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Hydrothermal synthesis of WO₃ film on rough surface to analyze methanol gas at room temperature

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Abstract

In this paper, we synthesized WO₃ thick films on a rough and smooth glass substrate by hydrothermal method and then heated to a temperature of 400-degree Celsius. Characteristic techniques such as XRD and SEM analysis were sequenced to determine the crystallite size and grain composition of the finished samples, respectively. We have discussed the results of the Rietveld refinement made using MAUD to determine useful information regarding the atomic sites, mesh parameters, and microstresses in the sample. Subsequently, FTIR analysis has been performed to note the critical bond vibrations associated with the material. AFM studies have also been included to determine the pore sizes and understand the surface-level differences between WO₃ films on rough and smooth substrates. The room temperature gas sensing mechanism was then discussed in the presence of humidity with methanol, ethanol, and benzene along with most of the targeted gases with different selective parameters at atmospheric pressure. We have tried to develop a theory incorporating the anomalous observation for the methanol gas sensing experiment and explained the future scope of this work.

1. Introduction

Gas sensing is one of the most widely researched problems owing to its need in the industry to detect leakage of hazardous gases [1, 2]. With advancements in computer simulations, synthesis, and characterization techniques, new materials are constantly being investigated for gas sensing applications. Over two decades of research have proven metal oxide semiconductors to be a promising alternative for such applications [3] because of their portability, low manufacturing cost, easy large-scale commercial production, compact size, and integration with basic electronics [4]. It is crucial to understand that a semiconductor’s sensitivity, which is basically the fluctuation in charge carrier concentration on the surface of the sample, is sensitive to the composition of the gas [5]. This correlates to a change in conductivity on the surface leading to the gas sensing phenomenon. This change in conductivity depends on various factors like morphology, the rate constant of surface reaction, surface roughness, etc [6]. Also, the structure of the metal oxide layers in sensing devices is crucial for the workings of gas sensors. Since catalysis is a surface phenomenon, larger surface areas provide a large reaction contact area between gas sensing materials and target gases [7]. The surface area modification is not just limited by the synthesis process but can also be achieved by introducing defects. For instance, the synthesis of WO₃ nanosphere by the facile method is accompanied by Fe doping produces particles with ultra-high surface areas (165 m² g⁻¹) [8]. This artificial defect in WO₃ could enhance the NO₂ sensing performance as compared to pure WO₃. The changes in the dimensions of the constituent particles can also be responsible for structural modifications. Since stoichiometric defects for WO₃ can be a key factor in introducing the gas sensing effect [9], WO₃ₓ nanowires and nanotube have been reported to show high gas sensing potential [10]. Interestingly, assembling the material as small grains can also boost the performance of gas sensors. The performance of WO₃ shown by Belkacem et al
[11], has been improved by introducing Co grains on the surface. They found changes in the conduction type of the sensors from n-type to p-type because of this defect. Finally, ozone gas was sensitivity was tested with this sensor which showed a high level of conductivity. Although oxide samples having a resistivity between $10^5$ and $10^8$ $\Omega$-cm at 300–400 °C will function as gas sensors [5], care needs to be taken when gas sensing experiments are carried out in the presence of such high temperatures as an increase in temperature makes the small grain to agglomerate into large entities decreasing both surface areas and catalytic properties of the material [7].

While talking about key factors responsible for gas sensing, it is also interesting to note the effects of humidity or the presence of water molecules on gas sensing properties. As mentioned in [12], the relative humidity (RH) significantly perturbs the sensitivity and resistance of the sensors. For tetrapod-shaped ZnO nanopowder sensor, the resistance increases gradually with increasing RH in a range of 32%–75%, while in a range of 75%–96% RH, the resistance decreases gradually with the increase of RH. Likewise, in some recent studies like [13], the authors have synthesized p-type MoS2 and MoS2-PEO composite sensors for direct applications in detecting humidity from human breath. This real-time humidity detection says a lot about how swiftly any material can react with the presence of water molecules in the vicinity of the sensor. On a similar account, in another study [14] the authors prepared a ternary rGO/N-MXene/TiO2 sensor for HCHO detection. Various levels of Humidity have been studied to show a correlation of gas sensing with atmospheric water vapors. Thus we can say that presence of water, in atmospheric form or in the interstitials of lattices, has a significant contribution to the sensing observations.

