Facile synthesis of Ag nanoparticles-decorated WO₃ nanorods and their application in O₂ sensing

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Abstract

Here we describe a two-step aerosol-assisted chemical vapor deposition (AACVD) synthesis method for the fabrication of Ag nanoparticles (NPs) decorated WO₃ nanorods (NRs), evaluating the use of different organometallic silver precursors. Physical property characterization techniques including XRD, SEM, TEM, and XPS were carried out to investigate the composition and morphology of the pristine WO₃ NRs and functionalized WO₃ NRs with Ag NPs. The results showed that uniform WO₃ NRs were obtained with a length of 600 nm to several μm and a diameter of 100–200 nm, and Ag NPs were well-dispersed on the surface of WO₃ NRs with the size of 6–20 nm. The nanostructured WO₃ thin films were synthesized and integrated directly onto alumina platforms via the AACVD method to fabricate gas sensors. Gas sensing performance was investigated towards different O₂ concentrations between 1% and 20% at various operating temperatures. The sensing response revealed that an increase in baseline resistance was observed for the Ag-decorated WO₃ sensors fabricated by using organometallic silver precursors, and the decoration of Ag NPs on WO₃ sensors improved sensing properties as compared to the undecorated ones. The possible formation process and sensing mechanism of the Ag NPs decorated WO₃ NRs are proposed.

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1. Introduction

O₂ sensors are in high demand for environmental monitoring, food security, health care, and industrial processing [1,2]. Nowadays, the widely used electrochemical-based O₂ sensors rely on the oxidation of Pb in the anode, which is highly toxic to the environment and should be replaced in the near future according to the “Restriction of Hazardous Substances Directive” (RoHS). Though Pb-free alternative electrochemical gas sensors to O₂ have been produced by introducing Zn, Fe, or Al, issues such as short lifespan and low sensitivity still remain. Meanwhile, the current alternative oxygen gas sensors still cannot meet the need for cost-effective, compact, and low-temperature working devices. Based on this, we previously deposited Ag/Ag₂O nanoparticles (NPs) on the surface of WO₃ nanorods to fabricate Pb-free gas sensors for O₂ measurement in a highly humid environment [3].

Metal-oxide semiconductor (MOS) gas sensors have been widely studied and used in gas detection fields due to the advantages of low cost, compact size, simple measurement, and easy production [4,5]. MOS nanomaterials can be divided into n-type and p-type metal oxide semiconductors based on their resistance response to gases classified as ‘oxidizing’ or ‘reducing’. Tungsten oxide (WO₃) is an important n-type MOS with a bandgap between 2.4 and 2.8 eV that has attracted wide attention due to its unique physical and chemical properties, and it has been used in gas sensing, electrochromic, photochromic, and catalytic fields [6,7]. It has been reported as an ideal candidate for the detection of various gases including NO₂ [8], NH₃ [9], H₂S [10], H₂ [11], and O₂ [3]. Therefore, here WO₃ is explored as a potential oxygen gas-sensing material to replace Pb-bearing ones.

Over the last few decades, many fabrication methods have been developed and used to prepare WO₃ nanostructures, including chemical vapor deposition [12], hydrothermal method [13], thermal evaporation [14], template-assisted growth [15], etc. Chemical vapor deposition (CVD), as a conventional technique for the synthesis of solid-state thin films, has been applied for many years. High-purity
materials with structural control at the atomic or nano-scale can be obtained by using the CVD method. However, the general lack of readily available volatile precursors and the difficulty in controlling the stoichiometry of the deposits hinder the further development of CVD technique. As an important branch of conventional CVD, aerosol-assisted chemical vapor deposition (AA CVD) technique uses aerosol droplets to transport the chemical precursors onto the substrate in the reactor with the aid of an inert gas carrier (usually N₂ or Ar) [16-17]. A wide range of low volatility or thermally unstable precursors can be used at an ambient atmosphere or low temperature due to the process relying principally on the solubility of the chemical precursor instead of volatility. Nano-thin films synthesized via AACVD show excellent control in particle size, crystallinity, porosity, and stoichiometry. Besides, the morphologies of the thin films can also be controlled by simply adjusting various reaction condition parameters such as deposition operating temperature, choice of solvent, and gas flow rate in the AACVD process. AACVD is commonly applied to synthesize metal oxide nanostructures for use in gas sensors [18].

