Enhanced humidity responsive ultrasonically nebulised $V_2O_5$ thin films

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Abstract
A large surface to volume ratio and easily accessible active reaction sites are key attributes for a good gas sensing material. Herein, we report synthesis, characterisation and humidity sensing properties of phase pure 420 nm thick low temperature (350 °C) polycrystalline $V_2O_5$ thin films deposited on quartz substrate by ultrasonic nebulized spray pyrolysis of aqueous combustion mixture (UNSPACM). The thin films were characterized by x-ray diffraction, Raman spectroscopy, atomic force microscope, field emission scanning microscope, transmission electron microscope, UV–visible spectroscopy and XPS. The highly porous and nanocrystalline characteristic of $V_2O_5$ thin films synthesized by this technique provide large surface to volume ratio and easily accessible active reaction sites making it a prominent material for gas sensing applications. The fabricated humidity sensor based on $V_2O_5$ thin films exhibited high sensitivity with good stability and reproducibility at room temperature. The sensor exhibited high sensitivity of 90.8% at 76% RH with response time of 35–60 s and recovery time of 7–54 s. We believe this method provides means for large-scale synthesis of $V_2O_5$ thin films for several gas sensing applications.

1. Introduction

Several oxides of vanadium such as $V_2O_5$, VO$_2$, $V_3O_7$, and VO exist with unique and interesting properties due to the existence of vanadium in different stable oxidation states (V$^{2+}$ to V$^{5+}$). Among them, $V_2O_5$, the most stable oxide, has attracted great interest owing to its layered structural nature, large optical band gap, good thermal stability, chemical stability and excellent electrochromic and thermoelectric characteristics [1–3]. $V_2O_5$ is known to be an n-type [2, 4, 5] semiconducting material. It crystallizes in $Pmmn$ space group of orthorhombic crystal system having lattice parameters of $a = 11.510$, $b = 3.563$ and $c = 4.369$ Å [6]. The 2D layered structure consists of layers weakly bound by the electrostatic forces along c axis of unit cell where each unit cell possesses two formula units [2, 6, 7]. Layers build up from VO$_2$ square pyramidal units sharing edges thereby making double chains along b-direction [6, 8, 9]. Chains are linked at the corners forming octahedrally coordinated VO$_6$ with different vanadium–oxygen distances emanating from three distinct oxygens; terminal V-O$_1$ (1.58 Å) doubly bound oxygen along c-direction, doubly V-O$_2$ and triply V-O$_3$ coordinated (1.77–2.02 Å) bridging oxygen in basal plane and weak V-O (2.79 Å) bonds between the layers [6, 7]. The spacing between the layers provides favorable sites for the intercalation of several species [10] into $V_2O_5$ making it a favorable material for numerous applications like gas sensing [11, 12], lithium-ion batteries [13] and catalysis [14]. Different synthesis techniques like atomic layer deposition [2], spray pyrolysis [15–20], sol-gel [21], spin coating [22], chemical vapor deposition [3], sputtering [23], pulsed laser deposition [24] and electron beam evaporation [25] are being employed to synthesize $V_2O_5$ thin films on different substrates. Generally, $V_2O_5$ thin films deposited at a substrate temperatures <300 °C are amorphous [1]. Crystallization temperature as well as thin film properties like optical band gap have been found to depend on growth method and nature of substrate (amorphous or crystalline) [1, 26]. Highly porous materials [27] most especially metal oxides [28] in thin film form have been
found to exhibit high humidity sensitivity owing to large surface to volume ratio [29, 30] and easy tunability of their optical and electronic properties [31]. Humidity sensors are employed in monitoring and regulating ambient humidity which plays a key role in our daily lives [27, 32]. They are used in numerous fields such as agriculture, semiconductor fabrication, food processing, drug manufacture and storage, preservation of antiques and paintings, cryogenic processes, packaging and regulation of humidity levels in living rooms [27, 33–37]. A semiconducting material possessing large surface to volume ratio coupled with easily accessible redox reaction sites is desirable for gas sensing application [31, 38]. The 2D layered nature and the spacing between layers in V$_2$O$_5$ provide favorable sites for the intercalation of several species into it, making V$_2$O$_5$ an appealing material for numerous sensing applications.

