 ppm isoprene and 100 ppm H₂.
6. Response and recovery of the sensor is caused by adsorption and desorption respectively. Hence recovery time can be improved by expediting the desorption step.
7. WO₃ particle size of <25 nm attributes to better charge transfer which translates to superior NO₂ sensitivity.

Acknowledgements

Authors would like to acknowledge financial support from National Science Foundation (award number CMMI-1265893). We would like to acknowledge Dr. Justin Roller at FEI Company for the HRTEM micrograph. The creative discussion with Mr. Leonard Bonville is highly appreciated. R.J. acknowledges the 2015 General Electric (GE) graduate fellowship.

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Figure captions

1. Simplified model explaining the NO₂ sensing phenomenon by monoclinic γ -WO₃. (a) Band bending after ionosorption of oxygen. E_C , E_F and E_V denotes the energy of conduction band, Fermi level and valence band respectively. qV_s and $2\Lambda_{\text{gas}}$ denotes the band bending height and thickness respectively. (b) Structure of γ -WO₃. (c) γ -WO₃ thin film deposited on a gold interdigitated electrode.
2. Arrangement of the Reactive Spray Deposition Technology for direct deposition of WO₃ on gold interdigitated electrodes.
3. Schematic of the gas sensing test setup.
4. (a) X-ray diffraction (b) Raman spectroscopy of WO₃ film directly deposited on gold interdigitated electrodes, both pre and post NO₂ test showing that there is no change in the structure of the film.
5. Microscopy images of WO₃ deposited by RSDT: (a) Cross-section of the WO₃ film on a Si substrate showing a thickness of 2.5 μm , (b) WO₃ film deposited on gold interdigitated electrodes, (c) higher magnification view of the WO₃ film on a gold line. Transmission electron microscopy (TEM) images of WO₃ films deposited by RSDT: (d) WO₃ primary particle size in the range 20-30 nm. Selected area diffraction pattern (SADP) is shown in the inset (e) high resolution image of a WO₃ particle showing lattice fringes corresponding to the (002) plane.
6. (a) Relation between sensor response (R_a = resistance of WO₃ film in pure air, R_g = resistance of WO₃ film in NO₂) and NO₂ concentration at different temperatures. (b) NO₂ sensing tests conducted at 0.17-5 ppm NO₂ in the air conducted at 300°C and 1500 sccm flow rate of gases. The tests shown above were conducted on the same sample.

7. Stability tests for WO_3 sensor conducted for 300 h at 0.5 ppm NO_2 in the air at 300°C .

8. NO_2 response as compared to other reducing analytes.

Table caption

1. Comparison of the WO_3 based NO_2 sensors prepared by different synthesis techniques.

Table 1

Synthesis method	Limit of detection (ppm)	Working temperature (°C)	Response converted to R_g/R_a	Response (used formula)	Response time	Reference
RSDT	0.17-5	300	4.44 (0.17 ppm) 6.58 (0.5 ppm) 7.37 (1 ppm) 8.07 (5 ppm)	R_g/R_a	7.2 s	This work
Sol-gel (WO ₃ on porous silicon)	0.05-2	25	R_a/R_g : 1.15 (0.05 ppm) 1.75 (0.5 ppm) 2.01 (1 ppm) 3.37 (2 ppm)	R_a/R_g	2 min	[72]
Sol-gel (WO ₃ on alumina)	0.05-2	150	1.65 (0.5 ppm) 2 (1 ppm) 2.67 (2 ppm)	R_g/R_a	2 min	[72]
DC magnetron sputtering (Porous WO ₃)	0.1-5	150	42.2 (1 ppm)	$(R_g - R_a)/R_a$	2 min	[73]
DC magnetron sputtering (Sputtered WO ₃)	0.1-5	200	8.2 (1 ppm)	$(R_g - R_a)/R_a$	2 min	[73]
Evaporation condensation	1-200	250	2 (1 ppm)	$(R_g - R_a)/R_a$	70 min	[13]
Drop coating	0.5-5 ppm	100 and 200	19.2 (1 ppm)	R_g/R_a	15 min	[32]

Glancing angle DC magnetron sputtering	0.1-2 ppm	250	4.4 (0.5 ppm)	R_g/R_a	15 min	[36]
Induction-heating oxidation of tungsten	1-8 ppm	110	5.5 (1 ppm)	R_g/R_a	10 min	[35]
PECVD	10-100 ppm	200	45 (10 ppm)	V_g/V_a (same as R_g/R_a)	50 s	[34]
Spray pyrolysis	10-100 ppm	200	1.5 (20 ppm)	$[(R_g - R_a)/R_a] * 100$	3 s	[31]

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Rishabh Jain is a Process Technology Development Engineer at Intel Corporation in Hillsboro, Oregon, USA. Dr. Jain obtained his Ph.D. in Materials Science and Engineering from University of Connecticut (UConn) in 2015 where he worked at the Center for Clean Energy Engineering as a graduate research assistant. His area of expertise is on the flame combustion synthesis of nanomaterial thin films for catalysts and gas sensors. In addition to that, Dr. Jain also excels in the electron microscopy and microstructural characterization of nanomaterials.

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