WO₃ nanorods (NRs) decorated with various noble metal NPs have been widely investigated and developed in many applications, especially in the gas sensing area [19,20]. Many studies have proved that the gas sensing response of a target analyte gas can be greatly enhanced by adding noble metal NPs onto the MOS sensing material and it has been demonstrated that AACVD is also a flexible technique that facilitates the implementation and functionalization of WO₃ NRs with many different noble metals [3,21,22]. In this paper, undecorated WO₃ NRs were prepared by using AACVD first and then noble metal additive, Ag, was further deposited onto the surface of the as-prepared WO₃ NRs. In previous work in this area, commercially available AgNO₃ was used to produce Ag/Ag₂O NPs decorating particles on nanostructured WO₃ [3], but that Ag-precursor was only capable of producing low loadings even at high precursor concentrations. To control Ag-loading, an alternative silver precursor is required. The organometallic silver precursors used here have previously been used to make Ag NP via a hydrothermal reaction [23] but never previously for AACVD and provide controllable deposition of Ag NP on the surface of WO₃ NRs. The composition and morphology of the as-deposited WO₃−x and WO₃ after annealing (AA) thin films were characterized by XRD, SEM, TEM, and XPS. The diameter of the Ag NPs was measured and the particle size distribution of the Ag NPs was counted. Finally, gas sensing performance towards oxygen for the bare WO₃ NRs and Ag-decorated WO₃ NRs were tested and the sensing mechanism of Ag-functionalized WO₃ towards O₂ is discussed.

2. Experimental

2.1. Preparation of sensing material and gas sensor

WO₃ NRs were synthesized using AACVD on the surface of alumina sensor platforms. The size of each platform was 2 × 2 mm with a thickness of 250 µm. Gold interdigitated electrodes were printed on one side of the platform and platinum heater on the other side. The cleaned platforms were placed close to the outlet of the rectangular AACVD reactor and preheated to 375 °C. Tungsten hexacarbonyl [W(CO)₆] (0.06 g, 0.17 mmol) was dissolved in a mixed solution of 10 mL acetone and 5 ml methanol. This solution was then transferred to a flask. After sonicating for 5 min, an aerosol was generated by an ultrasonic humidifier (2 MHz, Johnson Matthey Liquifog) at room temperature. A gas flow of N₂ (99.99%, BOC) was passed through the aerosol mist at a flow rate of 300 standard cubic centimeter per minute (sccm) to transport the aerosol droplets into the preheated reaction chamber, controlled by a mass flow controller (MFC, Brooks). Under these conditions, the precursor solution was fully transferred within 30 min. A shadow mask was used during the fabrication process, aiming to control the deposition area of the sensing materials. A set of nine alumina-based gas sensors can be arranged in the mask base at a time. Once the deposition was finished, the heater and humidifier were then switched off in sequence, and the sensors were naturally cooled down to room temperature under a flow of N₂. The as-deposited films on the surface of sensors were annealed in a muffle furnace for 2 h in air and heated up from room temperature to 500 °C at a rate of 10 °C/min to obtain WO₃ NRs. The reaction process of the AACVD technique is shown in Fig. 1. Organometallic silver metal precursors, silver 2-methyl-2-amino-propan-1-ol (Ag-AMP), silver 1-aminopropan-2-ol (Ag-AP), and silver 2-aminoethanol (Ag-EA), were synthesized according to the literature method [23] and then deposited via AACVD on the annealed WO₃ gas sensors at a heating temperature of 275 °C and N₂ flow rate of 170 sccm. Depositions with various volumes of the Ag precursor solutions were carried out to explore the effect of different

![Fig. 1. Schematic diagram of the reaction process of AACVD technique.](image-url)
Ag-loading on WO₃ gas sensors for gas sensing performance towards oxygen.