Methanol gas is used in potential applications such as fuel [15], wine industry, paint industry, and organic synthesis [16]. To date, many active materials have been exploited for room temperature methanol gas sensors such as alpha-iron oxide/polyaniline/PbS quantum dot [17], PANI–CdO nanocomposite [18], PANI–ZnO nanocomposite [19], polyaniline nanoparticles [20], carboxylated multi-walled carbon nanotube/polyaniline nanotube composite [21], Ferrite Cobalt (CoFe2O4) Porous Nanoparticles [22], TiO2 Nanotube-Reduced Graphene-Oxide [23], etc Here, there are some limitations in the use of polymers in gas sensors such as its stability, slow response time, non-solubility in solvents, and much more [21]. Research on composite materials for gas sensing has also been reported in many literatures. In [24], the authors have doped In2O3 with 17% SnO2 and used ITO as a substrate to detect methanol at room temperature. They have also brought about some modifications to the ITO, like applying copper as a catalytic layer which has shown even further improvement in sensitivity. Another research [17] talks about using conductive polymers for gas sensing purposes. Here, the α–Fe2O3/PANI/PbS QDs nanofilm was synthesized on an epoxy substrate with interdigital electrodes via hydrothermal and SILAR methods. Likewise, [25] talks about synthesizing hybrid TiO2 nanostructures with reduced graphene oxide for methanol sensing at 27 °C and concentration of 800 ppm. Again, [26] discusses the PANI-graphene micro/nanocomposites, where methanol concentrations of 500 ppm and 1000 ppm have been studied. The authors here mention very few effects of humidity on gas sensing and attribute this observation to the nature of the sensing material. Even the work in [27] and [28] discusses methanol gas sensors at room temperature with Gd1−xCaxFeO3 and carbon nanotubes as the sensing materials respectively. However, the limitations associated with these materials can be countered to some extent if metal oxide is used in gas sensors. The layer of metal oxide depends on the substrate surface, where if the surface is rough, the rate of diffusion reduces the magnitude of the surface roughness [29–31].

Metal oxides are promising candidates for gas sensing, however, the biggest hurdle towards it is to make them operate at room temperatures. The authors in [32] synthesized WO3-Nanolamella for NO2 sensing for which the operating temperature was around 200 °C. In [33] WO3-Pd composites have been studied for methanol and CO gas sensing for 350 °C. Similarly, [34] mentions the synthesis of WO3 nanocuboids for methanol gas sensing and its temperature range (80 °C–400 °C). Likewise, [35] and [36] also have much higher operating temperatures. Although some recent work done in [37] was carried out at room temperature. They have synthesized Pt-WO3 and unmodified WO3 as a comparative study for methanol gas sensing, where their sensitivity was 70%. That being said, methanol is a highly toxic gas and if it enters the human body of a human or an animal in an uncontrolled way, it can cause death [38]. This matter is very serious and some easy way should be found for it.

Therefore, in this paper, we have focused on the synthesis of methanol gas sensors that can run at room temperature, targeting industrial requirements. This is the first report of a WO3 film being made on a rough surface for methanol gas sensing. This paper, in response to methanol and other different gases, also sheds light on WO3’s structural, chemical, and room temperature gas-sensitive and superficial surface sensing class investigations.
2. Experimental

2.1. Materials
Sodium tungstate (Na$_2$WO$_4$·2H$_2$O), Hydrochloric acid (HCl), propylene glycol (PG (C$_3$H$_8$O$_2$)) was purchased from Loba Chemie and all the chemical reagents are of analytical AR grade. Glass plates (5 × 2 cm$^2$) were used as substrates. All aqueous solutions were prepared using double distilled water (DW).

2.2. Methodology
Na$_2$WO$_4$·2H$_2$O was used as a tungsten source for our deposited samples. Initially, 0.2 M Na$_2$WO$_4$·2H$_2$O was dissolved in 100 ml DW. It was then stirred for 20 min at a rate of 500 rotations per minute (rpm). When Na$_2$WO$_4$·2H$_2$O begins to dissolve, the rpm is gradually reduced. Then, 6 ml HCl was added to the mixture and stirred continuously for another 15 min. After lowering the RPM, 10 ml of PG solution was added and stirred continuously for another 30 min. It was then allowed to produce a precipitate. After the precipitate is formed, the solution is filtered to obtain a clear solution. This clear solution is further used to deposit a film on an ultrasonicated clean glass plate treated with acetone and methanol. Here, two types of glass plates were used namely smooth and rough surfaces where the glass surface was roughened using emery paper in one direction. The grid size of emery paper was 220 and the duration for roughening was 3 min. Further, the obtained clear solution and glass substrates were placed in an autoclave instrument for hydrothermal processing at 100 °C and 5 psi gauge pressure for 2 h. The autoclave is then cooled to room temperature and the film deposited on the glass substrates was heated to 400 °C for 2 h. Thus, annealed WO$_3$ films for smooth and rough surfaces were developed to study the gas sensing properties and it is indicated as WSA and WRA respectively throughout the paper.

