Impact of Ag on the Limit of Detection towards NH$_3$-Sensing in Spray-Coated WO$_3$ Thin-Films

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Abstract: Ag-doped WO$_3$ (Ag–WO$_3$) films were deposited on a soda-lime glass substrate via a facile spray pyrolysis technique. The surface roughness of the films varied between 0.6 nm and 4.3 nm, as verified by the Atomic Force Microscopy (AFM) studies. Ammonia (NH$_3$)-sensing measurements of the films were performed for various concentrations at an optimum sensor working temperature of 200 $^\circ$C. Enrichment of oxygen vacancies confirmed by X-ray Photoelectron Spectroscopy (XPS) in 1% Ag–WO$_3$ enhanced the sensor response from 1.06 to 3.29, approximately 3 times higher than that of undoped WO$_3$. Limit of detection (LOD) up to 500 ppb is achieved for 1% Ag–WO$_3$, substantiating the role of Ag in improving sensor performance.

Keywords: NH$_3$ sensing; oxygen vacancies; WO$_3$ films

1. Introduction

Various types of gas sensors, including chemoreceptive-, ionization-, acoustic-, and resonant-based sensors are gaining more attention in different sectors, such as environmental monitoring, food safety, medical diagnosis, and industrial applications [1–3]. Among these, chemoreceptive-based metal oxide semiconductors (MO$_x$) have received tremendous interest in gas sensing due to their high surface/volume ratio, as the gas reaction process is a surface phenomenon. Different MO$_x$, such as ZnO, SnO$_2$, WO$_3$, and TiO$_2$ [4,5] have been extensively studied for gas-sensing applications. Tungsten oxide (WO$_3$) has emerged as a potential MO$_x$ to detect the gases, such as NH$_3$, H$_2$, NO$_2$, CO, and alcohol vapors, because of their inherent properties, including excellent electrical conductivity, sensitivity, and selectivity [6,7]. To enhance the sensing performance further, doping is considered one of the possible approaches. Transition metal doping, such as Cr, Cu, Ag, and Pd, would induce the defects causing enrichment of oxygen vacancies via compensation mechanism. These metals act as promoters and increase the sensing properties via spill-over effect or Fermi-level mechanisms [8–10]. Godbole et al. [11] reported the NH$_3$-sensing properties of Pd/WO$_3$ films with the response of 0.27 at a working temperature of 225 $^\circ$C. Lu et al. [12] presented studies on NO$_2$-sensing properties of Ag–WO$_3$ nanoparticles and reported high sensitivity and better selectivity. Xu et al. [13] obtained a superior sensor response for Ag–WO$_3$ core-shell nanostructures towards alcohol vapor at a
working temperature of 340 °C. All these studies have shown that metal incorporated into WO$_3$ has enhanced the sensor performance.

In this regard, we have illustrated the NH$_3$-sensing performance of Ag–WO$_3$ films via the spray pyrolysis deposition technique. Ag is a noble metal that enhances the sensor response of WO$_3$ due to electronic sensitization mechanism [14]. Due to large area deposition, ease of operation, and cost effectiveness, spray pyrolysis is chosen to deposit films in this report. The availability of literature is scarce on Ag–WO$_3$ for NH$_3$ sensing, and one of the works published is on hydrothermal technique [14]. To the best of our knowledge, no reports on spray-deposited Ag–WO$_3$ films are accessible for NH$_3$ sensing. Therefore, our attempt has proved the possibility of these films for NH$_3$ sensing by spray pyrolysis. Though the literature is available on NH$_3$ sensing by metal-doped WO$_3$, the majority of the sensors work at high temperatures (>250 °C) and the reported detection limit is high [14–16]. Ammonia (NH$_3$), a reducing gas, is a major pollutant from the automobiles, fertilizer, and mining industries. According to the OSHA (Occupational Health and Safety Administration) report, the permissible limit for NH$_3$ is 35 ppm for 15 min [17]. High exposure to the gas for a long time will trigger lung- and kidney-related diseases, causing incurable damage to human health. In this context, we aimed to lower the operating temperature and detection limit, which are essential for the sensing applications. Thus, in the current work, we have reported spray-pyrolyzed Ag–WO$_3$ films as a promising candidate for NH$_3$ sensing at a working temperature of 200 °C with the detection limit of 500 ppb.

2. Experimental

Undoped and silver-doped tungsten oxide films (Ag–WO$_3$) were synthesized by the spray pyrolysis method. For undoped WO$_3$, ammonium metatungstate hydrate (99.99% purity) is dissolved in double-distilled water and a homogeneous solution is obtained. For Ag doping, silver nitrate was taken as a precursor, and doping was done at a 1 wt.%, 3 wt.%, and 5 wt.% ratio. Solution concentration was maintained at 0.01 M. Deposition parameters, such as substrate temperature and flow rate, were kept constant at 400 °C and 1 mL/min, respectively.

