UV Irradiation Influence on Hydrogen Sensors: V_2O_5 Thin Films Prepared by DC Magnetron Sputtering

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Abstract

In this study, DC Magnetron sputtered Vanadium Pentoxide thin films with Hydrogen gas-sensing properties have been focused, on solid-state gas sensors. We reported a novel approach that significantly improves the hydrogen sensing response of V_2O_5 thin film by illumination of UV light based on the UV light illumination gas response of the sensor change. The Sputtered V_2O_5 thin films have undergone various characterization processes, such as XRD, Raman, optical, EDX with SEM, and photoluminescence. The gas sensing response was calculated at room temperature of 27° C of Hydrogen gas concentration of 20 ppm, it remarkably enhanced the sensing performance under UV light irradiation by about 126%.

Keywords: Sputtering; UV irradiation; Hydrogen gas sensing response; sensitivity and selectivity;

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1. Introduction

The gas sensing behavior is one of the most significant applications in safety and precaution with common aspects gaining attention among researchers like the gas sensing field. Detection of toxic gases from industrial production, and environmental monitoring require a reliable sensor device. Recently, Metal Oxide Semiconductor (MOS) gas sensors have played a vital role detection of leakage of hydrogen in the field of hydrogen storage places and fuel cells. Vanadium can occur in numerous oxidation states of V^{5+}, $V^{4+,}$ and V^{3+}, which is easy for the preparation of V_2O_5 thin films with different electrical and chemical properties for a wide range of applications [1]. The Vanadium oxides (V_xO_y) are essentially different phases called Magneli phases, defined by the general stoichiometric formula V_nO_{2n-1} [2]. Vanadium Pentoxide (V_2O_5), particularly as a thin film form has drawn numerous applications due to the most stable state of V^{5+} and it has wide range of optical band gaps; chemical and electrical stability are some of the reasons that transform V_2O_5 a most favorable material for diverse applications like as gas sensing, storage device, cathode, catalysis, and electrochromic devices [3-6]. Several types of sensing material are used in semiconductor gas sensors [7-9], optical gas sensors [10-12], and solid electrolyte gas sensors [13] Various preparation methods exist, such as Electron beam evaporation [14], DC magnetron sputtering [15], chemical vapor deposition [16], spray pyrolysis[17.18] and spin coating [19].

Among the various types of preparation, we decided to prepare thin film in DC magnetron sputtering because of uniform deposition and top-down process. DC Magnetron sputtering was one of the most remarkable processing routes of V_xO_y thin film, because of the possibility of producing large-area deposition, good uniformity as well as good adherence to various substrates. Consequently, Most of the researchers focused on the development of gas sensors working at room temperature. The illumination of UV light on metal oxide semiconductors can change the surface electronic properties by generating charge carrier concentrations. It has been widely studied to improve the sensor sensitivity of various metal oxide semiconductors at ambient conditions. In this study, V_2O_5 thin films were deposited using DC Magnetron sputtering, and its sensor responsible for various conditions like the presence and absence of UV light was investigated. Meanwhile, the structural, and morphological properties of V_2O_5 films were studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM),

2. Experimental procedure

The V_2O_5 films were deposited on Silicon glass substrates by Homemade DC magnetron sputtering, using a Vanadium target (99.995%) purity. The deposition was performed presence of Ar and O_2 plasma with the temperature of the substrate maintained at 27°C. The pressure inside the deposition chamber was a base pressure of $2.5x10^{-5}$mbar, working pressure of $1x10^{-2}$ mbar oxygen pressure of $6.2x10^{-4}$ mbar, and the DC power was 66 W, deposition time of 25 min with an oxygen flow rate of 2.5 sccm. The V2O5 thin films that were deposited on silicon substrates were cleaned for 30 minutes with alcohol and acetone in an ultrasonic

The structural properties were analyzed using an instrument of X-ray diffractometer (Bruker D8 Advance) CuK_αwavelength of 1.5406A°. The morphological study was carried out using the SEM model of Quanta FEG 250. Argon-ion laser Raman spectroscopy with the wavelength of 200-2100nm LAB RAM HR Horiba France model. Optical transmittance and band gap energy of V_2O_5 were calculated at wavelengths between 300-3000 nm using UV-visible spectrophotometer models (Varian 5000). A Keithly digital Multimeter was used for electrical current measurement done by the microprobe station (Janis Microprobe Station) and data were taken with the Lab View program.

