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RESEARCH PAPER

The Effect of Substrate Temperature on the Nanostructured V_2O_5 Thin Films, Studying Their Structural, Optical Properties and Testing as Gas Sensors

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ABSTRACT

The current research aimed to improve the structural, optical, and sensing properties of vanadium pentoxide (V_2O_5) thin films produced via spray pyrolysis on varying substrate temperature (300–500 °C). Findings demonstrate that increasing the temperature drastically enhanced the crystal structure, as demonstrated by increased X-ray diffraction (XRD) peaks with the development of orthorhombic crystal structure. An increase in grain size is noted from approximately 16.5 nm at 300 °C to approximately 28.7 nm at 500°C according to the Scherrer equation, with a reduction in density of crystalline dislocations. The films showed quite low absorption in the visible region, with the optical energy gap (Eg) increasing from 3.15 eV to 3.7 eV as the temperature increased. This was attributed to quantum confinement and improved crystal development, and shown by AFM images of atom beam microscopy of a smooth surface with larger grain size and less defect on the surface at higher temperatures. In gas sensing tests, films deposited at 400 °C exhibited very significantly increased sensitivity to propane (C_3H_8) and carbon monoxide (CO) at 150 °C but had the highest sensitivity to nitric oxide (NO) at 50 °C. This is due to the process of redox reaction occurring on the surface of V_2O_5 in which reducing gases like CO enhance the conductivity by liberating electrons while oxidizing gases like NO lower the conductivity by capturing electrons. The thus research established that substrate temperature control during fabrication is necessary to achieve optimal features of V_2O_5 with a potential promising application for nonlinear optical devices, lithium batteries, and high-performance, low-cost gas sensors.

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INTRODUCTION

The modern research focused on applied physics have shown a growing interest in thin films of transition metal oxides because of their unique responses for varying optical and structural properties depending on the chemical composition and fabrication techniques needed to grow these films [1-3]. In this case V_2O_5, pentoxide, also looks like an interesting material because of its applications in energy storage, optical, and even sensing devices [4,5]. These features include, but are not limited to, multiple valence states (V^{5+}, V^{4+}), a wide optical bandgap (2.5 – 2.8 eV), [4] and stability both thermally and chemically, which

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makes him a perfect candidate for developing advanced materials such as rechargeable lithium batteries, supercapacitors, and infrared detectors.

The chemical, physical, and optical characteristics of V_2O_5 thinfilms is largely determined by the deposition parameters of the film like, concentration of the chemical solution, rate of the spray and temperature of the substrate [6]. For example, increasing the substrate temperature, leads to improved crystal structure as a result of enhanced mobility of atoms at the surface leading to more crystal grains of increased size and lowered structural defect. Study conducted by which examined the effect of temperature during the process of deposition, showed that increasing the temperature to 450C drove the formation of an orthorhombic crystal structure as observed by increased peak intensity in X-ray diffraction (XRD). Nonetheless, [7] Study of the effect of thermal annealing on films noticed that photosensitive properties including the refractive index are greatly influenced by film thickness and growth temperature. Ach high values of refractive indices were noted at smaller wavelengths (400nm) which is advantageous for the films to be used in nonlinear optical devices.

V_2O_5 films have been fabricated using a number of methods, such as: Pulsed laser deposition PLD: This produces highly crystalline films, but it is quite costly [8]. Spray pyrolysis [1]: A cheaper method that enables controlling the composition of chemicals and the thickness, which is applicable for large area layers. E-beam evaporation [9]: Guarantees clean films, but there is very poor control of the porous film structure.

The current investigation entails the study of the variations of the substrate temperature impact towards the morphological, optical, and gas sensing attributes of V_2O_5 films prepared utilizing the spray pyrolysis method.