Crystal structure and phase identification were performed via Rigaku SmartLab X-ray diffractometer with Cu Kα radiation at 40 kV, 30 mA. Raman analysis was performed using a Horiba JOBINYVON LabRAM HR spectrometer for the confirmation of structure. Morphological studies were performed via Innova SPM Atomic Force Microscope (AFM). AXIS ULTRA X-ray Photoelectron Spectroscope is used for oxidation state and composition studies. Gas sensing was conducted via dc probe measurements in an enclosed chamber (2.96 × 10$^4$ cm$^3$ by vol.) by purging synthetic air (79% N$_2$ + 21% O$_2$) and NH$_3$ to the sample. The flow of gas was controlled using programmable mass flow controllers (MFCs), and the overall flow was kept constant at 500 sccm. I-V measurements were performed via Keithley source meter 2450 using silver paste electrodes. Sensor response of the films was evaluated using the equation, ($\frac{R_a - R_g}{R_g}$). $R_a$ and $R_g$ suggest the film resistance in air and target gas (NH$_3$), respectively. Schematic representation of film synthesis and ammonia-sensing measurements of Ag–WO$_3$ film is represented in the Figure 1.
3. Results and Discussion

3.1. Structural and Morphological Analysis

Figure 2a–d represents the XRD pattern of Ag–WO₃ films at varied Ag doping levels. Diffraction peaks at the angles $24.1^\circ$, $33.9^\circ$, $49.6^\circ$, and $55.6^\circ$ correspond to (200), (202), (140), and (240) planes, indicating monoclinic phase ($\gamma$-WO₃) of WO₃ films (JCPDS card no. 43–1035) [12,18]. The appearance of sharp diffraction peaks implies that the deposited films have high crystallinity. The absence of any further peaks in the spectra endorsed the non-existence of any impurity phase in the prepared Ag–WO₃ films. All the films exhibited ‘a’ axis preferential orientation, i.e., along (200) plane. Evolution of (020) peak centered at $23.4^\circ$ is observed upon addition of Ag into WO₃. The introduction of Ag formed new nucleating centers for WO₃, ultimately retaining monoclinic structure. The crystallite size of the films was determined by employing the Scherrer formula [19] and it varies from 11.5 nm to 14.7 nm. The dislocation density and microstrain [19] were also evaluated and are presented in Table 1.

Since triclinic and monoclinic phases of WO₃ exhibit the same set of XRD peaks, we have conducted Raman measurements for further confirmation [20,21]. Figure 3 illustrates the Raman spectra of Ag–WO₃ films excited with the 532 nm laser source. Clear visibility of peaks at $\sim112$ cm$^{-1}$, $\sim134$ cm$^{-1}$, $\sim270$ cm$^{-1}$, $\sim325$ cm$^{-1}$, $\sim719$ cm$^{-1}$, $\sim806$ cm$^{-1}$, and $\sim963$ cm$^{-1}$, attributed to the different modes of vibrations in the WO₃ lattice. Peaks corresponding to $\sim719$ cm$^{-1}$ and $\sim806$ cm$^{-1}$ represent the asymmetric and symmetric stretching vibrational modes ($\nu_{as}$ and $\nu_{s}$) of O–W–O bonds and these are often referred to as the strongest monoclinic WO₃ modes [22]. Peaks located at $\sim270$ cm$^{-1}$ and $\sim325$ cm$^{-1}$ attribute to the O–W–O bending vibrational modes ($\delta$) and peaks below 200 cm$^{-1}$ contribute to the lattice vibrational modes [23]. All the films exhibit a peak at $\sim963$ cm$^{-1}$, which can be ascribed to the symmetric stretching vibration of terminal W=O bonds possibly associated with the clusters on the film surface [24,25]. The frequency of vibration of the W=O bond is predicted to be higher than that of the W–O bond since the W–O single bond is weaker than the W=O double bond. Raman measurements confirmed the monoclinic phase of Ag–WO₃ films.
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Table 1. Structural and morphological parameters of Ag–WO₃ films.

| Ag Conc. (wt.%) | 2θ, (200) | Crystallite Size D (nm) | Dislocation Density δ (×10¹⁵ m⁻²) | Microstrain ε (×10⁻³) | RMS Surface Roughness (nm) |
|----------------|-----------|-------------------------|------------------------------------|------------------------|--------------------------|
| 0              | 24.12°    | 13.0                    | 5.9                                | 2.7                    | 0.8                      |
| 1              | 24.16°    | 13.6                    | 5.4                                | 2.5                    | 4.3                      |
| 3              | 24.14°    | 11.5                    | 7.5                                | 3                      | 1.1                      |
| 5              | 24.14°    | 14.7                    | 4.6                                | 2.4                    | 0.6                      |