2.3. Methods
The film thickness was measured using the gravimetric method. The thicknesses of WSA and WRA films were estimated at 654 and 723 nm, respectively. A scanning electron microscope (SEM) was used to characterize morphologies of an as-prepared film (Hitachi S-4700 II, 25 kV). X-ray diffraction (XRD) pattern (Thermo ARLSCINTAG X'TRA with CuK$_\alpha$ irradiation wavelength = 0.154056 nm) was used to analyze the crystal structure. Fourier transform infrared (FTIR) spectroscopic studies were conducted using the Perkin Elmer IR spectrometer (500–4000 cm$^{-1}$). Surface roughness and surface topography of the samples were characterized by atomic force microscopy (AFM) mounted on top of a multi-axis piezoelectric positioning and scanning system with capacitive sensors from Physik Instrumente GmbH, Karlsruhe, Germany (PicoCube P-363.3.CD) that allows subnanometer resolution. A custom-made electronics module was used to communicate between the quadrupole diode, the piezoelectric controller, and the data acquisition boards on a personal computer. Data acquisition command modules and further data analysis routines were written using Igor Pro software from WaveMetrics (Portland, OR). We used the V-shaped, gold-coated reflective silicon-nitride cantilevers from Bruker (Billerica, MA) for measurements. The four-probe apparatus with semiconducting probe-tips was
employed in determining the IV characteristics of WO3 material in the presence of various gases in a saturated state. The determined amount (1000 ppm) of various gases (isopropyl alcohol (IPA), Benzene, Toluene, Acetone, Ethanol, Methanol) is injected in the chamber by a microsyringe. The experiment involving the determination of selectivity was conducted at a deck temperature of 31°C and at atmospheric pressure.

Table 1. (a) Summary of XRD analysis for WRA. (b) Summary of XRD analysis for WSA.

| Peak (2θ) | (h, k, l) | Multiplicity | d (Å)    |
|-----------|-----------|--------------|----------|
| 22.9832   | 002       | 2            | 3.8508   |
| 23.4553   | 020       | 2            | 3.7702   |
| 24.1839   | 200       | 2            | 3.6673   |
| 26.4542   | 120       | 4            | 3.3532   |
| 28.6444   | 112       | 4            | 3.1026   |
| 33.2632   | 022       | 4            | 2.6940   |
| 33.9739   | 202       | 2            | 2.6506   |
| 41.5394   | 222       | 4            | 2.1683   |
| 49.8154   | 400       | 2            | 1.8337   |

| Peak (2θ) | (h, k, l) | Multiplicity | d (Å)    |
|-----------|-----------|--------------|----------|
| 17.2437   | 020       | 2            | 5.1363   |
| 26.3661   | 111       | 8            | 3.3762   |
| 34.1104   | 040       | 2            | 2.6254   |
| 34.9273   | 200       | 2            | 2.5658   |
| 35.6746   | 002       | 2            | 2.5138   |
| 49.8239   | 042       | 4            | 1.8280   |
| 50.3451   | 202       | 4            | 1.8103   |
| 53.3596   | 222       | 8            | 1.7149   |
3. Results

3.1. Structural and morphological studies

XRD of WSA and WRA sample with its associated characteristics peaks of miller indices is shown in figure 1. WSA represents orthorhombic (JCPDS data file no. 01-087-2389) while WRA represents monoclinic (JCPDS data file no.83-0950) structure. [39]. According to Laue’s theory [40], the x-ray diffraction pattern shows maximum intensity when the incident wave-vector coincides with the reciprocal lattice vector of the crystal. Thus, a change in intensity correlates to a change in crystallinity. The smooth sample exhibits poor crystallinity as evident from small intensity peaks in figure 1. Rietveld refinement is done using the Marquardt model with the help of MAUD software for quantitative analysis for crystallite size, strain, etc shown in figure 2. The space group used for WO₃ is P2₁/c:b2 and with a line broadening model POPA LB [11].