MATERIALS AND METHODS

V_2O_5 Samples were prepared by depositing films on glass substrates under chemical spray pyrolysis (CSP). This preparation was carried out after cleaning the substrates with detergent, ethanol and distilled deionized water. The nozzle used in spraying also presents 15 cm distance from the substrates and a flow rate of 8 ml per minute. Compressed air with a pressure of 7 N/cm² as the carrier gas used. The spray solution initially contained a certain amount of VCl3 powder (99.9% purity) by dissolving it in 100 ml of deionized water. Thin films were obtained by preparing a solution of 0.1 M at different substrate temperatures (Ts=300-500° C) using a deposition spray rate of 10 mL/min. The reaction to form the thin films of V_2O_5 using CSP is expressed as:

$$4VCl_3\ (s) + 5O_2 \rightarrow 2V_2\ O_5(s) + 6Cl_2\ (g) \uparrow$$

The V_2O_5 thin films obtained are homogenous and free of pinholes while also showing sufficiently well adherence to the glass substrate. Interestingly enough, since vanadium enters as V_5^+ in the lattice V_2O_5, all the brilliant, pale honey seen on the glass substrate stands out as such. Fig. 1 shows

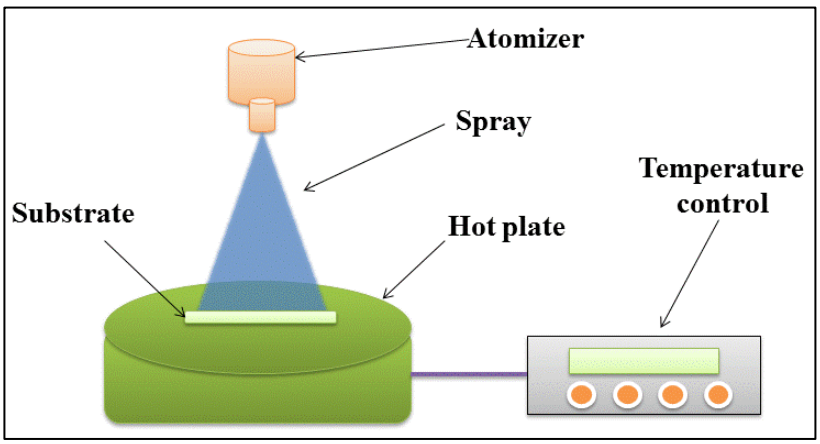

Fig. 1. Spray pyrolysis system diagram for preparation V_2O_5 thin film.

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a schematic of the thermal spraying mechanism used to prepare the samples in this research.

RESULTS AND DISCUSSION

By using a PANalytical X-Pert Pro MRD diffraction system, with Cu Kα radiation (λ = 1.54 Å), for the structural analysis of the V_2O_5 thin films. Fig. 2 shows the different XRD patterns of V_2O_5 thin films prepared at different substrate temperatures ranging from 300 to 500 °C.

The peaks at 20.14158, 21.64608, 30.65432, 37.78656 and 45.6392 correspond to the (001), (101), (301), (211) and (002) planes respectively. The patterns confirm the formation of V_2O_5 thin films with orthorhombic symmetry [10], where well-defined layered structure, JCPDS Card No. 00-