2.1.Gas-sensing setup

The V_2O_5 thin film was placed inside a homemade stainless-steel chamber connected with a well-equipped Keitheley Digital Multimeter for measurement of electrical current The prepared V_2O_5 thin film dimension was 1cmx1cm with good bottom aluminum electrical contact and it was mounted in a 750 ml air-tight chamber, where it was preheated using a temperature controller-based heater. The chamber was evacuated using a rotatory pump and then a testing procedure was done by the devices, Moreover, we had to wait for more than two hours resistance of thin films to become stable. The response was carried out in H_2 gas of concentrations of 20ppm gas, which was studied in a container with a volume of $250cm^3$ connected to a gas flow system. A mass controller device was used to control the concentration of H_2 gas. The sensors were also exposed to UV radiation while detecting H_2 gas. LED light source with a wavelength of 365nm (power density of 1 Wcm^{-2} is applied to V_2O_5 thin film for three minutes during the recovery time. The distance between the UV light and the sample is 7cm

centimeter. Initially, the samples were irradiated for 60 min with the UV-LED to stabilize the electrical resistance for comparison in terms of selectivity, this work considered performing NO_2, CO_2, and CO gas sensing measurements, under UV illumination at room temperature, for the concentration of 20ppm.

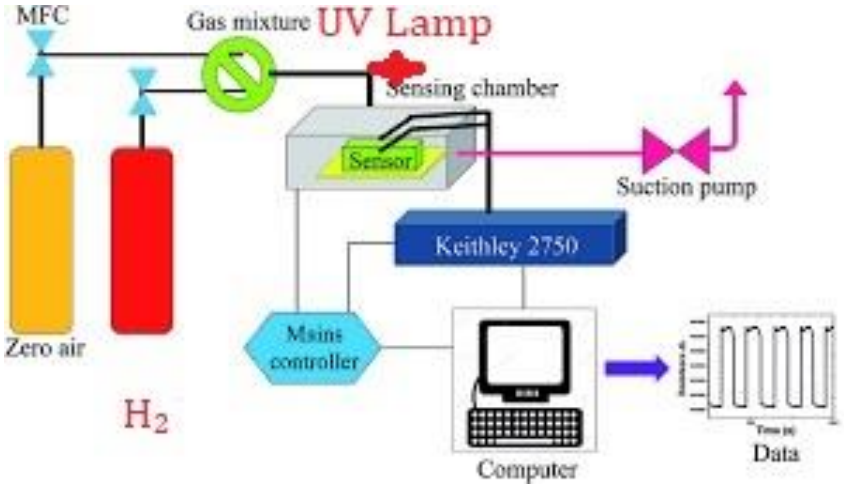
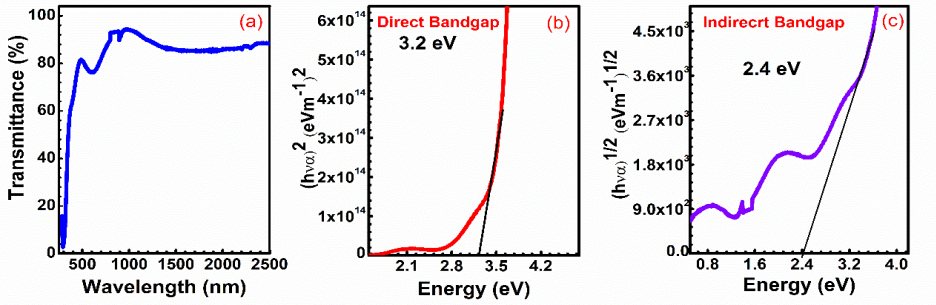