Once we obtain a satisfactory fitting with $R_w(\%) = 8.72$, we get the lattice parameter (a–c) equal to 7.334782 Å, 7.5404944 Å and 7.701753 Å with angles $\alpha = \gamma = 90^\circ$ and $\beta = 90.38561^\circ$.

Likewise, for WSA (space group: P m n b), the lattice parameters have the values of 5.2552 Å, 10.7413 Å and 5.1432 Å, with $\alpha = \beta = \gamma = 90^\circ$. In addition, tables 1 (a) and (b) depicts the d-spacing (interplanar spacing), miller indices (hkl), and multiplicity for each peak that reveals the proof of Bragg’s law. Accordingly, a decrease in d-spacing with 2 theta angles is attributed to the difference in the ionic radii of W and O ions [41]. The ionic radius of tungsten (0.64 Å) is smaller than the ionic radius of oxygen (1.40 Å). Thus, it implies from figure 1 that 2 theta shifts to lower values in WRA than WSA that increases the lattice volume of WRA [41]. Another important parameter to be studied is the micro-strain in the lattice. We know that the broadening of the peaks is due to the contributions of crystallite sizes ($\beta_1$) and micro-strain ($\beta_2$) [42]. From the Scherrer equation we have:

$$\beta_1 = \frac{k\lambda}{t \cos \theta}$$

where $\lambda$ is the wavelength of the incident radiation (Cu-K alpha radiation with wavelength 0.154184 nm), $t$ is the crystallite size, $\theta$ is the diffraction angle and $k$ is the proportionality constant, which is 0.9 for Gaussian fitting. Likewise, the broadening due to micro-strain is given by:

$$\beta_2 = 4\varepsilon \tan \theta$$

where $\varepsilon$ is the strain in the lattice due to the configuration and structure of atoms. Adding the two above equations and with little rearrangements we get,
where \( \beta_T \cos \theta \) is the net peak broadening. The above equation resembles an equation of a straight line on a plot of \( \beta_T \cos \theta \) versus \( 4 \sin \theta \) with \( \varepsilon \) (strain) being the slope and \( \frac{k\lambda}{l} \) being the y-intercept. Thus, the mean effective crystallite size and microstrain turn out to be 56.80 nm and \( 2.4 \times 10^{-3} \) for WRA and 72.88 nm and \( 4 \times 10^{-4} \) for the WSA sample.

Scanning electron microscopy (SEM) images for WSA and WRA samples (figure 3) represent the random arrangement of crystals. We observe a flat-cubic (rectangular) flake-like structure over the entire surface for both the samples (WSA and WRA). The WSA represents a small number of flake-like structures with large voids, however, the WRA represents a uniform arrangement of flake-like structures with low voids in which all the flakes accumulate in large numbers vertically. As a result, the surface area of the WRA film increases which produces a quantum confinement effect. This is due to the rough surface of the glass substrate that facilitates the growth of crystals in one direction.

We confirmed the formation and characteristics of our WO\(_3\) sample by studying the FTIR spectrum for both the WSA and WRA samples, as shown in figure 4. WRA specimens show sharp characteristic peaks (at 583 cm\(^{-1}\)) compared to (608 cm\(^{-1}\)) WSA. The blue shift (25 cm\(^{-1}\)) in the transmittance is due to the roughness of the film. When the wavenumber of WRA decreases, the length of the bond increases [43], this is noticeable from the
microstrain calculation. The change in bond length is caused by changes in the electro-negativity of the neighboring atoms. Evidence of changes in crystalline composition from a slight blue shift in this FTIR has already been given in x-ray diffraction studies. Furthermore, we also observe small yet characteristic peaks at 1634 cm\(^{-1}\) illustrating the presence of water on the surface. The small yet prominent peak at \(\sim 800\) cm\(^{-1}\) for both the samples reveal stretching of bridging oxygen \((\text{W}–\text{O}–\text{W})\) indicating the presence of strain in the lattice which is also brought about by the XRD analysis. Interestingly, here we also observe shifting in peaks for some frequencies. Since wavenumber is directly proportional to the energy of incident radiation that causes the observed bond resonance, the left shift of \(\nu(\text{O}–\text{H})\) for WRA (that is at 3366 cm\(^{-1}\)) as compared to that of WSA (that is at 3367 cm\(^{-1}\)) can be explained by stronger bonding and deeper penetration of water molecules with that of \(\text{WO}_3\) for WSA as compared to WRA. The same reasoning can be thought of for other peaks of the spectrum, indicating a greater presence of water for WSA than WRA. Table 2 talks about the characteristics of different peaks obtained by FTIR studies.