Figure 4a–d shows the topography and microstructures (3D view) of Ag–WO₃ films examined by AFM in tapping mode configuration. All the samples were scanned in the area of 0.5 × 0.5 µm². Figure 4b represents the topographical view of 1% Ag–WO₃. It suggests the coalescence of grains upon Ag incorporation forming larger globules of particles with the presence of voids. At 3% and 5%, Ag doping (Figure 4c,d), well-separated smaller grains are visible with almost uniform distribution. RMS surface roughness of the films was evaluated using NanoScope Analysis software and given in Table 1. Upon Ag doping, the roughness value of the films varied, and for 1% Ag–WO₃ higher value of roughness was recorded.
3.2. XPS Studies

Elemental composition and chemical state of Ag–WO₃ films (at 0% and 1% Ag conc.) were examined via the XPS technique. Figure 5a shows the deconvoluted spectra of W 4f split into spin-orbit doublet, namely W 4f_{7/2} and W 4f_{5/2} located at the binding energies (E_b) of 35.9 eV and 38.1 eV, respectively, in undoped WO₃ film. These represent the +6 oxidation state of W and another satellite peak at 40.5 eV indicates the W 5p{3/2} component corresponding to the same oxidation state [26]. The incorporation of Ag into WO₃ has led to the formation of +6 and +5 oxidation states of W as depicted in Figure 5b. Deconvolution of W 4f in Figure 5b has resulted in two pairs of doublets viz. one at 34.2 eV and 38.4 eV equivalent to W 4f_{7/2} and W 4f_{5/2}, respectively, for the +6 oxidation state of tungsten, and other pairs of doublets comprised of W 4f_{7/2} and W 4f_{5/2} centered at 32.4 eV and 36.5 eV are comparable to the +5 oxidation state of tungsten [27]. The peak positioned at 30.6 eV was assigned to the metallic tungsten [28]. If oxygen vacancy is present, electron density near neighboring W atoms intensifies, causing higher screening of its nucleus and consequently, the 4f energy level is predicted to be at lower E_b [23,27]. In the present studies, the shoulder associated with the W 4f is generated as a result of electrons emitted from W atoms near oxygen vacancies, and hence W atom has an oxidation state less than +6, resulting in the formation of sub-stoichiometric WO₃–x.

Figure 3. Raman spectra of Ag–WO₃ films.

Table 1. Structural and morphological parameters of Ag–WO₃ films.

| Ag Conc. (wt.%) | 2θ, (200) | Crystallite Size D (nm) | Dislocation Density (×10¹⁵ m⁻²) | Microstrain (×10⁻³) | RMS Surface Roughness (nm) |
|----------------|-----------|-------------------------|-------------------------------|---------------------|---------------------------|
| 0              | 24.12°    | 13.0                    | 5.9                           | 2.7                 | 0.8                       |
| 1              | 24.16°    | 13.6                    | 5.4                           | 2.5                 | 4.3                       |
| 3              | 24.14°    | 11.5                    | 7.5                           | 3                   | 1.1                       |
| 5              | 24.14°    | 14.7                    | 4.6                           | 2.4                 | 0.6                       |

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The deconvolution of O 1s spectra has produced 3 peaks (O₁, O₂, and O₃) in both WO₃ and 1% Ag–WO₃ films (Figure 5c,d) respectively. O₁ centered at Eₐ of 530.8 eV and 528.7 eV in WO₃ and 1% Ag–WO₃ respectively, was ascribed to O²⁻ in the lattice. Similarly, O₂ centered at 532.6 eV and 531.2 eV denote the lattice oxygen associated with the oxygen-deficient regions near W ions, which are generally referred to as oxygen vacancies (Vₒ) [29,30]. Area ratio of oxygen vacancies is estimated from peak area calculations as given below:

\[
\%Vₒ = \frac{O₂}{(O₁ + O₂ + O₃)} \times 100
\]

Vₒ for WO₃ and 1% Ag–WO₃ was found 35% and 45%, respectively. Hence, the studies inferred that oxygen vacancies increased by 10% in 1% Ag–WO₃. The least intense peaks centered at 534.7 eV and 532.8 eV, respectively in WO₃ and 1% Ag–WO₃, connected to the adsorbed oxygen species (O₂⁻, OH⁻) [30]. Figure 5e represents the characteristic peaks of Ag at Eₐ of 368 eV and 374.5 eV contributes to Ag 3d₅/₂ and Ag 3d₃/₂, respectively, in 1% Ag–WO₃. These peaks are assigned to the Ag⁰ / Ag¹⁺ states of silver [28,31].
atoms near oxygen vacancies, and hence W atom has an oxidation state less than +6, resulting in the formation of sub-stoichiometric WO$_3$-$x$.

