Integration of VLS-Grown WO₃ Nanowires into Sensing Devices for the Detection of H₂S and O₃

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ABSTRACT: The inspiration behind this research is the development of tungsten oxide (WO₃) nanowires based, highly sensitive and selective sensing devices directly on the active sensing platform. WO₃ one-dimensional nanowires were synthesized via the vapour-phase growth technique. This approach allows the production of well-aligned and uniform nanowires on alumina substrates with their diameter and length in the nanometer range. The morphological and structural properties of nanowires have been investigated by means of the field effect electron microscopy, grazing incidence X-ray diffraction, Raman spectroscopy, and X-ray photoelectron spectroscopy. Finally, the fabricated WO₃ nanowire sensing devices and their gas sensing performance were investigated in the presence of different oxidizing and reducing gases (especially environmental gases) at different temperatures. The WO₃ sensors demonstrate high performance toward H₂S and O₃ at the optimal working temperatures of 400 and 200 °C, respectively, with the detection limit in the ppb level.

INTRODUCTION

In the class of important n-type metal oxide semiconductors, tungsten oxide (WO₃) has attracted great attention due to its remarkable physical and chemical properties. These properties make WO₃ an ideal candidate for different applications such as electrochromic, photochromic, lithium batteries, and gas sensors. Moreover, it exhibits a wide band gap ranging from 2.7 to 3.6 eV, and this oxide is rather complex and can crystallize in a number of different phases and crystals. In the literature, numerous reports are available on the growth of WO₃ nanostructures in the form of nanoparticles, thin films, nanorods, and nanowires. To grow these nanostructures, hydrothermal reaction, sol–gel chemistry, thermal oxidation, pulsed laser deposition, and thermal evaporation are most commonly used. Interestingly, nanostructured WO₃ is vastly used in the area of gas sensing applications as it offers excellent reproducibility, low-power consumption, and enhanced sensor capabilities.

In fact, over the years, WO₃ has proved to be one of the important materials for the detection of toxic gases like NO₂, NH₃, H₂S, CO, etc. Among these, nitrogen dioxide (NO₂) is a typical air pollutant released by combustion facilities, automobiles, and aircrafts. According to the air-quality monitoring protocols (American standards) for NO₂, the concentration should be detectable in the range of 3–25 ppm. Moreover, the decomposition of NO₂ by solar irradiation is a common source of ozone (O₃) production. In many developed countries, the maximum safe concentration of ozone is 50 ppb for continuous exposure and 100 ppb for short-term exposure. Another important toxic gas is hydrogen sulfide (H₂S), often produced in coal oil, coal, or natural gas manufacturing. The threshold limit value (TLV) for H₂S is 10 ppm, while further exposure at concentrations higher than 100 ppm is dangerous to human life and can cause death. Therefore, reliable and low-cost sensors with high sensitivity and selectivity are in great demand for environmental safety and industrial control purposes.

The aim of this work is fabrication of ultrasensitive WO₃ nanowires based on gas sensors using a cost-effective and high-yield method, namely, the vapor–liquid–solid (VLS) technique. It presents several advantages such as the nonrequirement of precursors, lowered reaction energy, and requires only a furnace system and primary pumping for the growth of nanowires. Indeed, in the case of WO₃, this technique has been rarely used. In the present study, complete optimization of the growth process of the WO₃ nanowires is presented. In particular, the effect of different catalysts, substrate temperatures, and growth time on the surface morphology of the nanowires was investigated using scanning electron microscopy (SEM). The crystalline properties of the nanowires were assessed using the grazing incidence X-ray diffraction (GI-XRD), and at the same time, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were also used to study the surface chemical and structural properties of the WO₃ nanowires, respectively. Finally, WO₃ nanowires that exhibit the best crystalline and surface morphological properties were used to fabricate gas sensor devices for the detection of different concentrations of target gas analytes such as NO₂, H₂S, O₃, ethanol, and acetone.