Overall, the WRA pattern shows a slight change in FTIR. This is probably due to the increase in the number of atoms on the rough surface which increases the diffusion of IR from the film. In addition, as the peak position changes, changes occur in the length of the bond, which causes the atoms to vibrate. From this, the vibration-rotation interactions change. Higher vibrations increase the amplitude of the wave; Which makes it possible to squeeze and stretch the bond, making it beneficial for all gas sensing properties.

Atomic force microscopy characterization was also performed on the prepared samples. From figure 5, we can see that for WSA, there are multiple pores on the surface. The area of projection was 5 \(\mu\text{m}^2\) with a median surface thickness of 581.942 nm. The average pore size is estimated to be around 196.1 nm with an average depth of 100 nm and RMS roughness of 20.417 nm. These structural properties provide insight into the functioning of our samples as gas sensors. Multiple pores provide an effective increase in surface area for the target gas to

### Table 2. FTIR peaks for WSA and WRA samples for comparative study.

| WSA (cm\(^{-1}\)) | WRA (cm\(^{-1}\)) | Assignment |
|-------------------|-------------------|------------|
| 608.00            | 583.00            | \(\nu(\text{W}–\text{O}_{\text{inter}}–\text{W})\) bridging vibration of the corner-sharing \(\text{WO}_6\) octahedron [39] |
| 667.00            | 666.00            | \(\nu(\text{W}–\text{O}_{\text{inter}}–\text{W})\) vibration suggesting that the bridging oxygen play different roles [39] |
| 804.00            | 802.00            | \(\nu(\text{O}–\text{O})\) and \(\nu(\text{W}–\text{O}_{\text{inter}}–\text{W})\) stretching of the bridging oxygen [45] |
| 1039.00           | 1039.00           | \(W = O\) (terminal bonds) LO mode on the internal surface of the material [46] |
| 1460.00           | 1459.00           | considered as unusual values of the stretching \(\nu(\text{OH})\) and bending \(\delta(\text{OH})\) vibrations, indicating OH groups had strong bonds to either water molecules or surface oxygen atoms. [47] |
| 1634.00           | 1634.00           | Bending \(\nu(\text{H}–\text{O}–\text{H})\) vibration mode [45] |
| 3367.00           | 3366.00           | \(\nu(\text{O}–\text{H})\) stretching mode due to adsorption of the water molecule. [48][49] |

Stretching vibrations (\(\nu\)), in-plane bending vibrations (\(\delta\)).

Figure 6. Sensitivity of WRA as a response to different gases; inset showing resistance change in the sample for acetone, ethanol, methanol, and benzene before, during, and after the gas injection phase.
interact with the substrate, however, it also increases the likelihood of these gases getting trapped inside the surface. The reversibility of the sensor gets severely impacted with this modification as evident from figure 5(a). On the other hand, the WRA sample shows broader, smoother, and less intense surface modification which aids, not only in better sensitivity but also in reversibility since trapping of the gases is minimal. Figure 5(b) provides a good quantitative explanation of the same. The median height of the film is 969 nm, and the highest peak observed is 2.6 μm. This gives our gases even more surface area to interact with as compared to WSA. The size of the depressions here can be measured to be approximately 486 nm with an RMS roughness of 322 nm.

3.2. Gas sensing properties and mechanism

3.2.1. Selectivity

We interpreted the IV characteristics of the material in the presence of different gases to stress the gas selectivity criteria for our material shown in figure 6. The measured voltage ranged between 14–15V with the environmental temperature at 31 °C. This voltage range is studied to avoid any errors or fluctuation in sensing behavior that may occur for low voltages. This is also close to the standard value for a battery-operated gas sensor.