Figure 5. (a–e): XPS spectra of W, O, and Ag core levels in WO$_3$ and 1% Ag–WO$_3$ films.

3.3. Gas Sensing Properties

Operation temperature for WO$_3$ towards NH$_3$ was fixed by purging gas at various temperatures and calculating subsequent sensor response as presented in Figure 6a,b. Figure 6a represents the obtained graph for sensor current versus time wherein 5.03 ppm NH$_3$ is purged at 5 different temperatures: 100 °C, 150 °C, 175 °C, 200 °C, and 250 °C. An increase in temperature causes an increase in the sensor current, demonstrating the semiconducting nature of the WO$_3$ films. At 100 °C, the graph shows a straight line,
denoting no response for NH₃ due to the low thermal energy of the gas required for the chemisorption process. Low response was noted at 150 °C and 175 °C. An increase in the temperature to 200 °C has shown maximum response, and thereafter the response has decreased as indicated in Figure 6b. With the enhancement in the temperature, WO₃ started to respond, as enough thermal energy is provided for the surface reaction to occur by overcoming the activation energy barrier [32]. After the maximum response, a reduction in the sensing performance at 250 °C is due to the lower adsorption capability of gas molecules. In addition, it is observable that baseline stability was lost above 200 °C (Figure 6a). Hence, 200 °C is considered a suitable operating temperature for all the deposited films, and further studies were conducted at the same temperature.

Sensor response, rate of response, and recovery (τ_res and τ_rec) are the essential parameters that determine the efficiency of any sensor. Figure 7a–d depicts the transient response curves of Ag–WO₃ films (0%, 1%, 3% and 5% Ag conc.) for different NH₃ concentrations. Figure 7e shows the variation of sensor response with the NH₃ concentration. The sensor response for 5 ppm NH₃ was found to be 1.06, 3.29, 0.34, and 0.62 with the standard error.
of ±0.07 for undoped, 1%, 3%, and 5% Ag-doped WO$_3$ films, respectively. The highest response was recorded for 1% Ag–WO$_3$ with the $\tau_{res}$ of 5.5 min and $\tau_{rec}$ of 7.9 min. Doping of Ag reduced the detection limit from 1 ppm to 0.5 ppm (500 ppb) in 1% Ag–WO$_3$. 'Ag', being a noble metal, acts as a catalyst due to chemical sensitization and also causes electronic sensitization due to the interaction between Ag and WO$_3$, which might have induced the enhancement in the sensor response of the WO$_3$ film [9]. AFM studies revealed that 1% Ag–WO$_3$ showed higher surface roughness value (Table 1) compared to other Ag concentrations. Surface roughness is one of the parameters that can increase the surface to volume ratio of the films and thereby enhances the gas adsorption capacity [33]. M. Kumar et al. [34] and J. M. Lee et al. [33] observed similar results for CO and H$_2$-gas sensing, respectively. Augmentation in the sensing performance of 1% Ag–WO$_3$ could be accredited to improved oxygen vacancies upon Ag doping, which is confirmed by XPS analysis and also higher surface roughness and void formation on the film surface is proven by AFM, providing a greater number of adsorption centers for NH$_3$ [22,35]. Nevertheless, a decrease in sensor response beyond 1% Ag doping is connected to lower surface roughness of the films and catalytic efficiency of Ag, indicating that while Ag inclusion improves sensing performance, increasing the doping concentration above the optimum level may reduce catalytic efficiency [27]. Also, XPS revealed the possibility of Ag$_2$O formation upon Ag doping. When Ag concentration exceeds 1%, Ag$_2$O amounts might increase and cause an increase in the depletion layer width, deteriorating the sensor response of the films.

Selectivity and repeatability are the key factors that decide the performance of the sensors. Figure 8 represents the bar graph elucidating sensor responses of WO$_3$ and 1% Ag–WO$_3$ films towards various gases. These films are tested at a 5-ppm concentration towards NH$_3$, CO, CH$_4$, and NO$_2$. Both films showed the highest response to NH$_3$ indicating the selective nature of the deposited films towards ammonia among other gases. Repeatability measurements of about 5 cycles were performed for both WO$_3$ and 1% Ag–WO$_3$ films, shown in Figure 9a,b. Almost repeatable sensing characteristics were obtained 5 times for NH$_3$ purge at 5 ppm concentration, implying the stable response of the films. In comparison, sensing properties of the current work with the previously reported literature is given in Table 2. The WO$_3$ nanoflakes synthesized via spray pyrolysis detected the lowest NH$_3$ concentration to be up to 120 ppm at 150 °C [36], while the V-WO$_3$ films synthesized by soft chemical route exhibited a detection limit of 100 ppm towards NH$_3$ at 300 °C [37]. The Cr–WO$_3$ nanosheets synthesized by acidification with impregnation process detected 2 ppm NH$_3$ at 400 °C [38], whereas the WO$_3$–Fe$_2$O$_3$ nanocomposites by hydrothermal synthesis demonstrated NH$_3$ detection of 25 ppm at 300 °C [39]. In the present work, we were able to achieve lowest detection limit of 500 ppb towards NH$_3$ gas, keeping an operating temperature of 200 °C, which is a significant improvement in the sensing performance compared to the literature presented in Table 2.