2.2. Structural characterization

The crystalline structures of the synthesized thin-film materials were obtained by X-Ray Diffraction (XRD) (Bruker D8-Discover) equipped with a silicon strip detector using Cu Kα radiation (λ = 1.5418 Å) and operated at a current of 40 mA and a voltage of 40 kV. The X-ray diffraction patterns were collected with a scanning rate of 0.05°/s over a 20° to 70°. A field emission scanning electron microscope (FESEM) (JEOL JSM-6301/JSM-6300) was used to identify the morphology of the thin films from a top-down configuration after Au-coating. High-resolution transmission electron microscopy (HR-TEM) measurements were performed on a JEOL 2100 at a voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific) with a monochromatic Al Kα X-Ray source (1846.6 eV) was used to measure the elemental composition and electronic states of the elements. C 1s (284.8 eV) peak calibration is conducted for the referencing of the other peaks’ binding energy.

2.3. Gas sensing characterization

A predefined concentration of oxygen was obtained by diluting zero air (20% O₂) with nitrogen (99.999%) provided by the gas rig (Lehman Instrument, France). The variance in the concentration of oxygen was achieved by changing the flow rate of each gas using a mass flow controller (MFC, UFC 1100, Brooks) controlled by a computer program written in LabVIEW (National Instrument 2016). A water bubbler was added to the pathway of the tested gas mixture before entering the sensor chamber and used to simulate the humid environment. The resistance changes during the tests regarding different sensors while exposed to different concentrations of oxygen gas were monitored and recorded by a sensor management system AS-330 (Atmospheric Sensor Ltd, UK). By using this device, the sensing performance under different ranges of operating temperatures, test periods, and operating sequences can be carried out and analyzed. The time interval for the sensing test was 30 min of gas exposure. The oxygen concentration varied between 0% and 20%. The sensors were then purged with N₂ for 30 min to ensure their recovery to the baseline value of the initial resistance and stability before a new measurement was taken. The sensors’ response sensitivity was defined as being equivalent to Rₐg/Rₐ, where Rₐ is the resistance of sensor baseline in the nitrogen and Rₐg is the sensor resistance when the sensors are exposed to the target gas O₂.

3. Results and discussion

3.1. Material characterization

The XRD pattern of a plain alumina sensor platform without any deposition is shown in Fig. 2(a), which is identified as a combination of two materials obviously, corresponding to alumina and gold. Specifically, the diffraction peaks located at 25.6°, 35.2°, 37.8°, 43.4°, 52.6°, 57.5°, 66.5°, and 68.2° respectively attributed to (012), (104), (110), (113), (024), (116), (214) and (300) reflections, which are in good agreement with the standard reference pattern of hexagonal alumina (JCPDS # 82-1467). The rest of the peaks positioned at 38.3°, 44.6°, and 64.7° can be indexed to (111), (200), and (220) planes and match well with the reference pattern of cubic gold (JCPDS # 01-1174). It is worth highlighting that alumina is the base of the sensor platform and gold comes from the electrodes. The XRD patterns of as-deposited sub-stoichiometric tungsten oxide (WO₃-x) and WO₃ after annealing (WO₃ AA) on the alumina substrates are put together in Fig. 2(b) for comparison. Regardless of the peaks attributed by Al₂O₃ and Au, two highlighted peaks at 23.5° and 48.1° correspond to (010) and (020) reflections respectively, suggesting the formation of monoclinic phase structure of WO₃-x after annealing [24]. While the diffraction peaks of WO₃ AA can be indexed to monoclinic WO₃ (JCPDS # 72-0677). The strong peak at 23.1° and two relative weak peaks at 23.6° and 24.3° are ascribed to (002), (020), and (200) reflections, showing the preferred orientation along the (002) direction of WO₃ NRs deposited on the alumina substrate after annealing. Fig. 2(c) shows the XRD patterns of as-deposited Ag-decorated WO₃ gas sensors. Three organometallic Ag metal precursors with 10 μL of the initial precursor solution were deposited on the annealed WO₃ sensors at a N₂ flow rate of 170 sccm and the reaction temperature was 275 °C. No significant difference was found after the deposition of Ag-precursors on WO₃ gas sensors, the diffraction peaks of silver (38.2°, 44.3° and 64.5°, JCPDS # 87-0718) overlap with the peaks of gold (38.3°, 44.6° and 64.5°, JCPDS # 01-1174) from the electrodes contained on the surface of the gas sensor.

