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# A Novel Room-Temperature Carbon Dioxide ($CO_2$) Gas Sensor Based on Tungsten Oxide ($WO_3$) rods via Pulsed Laser Deposition

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**ABSTRACT**

Room temperature Carbon dioxide $CO_2$ gas sensor was fabricated on Tungsten Oxide ($WO_3$) nanorod thin film. Copper Oxide (CuO) nanostructure on quartz was used as substrate to grow $WO_3$ nanorod by Pulsed Laser Deposition method . The role of CuO substrate on the grown shapes of $WO_3$ films and enhanced sensing as well is discussed here. FESEM and XRD were used to characterize the films. $WO_3$ nanorod-based gas sensor exhibits excellent RT Sensitivity (109 %) to $CO_2$ gas at 105 ppm because of effective interaction of ($WO_3$) film morphology with ($CO_2$). The $WO_3$ nanorod sensor showed remarkably enhanced response under gas flow conditions (23,62 and 105 ppm) due to availability of additional adsorption sites and oxygen vacancies. The sensor shows fast response with a response time of 3 s and a decay time of 1.7 s.

**Keywords:** *$WO_3$ nanorods, $CO_2$ gas sensor, Sensitivity*

## 1. INTRODUCTION

Due to its oxygen-deficient n-type wide band gap semiconductor material with an electronic band gap of ~2.6–3.0 eV, tungsten oxide ($WO_3$) has become one of the most important functional components in the gas sensor devices. Depending on the size and dimensionality in nanostructure because of the quantum effect of one dimensional, $WO_3$ have attracted a lot of interest due to their exceptional optical and electronic properties [1-3], sensor to the gases like xylene, $NO_2$ gas, CO, $NH_3$, and VOCs ,this morphology enhanced the performance of gas sensors [4-9] and biosensor applications [10-12]. Narrower bandgaps can facilitate charge carrier activation at room temperature, to achieve effective gas sensing performance, but may impact selectivity[13]. Wider bandgaps contribute to enhanced chemical and thermal stability but they often necessitate higher operating temperatures. $WO_3$ exhibits exceptional sensitivity to both oxidizing gases and reducing gases such as nitrogen dioxide ($NO_2$), sulfur dioxide ($SO_2$), ozone ($O_3$) and carbon monoxide (CO), ammonia ($NH_3$), hydrogen sulfide ($H_2S$) and volatile organic compounds (VOCs) [14] At low operating temperatures, tungsten trioxide ($WO_3$) has shown great stability, repeatability, and sensitivity, making it a potential material for gas sensor applications. [15]. Various synthesis approaches have been performed to fabricate and applications of one –dimensional (1D) $WO_3$ nanostructure such as hydrothermal route [16, 17], by a microwave-assisted hydrothermal method [18, 19],sol-gel method [20, 21]

Among the most important approaches for the growing of uniformly distributed of nano-sized cube-shaped and nanorods $WO_3$ to be used in gas sensing applications was the pulsed laser deposition method (PLD) [22-24]. The preparation of $WO_3$ with this process has a number of benefits over other approaches, its ensuring the proper tungsten-to-oxygen ratio in $WO_3$ by controlling their stoichiometric transfer from the target to the substrate[22], PLD makes it possible to control over the morphology, grain size, and surface roughness by adjusting deposition parameters including substrate temperature and oxygen partial pressure[23] and due these advantages $WO_3$ present itself as a material that looks promising for use in sensing applications , through which nano-sized cube-shaped and nanorods plays an important role in achieving the main objective of such devices ,high crystalline in addition to the size and dimensionality of such nanostructures are the two advantages using such method .The formation of $WO_3$-based gas sensor has attracted considerable attention, which includes $NO_2$ gas Sensors [7, 19, 22]. A hydrogen sensing with Multilayer porous Pd-$WO_3$ was fabricated [20], the showed a high sensitivity of Pd- WO3 films for 1000 ppm H2 and a fast response time (7 s) at the temperature of 250 °C.