Fig.1 shows the gas-sensing setup

3. Material characterisation

3.1. Optical analysis

Optical studies of DC Magnetron sputtered vanadium oxide thin film sensor were performed using a wavelength range of 300nm to 3300 nm a UV-Vis spectrophotometer. Fig. 2(a) shows the transmittance of V_2O_5 thin film nearly 87%. Enhanced optical transmittance was observed in the range of wavelengths from 320 to 500nm. The coefficient of absorbance is given by the relation $(\alpha h\nu)^2 = A(h\nu - E_g)^n$ Where E_g is energy gap, h ν is photon energy, A is constant, and 'n' depends on the type of optical transition. Fig YY shows that $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ vs photon energy graphs for V_2O_5 thin films from which direct and indirect bandgap energy (E_g) values of the samples were determined from Taue's plots shown in Fig.2 (b &c) by extrapolation of the linear plots of at absorption coefficient (α) equal zero and the calculated values of direct and indirect bandgap values are 3.2eV and 2.4eV. In previous reports, the direct band gap of V_2O_5 thin films was calculated to be 2.22 eV from the plot of $(\alpha h\nu)^2$ versus hν [20,21].



Fig,2 (a) Transmittance spectra, (b & c) Taue's plot for optical direct and indirect band gap of V_2O_5

3.2.XRD analysis

The structural analysis of the V_2O_5 thin films has been analyzed under an X-ray diffraction study as shown in Fig.3, The XRD pattern shows V_2O_5 thin films of strongly amorphous nature and it was confirmed by (JCPDS card No.41-1426) data. Moreover, the amorphous nature exists at a small angle with a wider diffraction pattern due to the oxygen flow in the deposition process. The substrate temperature does not require enough to provide the necessary thermal energy to the atom to find the locations for further bonding, resulting in an amorphous structure [22].

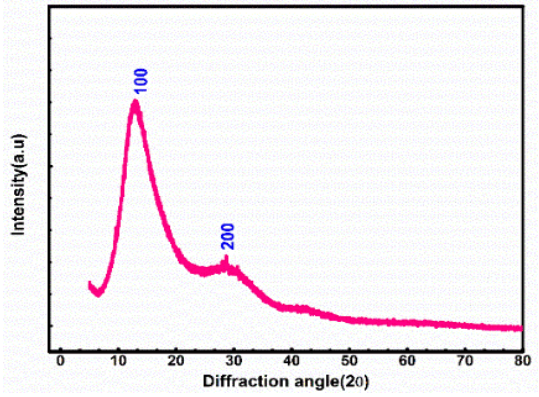


Fig.3, XRD pattern of V_2O_5 thin film

Previous report, the XRD pattern showed that DC reactive sputtered thin films of crystalline nature at 200°the deposition of the crystalline V_2O_5 phase occurs at around 200 °C in the case of DC reactive magnetron sputtering [23]. Modern surveys of RF magnetron sputtered V_2O_5 thin films also showed that as grown at room temperature have an amorphous structure [24].

3.3. Raman analysis

Fig.4, shows Raman spectra of V_2O_5 thin films noted at room temperature. The Raman spectra of the V_2O_5 thin films featured peaks at wavenumbers 151, 285, 410, 531, and 711. 769, 914 which were consistent with wavenumber values reported for crystalline V_2O_5.The connecting V-O bond is shown to have the highest stretching frequency of 769 cm^{-1}. The 531 and 410 cm^{-1} bands are attributed medium-range frequency of contributed V-O-V stretching mode, consistent with the medium range of order. The strong intensity shifted towards the low-frequency range of 285 cm^{-1} in a V-O-V bending mode, also which shows decreasing crystalline size.