The well-known gas detection mechanism of metal oxide gas sensors involves the resistance variations caused by the chemisorption of gas molecules on the sensor surface. Depending on the operating temperature, WO$_3$ exposure to the synthetic air produces molecular/atomic oxygen ions ($O_2^−, O^−,$ and $O^2−$). Electron transfer from the surface of the WO$_3$ to the adsorbed oxygen species creates a band bending region called the depletion layer, resulting in a decrease in the carrier concentration of the film and an increase in the resistance. Later, when WO$_3$ is subjected to NH$_3$ exposure, the depletion layer width decreases due to the release of electrons back to the WO$_3$. As Ag–WO$_3$ is exposed to NH$_3$, the depletion layer further decreases due to the electronic sensitization mechanism giving rise to an increment in carrier concentration and a reduction in surface resistance. Figure 10 illustrates the schematic representation of the sensing mechanism. Specific reactions involved in the process are governed by the equations given below [14,35]:

$$O_2(gas) \rightarrow O_2(ads) \quad (1)$$

$$O_2(ads) + e^- \rightarrow O_2^- \quad (2)$$


\[ \text{O}_2^- + e^- \rightarrow 2\text{O}^- \quad \text{(3)} \]

\[ 4\text{NH}_3(g) + 5\text{O}_2^- \rightarrow 4\text{NO} + 6\text{H}_2\text{O} + 5e^- \quad \text{(4)} \]

\[ 2\text{NH}_3(g) + 3\text{O}^- \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 3e^- \quad \text{(5)} \]

Sensor response, rate of response, and recovery (\( \tau_{\text{on}} \) \( \tau_{\text{off}} \)) are the essential parameters that determine the efficiency of any sensor. Figure 7a–d depicts the transient response curves of Ag–WO\(_3\) films (0%, 1%, 3% and 5% Ag conc.) for different \( \text{NH}_3 \) conc. concentrations. Figure 7e shows the variation of sensor response with the \( \text{NH}_3 \) concentration. The sensor response for 5 ppm \( \text{NH}_3 \) was found to be 1.06, 3.29, 0.34, and 0.62 with the standard error of \( \pm 0.07 \) for undoped, 1%, 3%, and 5% Ag-doped WO\(_3\) films, respectively. The highest response was recorded for 1% Ag–WO\(_3\) with the \( \tau_{\text{on}} \) of 5.5 min and \( \tau_{\text{off}} \) of 7.9 min.

Doping of Ag reduced the detection limit from 1 ppm to 0.5 ppm (500 ppb) in 1% Ag–WO\(_3\). 'Ag', being a noble metal, acts as a catalyst due to chemical sensitization and also causes electronic sensitization due to the interaction between Ag and WO\(_3\), which might have induced the enhancement in the sensor response of the WO\(_3\) film [9]. AFM studies revealed that 1% Ag–WO\(_3\) showed higher surface roughness value (Ref. Table 1) compared to other Ag concentrations. Surface roughness is one of the parameters that can increase the surface to volume ratio of the films and thereby enhances the gas adsorption capacity [33]. M. Kumar et al. [34] and J. M. Lee et al. [33] observed similar results for CO and H\(_2\)-gas sensing, respectively.

Augmentation in the sensing performance of 1% Ag–WO\(_3\) could be accredited to improved oxygen vacancies upon Ag doping, which is confirmed by XPS analysis and also higher surface roughness and void formation on the film surface is proven by AFM, providing a greater number of adsorption centers for \( \text{NH}_3 \) [22,35]. Nevertheless, a decrease in sensor response beyond 1% Ag doping is connected to lower surface roughness of the films and catalytic efficiency of Ag, indicating that while Ag inclusion improves sensing performance, increasing the doping concentration above the optimum level may reduce catalytic efficiency [27]. Also, XPS revealed the possibility of Ag\(_2\)O formation upon Ag doping. When Ag concentration exceeds 1%, Ag\(_2\)O amounts might increase and cause an increase in the depletion layer width, deteriorating the sensor response of the films.