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RESULTS

Optimization of the Growth Process and the Surface Morphological Characterization of Nanowires. Scanning electron microscopy has been employed to study the surface morphology of WO₃ nanowires grown under different experimental conditions. In particular, we have studied the influence of different catalysts, substrate temperatures (Tₛ), as well as the effect of deposition time on the growth of nanowires. Figure 1 reports the SEM images of WO₃ nanowires grown with Au and Pt catalysts at an evaporation temperature of 1100 °C. The substrates were kept at two different temperatures, Tₛ = 525 and 580 °C, and the deposition was carried out for 15 min.

It can be clearly observed from Figure 1 that both the type of catalyst and the substrate temperatures have a great influence on the growth of nanowires. In the case of a platinum catalyst, no growth of nanowires was observed at both Tₛ = 525 and 580 °C. On the other hand, using Au as a catalyst, the WO₃ nanowire growth covering the whole alumina substrate has been observed. In particular, nanowires grown at Tₛ = 525 °C possess a diameter in the range of 10−30 nm and length less than 100 nm. With the increase in Tₛ (at 580 °C), the nanowires start to grow longer when compared to the ones at lower temperatures.

Further investigations reveal that the growth of nanowires using the Pt catalyst can be observed only at higher substrate temperatures. Figure 2 reports the growth of WO₃ nanostructures on both Au and Pt catalysts at a substrate temperature of 700 °C. In comparison, both exhibit similar morphology (nanorods), while the density of grown structures was low in the case of Pt as compared to that of Au. Hence, the substrate temperature of 525 °C and Au as a catalyst have been found suitable for the growth of nanowires.

Furthermore, the effect of deposition time, while keeping the other conditions constant (1100 °C, Ar = 100 sccm, Tₛ = 525 °C, P = 1 mbar), on the growth of WO₃ nanowires has been investigated. Figure 3 shows the comparison of nanowires grown using Au catalyst at two different deposition times (15 and 20 min). The nanowires prepared with a longer deposition time (20 min) are denser as they grow longer, with their length in the micrometer range. On the other hand, nanowires prepared with a shorter deposition time (15 min) possess length and diameter in the nanometer range. The dimensions and the morphology of nanowires grown on the Au catalyst at these experimental conditions (1100 °C, Ar = 100 sccm, Tₛ = 525 °C, P = 1 mbar, deposition time = 15 min) are suitable for fabricating conductometric sensing devices. Hence, these WO₃ nanowires were used for further characterizations and sensor device fabrication.

Structural Characterization of Nanowires Using GI-XRD and Raman Spectroscopy. GI-XRD analysis was performed to study the crystalline structure of WO₃ nanowires. Figure 4 represents the GI-XRD pattern recorded for WO₃ nanowires, which indicates the presence of WO₃ and the Au catalyst. The extra peaks observed in the spectra indexed with (*) correspond to the alumina substrate. The crystallographic planes of WO₃ nanowires and their corresponding values of 2θ equal to 23.08, 24.21, 26.52, 28.72, 34.04, 41.69, 47.20, 50.44, and 55.82° are attributed to the (001), (200), (110), (111), (220), (121), (221), (240), and (132) crystallographic planes, respectively. According to the literature and JCPDS data file
no. 05-0392, these spectra indicate the growth of the monoclinic phase of WO3 nanowires.27,28

On the other hand, Figure 5 reports the Raman spectrum of WO3 nanowires along with the spectra of the alumina substrate. WO3 peaks were clearly observed at 807, 708, 328, and 270 cm$^{-1}$. Compared to the literature,29 the peaks observed at 807 and 708 cm$^{-1}$ represent the monoclinic crystalline phase of WO3 that corresponds to the W−O−W stretching vibrations of the bridging oxygen. On the other hand, peaks at 328 and 270 cm$^{-1}$ belong to bending vibrations of O−W−O bonds.30