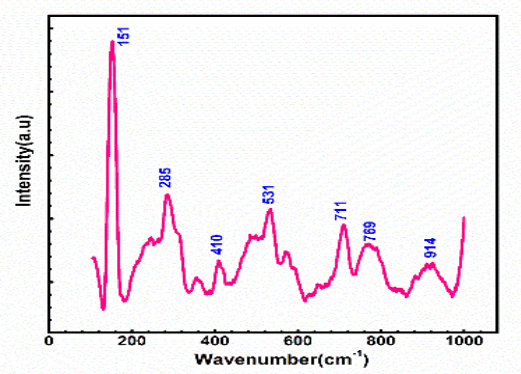


Fig 4 Raman Spectra of V_2O_5 thin films

3.4. Surface morphology studies (EDAX-SEM)

EDAX studies were performed to determine the elemental composition of the DC Magnetron sputtered V_2O_5 thin film. The composition of vanadium and oxygen was confirmed by EDAX analysis tools and atomic weight percentages are calculated as V 45.5%.O 19.1% Na 20.5% for vanadium and oxygen respectively from this study samples are specific contents values from EDX analysis. The surface morphology of the V_2O_5 thin film has been analyzed with the SEM images shown in Fig.5. The V_2O_5 thin films are pure homogeneous without any pinholes or cracks and cover the substrate well. Agglomeration of particles affects the uniformity of the V_2O_5 thin films. The particles are flower-like in shape being two-dimensional they possess a higher surface-to-volume ratio and from SEM analysis particle size was of the order of 100 – 150 nm.

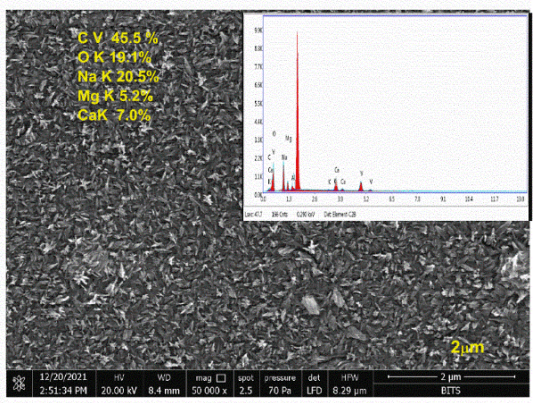


Fig.5, SEM EDX image of V2O5 thin film

3.5.PL Study

Photoluminescence (PL) spectroscopy is a non-destructive and contactless convenient instrument that presents essential information on the photochemical, electronic structure, optical, and point defects in the interfacial region of semiconductor materials. The PL spectrum is suitable for examining defects impurity levels and structure as prepared V_2O_5 thin films. Fig.6, shows PL spectra of V_2O_5 thin films wavelength range from 394 to 523 nm calculated at ambient temperature conditions by using excitation wavelength 350 nm. The PL spectra of the V_2O_5 thin film show an intense peak at 394 nm. The non-stoichiometric and oxygen-deficient V_2O_5 films are obtained. The high density of oxygen vacancies interacting with interfacial V_2O_5 thin films at room temperature conditions which the formation of a considerable number of trapped states within the band gap, giving rise to high PL intensity.

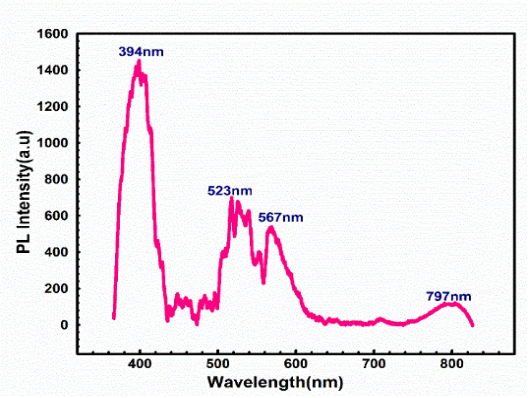


Fig 5 shows the photoluminescence spectrum

4. Results and Discussion

4.1. Gas sensing mechanism

The sensing mechanism of V_2O_5 thin films the resistive gas sensor is the change in electric current when the target gas passes through the surface of the samples, the microscopic presence of the electron transfer on the surface of the materials during the H2 adsorption and