Figure 7. (a–d): Transient response curves of Ag–WO\(_3\) films and (e) sensor response of the films at various \( \text{NH}_3 \) concentrations with error bars.
cess detected 2 ppm NH$_3$ at 400 °C \cite{38}, whereas the WO$_3$–Fe$_2$O$_3$ nanocomposites by hydrothermal synthesis demonstrated NH$_3$ detection of 25 ppm at 300 °C \cite{39}. In the present work, we were able to achieve lowest detection limit of 500 ppb towards NH$_3$ gas, keeping an operating temperature of 200 °C, which is a significant improvement in the sensing performance compared to the literature presented in Table 2.

![Figure 8](image-url)  
Figure 8. Representation of selectivity studies for WO$_3$ and 1% Ag–WO$_3$ with error bars.

![Figure 9](image-url)  
Figure 9. Repeatable sensing characteristics of (a) WO$_3$ (b) 1% Ag–WO$_3$ at 5 ppm NH$_3$ concentration.

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$$O_{3}^- \rightarrow O_{4}^-$$

Table 2. NH$_3$-sensing properties of the present work and reported in the literature.

| Material       | Method of Deposition | Limit of Detection | Operating Temperature (°C) | Reference |
|----------------|----------------------|--------------------|-----------------------------|-----------|
| Pd–WO$_3$ films | Spray pyrolysis       | 10 ppm             | 225                         | \cite{9}   |
| Ag–WO$_3$ nano-rods | Hydrothermal       | 50 ppb             | 450                         | \cite{12} |
| WO$_3$ nanoflakes | Spray Pyrolysis        | 120 ppm            | 150                         | \cite{36} |
| V–WO$_3$ films  | Soft-chemical route   | 100 ppm            | 300                         | \cite{37} |
| Cu–WO$_3$ films | Soft-chemical route   | 100 ppm            | 200                         | \cite{37} |
| Cr–WO$_3$ nanosheets | Acidification with impregnation | 2 ppm   | 400                         | \cite{38} |
| WO$_3$–Fe$_2$O$_3$ nanocomposites | Hydrothermal | 25 ppm             | 300                         | \cite{39} |
| Ag–WO$_3$ films | Spray pyrolysis       | 500 ppb            | 200                         | This work |
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| WO$_3$ nanoflakes      | Spray Pyrolysis      | 120 ppm            | 150                         | [36]      |
| V–WO$_3$ films         | Soft-chemical route  | 100 ppm            | 300                         | [37]      |
| Cu–WO$_3$ films        | Soft-chemical route  | 100 ppm            | 200                         | [37]      |
| Cr–WO$_3$ nanosheets   | Acidification with impregnation | 2 ppm | 400                         | [38]      |
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| Ag–WO$_3$ films        | Spray pyrolysis      | 500 ppb            | 200                         | This work |

Figure 10. Sensing mechanism involved between the grains of WO$_3$ and Ag–WO$_3$ films.

4. Conclusions

Spray pyrolyzed Ag–WO$_3$ films were investigated for NH$_3$ sensing at different concentrations. XRD spectra depicted the monoclinic phase of deposited films, which was further verified by Raman analysis. Oxygen vacancies, higher surface roughness, and void-like structures of 1% Ag–WO$_3$ contributed to enhancement in the sensor response value. Selectivity studies of WO$_3$ and 1% Ag–WO$_3$ towards NH$_3$, NO$_2$, CH$_4$, and CO exhibited an excellent response to NH$_3$ compared to other gases. Spray deposited Ag–WO$_3$, as a unique approach for NH$_3$ sensing, produced a superior response at a low operating temperature of 200 °C with a detection limit in the sub-ppm levels.