This work presents synthesis, characterization, and humidity sensing properties of high-quality low temperature (350 °C) polycrystalline V$_2$O$_5$ thin films synthesized by UNSPACM, a simple, large area and cost-effective deposition technique. The technique besides being cheap, is scalable, compatible, flexible and yields highly porous films suitable for gas sensing applications due to its enhanced surface to volume ratio. It also provides easy way to dope any element in any stoichiometry of interest through solution [15] without having the need for complex equipment and with no vacuum or special substrate requirements. It further provides an advantage over other reported spray pyrolysis techniques [15, 16, 18–20] by combining solution combustion synthesis (SCS) and spray pyrolysis methods. The self-propagating elevated temperature reaction characteristic of SCS aids complete conversion of precursors into products resulting into high quality thin films [39]. Taking into consideration large area deposition of the films and scalable deposition of V$_2$O$_5$ thin films through UNSPACM for industrial applications is less exploited coupled with excellent sensing properties of V$_2$O$_5$, it becomes useful to investigate humidity sensing properties of low-cost large area V$_2$O$_5$ thin films deposited by this technique. The as-synthesized V$_2$O$_5$ thin films were used to fabricate humidity sensor and its sensing properties were studied using an in-house built sensing setup. The V$_2$O$_5$ films exhibited enhanced sensitivity, stability, fast response and recovery times towards humidity at ambient conditions without going for tedious complex and complicated lithographic designs and with no special substrate requirement.

2. Experimental

2.1. Synthesis

Porous V$_2$O$_5$ thin films were deposited on pre-cleaned quartz substrate at 350 °C by UNSPACM. Precursor solution (aqueous combustion mixture) was made by taking stoichiometric amounts of vanadyl nitrate (oxidizer) and urea (fuel) dissolved in few ml of distilled water. Vanadyl nitrate was obtained by adding few drops of concentrated nitric acid in ammonium metavanadate. Measurements were done ensuring maximum exothermicity whereby the ratio of oxidizer to fuel was one [39]. Reaction scheme leading to the formation of V$_2$O$_5$ is as shown below.

$$2\text{VO(NO}_3\text{)}_3 + 5\text{CH}_4\text{N}_3\text{O} \rightarrow \text{V}_2\text{O}_5 + 8\text{N}_2 + 10\text{H}_2\text{O} + 5\text{CO}_2$$

The precursor solution was taken into specialized glass setup and nebulized using 2.5 MHz frequency ultrasonic nebulizer (Mystique Air Sep USA). The schematic of the setup is given elsewhere [40]. N$_2$ gas kept at a flow rate of 1000 sccm was used to carry ultrasonically nebulized mist into the substrate kept at 350 °C. The droplets pyrolyzed immediately upon reaching the hot substrate. Film deposition was done for 10 min. V$_2$O$_5$ forms when droplets reach the hot substrate owing to the high exothermic and self-propagating nature of the reaction.

2.2. Characterization

Structural analysis of thin films was done using x-ray diffraction X’Pert-PRO PANalytical instrument with Cu-K$_\alpha$ radiation (1.5418 Å) at a scan rate of 2° per minute. Phase formation was further confirmed from Raman spectra of the thin films measured at room temperature in 50–1100 cm$^{-1}$ range (Horiba JobinYvon HR-Raman-123 microPL spectrometer at 532 nm wavelength). Morphology and microstructure of thin films was investigated by Inspect F50 field emission scanning electron microscope and JEOL 2100 F transmission electron microscope operated at 20 and 200 kV respectively. Surface roughness of the films was measured using non-contact mode A.P.E Research A100-AFM atomic force microscope. Veeco Dektak 6 M surface profilometer was used to measure the film thickness. Optical characterization of the thin films was done by Perkin Elmer-Lambda 750 UV-Vis-NIR spectrophotometer. The chemical electronic states of thin films were analyzed by x-ray photoelectron spectroscopy (XPS) measurements conducted using axis ultra DLD (from Kratos) high resolution instrument with automatic charge neutralization equipped with MgK$_\alpha$ radiation (1253.5 eV). XPS data was fitted using XPS Peak41 software [41].
2.3. Humidity sensing