desorption mechanism, whereas the composite material V_2O_5 thin film was is exposed to air the oxygen molecules in the air adsorb on to the surface of the materials [25], Meanwhile, oxygen molecules have a strong affinity of electrons detached from the conduction band. The H_2 gas combines with oxygen ions adsorbed proceeding the surface of the material, releasing electrons back to the conduction band of the materials, growing the carrier concentration, the width depletion layer decreasing and reducing the resistance of the material [26]. When UV light was exposed to hydrogen gas at a balanced condition of Fermi level, the conduction band electrons in the V_2O_5 thin film were responsible for the depletion region formation and also increased width of the potential barrier, In addition, the adsorption capacity of hydrogen molecules due to large surface area contributed a larger number of vacancy active sites, The more number of electron return to the conduction band of material which increases adsorption capacity of Hydrogen molecules, which further decreases the number of materials in the target gas resistance, due to this reason, gas sensing response improving.

4.2. Gas Sensing response of V_2O_5 thin film

The H_2 gas sensing response of the V_2O_5 thin film was evaluated both with and without UV illumination at a low operating temperature of 27°C. The gas sensor exhibited increased sensitivity to hydrogen at room temperature under both dark and UV illumination conditions. Interestingly, the results indicated higher sensitivity when the sensor was exposed to UV light compared to dark conditions. Further details of the gas sensing properties are provided in Table 1.

Cycles	Ist (UV- OFF)		2nd (UV-ON)		3rd (UV-ON)	
H_2 concentrations 20 ppm	H_2-IN	H_2-OUT	H_2-IN	H_2-OUT	H_2-IN	H_2-OUT
Current (µA)	0.836	1.69	0.942	1.981	0.989	2.25
Gas Sensing response (%)	84.4		104		126	

Table,1 shows the gas sensing response of V_2O_5 thin film

The gas-sensing response measurement incorporated varying UV light intensities. Under room temperature conditions, the electrical current of the V_2O_5 thin film sensor exhibited a proportional increase in the presence of UV irradiation, influencing the gas sensing response, as depicted in Fig. 6 (a, b, c, & d). The heightened photoelectric current, corresponding to increased UV light intensity, resulted from the rising electron concentration at the conduction band. Subsequently, the gas-sensing properties of the V_2O_5 thin films were examined when exposed to a hydrogen concentration of 20 ppm diluted in dry air at room temperature under specific UV light conditions.

During the initial cycle without UV light illumination, the impact of 20 ppm hydrogen gas caused a fluctuation in electrical current. Before the introduction of H_2 gas, the current measured 0.836µA, reaching a peak of 1.69µA upon exposure to H_2 gas. The gas sensing response during this cycle was nearly 84.4%, as depicted in Fig. 6b. In the subsequent cycle, UV light was employed during the exposure to H_2 gas, increasing electrical current. The calculated values were 0.942µA (H_2-IN) and 1.981µA (H_2-OUT). The gas sensing response for this scenario was approximately 104%, as illustrated in Fig. 6c.

The same procedure was repeated with UV light exposure to the V_2O_5 thin film sensor, leading to a current variation from 0.989µA (H_2-IN) to 2.25µA (H_2-OUT). The gas sensing response increased to 126%, as shown in Fig. 6d.