Fig. 3(a) shows the surface morphology of a bare sensor, which reveals that the sensor is made up of interdigitated Au electrodes and alumina-based substrate. Fig. 3(b) illustrates the cross-section of
as-deposited \( \text{WO}_3 \) thin films. A high density of randomly oriented rod-like morphology can be observed. \( \text{WO}_{3-x} \) NRs show slender structure with a diameter of about 80 nm and a length ranging from 700 nm to several micrometers. It is noteworthy that some slim rods are self-assembled into bundled aggregates in the marked area, which may be ascribed to the high surface energy of the single nanorod with a high length-to-diameter ratio during the preparation process [25]. The surface morphologies of as-deposited \( \text{WO}_{3-x} \) thin film before and after annealing are shown in Fig. 3(c) and 3(d). From Fig. 3(c), it can be seen that a thick layer of nonaligned \( \text{WO}_{3-x} \) NRs is formed on the surface of the sensor. The distribution of \( \text{WO}_3 \) NRs becomes dense after annealing (Fig. 3(d)).

The microstructure of the \( \text{WO}_{3-x} \) and \( \text{WO}_3 \) NRs was examined by HRTEM, and the corresponding results are shown in Fig. 4. In Fig. 4(a), the \( \text{WO}_{3-x} \) shows a decrease in diameter from 110 nm to 20 nm, which we have previously observed [26], and with a length of 2.14 \( \mu \)m along the growth direction (bottom to top), which is perpendicular to the substrate. From the inset picture in Fig. 4(a), the lattice spacing of 0.362 nm can be observed, which can be attributed to the (010) plane of monoclinic \( \text{WO}_{3-x} \), indicating that the growth direction of \( \text{WO}_{3-x} \) NRs was along [010] direction. The sharp heads of the nanorod structure disappeared and long nanorods tend to break into short pieces after annealing at 500 °C in the air for 2 h as is shown in Fig. 4(c). Obviously, the surface of the \( \text{WO}_3 \) NRs became slightly coarser and rough. The lattice fringes in the inset of Fig. 4(c) revealed the \( \beta \)-spacing of 0.385 nm and could be ascribed to the (002) planes of monoclinic \( \text{WO}_3 \) [JCPDS # 72-0677], demonstrating that the growth direction of \( \text{WO}_3 \) NRs was along [002] direction, which is in good agreement with the characterization analysis of XRD. Based on the two groups of interplanar spacings, it can be concluded that lattice parameters are influenced by the oxidation of \( \text{WO}_{3-x} \) to \( \text{WO}_3 \) during the annealing process.

SEM characterizations of as-deposited Ag-decorated \( \text{WO}_3 \) gas sensors via organometallic Ag metal precursors, including Ag-AMP, Ag-AP, and Ag-EA with different amounts of precursor solution used for deposition, are shown in Fig. 5. It can be clearly seen that many spherical-shaped Ag NPs are uniformly decorated on the surface of \( \text{WO}_3 \) NRs. In particular, the coverage of the NPs on the surface of \( \text{WO}_3 \) NRs increases gradually as the amount of the initial precursor increases and becomes almost saturated when the dosage reaches 10 \( \mu \)L. No obvious morphology change for Ag NPs is found with the increase of precursor solution. Besides, it seems like the deposition of different organometallic Ag metal precursors has no visible influence on the morphology of \( \text{WO}_3 \) NRs. Further information about the microstructure of the Ag NPs and the \( \text{WO}_3 \) NRs was characterized by TEM. TEM images of Ag/\( \text{WO}_3 \) sensors with different loadings produced using the Ag-AMP precursor are shown in Fig. 6. It can be observed that the diameter of \( \text{WO}_3 \) NRs is about 100–200 nm. The clear lattice fringes can be seen in two insets in Fig. 6(b) with interplanar spacings of 0.385 and 0.235 nm, corresponding to the (002) plane of \( \text{WO}_3 \) and (111) plane of Ag. The surface of \( \text{WO}_3 \) NRs is homogeneously covered with well-dispersed spherical Ag NPs. The particle size distribution of the Ag NPs with different loadings was counted and the result is shown in Fig. 7.