Room temperature humidity sensing studies on the films were conducted in a simple in-house built computer-controlled sensing system (figure 1) comprising of dry gas cylinder, mass flow controllers (MFC 1, MFC 2 and MFC 3) attached to mass flow regulator, bubbler containing water, solenoid valves (S1 and S2) attached to solenoid controller, test chamber, sensor holder and data acquisition system. The contacts of the V$_2$O$_5$ humidity sensing device were fabricated by applying a small amount of silver paste on corners of V$_2$O$_5$ thin film (figure 1). The linear nature of current-voltage curves confirmed the ohmic nature of contacts. The humidity sensing setup has two lines leading to the sample: (i) MFC 1 and S1, and (ii) MFC 2, MFC 3, Bubbler (water) and S2. First line which leads flow of dry air alone is taken as background. Second line is humid air attained by bubbling dry air through MFC 3 in to water, and relative humidity was controlled by adjusting the flow of dry air in MFC 2. The solenoid valves 1 and 2 are coupled through timed solenoid controller, which makes only one line active at a time.

The relative humidity is controlled by dry air flow through MFC 2 and the time of exposure to the humid air is controlled by solenoid valve controller. The RH levels were monitored using Generic E_14009384 220 V Digital Air Humidity Controller. The relative humidity (RH) of 25, 44, 58, 62 and 76% were attained and maintained at room temperature (25 °C). The change in conductivity of V$_2$O$_5$ thin film was measured with a Keithley 6430 Source Meter SMU instrument at different RH atmospheres. This setup can be adopted for studying sensing properties of bulk or thin films for volatile organic compounds and other analytes of interest.

3. Results and discussion

3.1. X-ray diffraction

Figure 2(a) shows the XRD pattern of V$_2$O$_5$ thin films. The optimized deposition temperature of 350 °C was deduced after depositing thin films at several substrate temperatures (250 °C–450 °C). Films deposited below 350 °C were found to be amorphous while thin films deposited at substrate temperature > 350 °C were crystalline. Grain growth was seen to increase with deposition temperature. Thin films were polycrystalline and preferentially oriented in (001) direction. This was demonstrated by highest intensity peak at 2θ value of 20.32°. All diffraction peaks were indexed to Pmmn space group of orthorhombic V$_2$O$_5$ crystal system (JCPDS #77-2418) [42]. No any characteristic impurity peaks nor of any other vanadium oxides was observed revealing phase purity of synthesized V$_2$O$_5$ thin films. Average crystallite size, D of thin films was estimated by Scherrer’s formula [43, 44], given by $D = \frac{K \lambda}{(\beta \cos \theta)^2}$, where 2θ is Bragg’s angle, K is Scherrer’s constant taken in this case to be 0.9 [44], λ represents the wavelength of x-ray radiation used (CuK$_\alpha$ = 1.5418 Å), β is the peak’s full width at half maximum while ω is instrumental broadening recorded for standard silicon sample. Average D value was determined to be 22 ± 0.5 nm. Dislocation density, δ expressed as length of dislocation lines per unit length.
volume of crystal was calculated from the relation 

\[ d_0 = D^2 \] 

where \( D \) is crystallite size and its value was found as 

\[ \delta = 2.06 \times 10^{-3} \text{ lines/nm}^2 \]

This small dislocation density confirms good crystallinity of the synthesized V\(_2\)O\(_5\) thin films [20]. Achievement of high crystalline films at such a low temperature (350 °C) can be attributed to the exothermic nature of the combustion reaction where the local temperature can be higher. However, the high temperature exposure lasts for a very short time avoiding crystalline growth, thereby resulting in high surface area. Instantaneous evolution of gases not only results in porous microstructure but also quenches the product thereby preventing grain growth.