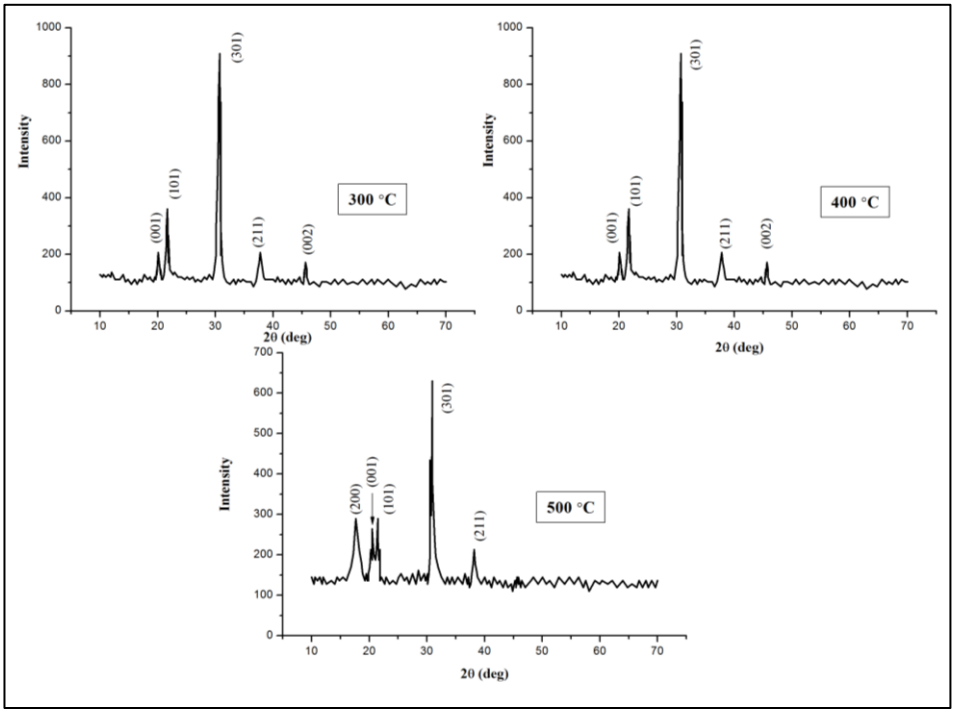

Fig. 2. XRD spectra of V_2O_5 thinfilm at different substrate temperature.

Table 1. Crystalline size (D), Lattice Strain (ε), Dislocation Density (δ), of V_2O_5 thinfilm at different substrate temperature.

Variation of Temperatures (°C)	(hkl)	2θ(deg)	FWHM	D (nm)	δ ×10^{-3} (nm^{-2})	ε×10^{-3}	Avg. D (nm)	Avg. δ	Avg. ε
300	001	20.1415	0.3817	21.1363	2.2384029	9.37862	20.6312	2.80896	7.31349
	101	21.6460	0.3933	20.5633	2.3649087	8.97715			
	301	30.6543	0.4975	16.5566	3.6479967	7.92050			
	211	37.7865	0.5760	14.5773	4.7059303	7.34361			
	002	45.6392	0.2842	30.3225	1.087597	2.94757			
400	001	20.1415	0.3817	21.1363	2.238403	9.37862	20.6310	2.80902	7.31357
	101	21.6460	0.3933	20.5627	2.365029	8.97738			
	301	30.6543	0.4975	16.5563	3.648143	7.92066			
	211	37.7865	0.5760	14.5773	4.70593	7.34361			
	002	45.6392	0.2842	30.3225	1.087598	2.94757			
500	200	18.6539	0.2880	27.9490	1.280165	7.65256	23.5220	2.348077	7.585447
	001	20.8345	0.2747	29.3981	1.157073	6.52103			
	101	21.5312	0.4886	16.5478	3.65187	11.2142			
	301	30.45285	0.54846	15.0117	4.437521	8.792073			
	211	37.60079	0.29237	28.70345	1.213757	3.747273			

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001-0359.

Fig. 2 shows the X-ray diffraction (XRD) spectra of V_2O_5 thin films, which show peaks characteristic of the polycrystalline phase. Increasing the substrate temperature increased the crystallinity of the thin film. The increased density resulting from grain growth is related to the increased crystallinity resulting from higher substrate temperature.

The thin films show preferential growth along the (301) direction as an increase of the substrate temperature. Fig. 2 depicts how the intensity ratio (301) to (002) varies with substrate temperature. the fluctuation in intensity of diffraction peaks becomes more pronounced at a substrate temperature of 400 °C.

Fig. 2 shows that as the substrate temperature increases, the intensity of the (301) plane increases sharply up to 400 °C, beyond which it starts to decline at higher substrate temperatures. However, the intensity of the (101) plane is increased with increasing substrate temperature signifying some effect of crystal orientation [11].

By Scherer's equation(2), mean grain size of as-deposited films was determined [12]:

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \tag{2}$$

where β is full width at half maximum (FWHM) in radians along the (301) of the XRD peak, k denotes the wave length of the X-ray (kcuka = 1.5406 Å), and h means the Bragg diffraction