**Figure 5.** Raman spectra of WO3 nanowires in comparison with an alumina substrate.

X-ray Photoelectron Investigation of WO3 Nanowires. The surface composition and the chemical states of the elements in the WO3 nanowire sample were investigated by the XPS technique. The survey scan spectrum in Figure 6a of WO3 nanowires indicates that the surface of the sample is mainly composed of tungsten, gold, and oxygen elements with carbon contamination. In particular, the peak observed at 284.3 eV is attributed to the presence of carbon,31 which is a commonly adsorbed compound on the surface of the sample at room temperature. On the other hand, Figure 6b represents the W 4f spectra with two prominent peaks at 35.3 and 37.4 eV for W 4f$^{7/2}$ and W 4f$^{5/2}$, respectively.32 These 4f doublet peak lines are separated by a binding energy of 2.1 eV, which is in line with the literature33 and represents the +6 oxidation state of tungsten.34 Figure 6d shows the O 1s peak that can be resolved into two components, one at 530 eV and the other observed at 532.6 eV.32 The O 1s peak at 530 eV corresponds to the oxygen in the lattice and O$^{2-}$ ions, while the peak at 532.6 eV might be observed due to O$^{2-}$ and O$^{-}$ ions in the oxygen-deficient region.

Furthermore, the XPS study also shows the presence of Au catalysts on the WO3 nanowire sample. The Au 4f (Figure 6c) peaks at 83.6 and 87.3 eV were assigned to two different states of gold, i.e., Au 4f$^{7/2}$ and Au 4f$^{5/2}$, respectively.34

Gas Sensing. In the present work, WO3 nanowire sensors were tested toward different reducing (CO, ethanol, acetone, and H2S) and oxidizing (NO2 and ozone) gases. It is well known that in the sensor technology, selectivity is an important aspect and is usually very hard to achieve. However, it is somehow possible to enhance the selectivity of the devices by changing the operating temperature, and hence tuning the performance of the sensing device toward the specific target compounds. The WO3 nanowire sensors were operated within a range of temperatures to identify the optimal one for each target gas. Then, at that optimal working temperature (unique value for each gas), sensors were used to detect different concentrations of gas, and the collected data were used to draw calibration curves from which the lowest detection limit has been calculated.

To find the optimal working temperature of a sensor, response vs temperature curves for different gases are shown in Figure 7. The response of WO3 sensors was calculated by using eqs 4 and 5 with respect to the different operating temperatures at a fixed relative humidity of 50% at 20 °C. We decided to keep humidity constant during these preliminary investigations at a value close to the application requirements. Different concentrations of gases have been chosen according to their exposure limits. For example, as reported in the introduction, TLV for H2S is 10 ppm.

![Figure 6](image_url)  
**Figure 6.** XPS spectra of (a) survey scan, (b) W 4f, (c) Au 4f, and (d) O 1s acquired at room temperature.
Therefore, in Figure 7, each concentration was chosen according to the limit for that specific gas over which it became either dangerous to human health or to the environment. It can be clearly observed from Figure 7 that WO$_3$ nanowires show the highest response toward H$_2$S at an optimal working temperature of 400 °C, while at 200 °C, sensors show a higher response toward O$_3$. Thus, modulating the operating temperature can indeed promote a partial selectivity between O$_3$ (at a lower temperature) and H$_2$S (at a higher temperature).

Figure 8a,b shows the dynamic response of WO$_3$ nanowires toward H$_2$S and O$_3$ gases at their optimal working temperatures. The sensors show a decrease in the electrical conductance on the exposure of O$_3$ (oxidizing gas), while for H$_2$S (reducing gas), the conductance increases. This shows the typical behavior of n-type semiconductors.$^{35-37}$

Furthermore, Figure 9 reports the calibration curve, i.e., response vs gas concentration, for H$_2$S and ozone at their optimal work temperatures. The experimental data for calibration graph were well fitted by the typical power-trend relationship for metal oxide sensors,$^{38}$

\[
\text{response} = A\text{[gas concentration]}^B
\]

where $A$ and $B$ are constants typical of the sensing material and the stoichiometry of the involved reactions. Table 1 reports the values of coefficients $A$ and $B$ along with the estimated detection limits for target gases O$_3$ and H$_2$S by considering a response of 1 as the minimum response to have a detectable signal.