### 3.2. Raman spectroscopy
Phase formation of the thin films was further confirmed from Raman spectroscopic measurements. Figure 2(b) shows Raman spectra of V\(_2\)O\(_5\) thin films recorded at room temperature. The Raman spectra of the films featured ten peaks at wavenumbers 102, 145, 197, 284, 304, 404, 482, 528, 701 and 995 cm\(^{-1}\) which were consistent with wavenumber values reported for crystalline V\(_2\)O\(_5\) [6, 17, 46]. The peaks were assigned to different bending and stretching vibrational modes of V\(_2\)O\(_5\) as given in Table 1. 

### Table 1. Raman active modes for as-deposited V\(_2\)O\(_5\) thin films.

| Symmetry      | Wavenumber (cm\(^{-1}\)) | Assignment | Ref [6] | Ref [46] | Ref [47] | This work |
|---------------|---------------------------|------------|---------|---------|---------|-----------|
| \( T_{1u} \)  | A\(_g\)                    | 98         | 101     | 98      | 102     |           |
| \( T_{2u}, R_{2u} \) | B\(_{1g}\), B\(_{2g}\) | 142        | 145     | 145     | 145     |           |
| \( T_{1g}, R_{1g} \) | B\(_{1g}\) | 194        | 198     | 194     | 197     |           |
| \( \delta(V-O)\) | B\(_{1g}\), B\(_{3g}\) | 281        | 284     | 281     | 284     |           |
| \( \delta(V=O)\) | A\(_g\)                    | 300        | 305     | 300     | 304     |           |
| \( \delta(V-O)\) | A\(_g\)                    | 403        | 406     | 405     | 404     |           |
| \( \delta(V=O-V)\) | A\(_g\) | 476        | 484     | 470     | 482     |           |
| \( \nu(V-O)\) | A\(_g\)                    | 526        | 531     | 520     | 528     |           |
| \( \nu(V=O)\) | B\(_{1g}\), B\(_{3g}\) | 698        | 704     | 694     | 701     |           |
| \( \nu(V=O)\) | A\(_g\)                    | 992        | 996     | 992     | 995     |           |

A\(_g\) mode and 6 modes of B\(_{1g}\), B\(_{3g}\) symmetry are not observed.

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Figure 4. (a) TEM image of synthesized V$_2$O$_5$ thin films, (b) Selected area electron diffraction pattern, (c) HRTEM image and (d) EDS spectrum of the sample.

The selected area electron diffraction (SAED) pattern given in figure 4(b) reveals polycrystalline nature of V$_2$O$_5$ thin films. The lattice spacings at 0.433, 0.401, 0.341, 0.261, 0.204, 0.191 and 0.178 nm obtained from selected SAED pattern correspond to d-spacings of (001), (101), (110), (310), (202), (600) and (020) crystal planes respectively proving the polycrystalline characteristic of thin films.

The high-resolution transmission electron microscope image shown in figure 4(c) demonstrates 0.433 nm lattice spacing corresponding to (001) crystal plane indicating preferential orientation of thin films in (001) direction. These observations agree with XRD planes of orthorhombic V$_2$O$_5$, space group $Pmmn$ shown in figure 2(a). The EDS spectrum is shown in figure 4(d); it confirms the presence of vanadium (V) and oxygen (O) in the sample.