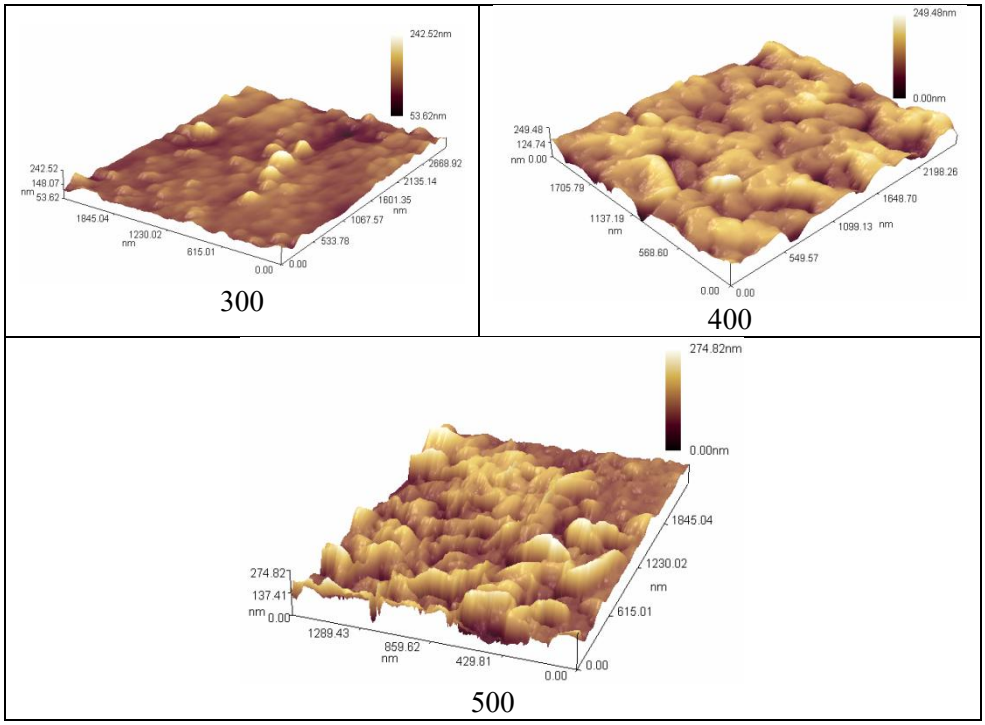

Fig. 3. AFM topographies of V_2O_5 thinfilm at different substrate temperature.

Table 2. Lattice parameters of V_2O_5 thin films.

Substrate temperature (°C)	Lattice parameters		
	a (A)	b (A)	c (A)
300	7.98	6.5	4.53
400	7.93	6.9	4.4
500	7.9	7.1	4.28

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angle. Table 1 summarizes the data obtained from the XRD diffraction study.

In general, the lattice parameters have been computed from the following formulae [13]:

$$d_{hkl} = \frac{1}{\sqrt{(h^2/a^2) + (k^2/b^2) + (l^2/c^2)}} \quad (3)$$

Let a = b = c for an orthorhombic lattice. the (hkl) being the Miller indices of the reflecting planes observed in the XRD diffraction spectrum, and dhkl their interplanar distances. The findings are presented in Table 2.

Most importantly, the strains arising from the misfit markedly influence the structural characteristics due to the geometric discrepancies at the interphase boundaries between crystalline lattices of films and substrates. Such forces might induce strains in the films. The strain (ε) value of the V_2O_5 film for the (301) peak is calculated with the following formula [14]:

$$\varepsilon = (\beta \cos\theta)/ 4 \quad (4)$$

where β is the full-width at half maximum of the peak in question. The computed values for the (301) peak are shown in Fig. 1. Strain increases with the increase in substrate temperature.

Dislocation density (δ), defined as the length of dislocation lines per unit area (m^{-2}), is then calculated through eq.5 [15]. The dislocation density of the film for the (301) peak is calculated by the following equation:

$$\delta = 1/D^2 \quad (5)$$

The lower d value is about 3.64799676 m-2 for deposition at 300°C on the (301) peak, while the upper value is 4.437521 m^{-2} for deposition at 500°C. Refer to Table 1. This confirms there is an inverse relationship between the size of the crystal and the density of dislocations. The importance of dislocation density is then explained in the fracture of the grain. An increase in strain, which occurs at the same time as the increase in grain boundaries, also gives rise to an inverse relationship with grain size.

Fig. 3 shows the AFM topographies of the V_2O_5 thin film. Each film was characterized by similar forms of small grains and low surface roughness. The crystallinity of the film increases, and the size of the crystallites increases with more time of deposition. Such a finding is in agreement with the data of the XRD presented in Fig. 1.

