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Ultra-low NO_2 detection by gamma WO_3 synthesized by Reactive Spray Deposition Technology

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ABSTRACT

A porous tungsten oxide (WO_3) NO_2 sensor was developed by a one-step flame based process called Reactive Spray Deposition Technology (RSDT). This nano-crystalline WO_3 film was deposited directly on gold interdigitated electrodes. The sensing characteristics of this NO_2 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 (~7s) and recovery time (~5 min), respectively. The stability of the sensor was evaluated for 300 h in 0.5 ppm NO_2 at 300 °C in (2000 response-recovery cycles). The sensor was stable up to 6 days (~150 h) of continuous operation and degraded between 150–300 h. The morphology and surface properties of the WO_3 film were investigated with XRD, Raman spectroscopy, BET, SEM, TEM, and HRTEM.

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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], natrium superionic conductor (NASICON) [11], In_2O_3 [12], and WO_3 [13], have been used for NO_2 gas sensing. Among metal oxides, WO_3 is considered to be a good candidate for low concentration NO_2 sensing.

WO_3 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,

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, natrium superionic conductor; PECVD, plasma-enhance chemical vapor deposition; PEL, permissible exposure limit; THF, tetrahydrofuran; ICDD, International Centre for Diffraction Data.

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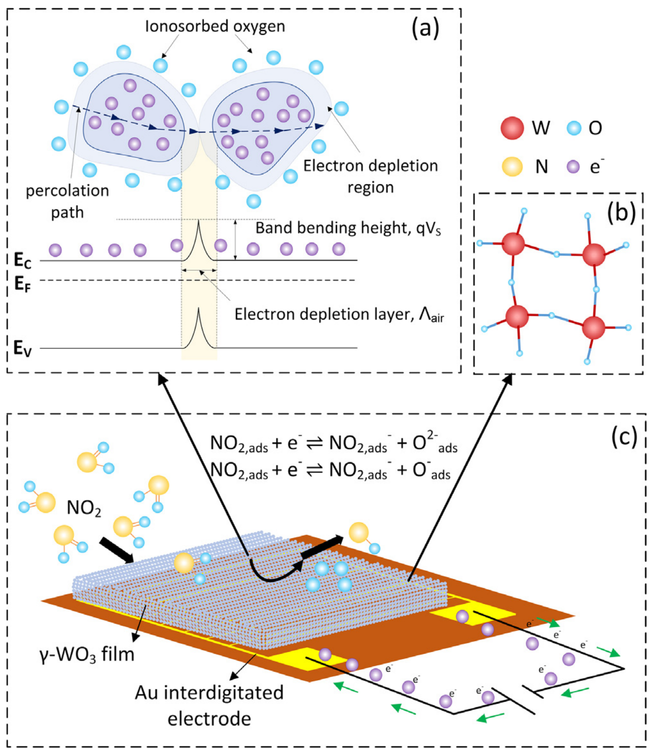

Fig. 1. Simplified model explaining the NO_2 sensing phenomenon by monoclinic γ-WO_3. (a) Band bending after ionosorption of oxygen. E_C, E_F and E_V denotes the energy of conduction band, Fermi level and valence band respectively. qV_S and $2\Lambda_{gas}$ denotes the band bending height and thickness respectively. (b) Structure of γ-WO_3. (c) γ-WO_3 thin film deposited on a gold interdigitated electrode.

optical and magnetic behaviors which are favorable for particular applications. Gas sensing property of WO_3 was discovered for the first time by Shaver, in 1967 when he observed a change in conductivity of WO_3 thin film in presence of low concentration of H_2. Since then *n*-type WO_3 has been extensively used for sensing H_2 [18], H_2S [19], NO_X [13,20], NH_3 [21], O_3 [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. WO_3 film deposited interdigitated electrodes possesses both receptor and transducer functions, where the reaction of the NO_2 species takes place on the WO_3 film (receptor function) and the adsorbed NO_2 changes the resistance (transducer function) of the sensing film. This change in resistance can be correlated with the concentration of NO_2. The response (S) for NO_2 is calculated as the ratio of the resistance of the WO_3 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 NO_2 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 WO_3 and NO_2. Fig. 1 depicts the mechanism. At elevated temperature, oxygen from the air is adsorbed on the WO_3 surface. Since a constant voltage is applied externally on the WO_3 film, the electrons are exchanged from the conduction band of WO_3 to the adsorbed oxygen causing them to convert to ionosorbed species. NO_2 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:

$$NO_2 + e^- = NO^+ + O^{2-}{}_{ads}(\text{below}150\,^\circ C),$$

$$NO_2 + e^- = NO^+ + O^-{}_{ads}(150\text{–}500\,^\circ C)[29].$$

This causes the formation of an electron depletion region around the individual WO_3 particle, also known as space-charge layer, Λ_{gas} [30]. At the junction of two particles a larger electron depletion layer ($2 * \Lambda_{gas}$) is formed causing conduction band bending of WO_3 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 WO_3 film resistance.

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 γ-WO_3 films directly on gold interdigitated electrodes. The RSDT process allows the flexibility to create γ-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 (λ_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 to 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

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