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Fig. 3. SEM images of (a) bare alumina sensor, (b) cross-section of as-deposited \( \text{WO}_3 \) thin films on alumina platform, (c) as-deposited \( \text{WO}_{3-x} \) and (d) \( \text{WO}_3 \) AA on alumina sensor.
can be found that the diameter of Ag NPs is mostly distributed between 6 and 20 nm irrespective of the precursor amount. EDS element mapping was carried out to study the elemental composition of the as-deposited Ag/WO₃ on the alumina gas sensor platform. From the EDS spectrum of the sample shown in Fig. 8, four main elements, including Au, W, O, and Ag were detected. Particularly, the presence of a large amount of Au elements is derived from the use of a gold TEM grid and the gold electrode from the sensor substrate. Corresponding EDS elemental mapping is shown in Fig. 8(a-d), illustrating that W, O, and Ag are all well distributed along the Ag NPs decorated WO₃ NRs.

The elemental electronic state and the composition of as-deposited WO₃₋ₓ, annealed WO₃ thin films, and Ag NPs were conducted through XPS analysis. Fig. 9 displays the W 4f and O 1s core-level spectra recorded from the as-deposited WO₃₋ₓ and WO₃ AA films on alumina sensor platform. As is shown in Fig. 9(a), two doublets of W 4f are obtained after fitting the spectra for as-deposited WO₃₋ₓ. The peaks at 35.7 and 37.8 eV are associated with W 4f⁷/₂ and W 4f⁵/₂ for the W⁶⁺ oxidation state respectively, referring to the existence of stoichiometric WO₃. The low-intensity ones at 34.7 and 36.9 eV demonstrate the presence of the sub-stoichiometric WO₃₋ₓ. After annealing, the W 4f spectra on the sensor shown in Fig. 9(b) reveal only two intense peaks at 35.4 and 37.5 eV, corresponding to W 4f⁷/₂ and W 4f⁵/₂ for the W⁶⁺ oxidation state [27]. The results prove the presence of only stoichiometric WO₃. As displayed in Fig. 9(c,d), the peak located at 530.7 and 530.3 eV can be attributed to the lattice oxygen in the as-deposited WO₃₋ₓ and WO₃ AA on alumina. Fig. 10 displays the XPS spectra of the Ag3d regions for all three organometallic Ag metal precursors with different volumes of initial precursor solution and their corresponding area ratio of Ag3d to W4f regions. For all samples, two clear peaks at around 374.2 and 368.1 eV are identified clearly and can be assigned to Ag3d₃/₂ and Ag3d₅/₂ respectively. Some small chemical shift for the Ag core level has been observed with different amounts of loadings, which can be attributed to the initial state effect caused by the size of the Ag NPs [28]. For Ag NPs, a 0.5–2 eV chemical shift has been observed for small particles as compared to the core levels of respective bulk Ag crystals [29]. It can be found that the intensity of the Ag peaks for all

![Fig. 4. HRTEM images of (a-b) as-deposited WO₃₋ₓ NRs and (c-d) annealed WO₃ NRs.](image-url)
three organometallic Ag metal precursors increases as the amount of precursor increases. Fig. 10(d-f) show an increase in silver deposition on WO₃ as the amount of Ag precursor solution increase. This would be an important improvement over our previous use of AgNO₃ as a silver precursor, where it was very difficult to alter the amount of Ag/Ag₂O deposited even by changing the amount of precursor. However, it is also worth noting that the increase of area ratio of Ag3d to W4f regions becomes smaller with the further increase of Ag precursor amount.