Investigation of ambient $CO_2$ Gas in $WO_3$ Nanostructures properties of 1D-nanostructures of $WO_3$ shows the $CO_2$ diffusion strongly depends on the morphology of the WO3. This isotope selective capability can be utilized for isotopic fractionation in a gas [24]. Low temperature CO gas sensor nanostructured WO3 thin films doped with Fe have been developed by thermal evaporation method[8], a good response to various concentrations (10–1000 ppm) of CO has been achieved with WO3 film at a low operating temperature of 150 °C. Experimental and theoretical studies on $CO_2$ sensing properties of WO3 powder were performed [25] , the maximum sensing response is obtained at 500 ppm of $CO_2$, when operated at 300 °C . The synthesis of $WO_3$ with different dimensionalities, then introduce the gas sensing towards different types of gases and the corresponding mechanisms, was introduced by Huiwu Long et al [26]

Our study aimed to fabrication and characterization of ultra-long 1D $WO_3$ via two steps, in 1st step CuO nanostructures are deposited on quartz substrates using the vacuum thermal evaporation, and then pulsed laser deposition was used to deposit WO3 on CuO substrate in the 2nd step . The structural properties of the sample were measured using Field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD) measurements. $CO_2$ gas sensor based on MSM were fabricated, the aluminum (Al) contacts were deposited by vacuum thermal evaporation, representing the metal. The influence of WO3 structure and length on the sensing characteristics, and the performance of the fabricated Al-WO3/CuO-Al gas sensor have been investigated in detail. This work offers a new approach for the design and fabrication of WO3 room temperature gas sensor with optimized structural stability and performance.

## 2. EXPERIMENTAL PROCEDURE

After cleaning the quartz substrates were placed over the substrate holder at a distance of 20 cm away from the tungsten boat contains high-purity copper powder was then thermally evaporated on the substrate under 2.2 x 10-5 mbar using vacuum thermal evaporator. The resulting sample (Cu/quartz) was successively transferred into a thermal tube furnace for oxidation at 700 °C, and then CuO cooled to room temperature. The resulting CuO/quartz film was used as the substrate to grow WO3 nanostructure.

The Tungsten oxide thin-films are prepared by PLD technique. The fundamental wavelength of Nd:YAG laser with a pulse width of 10 ns is used for the ablation of high purity tungsten metal target mounted on a linear ultra-high vacuum (UHV) translation stage. A plano-convex lens of 50 cm focal length is used for focusing the laser on the target. A vacuum chamber evacuated to a base vacuum of $4.6\times10-5$ mbar is used for the deposition purpose. The resulting sample ($WO_3$/CuO/quartz) was successively transferred into a thermal tube furnace for oxidation at 700 and 900 °C, and then WO3 cooled to room temperature.

Using a metal mask and vacuum thermal evaporation, aluminum (Al) contacts were deposited by vacuum thermal evaporation using a metal mask based on the pattern of the contact structure. After that, the device was annealed for five minutes at 425°C.SEM, techniques (TESCAN MIRA3, France), the properties of the WO3 and CuO nanoparticles were examined with an X-ray diffractometer (Phillips PANanaltical X'pert, Holland).

The MSM gas sensor consists of two interdigitated electrodes with four fingers each. Each finger has dimensions of 230 mm for breadth, 3.3 mm for length, and 400 µm for separation. Vacuum thermal evaporation was used to make aluminum (Al) contacts using a metal mask made utilizing the pattern of the contact structure.

The gas test system contains from open cylinder made of stainless steel with a diameter of 19 cm and a height of 7.5 cm. has an entrance for gas to exposing it to the symbols. After open the cover of test chamber we placed the sample on the heater. A rotary pump was used to evacuate the chamber of gas sensor with 1 mbar approximately. Switch on heater reach to the required temperature. The bias voltage Applied was 5 volts between both sides of electrodes. To control gas flow we used needle valves to reach gas flow conditions (23, 62 and 105 ppm). Resistance was changed for different operating temperature (RT, 50$^o$C and 100$^o$C) registered by a digital multimeter attached to a computer.

## 3. RESULTS AND DISCUSSION

The morphology of the deposited $WO_3$ on the CuO shown in Fig. 1(a and b). It's clearly seen that the nano-sized cube-shaped and nanorods $WO_3$ by the pulsed laser deposition of metal tungsten and oxidized at 700 and 900 °C successively , the morphology of the grown WO3 nanostructure displays nano-sized cube-shaped and nanorods with high density and good quality. Note that the mean diameter of these rods ~500 nm was observed, the length of these nanorods is about 10 µm.