The absorbance differences between the samples of vanadium oxide thin films are shown in Fig. 4 against the wavelengths λ at different substrate temperatures. The absorbance spectrum indicates that vanadium oxide films have very low absorbance within the visible region; this

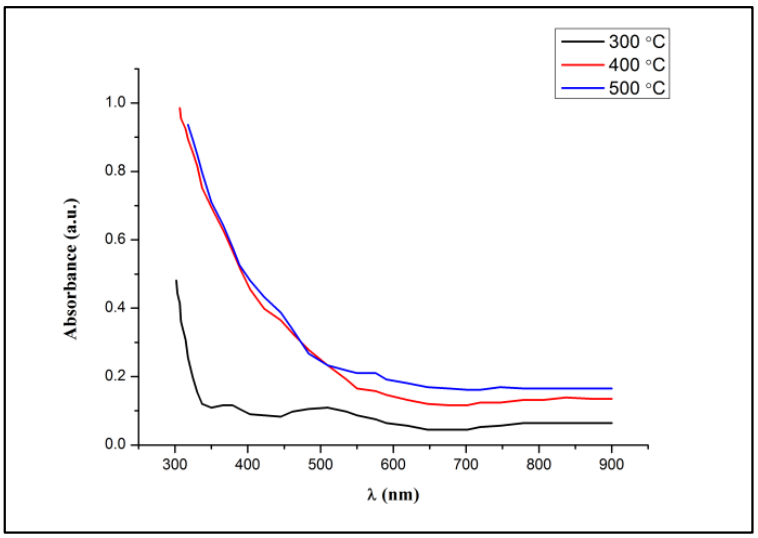

Fig. 4. Optical Absorbance versus wavelength for V_2O_5 films with different substrate temperatures.

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is one of the characteristics of vanadium oxide. Morphological changes may be responsible for this and decrease in the hydroxide accumulation along grain boundaries.

Using UV-visible absorption spectrum and the Tauc relation, the energy gap shown in Fig. 2 is the property of the produced vanadium oxide thin films corresponding to different substrate temperatures. Absorption coefficient (α) is to be calculated first as per relation [16] in order to obtain band gap (Eg) values of films.

$$\propto = (1/t) \times \ln(1/T) \quad (6)$$

where t is the film thickness and T is the transmittance. The following relation [17] yields the optical band gap of the V_2O_5 thin film:

$$\propto h\nu = A(h\nu - Eg)^{1/2} \quad (7)$$

where a constant is denoted by A and photon energy by hν. Plotting $(\alpha h\nu)^2$ against (hν) and projecting the linear portion of the plot to zero absorption ($(\alpha h\nu)^2 = 0$) yields the Eg value.

The as-deposited thin film presented an energy gap of 3.15 eV, which is greater than the 2.4 eV reported elsewhere [18]. At the nanoscale, quantum confinement effect takes place. Following annealing, in the case of the sample, there appears to be a shift of the absorption edge to longer wavelengths, with more pronounced sharpening of the edge at 500 °C substrate temperature, which may have arisen due to favoring crystal growth and decreasing crystal defects as the substrate temperature was increased, thus reducing the energy of the tails close to the energy band edge. So another cause that may have raised an optical energy gap to 3.7 eV is the increasing crystalline size with the rise in temperature as in Fig. 5.

Different substrate temperatures were employed in gas-sensitive V_2O_5 film preparation using the chemical vapor deposition (CP) process. To study gas sensing behaviors, I have selected for analysis sample 2 fabricated in this study as a gas sensor device at a substrate temperature of 400 °C.

To optimize sensor operating temperature, the temperature was varied between 50 and 150 ◦C with increments of 50 ◦C. These experiments were conducted by inoculating a definite total of several test gases (C_3H_8, CO, NO) into a chamber [19]. The sensitivity of V_2O_5-based gas sensors was determined for different concentrations of C_3H_8 (1500 ppm), CO (250 ppm), and NO (900 ppm) at raised temperatures. The equation used for the calculation of the sensitivity was S_gas = (Ggas − Gair)/Gair, with Ggas being defined as the gas conductance response (during the presence of the gas) minus Gair which is in belief of air conductance at the beginning of contact time.