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References
1. Vinayakumar, K.B.; Martins, M.; Gaspar, J.; Hutter, T. Ionization Potential Tunable Pyroelectric Ambient Pressure Multi-Gas Detection Platform. In Proceedings of the IEEE International Conference on Micro Electro Mechanical Systems, Gainesville, FL, USA, 25–29 January 2021; pp. 795–798. [CrossRef]
2. Qi, X.; Liu, J.; Liang, Y.; Li, J.; He, S. The response mechanism of surface acoustic wave gas sensors in real time. Jpn. J. Appl. Phys. 2019, 58, 014001. [CrossRef]
3. Vinayakumar, K.B.; Gund, V.; Lambert, N.; Lodha, S.; Lal, A. Enhanced lithium niobate pyroelectric ionizer for chip-scale ion mobility-based gas sensing. In Proceedings of the 2016 IEEE Sensors, Orlando, FL, USA, 30 October–3 November 2016; pp. 3–5. [CrossRef]
4. Liu, H.; Shen, W.; Chen, X. A room temperature operated ammonia gas sensor based on Ag-decorated TiO2 quantum dot clusters. RSC Adv. 2019, 9, 24519–24526. [CrossRef]
5. Ravichandran, K.; Santhosam, A.J.; Sridharan, M. Effect of tungsten doping on the ammonia vapour sensing ability of ZnO thin films prepared by a cost effective simplified spray technique. Surf. Interfaces 2020, 18, 100412. [CrossRef]
6. Jeevitha, G.; Abhinaya, R.; Mangalaraj, D.; Ponpandian, N.; Meena, P.; Mounasamy, V.; Madanagurusamy, S. Porous reduced graphene oxide (rGO)/WO3 nanocomposites for the enhanced detection of NH3 at room temperature. Nanoscale Adv. 2019, 1, 1799–1811. [CrossRef]
7. Tesfamichael, T.; Piloto, C.; Arita, M.; Bell, J. Fabrication of Fe-doped WO3 thin films for NO2 sensing at lower operating temperature. Sens. Actuators B Chem. 2015, 221, 393–400. [CrossRef]
8. Nakarungsee, P.; Strirattanapibul, S.; Issro, C.; Tang, I.M.; Thongmee, S. High performance Cr doped ZnO by UV for NH3 gas sensor. Sens. Actuators A Phys. 2020, 314, 112230. [CrossRef]
9. Yu, H.; Li, J.; Li, Z.; Tian, Y.; Yang, Z. Enhanced formaldehyde sensing performance based on Ag@WO3 2D nanocomposite. Powder Technol. 2019, 343, 1–10. [CrossRef]
10. Zeng, Y.; Hua, Z.; Tian, X.; Li, X.; Qiu, Z.; Zhang, C.; Wang, M.; Li, E. Selective detection of methanol by zeolite/Pd-WO3 gas sensors. Sens. Actuators B Chem. 2018, 273, 1291–1299. [CrossRef]
11. Godbole, R.; Godbole, V.; Bhagwat, S. Palladium enriched tungsten oxide thin films: An efficient gas sensor for hazardous gases. Eur. Phys. J. B 2019, 92, 78. [CrossRef]
12. Lu, R.; Zhong, X.; Shang, S.; Wang, S.; Tang, M. Effects of sintering temperature on sensing properties of WO3 and Ag–WO3 electrode for NO2 sensor. R. Soc. Open Sci. 2018, 5, 1–11. [CrossRef]
13. Xu, L.; Yin, M.L.; Liu, S. Superior sensor performance from Ag@WO3 core-shell nanostructure. J. Alloys Compd. 2015, 623, 127–131. [CrossRef]
14. Yuan, Z.; Zhang, J.; Meng, F.; Li, Y.; Li, R.; Chang, Y.; Zhao, J.; Han, E.; Wang, S. Highly Sensitive Ammonia Sensors Based on Ag-Decorated WO3 Nanorods. IEEE Trans. Nanotechnol. 2018, 17, 1252–1258. [CrossRef]
15. Castillo, C.; Cabello, G.; Chornik, B.; Huentupil, Y.; Buono-Core, G.E. Characterization of photochemically grown Pd loaded WO3 thin films and its evaluation as ammonia gas sensor. J. Alloys Compd. 2020, 825, 154166. [CrossRef]
16. Van Tong, P.; Hoa, N.D.; Van Duy, N.; Le, D.T.T.; Van Hieu, N. Enhancement of gas-sensing characteristics of hydrothermally synthesized WO3 nanorods by surface decoration with Pd nanoparticles. Sens. Actuators B Chem. 2016, 223, 453–460. [CrossRef]
17. National Institute for Occupational Safety and Health; Centers for Disease Control; U.S. Department of Health and Human Services. Occupational Safety and Health Guidelines for Ammonia. In Proceedings of the IEEE International Conference on Micro Electro Mechanical Systems, Gainesville, FL, USA, 25–29 January 2021; pp. 795–798. [CrossRef]
18. Anusha acknowledges the Indian Nano electronics User Program (INUP), supported by the Ministry of Human Resource Development (MHRD), Govt. of India, located at the Indian Institute of Science, Bengaluru for providing the facilities to carry out a part of the work.
23. Bittencourt, C.; Llobet, E.; Ivanov, P.; Vilanova, X.; Correig, X.; Silva, M.A.P.; Nunes, L.A.O.; Pireaux, J.J. Ag induced modifications on WO$_3$ films studied by AFM, Raman and x-ray photoelectron spectroscopy. J. Phys. D Appl. Phys. 2004, 37, 3383–3391. [CrossRef]

24. Shigesato, Y.; Murayama, A.; Kamimi, T.; Matsuhiro, K. Characterization of evaporated amorphous WO$_3$ films by Raman and FTIR spectroscopies. Appl. Surf. Sci. 1988, 34, 804–811. [CrossRef]

25. Ex, C.; Juan, S.; Km, M.; Claudio, S.; Manuel, S.; Av, U. Obtaining of films of tungsten trioxide (WO$_3$) by resistive heating of a tungsten filament. Superf. Vacio 2008, 21, 12–17.