The gas sensing mechanism for the detection of H$_2$S and O$_3$ can be explained based on the conduction changes originated from the adsorption/desorption process upon the interaction with analytes.$^{35,39,40}$ When the n-type WO$_3$ nanowire system is exposed to the ambient air, a chemisorption of oxygen molecules on the surface occurs, resulting in the formation of adsorbed O$_2^-$, O$_3^-$, and O$_2^{2-}$ ions,$^{12,41}$ among which, in the temperature range of 150 < $T$ < 400 °C, O$_3^-$ ions dominate the surface, while at a higher temperature, O$_2^{2-}$ adsorbents dominate the oxide surface.$^{42}$ These adsorbed ions start capturing electrons from the outermost region of WO$_3$, due to which the electron concentration starts to decrease, resulting in the formation of the electron depletion layer (Figure 10a).

As a consequence of this reaction, extra electrons were donated back to WO$_3$, resulting in a decrease in the depletion layer

![Figure 7. Temperature dependence response of WO$_3$ sensing device measured with a relative humidity of 50% at 20 °C.](image-url)

![Figure 8. Dynamic response of WO$_3$ sensing devices toward reducing gases (a) hydrogen sulfide (10–20 ppm) at 400 °C and (b) ozone (50–150–300 ppb), measured at 200 °C with a relative humidity of 50% at 20 °C.](image-url)

![Figure 9. Detection trend lines for the WO$_3$ devices toward H$_2$S (400 °C) and O$_3$ (200 °C). The relative humidity was 50% at 20 °C.](image-url)

| gases | working temp. (°C) | $A$ | $B$ | detection limit |
|-------|--------------------|-----|-----|----------------|
| H$_2$S | 400                | 4.0 | 1.3 | 0.36 ppm       |
| O$_3$  | 200                | 1800| 1.8 | 0.017 ppm (17 ppb) |

![Table 1. Calibration Curve Coefficients and Detection Limits of the WO$_3$ Sensor Toward H$_2$S and O$_3$.](image-url)
Due to the highly accepting character of O₃, the concentration of the surface-adsorbed O⁻ ions increases, which in turn increases the electron depletion layer thickness and decreases the sensor conductance upon ozone exposure (Figure 10b).

**Comparison with the Literature.** Furthermore, the sensing performances of the nanowire sensors toward H₂S and ozone have also been compared with the literature reported in Table 2. Although the optimal working temperature for WO₃ nanowires toward H₂S was found to be 400 °C, for a clear analysis, we have compared the response of WO₃ nanowire sensors at 300 °C against the reported literature. Sensing data in Figure 10 for H₂S show that our sensing devices have a superior performance even at temperatures lower than their optimal one (300 °C). Indeed, WO₃ nanowire sensors exhibit a response double than that of the highest reported value in the literature.

On the other hand, in the case of O₃ gas, very few reports have been found in the literature. Different types of WO₃ sensing devices for the detection of O₃ have been reported in the literature such as in the form of thin films and nanorods. The optimal working temperature was found to be quite similar to the other reported values (Table 2). However, the response of our WO₃ nanowire sensors is 100 times higher as compared to the literature data at the ppb level of O₃.

### CONCLUSIONS

The WO₃ nanowires were successfully grown using a simple, highly productive VLS method on the Au-deposited alumina substrate, having a diameter in the range of 20–30 nm. GI-XRD and Raman spectroscopy studies confirm the monoclinic phase of WO₃ nanowires. The observation of two distinct W 4f peaks in the XPS spectra shows that the tungsten (W) is in the +6 oxidation state. Finally, the WO₃ nanowire sensor shows the best performance toward H₂S and ozone at optimal working temperatures of 400 and 200 °C, respectively. Indeed, the control on the working temperature of the sensors results in tuning the selectivity of the device toward a specific gas. The sensors showed a response of 103 toward 10 ppm of H₂S, while in the case of ozone, at 300 ppb, the highest response was found to be 170. Considering the lowest response value