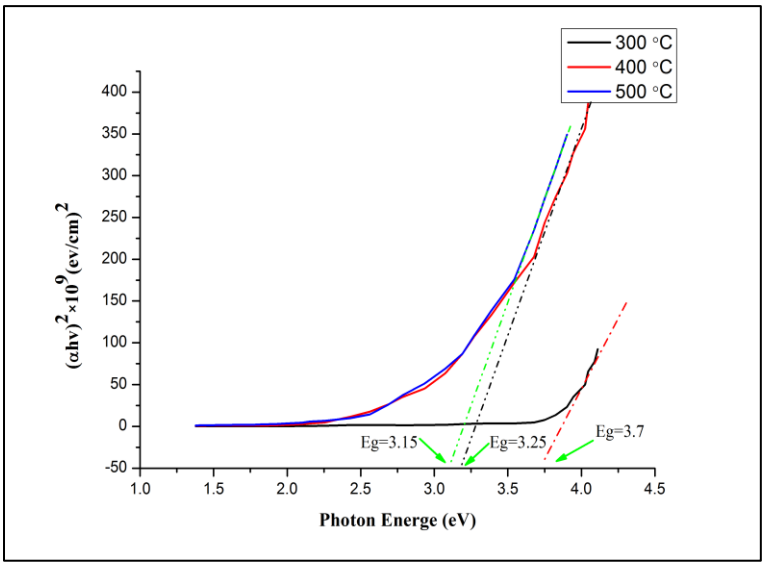

Fig. 5. The optical band gap of V_2O_5 thin films deposited by different substrate temperatures.

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$$S_{gas} = G_{gas}/G_{air} = R_{air}/ R_{gas} (=R_{gas} - R_{air}) \quad (8)$$

Fig. 6(a) presented gas sensitivity values for the V_2O_5 film to C3H8, prepared at a substrate temperature of 400 °C. The investigation confirmed that 150 °C was the preferred operating temperature for a V_2O_5 gas sensor in the detection of C3H8 gas. As indicated in Fig. 6(b), with an increase in working temperature, sensitivity goes up, suggesting that CO gas sensitivity had a maximum at 150 °C.

Since CO and C_3H_8 gases both led to an increase in sensitivity, it is assumed that the process involves the adsorption of a decreasing gas molecule either on the oxide surface itself or on some specific catalysts [19,20]. As per Eq. (9) shown, this means that an adsorbing CO molecule interacts with a surface oxygen ion (O−) to release a trapped electron into the V_2O_5 conduction band thereby increasing conductance.

$$CO_{gas} + \frac{1}{2O_{2\ surface}} \rightarrow CO_{2\ gas} + e^{-} \quad (9)$$

As indicated by [19], it is the V_2O_5 surface, with surface oxygen ions, on which the oxidation of NO gas arisen. In the course of this process, an adsorbing NO molecule interacted with a surface oxygen ion, consuming an electron and forming NO_2 molecules (Eq. (10)). When it comes to surface oxygen ions, the absorbent NO2 molecules created Surface acceptance levels that were deeper. However, O_2^- ions transfer some bound electrons to physisorbed NO_2 molecules, forming NO_2^- species (Eq. (11)), which is accompanied by the lowest conductance [19], while the majority of the NO molecules would react directly with surface V_2 ions (Eq. (12)). The following can probably be