Supposed growth mechanism: A reasonable growth mechanism of 1D $WO_3$ nanostructures formation in our experiments can be divided into two parts: nucleation and growth, as the temperature of the furnace was reached to 700 and 900 oC under the ambient oxygen which will react with tungsten to form the nucleus of the WO3 with the cylindrical bases, which appear to be the rods' roots, grew layer by layer on the cylindrical bases that emerged from the middle of these nuclei. The formed tungsten grains on CuO substrate, will be no significant lattice mismatch between them leading to the condensed and nucleated in the form of $WO_3$ nano-sized cube-shaped Figure 1(a). As the reactant concentration increases $WO_3$ nuclei individually grow in upward direction in the form of nanorods the neclui become larger so these rods will longer.

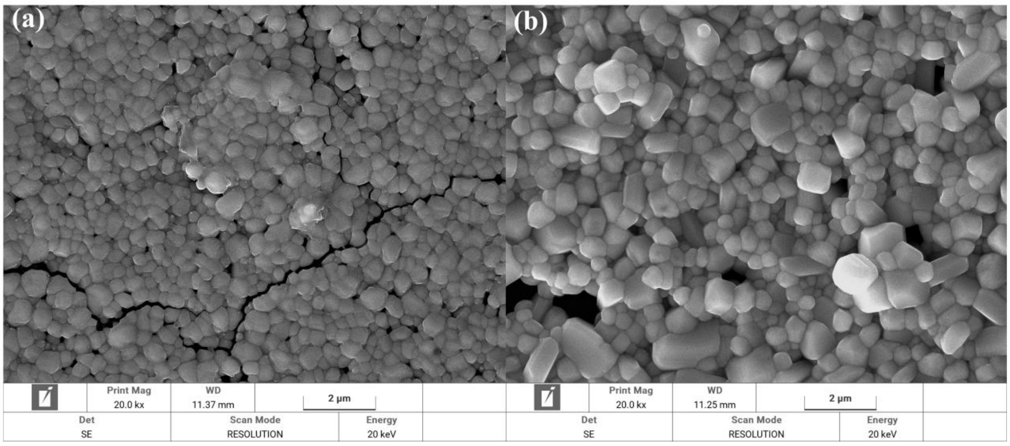


**Figure 1**. FESEM images of $WO_3$ grown on CuO substrate at (a) 700 °C and (b) at 900 °C.

Figure 2 shows the typical XRD patterns of the $WO_3$ nanostructures grown on the CuO . The XRD pattern of $WO_3$ nanostructured grown on CuO using the pulsed laser deposition method is shown in Fig. 2. All the observed diffraction peaks are match very well with the standard card to the monoclinic phase of $WO_3$ (JCPDS Card No. 83-0951) [27]. The high intensity of observed peaks , are sharp enough to reveal the crystallinity of $WO_3$ and other peaks due to CuO phases are detected, with no impurity peaks indicating good purity of the as-synthesized product.

The XRD pattern of $WO_3$ film deposited at 700 °C. The pronounced high and low intensity $WO_3$ diffraction peaks with different intensities are observed, the relatively higher diffraction intensity obtained at (011) plane indicates that the preferred growth orientation is towards this direction. When the temperature increases, the structure of the $WO_3$ films forms crystalline state, it can be seen that the film has a sharp peak at (101) accompanied by two small peaks at other diffraction planes which proves that the crystallization has improved.

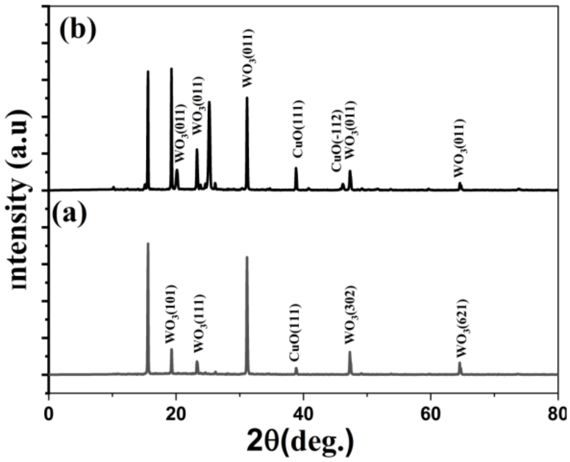


**Figure 2**. The XRD patterns of $WO_3$ grown on CuO substrate at (a) 700 °C and (b) at 900 °C.

Figure 3 shows the real-time on/off switching was measured by applying a $CO_2$ gas with flow conditions (23, 62 and 105 ppm).