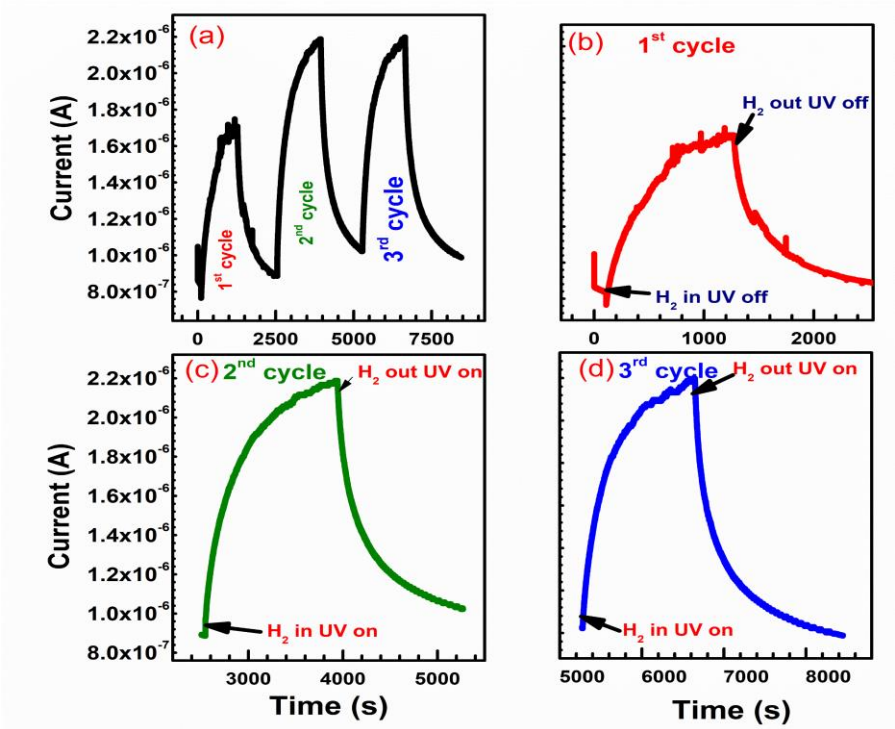


Fig.6 H_2 Sensing response (a) Three cycles (b) First cycle without UV Irradiation (c, d) second and third cycle with UV irradiation

4.4. Selectivity

The selectivity of V_2O_5 thin film to detect a particular gas, In this study only four gases were detected by the DC Magnetron sputtering method namely Hydrogen, Carbon dioxide, Nitrogen oxide, and Carbon monoxide, The comparative histogram for the selectivity of V_2O_5 thin film at 20ppm of each is shown in Fig.7, From the study that DC magnetron sputtered V_2O_5 thin film has good sensing behavior towards Hydrogen.

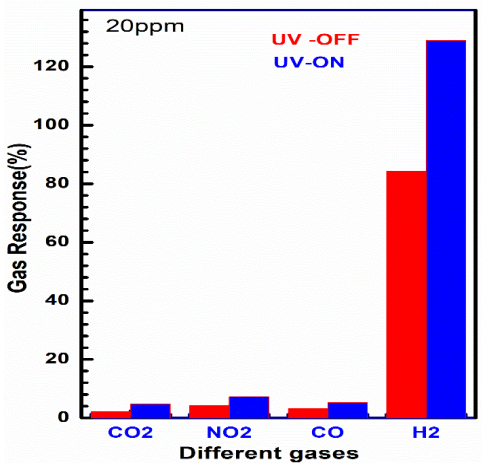


Fig.7, selectivity graph for different gases of V2O5 thin film

5. Conclusion

The DC Magnetron sputtered V_2O_5 thin films metal oxide gas sensor to investigate hydrogen gas sensing response examined with presence and absence of UV Light irradiation effect under room temperature. The V_2O_5 thin film structural, morphological, and optical properties are investigated. From X-ray diffraction analysis sputtered V_2O_5 thin film polycrystalline nature, and morphological investigation shows a small flower-like structure. The band gap energy of thin film calculated direct band energy 3.2eV and indirect band gap2.4eV respectively. The UV light (365nm, 3,4 mW/cm2) was irradiated to V_2O_5 thin film sensor materials The sensor also exhibited good repeatability for H_2 gas detection and good selectivity concerning reducing gases.

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Author contributions

Both authors contributed to the study conception and design, Material preparation, data collection, and analysis were performed by A. Paramesvaran and M. Balachandramohan. Both authors read and approved the final manuscript.

Availability of Data

The datasets analyzed during the current study are available from the corresponding author upon reasonable request.

Declarations

The author declares that there is no conflict of

interest.

Ethical Compliance

The authors declare that there is no ethical compliance.

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