3.2. Gas sensing properties

Gas sensing tests were carried out to different oxygen concentrations ranging from 0% to 20% (200,000 ppm) in an ambient environment (~50% RH) for all undecorated and Ag-decorated WO₃ sensors at operating temperatures varying from 150 to 300°C. The relative humidity (RH) was maintained at 50% and the temperature interval was set at 25°C to examine the sensors' sensing properties. Dynamic response-recovery curves of all Ag-AMP/WO₃, Ag-EA/WO₃, Ag-AP/WO₃, and undecorated WO₃ sensors towards various O₂ concentrations (1–5–10–15–20%) are shown in Fig. 11. It should be pointed out that the sensors of AgAMP 5 μL, AgAMP 1 μL, AgAP 3 μL, and AgEA 1 μL did not successfully pass the sensing tests due to sensor failure to measure resistance through the sensor, heater or both. Obviously, the resistance of all sensors increased upon exposure to O₂ that reduced when subsequently exposed to N₂, revealing a typical n-type semiconductor behavior. In general, the absolute change in resistance on exposure to O₂ of the sensors decorated using organometallic silver increases with the increasing amount of silver precursors. For the sensors decorated by Ag-AMP and Ag-EA, the amount of 3 μL shows the largest resistance change, while the largest resistance change is observed for 10 μL decorated by Ag-AP. Moreover, the absolute resistance simultaneously increases with the increase of O₂ concentration under the specific temperature, indicating the improvement of sensor response.

Fig. 11(b) shows the response of Ag-AMP 3 μL/WO₃ and WO₃-based sensors at different operating temperatures under the O₂ concentration of 20%. Both sensors exhibit an improvement in the sensor response with the increase of working temperature from 150° to 250°C. For all the WO₃ sensors, the highest sensing response is obtained at 250 or 300°C with a value of about 4, while for the Ag-AMP 3 μL/WO₃ sensor, the highest response of 4.4 is found at 300°C. For the 10 μL Ag-AP decorated WO₃ sensor, the maximum response value of 5 is found at around 240°C (Fig. 11(d)). It is worth noting that the response decreases sharply in the temperature interval of 250–275°C and then increases again with the further increase in working temperature, which may be attributed to the change of Ag NPs size under high temperatures and thus affects the sensing performance of the Ag/WO₃ sensors. Besides, for the Ag-EA 3 μL/WO₃ sensor, two max response peaks were found with the response value of 4.4 and 4.7 at 200 and 250°C, respectively (Fig. 11(f)). The small response peak located at 200°C could be attributed to the phase change of Ag NPs in bulk with larger particles, and the higher peak positioned at 250°C refers to the sensing response for Ag NPs with smaller size. Ag forms Ag₂O upon exposure to O₂ over the surface but the obtained Ag₂O tends to decompose and form Ag and O₂.

Fig. 5. SEM images of as-deposited Ag/WO₃ sensors by using (a-d) Ag-AMP, (e-h) Ag-AP and (i-l) Ag-EA as precursors with various amounts of the initial precursor solution. (a, e, i) 1 μL, (b, f, j) 3 μL, (c, g, k) 5 μL and (d, h, l) 10 μL.
when the temperature is over 190 °C [30]. Hence at lower temperatures, the silver should be oxidized to Ag₂O, while at high temperatures, it should be decomposed to metallic Ag. However, Barsan et al. [31] concluded that the surface energy of Ag nanostructure may enable Ag₂O to be stable at temperatures from 190 to 700 °C in the air for small-size Ag NPs. Moreover, another published paper reports that Ag was oxidized into Ag₂O at an oxidation temperature of about 350–500 °C [32]. The O₂ response of Ag NPs decorated WO₃ sensors may therefore be directly related to the size, phase, and proportion of Ag/Ag₂O NPs [33–35], and the working temperature is the critical factor to influence these variables. Hence such temperature-induced phenomena might be the cause of the difference between the Ag-AMP 3 μL/WO₃ sensor in Fig. 11(b) where the sensitivity continues to increase with increasing working temperature for whereas fluctuations in response are observed for Ag-AP 10 μL/WO₃ and Ag-EA 3 μL/WO₃ in Fig. 11(d) and 11(f).