As can be seen, our material reacts strongly with methanol as compared to other gases. The high sensitivity for only one gas proves the application of our material in an industrial setting with a mixture of gases at room temperature. Often, a space-charge layer model helps us in understanding the mechanism of gas sensing for metal-oxide semiconductors [50]. Here we notice an interesting observation as compared to other works of literature in this domain, that is, an increase in resistivity for alcohols. Before discussing the mechanism, it is worthy to note the presence of surface water and interstitially trapped water molecules. As evident from FTIR data, the peaks in the range of ∼1600 cm⁻¹ to ∼3500 cm⁻¹ correspond to the water and OH⁻ molecules in our material at room temperature. As given in [51], there are two types of water adsorption. Most of the water is weakly bonded to the surface and is eliminated with the evacuation at room temperature and slight heating. At the same time, we also have water that is trapped in the microporous structure of the oxides which is evaporated on heating above 400 °C. As gas sensing is primarily a surface phenomenon, the water trapped in such microporous structures cannot contribute much to the changes in surface conductivity. Since we have observed a resonance at 1634 cm⁻¹, we can confirm the presence of water molecules, as a result of weakly held hydrogen bonds, on the surface of WO₃. This is certainly because of using PG in the synthesis phase, which captures additional moisture on the surface of WO₃ and thus preventing water from an easy escape even after exposure to an open environment. The oxygen atom in the water molecule fills the oxygen vacancies in WO₃, resulting in oxidation of the surface. Similar observations with respect to NO₂ and CO, along with a complete discussion are provided in [52]. The following reaction depicts the increase in resistance as a consequence of reduction:

\[ H_2O(gas) + V^- \rightarrow 2e^- \rightarrow O_0 + H_2(gas) \]

where V⁺ is the ionized oxygen vacancy and O₀ is the lattice oxygen. Now, when methanol is introduced into the closed chamber, the hydrogen from water and oxygen from methanol gets bonded through hydrogen bonding [53] and as a result, we have the methanol-water species distributed all over the surface. As given in [52], just like CO, methanol doesn’t compete with water for reaction partners on the WO₃ surface. Unlike acetone, which is a poor reducing agent, methanol finds even more reaction partners on the WO₃ surface than dry air. This hydrogen-bonded methanol-water species further act as electron-withdrawing pairs due to the positive inductive effect [54], which gives rise to an even further increase in resistivity of the WO₃ sample. Thus, the presence of water and methanol both contribute to the widening of the band-gap for our n-type material.

Figure 7. Resistance voltage characteristics of (a) WSA and (b) WRA for (i) environment saturated with methanol gas, (ii) before the injection of methanol, and (iii) after the injection of methanol.
3.2.2. Voltage response

We have compared the performances of WSA and WRA samples in terms of methanol exposure of 8 min. Figure 7 depicts the behavior of resistivity as a function of voltage in the range 14V to 15V for methanol. We can see a clear distinction between their counterparts when the gas is present and absent. This difference can be optimized using instrumentation amplifiers for practical applications.

As was summarized above, the methanol-water species acting as electron-withdrawing centers accumulated on the surface of WO$_3$ along with the presence of water, satisfy the oxygen vacancies. Thus, an increase in resistivity is observed for the material with a sensitivity of 175% as determined by the sensitivity equation:

$$S = \frac{R_g - R_{bg}}{R_{bg}} \times 100$$

Where $R_g$ is the resistance measured in the presence of gas and $R_{bg}$ is the measured resistance before injecting gas in the environment (i.e. the background gas). The resistance-voltage performance of WRA samples is compared with that of WSA samples which clearly shows a characteristic distinction. Although the sensitivity of WSA samples shows promising results: 350%, we see poor reversible behavior. Since FTIR results reveal greater water molecules penetration for WSA as compared to WRA, we can say that the methanol molecules get trapped as a result of their hydrogen bonding with H$_2$O. In other words, the greater the concentration of water in the sample, the greater is its ability to retain methanol molecules in the micropores and the surface even after the evacuation of gas. This is an undesirable property for sensing and thus, in a practical setting, a WSA sample may not be a suitable choice as a gas sensor.

In Figure 8, we have also shown a detailed comparison of WSA and WRA of the next two reactive gases, Ethanol and Benzene. We observe unstable behavior for WSA before injecting the gases at room temperature. On the other hand, WRA performs significantly well for both gases. This tells us about the reversibility of the
sensor; at room temperature, WSA simply traps gases in a huge amount which makes it undesirable for any use in the gas sensing technology. At elevated temperatures, this phenomenon even worsens leading to poor data.