The existence of silicon (Si), carbon (C) and copper (Cu) is due to substrate and carbon-coated copper grids used for TEM analysis.
3.4. Optical
Figure 5(a) shows the diffuse reflectance (DRS) of V$_2$O$_5$ thin films recorded at 200–1200 nm of wavelength. Kubelka-Munk function, KM was used to convert DRS into absorption spectra [49, 50]. KM at any wavelength is expressed as $F(R_{\infty}) = \frac{R_{\infty} - R_{\infty}^2}{2R_{\infty}}$ where $R_{\infty}$ is reflectance of the films relative to reference material ($R_{\text{sample}}/R_{\text{reference}}$), $\alpha$ is absorption coefficient while $S$ is scattering coefficient. The absorption band edge observed at around 560 nm (figure 5(a)) corresponds to the band gap of V$_2$O$_5$. The band gap (optical) of V$_2$O$_5$ thin films was estimated to be 2.22 eV from the plot of $(\alpha h\nu)^2$ versus $h\nu$ (direct band gap) [51, 52]; then extrapolating linear section of the curve to reach horizontal axis as presented in figure 5(b) (Tauc plot).

This value agrees with reported band gap values for V$_2$O$_5$ thin films [1].

3.5. X-ray photoelectron spectroscopy
Figure 6(a) presents survey spectrum of the thin films from which peaks corresponding to O1s, V2p$_{3/2}$ and V2p$_{1/2}$ core-level spectra were identified. The adventitious C1s peak present at binding energy (BE) of 284.8 eV was taken as a reference. O1s and V2p peaks were then calibrated based on this value.

The background was subtracted by applying Shirley background function (figure 6(b)). V2p$_{3/2}$ peak occurred at BE of 517.6 eV with FWHM of 0.9 eV while V2p$_{1/2}$ peak appeared at BE of 524.9 eV with FWHM of 2.3 eV. These peak positions together with the difference in energy between the V2p$_{3/2}$ and V2p$_{1/2}$ peak values which is 7.3 eV are characteristic of V$^{5+}$ oxidation state [2, 53, 54]. The absence of any other oxidation state in the XPS spectra of the sample further confirms the high quality of V$_2$O$_5$ thin films. The O1s peak appearing at BE of 530.3 eV with FWHM of 1.1 eV is attributed to lattice oxygen while O1s peak occurring at BE of 531.8 eV with FWHM of 1.5 eV is ascribed to atmospheric oxygen present due to CO$_2$ or H$_2$O [55, 56].
3.6. Sensing

The humidity sensing properties of V2O5 thin films were studied by fabricating a two-probe device which was introduced to various relative humidity (RH) environments achieved by mixing dry air with humid air obtained by bubbling dry air through water at a controlled flow rate. The schematic of humidity sensing set up used is given in figure 1. Our method provides an easy way of attaining and maintaining various relative humidity environments thus providing better room for reproducibility of the results. Figure 7(a) shows room temperature current-voltage characteristics of the sensor at different RH environments ranging from dry air to high humid atmosphere (76% RH). The curves are linear proving ohmic characteristic of the contacts. It is also clear from current-voltage curves that current of V2O5 humidity sensor increases with increase in relative humidity which is consistent with reports for n-type semiconducting humidity sensors [32].

Further testing was conducted which gave fundamental results on important parameters which characterize sensing device notably sensitivity, response time, recovery time and reproducibility. Figure 7(b) gives device response on exposure to different humidity environments ranging from dry air (5% RH) to various higher RH environments of 25, 44, 58, 62 and 76% at 25 °C. Upon exposure of the device to moist air of 25% RH from dry air (5% RH), current increased drastically and stabilized at a value higher than that exhibited by dry air. Interestingly, on switching off the device back to dry air, current sharply decreased and stabilised at baseline current value of dry air. This quick response and recovery were repeating for several cycles of switching the device from dry air to moist air and vice versa showing greater reproducibility and stability of the sensor; only few representative cycles are given in figure 7(b) to avoid clutter. A similar response trend with enhanced current was noted when the device was subjected to much higher humid air of 44, 58, 62 and 76% RH. The current increased with increase in RH as given in figure 7(c). We tested performance of the device after four months and results were repeating, which further confirms its greater stability and reproducibility.