### 3.3. Growth mechanism of the Ag decorated WO₃ NRs

As is well known, two main concepts are often used for the preparation of MOSs, namely 'top-down' fabrication and 'bottom-up' synthesis [36]. Especially, AACVD is considered as the typical 'bottom-up' approach to generating large-scale nanomaterials, which is based on the growth of structures through the assembly of atoms derived from chemical precursors. The basis of AACVD is the atomization of liquid precursor which is transported by a flow of inert carrier gas to the substrate. The solvent then undergoes rapid vaporization, forming precursor vapors at elevated temperatures, the vapors start to react and decompose forming a thin film on the substrate. Film morphology such as nanostructured rods is dependent on the solvent used and the deposition temperature.

It is widely accepted that the formation of WO₃ NRs follows the catalyst-free direct vapor-solid (VS) mechanism [37]. Fig. 12 shows
the growth mechanism for Ag-decorated WO₃ NRs. First of all, vapor phase WO₃ is obtained via the direct oxidation of the tungsten organic precursor. The generated WO₃ vapor is carried by the N₂, followed by the formation of localized crystals at the incipient stages. Then, the WO₃ polycrystalline layer tends to form on the surface of alumina sensing substrate, and the polycrystalline layer in the morphology of thin films consists of NPs, which can serve as seeds and is vital for the nucleation and subsequent growth of WO₃ NRs [38]. The nanostructured film can offer energetically favorable planes for the nucleation of the NRs end caps. Furthermore, it can provide pathways for surface diffusion of subsequently condensed vapor species to the surface of WO₃ NRs. The loosely packed [010] crystallographic planes are considered as the preferred grow surface owing to the relatively high surface energy and fast growth rate. As a result, the nanorods with single crystals lift and exhibit a high length-to-diameter ratio. Especially, the growth of WO₃ NRs is crossed like a lawn due to the rough surface of the initial polycrystalline layer. Based on the observation of the cross-section in Fig. 3(b), the lawn-structured WO₃ thin film is generated. Besides, it should be clear that some factors such as the degree of supersaturation, the transfer rate of WO₃ vapor, availability of nucleation sites, and temperature gradient across the substrate are crucial during the nucleation and growth of WO₃ NRs.

After the successful synthesis of WO₃ NRs, organometallic silver precursors were used to deposit Ag NPs on the surface of WO₃ NRs. WO₃ NRs with a high length-to-diameter ratio have high surface energy, which can act as active attachment sites to attract organometallic silver vapor molecules. Since the heating temperature in the AACVD reactor is relatively high, the Ag-containing precursors will decompose and generate Ag NPs. Besides, the WO₃ NRs are fully exposed to the environment of organometallic silver vapor, and thus the decoration of Ag NPs is well-dispersed. With the volume increase of the Ag precursor solutions, the loading of Ag NPs becomes densely packed.

3.4. Gas sensing mechanism

For most of the chemiresistive metal oxide gas sensors, a band bending model based on the surface chemistry of highly reactive ionosorbed species (O₂⁻, O⁻ or O²⁻) was usually put forwards to illustrate the gas sensing mechanism [39]. However, it has been proved that the classical band bending model is inappropriate for
WO$_3$-based sensors, in which surface lattice oxygen instead of surface adsorbed charged oxygen species reacts with the adsorbed target gases to create oxygen vacancies that rapidly diffuse into the bulk and modulate the conductivity [40]. Frederick et al. [41] developed a "bulk conduction mechanism" to explain the gas sensing behavior that the resistance change of the gas sensors should be attributed to the change of oxygen vacancy concentration in the nanomaterial. In the framework of this bulk conduction mechanism, in the starting N$_2$ ambient, there is a higher concentration of oxygen vacancies on the surface of Ag/WO$_3$ sensors and hence higher conductivity, then after the sensor is exposed to O$_2$, there will be a lower concentration of oxygen vacancies due to vacancy healing (Fig. 13(a)).