3.2.3. Temperature response

After observing the anomalous mechanism at room temperature, it is worthy to investigate the functioning of WO₃ at slightly elevated temperatures, that is, above 60 °C shown in figure 9. At this temperature, the water molecules leave the surface of WO₃. Thus, we no longer have additional oxygen molecules from water to withdraw electrons from the conduction band and increasing the resistivity. Following the evaporation of water, we can also expect a direct reaction between the surface and the target gas, as opposed to the prior condition where there was an intermediating water molecule on the surface.

As we increase the temperature beyond 60 °C, we notice a sharp decrease in resistance to the methanol atmosphere. This can be attributed to the expected behavior of WO₃ in sensing alcohol as suggested in multiple works of literature [55]. This phenomenon is due to the chemisorption of methanol on the surface of WO₃ at a molecular level [56]. Since CH₃O⁻ is a good nucleophile, it donates electrons to W⁶⁺ oxidized sites on the surface to form weak covalent bonds. This electron donation (that is the charge carrier donation) causes a reduction in the depletion band of WO₃ which finally results in an increase in conductance. On similar grounds, we can argue about the formation of ethoxy species on the surface of WO₃ contributing to the gas sensing of ethanol, however, due to its high-temperature requirements (∼200 °C), only a fraction of such species could occupy the metal oxide surface in this temperature range. When entering the domain of high-temperature gas sensing, this effect of ethoxy species bonding with surface atoms of WO₃ is more pronounced as given in [49, 55].

Starting from the room temperature (i.e. at 31 °C), we carry out the sensitivity observations for methanol as the target gas. From figure 10, a clear correlation is observed for temperature in the range from 30°C–80°C. This is the exact range where the evaporation of water can be thought to be the fastest. This re-establishes our claim about the anomalous behavior of the WO₃ gas sensor in the presence of water molecules. Beyond 80 °C, we
detect a decrease in resistance for the sensor during the methanol gas environment, which aligns with the existing literature. It is interesting to note that at a higher temperature, i.e. at 130 °C, the sensitivity drastically decreases. This can be due to the increase in bond vibration of WO$_3$ molecules which makes our sensors difficult to trap the methanol gas for detection.

4. Discussions

Due to the roughness of the surface, the grain boundary at high-angle increases. When the deposition of WO$_3$ begins, nucleation mainly occurs at the site where there is an irregularity on the surface [57]. Thus, the crystal lattice decorates the radicals on the surface. This means that a constant accumulation of W and O atoms on a rough surface (through nucleation and growth of crystals) increases the degree of grain boundary at a high angle [57].

From figure 3, the volume of one flake of WSA and WRA is calculated as 0.148 and 0.064 cm$^3$, respectively. Considering the density of WO$_3$ as 7.2 g cc$^{-1}$ [58], the individual flakes can be estimated as 1062 $\times$ 10$^{-12}$ and 461 $\times$ 10$^{-12}$ g for WSA and WRA, respectively. With this, we can estimate the surface area to weight ratio which is equal to 0.083 and 0.135 m$^2$ per unit gram for WSA and WRA samples. Here a larger value of the WRA’s surface-to-weight ratio indicates that more particles exist on the surface resulting in more gas-interaction sites [57]. Another important point to be mentioned is the interstitial voids between each grain as a consequence of the random orientation of the WO$_3$ flakes. Figure 3 shows a distance of 4–10 μm and 0.5–4 μm between the voids for the WSA and WRA samples, respectively. During the high concentration injection of gases, these voids help to carry the gas molecules to a deeper level, thereby increasing the pure surface of the corresponding film [57]. Moreover, the large size of the voids in the WSA creates interference and the gas quickly diffuses to the film’s surface, while the small voids in the WRA help the gases to reach even deeper levels, increasing the net chemisorption area of the film.

The usual explanation for the variation in nucleation rate is that a coarse substrate exceeds the surface area over a flat layer so that more molecules can be dispersed and heterogeneous nucleation can occur [59]. Rough surfaces reduce the stress of the crystal-substrate surface than flat surfaces, so more WO$_3$ crystals can contact the surface. Therefore, although the method of making both the films is the same, the higher the volume of WO$_3$, the more crystal sites there are on the rough surface. Due to the pressure on the crystal sits on each other, the critical volume of the internal WO$_3$ crystal site becomes smaller. Therefore, even if the bond length is increased, the bond vibration is affected by the nearby electronegative atom, which requires less energy to break the WO$_3$ bond. The same thing happens in a flat substrate in the very opposite way which requires more energy.