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**Table 2. Literature Comparison of WO₃ Nanostructures for H₂S and O₃ Sensing**

| Structure          | Method                          | Gas (type and concentration) | Loading     | Response     | Temperature | Ref. |
|--------------------|---------------------------------|------------------------------|-------------|--------------|-------------|-------|
| WO₃ nanorods       | hydrothermal/impregnation method | H₂S_10 ppm                   | Ru loaded   | ≈20 ppm@350 °C | 47          |
| rGO/WO₃ nanosheets | hydrothermal method             | H₂S_40 ppm                   | rGO loaded  | ≈40 ppm@330 °C | 48          |
| Cu/WO₃ nanowires   | thermal evaporation and sputtering | H₂S_100 ppm                 | CuO loaded  | ≈1.5 ppm@200 °C | 26          |
| WO₃ nanowires      | evaporation–condensation technique | H₂S_20 ppm                 | Cr doped    | ≈153 ppm@80 °C | 49          |
| Cr/WO₃ microspheres| hydrothermal method             | H₂S_100 ppm                 | Co loaded   | ≈3.5 ppm@250 °C | 36          |
| WO₃ film           | RF magnetron sputtering          | O₃_0.8 ppm                   | Co loaded   | ≈6.8 ppm@250 °C | 50          |
| WO₃ thin film      | RF sputtering                    | O₃_0.8 ppm                   |              | ≈19 ppm@200 °C | 51          |
| WO₃ thin film      | sol–gel                         | O₃_0.8 ppm                   |              | ≈15 ppm@200 °C | 51          |
| WO₃ thin film      | evaporation                      | O₃_0.8 ppm                   |              | ≈3 ppm@200 °C  | 51          |
| WO₃ thin film      | RF sputtering                    | O₃_0.8 ppm                   |              | ≈10 ppm@400 °C | this work   |
| WO₃ nanowires      | vapor phase growth               | H₂S_10 ppm                   |              | ≈20 ppm@400 °C | this work   |
| WO₃ nanowires      | vapor phase growth               | O₃_0.3 ppm                   |              | ≈170 ppm@200 °C | this work   |
equal to 1 for each gas, the WO₃ nanowire sensors have detection limits in the ppb level that proves a superior performance compared to the literature reports.

**EXPERIMENTAL SECTION**

**Substrate Preparation.** Alumina substrates (4 mm², 99% purity, Kyocera, Japan) were used to grow tungsten oxide nanowires. Prior to the growth process, the substrates were ultrasonically cleaned with acetone and dried using synthetic air.

**Growth of WO₃ Nanowires.** For the synthesis of WO₃ nanowires, an ultra-thin layer of noble metal catalysts was deposited using magnetron sputtering on alumina substrates. To optimize the growth process of WO₃ nanowires, two different metal catalysts, namely platinum (Pt) and gold (Au), were used. Different deposition conditions were employed to deposit these metal catalysts to obtain the same approximate thickness. These conditions are Ar plasma = 7 sccm, radio frequency (RF) magnetron sputtering, 70 W, and 5 s for gold, whereas for platinum, Ar plasma = 7 sccm, direct current (DC) magnetron sputtering, 70 W, and 2 s.

After catalyst deposition, WO₃ nanowires were grown via the vapor–liquid–solid (VLS) method. This whole growth process was performed in an alumina tubular furnace (custom design based on the commercial Lenton furnace). The WO₃ powder (99.9% purity, Sigma-Aldrich) was used as the source material. The metal oxide powder was placed at the center of the tubular furnace at a given temperature to promote evaporation. The catalyst-deposited substrates were placed at a lower temperature when compared to the evaporation temperature of the source material. Inert argon gas was used as a carrier gas to transport these WO₃ vapors toward the catalyzed alumina substrates. The growth of WO₃ nanowires was carried out at an evaporation temperature of 1100 °C, 1 mbar of pressure, and 100 sccm of argon flow. The substrate temperature was varied from 500 to 700 °C and deposition was carried out for 15 and 20 min to acquire the preferable surface morphology of nanowires.