The role of catalyst particles in sensitizing MOSs has been discussed in the context of two mechanisms, namely chemical and electronic sensitization [42]. By adding Ag NPs to the surface of
the possible contribution in sensitivity to oxygen can be ascribed to the function of electronic sensitization derived from the interface between Ag NPs and the WO$_3$ surface and the effect of chemical sensitization of Ag NPs (spill-over effect). The data found in the literature showed a relatively low work function of Ag (4.26 eV) [43] and a high work function of WO$_3$ (5.7 eV) [44], resulting in electrons transferring from Ag NPs to n-type semiconductor WO$_3$ (electronic sensitization) in order to equalize the Fermi level, as shown in Fig. 13(b), which would lead to a decrease in baseline resistance. Conversely, more oxygen molecules can be adsorbed by the Ag/WO$_3$ surface through a spill-over type mechanism under chemical sensitization, reducing the oxygen vacancy concentration, which will increase the baseline resistance. The net dramatic increase in the baseline resistance indicates that the spill-over effect is more dominant (increases baseline resistance) here than electronic sensitization (decreases baseline resistance). Hence the introduction of Ag NPs will enrich the surface with lattice oxygen, which will lead to the decline of vacancy concentration and the increase of initial resistance of Ag/WO$_3$ sensors [45].
Fig. 11. Sensor resistance changes of (a) Ag-AMP/WO₃ sensors, (c) Ag-AP/WO₃ sensors, and (e) Ag-EA/WO₃ sensors to various O₂ concentrations (1–5–10–15–20%) at different operating temperatures ranging from 150°C to 300°C with an undecorated WO₃ for comparison; (b) response of WO₃ and Ag-AMP 3 μL/WO₃ sensor to 20% O₂ as a function of operating temperatures; (d) response of WO₃ and Ag-AP 10 μL/WO₃ sensor to 20% O₂ as a function of operating temperatures; (f) response of WO₃ and Ag-EA 3 μL/WO₃ sensor to 20% O₂ as a function of operating temperatures.
**Fig. 12.** Schematic model of the growth mechanism for Ag-decorated WO₃ NRs.

**Fig. 13.** (a) Energy band structure schematic diagrams of Ag and n-type WO₃ semiconductors. (b) Schematic model of depletion layer for undecorated WO₃ NRs and Ag decorated WO₃ NRs when exposed to N₂ and O₂.
4. Conclusions

Ag NPs-decorated WO₃ NRs using organometallic silver as the precursor was successfully deposited on the alumina sensor platform in a two-step synthesis method via AACVD. The physical property characterization results showed that no obvious Ag peaks were found in the XRD patterns of an Ag-decorated WO₃ gas sensor due to the overlap of Au peaks. XPS analysis demonstrated that metallic Ag NPs were formed on the surface of WO₃ NRs. Together with the SEM images, it can be observed that the coverage of spherical Ag NPs adhered on the surface of WO₃ NRs increased with the increase of precursor amount and tend to approach saturation when the dosage reaches 10 μL. The diameter of the Ag NPs is mainly ranging from 9 to 13 nm while the diameter of WO₃ NRs is about 100–200 nm and the length is varying from 600 nm to several μm. Although gas sensing measurements indicated that no significant enhancement was found for the Ag-decorated WO₃ NRs in the O₂ sensing response as compared to the bare WO₃ NRs, the preparation process of Ag NPs-decorated WO₃ NRs is very informative because the silver loading can be controlled simply by altering the silver precursor amount. Further development and investigation on sensor selectivity, stability, and cross-sensitivity to other gases need to be studied in the future to make Ag-decorated WO₃-based materials a potential oxygen gas sensor.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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