26. Cai, G.-F.; Wang, X.-L.; Zhou, D.; Zhang, J.-H.; Xiong, Q.-Q.; Gu, C.-D.; Tu, J.-P. Hierarchical structure Ti-doped WO$_3$ film with improved electrochromism in visible-infrared region. RSC Adv. 2013, 3, 6896–6905. [CrossRef]

27. Wang, Y.; Cui, X.; Yang, Q.; Liu, J.; Gao, Y.; Sun, P.; Lu, G. Preparation of Ag-loaded mesoporous WO$_3$ and its enhanced NO$_2$ sensing performance. Sens. Actuators B Chem. 2016, 225, 544–552. [CrossRef]

28. Adilakshmi, G.; Reddy, R.S.; Reddy, A.S.; Reddy, P.S.; Reddy, C.S. Ag-doped WO$_3$ nanostructure films for organic volatile gas sensor application. J. Mater. Sci. Mater. Electron. 2020, 31, 12158–12168. [CrossRef]

29. Ta, T.K.H.; Tran, T.N.H.; Tran, Q.M.N.; Pham, D.P.; Pham, K.N.; Cao, T.T.; Kim, Y.S.; Tran, D.L.; Ju, H.; Phan, B.T. Surface Functionalization of WO$_3$ Thin Films with (3-Aminopropyl)triethoxysilane and Succinic Anhydride. J. Electron. Mater. 2017, 46, 3345–3352. [CrossRef]

30. Yu, W.; Shen, Z.; Feng, F.; Lu, Y.; Ge, M.; Fu, X.; Sun, Y.; Chen, X.; Dai, N. Improving gas sensing performance by oxygen vacancies in sub-stoichiometric WO$_{3-x}$. RSC Adv. 2019, 9, 7723–7728. [CrossRef]

31. Baig, U.; Gondal, M.A.; Rehman, S.; Akhtar, S. Facile synthesis, characterization of nano-tungsten trioxide decorated with silver nanoparticles and their antibacterial activity against water-borne gram-negative pathogens. Appl. Nanosci. 2020, 10, 851–860. [CrossRef]

32. Zhang, G.; Li, C.; Cheng, F.; Chen, J. ZnFe$_2$O$_4$ tubes: Synthesis and application to gas sensors with high sensitivity and low-energy consumption. Sens. Actuators B Chem. 2007, 120, 403–410. [CrossRef]

33. Kumar, M.; Singh, B.; Yadav, P.; Bhatt, V.; Kumar, M.; Singh, K.; Abhyankar, A.C.; Kumar, A.; Yun, J.-H. Effect of structural defects, surface roughness on sensing properties of Al doped ZnO thin films deposited by chemical spray pyrolysis technique. Ceram. Int. 2017, 43, 3562–3568. [CrossRef]

34. Lee, J.M.; Lee, W. Effects of surface roughness on hydrogen gas sensing properties of single Pd nanowires. J. Nanosci. Nanotechnol. 2011, 11, 2151–2154. [CrossRef] [PubMed]

35. Arun Kumar, K.D.; Valanarasu, S.; Ponraj, J.S.; Fernandes, B.J.; Shkir, M.; AlFaify, S.; Murahari, P.; Ramesh, K. Effect of Er doping on the ammonia sensing properties of ZnO thin films prepared by a nebulizer spray technique. J. Phys. Chem. Solids 2020, 144, 109513. [CrossRef]

36. Kolhe, P.S.; Mutadak, P.; Maiti, N.; Sonawane, K.M. Synthesis of WO$_3$ nanoflakes by hydrothermal route and its gas sensing application. Sens. Actuators B Chem. 2020, 344, 111877. [CrossRef]

37. Jiménez, I.; Vilà, A.M.; Calveras, A.C.; Morante, J.R. Gas-sensing properties of catalytically modified WO$_3$ with copper and vanadium for NH$_3$ detection. IEEE Sens. J. 2005, 5, 385–390. [CrossRef]

38. Wang, S.; Zhang, H.; Li, H.; Wu, R.; Hua, Z.; Wu, Y.; Tian, X. NH$_3$ sensing properties with Cr-loaded WO$_3$ nanosheets. Chem. Lett. 2020, 49, 1421–1425. [CrossRef]

39. Dien, N.D.; Phuoc, L.H.; Hien, V.X.; Vuong, D.D.; Chien, N.D. Hydrothermal Synthesis and Ammonia Sensing Properties of WO$_3$/Fe$_2$O$_3$ Nanorod Composites. J. Electron. Mater. 2017, 46, 3309–3316. [CrossRef]