When the WO$_3$ film is exposed to methanol gas while studying temperature response, the rough surface increases surface area with an increasing number of gas-interaction sites. Here, some short-term reactions take place to form strong hydrogen bonds [17]. The electropositive hydrogen atoms of the methanol molecule are attached to the WO$_3$ electronegative oxygen atom, which improves the internal conductivity of the sensor required for methanol gas. In addition to these gas interactions, regular electron exchange also contributes to changing the resistance of methanol and air. These interactions are responsible for increasing the conductivity of sensors in methanol gas [20].

When WO$_3$ films are exposed to the methanol gas, WSA and WRA samples have similar effects due to the same morphology. However, in the case of coarse specimens, the longer the bond length, the higher the vibratory state, according to the FTIR study. Here, the bond dissociation energy ($E_d$) of WO$_3$ and methanol plays an important role. $E_d$ of Single W-O is 720 ± 71 kJ mol$^{-1}$ [60]. In WO$_3$, having three W-O bonds, the total $E_d$ is 2160 ± 71 kJ mol$^{-1}$. By comparison, methanol has three C–H, one C–O, and one O–H bonds (415 kJ mol$^{-1}$, 356 kJ mol$^{-1}$, and 463 kJ mol$^{-1}$), giving an average $E_d$ of 2064 kJ mol$^{-1}$ [60]. Thus, it is observed that WO$_3$ has higher $E_d$ than methanol. When methanol gas is supplied onto WO$_3$ films, the excess $E_d$ is reduced by the vibration of the bond length in WO$_3$ (104 ± 71 kJ mol$^{-1}$). At one level, the bond energy of WO$_3$ becomes exactly equal to the bond energy of methanol, which creates resonance. For this reason, WO$_3$ films here are sensitive to methanol gas at room temperature.

The films also exhibit high environmental stability as no quality degradation was observed even after a long duration of time.

5. Future Scope

Since humidity and substrate roughness can greatly impact the gas sensing of methanol, it can be worth investigating a quantitative relationship between the water vapors, substrate modification, and gas sensing characteristics. A time-based measurement can also be studied along with this to understand the mechanism in
greater detail. Upon considering the application of WO$_3$ material, especially for a thin film gas sensor, our work presented here may cast a new perspective on this subject.

6. Conclusion

This is the first report of the synthesis of a WO$_3$ film on a rough surface by hydrothermal method to detect methanol gas at room temperature. XRD studies suggest a monoclinic structure of WO$_3$, and morphological studies have shown a flat-cubic (rectangular) flake-like structure. From the FTIR data, the vibrations in the bonds and the presence of water molecules on the surface of WO$_3$ are evident. We saw inconsistent readings for alcohol, primarily methanol and ethanol, i.e., a large gas-interaction site provided by the rough surface shows a high reaction of the sensor. Water holding capacity depends on the form of the substrate; It has been found that water penetrates deeper and is strongly binding for a smooth substrate compared to a rough surface. As a result, the oxygen spaces of WO$_3$ are filled with oxygen from water molecules which reduces the capacity of the charge carriers (electrons). Further, the methanol molecules associated with surface water molecules by hydrogen bonding act like electron-withdrawing species which further increases the resistivity. However, the oversaturation of water makes the smooth substrate sample undesirable for gas sensing application due to poor reversibility. The presence of moisture and its effect on gas sensitivity can be experimentally proved by heating the WO$_3$ sample above 60°C, as water molecules evaporate from the surface. Once this happens, we have the reactive methoxy species chemisorbed on the WO$_3$ surface, resulting in a decrease in resistivity. Thus, rough surfaces easily facilitate sensitivity to methanol gas, improve selectivity, sensor repetition, and increases chemical stability. Finally, this work emphasizes that WO$_3$ on rough glass can be a good candidate for room temperature methanol gas sensing applications useful for industrial and various other field operations.

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Data availability statement

No new data were created or analyzed in this study.

Author Contributions

All authors listed have made a substantial, direct, and intellectual contribution to the work, and approved it for publication.

Compliance with ethical standards

Conflict of Interest

The authors declare that they have no conflict of interest.

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