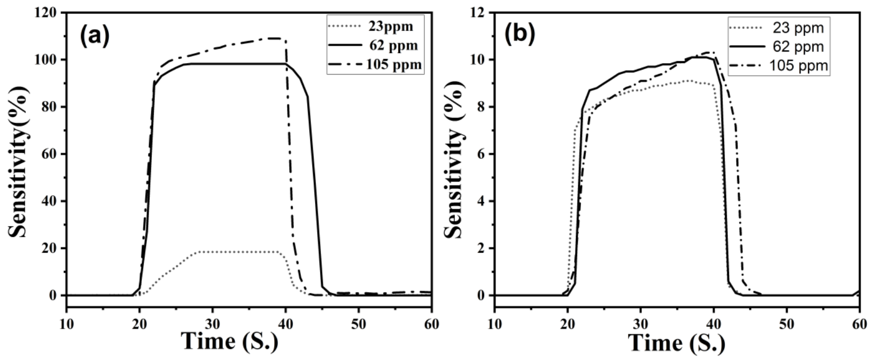


**Figure 3**. The Sensitivity of the (Al- $WO_3$ -Al) gas sensor measured under 23, 62 and 105 ppm $CO_2$ gas flow.

The measured sensitivity showed a rapidly increasing value upon exposure to $CO_2$, and the sensitivity decreased in the absence of gas flow conditions. The detection of oxidizing gas as in the case of $CO_2$ the sensing response of $WO_3$ is defined as [8, 25]

$$S\% = \frac{R_g - R_{air}}{R_g} X100 \qquad (1)$$

Where Ra and Rg are the electrical resistance of the sensor in air and in $CO_2$, respectively. Response and recovery times are the times required for the sensor to reach 90% and 10% of the maximum resistance change respectfully. The response and recovery times of the $WO_3$ nanostructure switches are listed in Table 1.

**Table 1** Values of shows the gas flow-dependent responses of Al- WO3-Al

| Gas flow ppm | WO3 rods | | | WO3 cube-shaped | | |
|---|---|---|---|---|---|---|
| | Rise time (s) | Decay time (s) | Sensitivity (%) | Rise time (s) | Decay time (s) | Sensitivity (%) |
| 23 | 6.9 | 2.18 | 18.4 | 3.7 | 1.9 | 9.1 |
| 62 | 2 | 4.9 | 98.2 | 5.2 | 1.7 | 10.1 |
| 105 | 2 | 1.7 | 109 | 11.5 | 3.6 | 10.3 |

We observed the sensitivity of Al- WO3-Al was increase under room temperature with increasing gas flow, indicating that the $WO_3$ NRs has good response. A high sensitivity could be attributed to gas-induced electron-hole generation at the depletion area of WO3 NRs, particularly near the heterostructure interface when a gas is transited into Al- WO3-Al. Based on the results listed in Table 1, the device displays a fast pulse response with a short rise time and decay time. The rise time decreased as the gas flow increased as for the decay time, it also decreases.

## 4. CONCLUSIONS

In summary, we demonstrate the fabrication room temperature CO2 gas sensor based on highly dense WO3 cube-shaped and nanorods grown on CuO/quartz substrates. The WO3 structures were investigated and showed a good crystalline purity. The exceptional quality of the produced gas sensor has been attributed to the $WO_3$ structure. Furthermore, due to the presence of oxygen in CuO, it is difficult for it to migrate into $WO_3$ rods. The produced Al- $WO_3$-Al gas sensor demonstrated strong $CO_2$ sensitivity. The sensitivity (S) was found to be 109 % at room temperature, which is an indicator of high gas response. Under 105 ppm $CO_2$ gas flow, the device showed a relatively fast response (2 s) and recovery (1.7s) times for gas response.

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