Conductivity of semiconductor device sensors is dependent upon the humidity levels the sensor is subjected to; it can be electronic or protonic [27, 32]. Water adsorption in V2O5 is considered as an intercalation phenomenon to form V2O5.nH2O due to its layered structural nature [1, 3]. On exposure to low humidity atmospheres, less quantity of water molecules get trapped into the layers. They are too far apart for H\(^+\) to move freely between immobile chemisorbed and first physisorbed water layers. Electron hoping thus prevails characterised by low sensor conductivity [32]. At high humidity levels large quantity of water molecules gets intercalated, protons freely move at higher-level physisorbed water layers according to Grotthuss mechanism [32, 57] and protonic conductivity prevails over electronic one. The formation of more physisorbed water layers at higher humidity enhances diffusion of protons through array of hydrogen-bonded water molecules which leads to increased protonic conductivity [58]. The high conductivity at higher humid environments is due electrons donated by the more physisorbed water molecules onto n-type V2O5 thereby pushing Femi level closer.
The fabricated humidity sensor based on the as-synthesized V2O5 thin films demonstrated excellent humidity sensing performance at 97.2% RH, which is better than that previously reported [2, 29]. Response time and recovery time (defined as time required to reach 90% of final equilibrium value) [62] were determined by fitting one cycle of RH response curves (figure 7(c)) for rise and fall rate constants using first order differential equations expressed as \( I(t) = I_{\text{rise}} + \alpha e^{\beta t} \) and \( I(t) = I_{\text{fall}} - \beta e^{-(t-\tau)} \) respectively [63] where \( \alpha \) and \( \beta \) are scaling constants, \( \tau \) is time constant, \( t \) is time for ON or OFF cycles and \( I_{\text{dry air}} \) is sensor current in dry air. The response time and recovery time were determined to be 35–60 s and 7–54 s respectively. We have compared the performance of our device with that of previously reported oxide-based humidity sensors in table 2 [2, 3, 29, 59–62, 64, 65]. Our device exhibits high sensitivity (90.8%) at relatively low RH (76%) which signifies better humidity sensing performance than that of V2O5 thin films/nanosheets [2, 29] and other previously reported oxide based humidity sensors [59, 60, 62, 64]. The response/recovery times of our device are also faster than those of other oxide-based humidity sensors reported [29, 59, 61, 62, 65].

This deposition technique provides a simple and cost-effective scalable way of synthesizing V2O5 thin films for various sensing applications. The films obtained were highly porous and nanocrystalline in nature, which provides large surface to volume ratio and easily accessible active sites making this a prominent deposition technique for various gas sensing applications. Gas sensing set up described in this work can easily be adopted for sensing various volatile organic compounds, by simply keeping analyte of interest in the bubbler.

### 4. Conclusion

We have synthesized and comprehensively characterized low temperature (350 °C) crystalline V2O5 thin films on quartz substrate by simple and cost-effective deposition technique; ultrasonic nebulized spray pyrolysis of aqueous combustion mixture. The thin films were characterized by XRD, Raman spectroscopy, UV-Visible spectroscopy, scanning electron microscope and transmission electron microscope. Morphological investigation revealed porous and nanocrystalline nature of V2O5 thin films, a suitable phenomenon for gas sensing performance due to their enhanced surface to volume ratio. In-house built setup was used to study humidity sensing properties of thin films. The fabricated humidity sensor based on the as-synthesized V2O5 thin films demonstrated excellent humidity sensing properties. It exhibited fast response and recovery time of 35–60 s and 7–54 s respectively and high sensitivity of 90.8% at 76% RH. These results exhibit high performance of V2O5 thin films opening avenues for large-scale preparation of V2O5 thin films for several sensing applications.

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