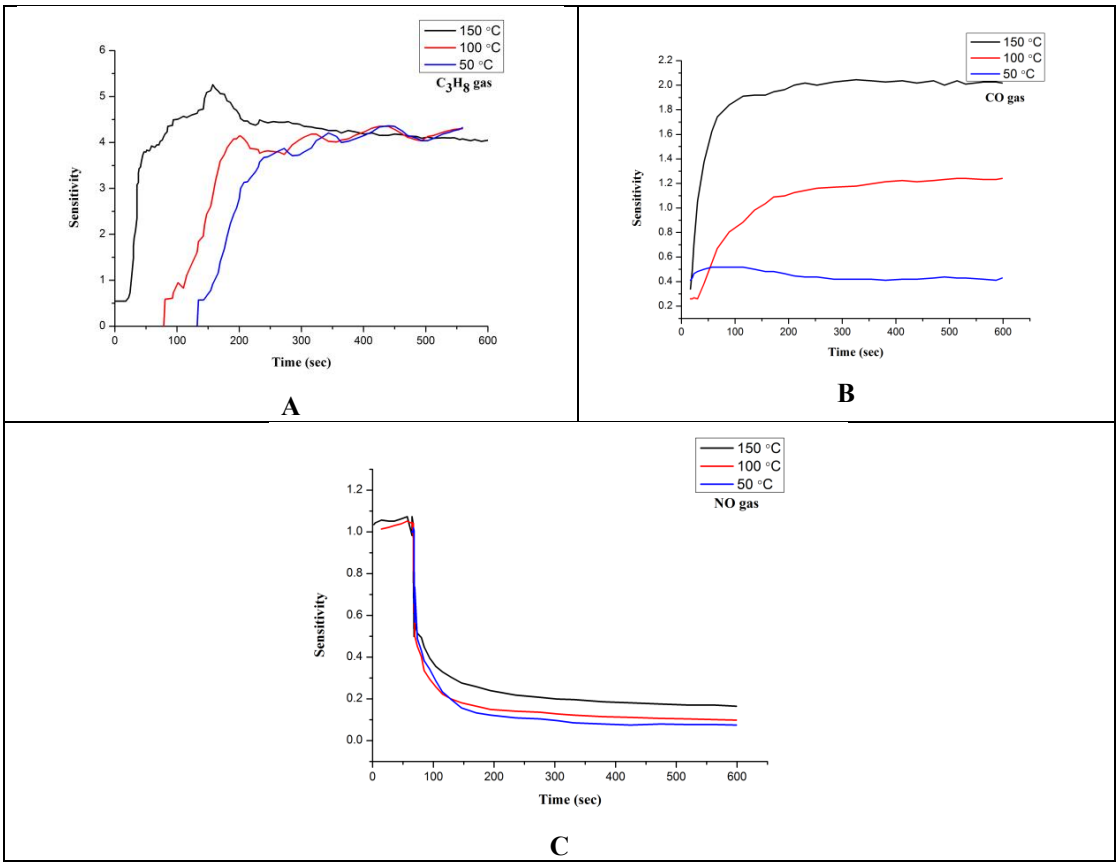

Fig. 6. Sensitivity properties of V_2O_5 thin film sensors prepped at substrate temperature 400 °C for (a) C_3H_8, (b) CO and (c) NO gases.

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the overall reactions:

$$NO_{gas} + O_{2\ surface} + e^- \rightarrow NO_{2\ gas} - \quad + O^- \quad (10)$$

$$NO_{2\ gas} + e^- \rightarrow NO_2 - \quad (11)$$

$$NO_{2\ gas} + O_{2\ surface} + 2e^- \rightarrow NO_2 - \quad + 2O^- \quad (12)$$

At these test conditions of working temperature 50 ◦C, one record sharp sensitivity of V_2O_5 films at 60s NO gas exposure. As the sensor working temperature increases, sensitivity and response towards NO gas drop. Thus, 100, 150, and 50 ◦C were thought to be the optimum working temperatures for C_3H_8, CO, and NO gases, respectively. Such V_2O sensors are low-cost and simple for fabrication. Such CP technique, which shows remarkable gas detection performance could easily be distributed into metal oxide gas sensors.

CONCLUSION

This study proved the influence of substrate temperature (300-500 degrees Celsius) on the structural, optical and gas sensing properties of V_2O_5 thin films obtained by spray pyrolysis. Increasing substrate temperature improved crystallinity since more XRD peaks associated with the orthorhombic phase appeared. The grain size increased from around 16.5 nm, for 300ç, to about 28.7 nm at 500 °C, accompanied by reduced dislocation density, indicating better crystal quality. The films showed little absorption in the visible and increased in optical bandgap with increasing temperature from 3.15 eV to 3.7 eV, attributed to quantum confinement effects and lesser defects. From the AFM analysis, smoother surfaces and bigger grains were found with increased temperature which correlates with these structural improvements. Gas-sensing evaluations showed that films present sensitivity with respect to temperature: thus for films deposited at 400°C maximum sensitivity at 150°C was found for C_3H_8 and CO while for NO it was at 50 °C. This is attributed to redox interactions on the surface of the V_2O_5, which in the presence of reducing gases such as CO serve to release electrons and enhance conductivity while electrons are consumed in the case of oxidizing gases, for instance, NO, thus decreasing conductivity. These results underline the predominant role of substrate temperature influencing the features of V_2O_5 films and put it across as an economic, high-performance material for nonlinear optical devices, lithium-ion batteries, and selective gas sensors. In future studies, hybrid deposition techniques or doping can be employed to boost sensitivity and stability even further.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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