**Characterizations.** A field-emission scanning electron microscope LEO 1525 (Gemini model; Carl Zeiss AG, Oberkochen, Germany) was operated at 3–5 kV to investigate the surface morphology of the nanowires. The GI-XRD technique (Empyrean diffractometer, PANalytical, the Netherlands) was used to investigate the crystalline structure of WO₃ nanowires. The GI-XRD was performed in a glancing angle mode, with 1.5° incident angle using Cu-LFF (λ = 1.5406 Å) operated at 40 kV to 40 mA. The spectra were recorded by a parallel-plate collimated proportional Xe detector with a nickel large-β filter, in the range of 20–70°. Near-ambient pressure X-ray photoelectron spectroscopy (SPECX GmbH, Germany, Al Kα monochromatized source) allow the chemical analysis of the surface of the materials in the hundreds pascals range atmosphere. In our experiment, the pressure inside the cell was 300 Pa, the atmosphere composition was 80% nitrogen and 20% oxygen to simulate in-operando working conditions, and measurements were performed at room temperature. All reported binding energy data were calibrated using the C 1s peak of the residual C contamination at the surface of the materials. Further, for the fitting and analysis of XPS data, KolXPD software has been used. Moreover, Raman spectra of WO₃ nanowires were measured using a HORIBA monochromator iHR320 configured with a grating of 1800 g mm⁻¹, coupled to a Peltier-cooled Synapse CCD. An He–Cd laser (442 nm) was focused on the samples by a fiber-coupled confocal optical microscope (HORIBA) at 100x magnification. The spectra of the nanowires were recorded in the wavelength range of 200–1000 cm⁻¹.

**Sensor Fabrication and Gas Sensing Measurement.** A set of WO₃ nanowire samples was prepared for gas sensing applications. To fabricate the sensing device, TiW alloy pads were deposited by DC magnetron sputtering (70 W argon plasma, 300 °C, 5.5 × 10⁻³ mbar, and 3 min), which improves the mechanical adhesion during the soldering process. Afterward, interdigitated platinum contacts were deposited on the top of nanowires by using the same parameters as described before the deposition time of 20 min.

Metal oxide surface reactions are strongly thermally activated and thus the sensing performance of WO₃ nanowires is also strongly influenced by the temperature. Therefore, to enable the test of these WO₃ sensors in a wide range of temperatures, a platinum heater was deposited on the backside of the samples, via the same process used for the contacts deposition. The prepared sensor devices were finally mounted on transistor outline packages using electrosoldered gold wires. To stabilize the contact material, the sensors were aged at 400 °C for 72 h prior to the electrical measurements. Such transducers were prepared using thin- or thick-film technologies; the temperature uniformity is good, but unfortunately the power consumption is quite high, in the range of 180–490 mW for 200–400 °C for a 2 × 2 mm² substrate.

A flow-through technique was used to investigate the conductometric sensing response of the fabricated devices. A lab-made stainless steel chamber (1 L volume) was used to test the sensors. To minimize the effect of external temperature variations, the temperature of the chamber was set at 20 °C. The temperature of the sensors was controlled by modulating the electric power applied to the heater by Thrulby-Thaner PL330DP power supplies. After the placement of all of the sensors inside the test chamber, they were heated at the desired working temperature for 8 h for thermal stabilization. All test gases came from certified bottles, supplied by SIAD SpA (Italy), and they were mixed with a carrier of dry synthetic air by mass-flow controllers (MKS Instrument, Germany), maintaining a 200 sccm total flow. A fixed voltage of 1 V was applied to the sensors (Agilent E3631A power supply), measuring at the same time the conductance of each sensor using pico-ammeters (Keithley 486). The response is determined by the variation of the conductance using the following formulae for oxidizing gas

\[
\text{response} = \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} = \frac{G_{\text{air}} - G_{\text{gas}}}{G_{\text{gas}}}
\]

(4)

and reducing gas

\[
\text{response} = \frac{G_{\text{gas}} - G_{\text{air}}}{G_{\text{air}}}
\]

(5)

where \(R_{\text{gas}}\) and \(G_{\text{gas}}\) are, respectively, the sensor resistance and conductance in the presence of the gas, and \(R_{\text{air}}\) and \(G_{\text{air}}\) in synthetic air.

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Nanorods and Nanoparticles.

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Films.

Gas Sensor. Synthesized via a Sol

Characterization of Tungsten Oxide Thin Films Produced by Spark

of Sub-Micron Porous WO₃ Spheres.

Part 1

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