Structural, Optical and Morphological Properties Of Zn And Mg Co-Doped V₂O₅ thin Film nanostructures

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**Abstract:** The research study reveals metallic co-doping of Zinc(Zn) and Magnesium (Mg) on vanadium pentoxide(V₂O₅) thin film nanostructures by spray pyrolysis deposition technique. The study findings have been made into how the morphological, structural and optical properties of the materials change for the different co-doping percentage of 1%, 3%, 5%, 10% of Zn-Mg. X-ray diffraction (XRD) clearly shows an orthorhombic crystalline structure with polycrystalline nature. The dopant Zn and Mg infused into the V₂O₅ matrix and is confirmed by EDAX images. A field emission scan electron microscope was used to examine surface morphology which reveals that grain structure has been modified by increasing the doping content. It is evident from the atomic force microscopy (AFM) images that the effect of Zn and Mg on V₂O₅ thin film has enhanced surface roughness. The transmittance and energy bandgap (Eg) of the film found to be decreased with an increase in doping concentration whereas absorbance varies with doping levels. The research findings suggest that the Zn-Mg co-doped V₂O₅ thin films could be a potential source for energy, optical and sensor-based device applications.

**Keywords:** Spray Pyrolysis; Co-doped V₂O₅; XRD; Crystallinity; FESEM; Surface morphology.

1. **INTRODUCTION**

The advancement in the field of nanomaterials like transition metal oxides V₂O₅ and their physiochemical properties has attracted the attention of researchers in recent years[1-4]. The area of application of metal oxide-based V₂O₅ devices is mainly in storage devices, UV detectors, sensors, electro-optical devices, energy harvesters, transistors, piezoelectric devices etc. The V₂O₅ properties like electrical resistivity, n-type conductivity, magnetic susceptibility, high specific power, transmission, high energy density, variable oxidation states of V₂O₅ make the above applications possible [5-14].

Recent research on various oxides of vanadium ions could vary the properties by anoxide surface formation and chemisorption [15-18]. The electric conductivity of V₂O₅ will enhanced during interaction with reducing gases during which V⁵⁺ species changes to V⁴⁺. The concentration of oxygen nonstoichiometric (V₂O₅-x) due to oxygen vacancies are responsible for the semiconducting properties of V₂O₅.

Doping is a key part of evaluating the physical properties and uses of semiconductors. This concept has been empirically demonstrated by evidence-based applications in the industries of semiconductors. Minor proportions of impurities affect the carrier ions and electrical conductivity of substances. The solution of bipolar doping and compensation problems in semiconductors is proposed for co-doping. Co-doping in particular can be effective in improving the solubility of dopant, increasing activation rates by reducing acceptors and donorising energies and increasing carrier mobility [19, 20].

Zinc and magnesium were added to enhance the optical, structural, electrical and morphological properties of V₂O₅ thin film. Both Zn and Mg ions easily enter into V₂O₅ crystal lattice and substitute the V²⁺ position of the crystal because the ionic radius of these transition metals element which are substantially lower than that of V²⁺. The spray pyrolysis thin film deposition method is followed to study how a Zn and Mg co-doping allows easy control and replace desired elements within required amounts in the precursor solution and affects the morphological, microstructural and optical properties of V₂O₅ thin films.

The grain size and crystallinity of the thin films will decide the selectivity and sensitivity of a gas sensor which is measured in terms of change in the resistivity of a gas when it comes in contact with an oxide layer [21].
Considering this co-doping by spray pyrolysis method is ideally suited for thin film deposition based on V₂O₅. It is important to find new appropriate doping substances that do not change much of the structure of the V₂O₅ crystals to obtain V₂O₅ thin film which has wide optical band gap with improved electrical conductivity. The work is focused on the fabrication and study of structural properties of Zn and Mg co-doped for the development of devices on sensors and energy-based applications.

2. EXPERIMENTAL WORK
2.1 Sample Preparation
The thin films of pure V₂O₅ and Zn-Mg co-doped with varying percentages in equal volumes were fabricated by spray pyrolysis method on substrate material like glass.[22] The concentrated HCl is added in drops to ammonium metavanadate in 100ml distilled water with concentration of 0.02 M, the standard solution of V₂O₅ was prepared. By adding V₂O₅ precursor solutions with magnesium chloride (MgCl₂) and zinc acetate(Zn(CH₃COO)₂·2H₂O) in equal quantities, Zn-Mg co-doped thin films of 1%, 3%, 5% and 10% concentrations were fabricated. The solution is continuously sprayed on the well-purified glass substrate surface at 350°C.[23]
The conditions for depositing the thin films on glass substrate are listed in Table 1. The thickness of approximately 200 nm of thin films was prepared and maintained for about 350 °C for about one hour in a heated air oven to clear other impure residuals that exist in the solutions.

<table>
<thead>
<tr>
<th>spray Parameters</th>
<th>Optimum Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass substrate temperature</td>
<td>350°C</td>
</tr>
<tr>
<td>Ammonium metavanadate</td>
<td>0.02 M</td>
</tr>
<tr>
<td>Solution concentration of Magnesium chloride</td>
<td>0.02 M</td>
</tr>
<tr>
<td>Solution concentration of Zinc acetate</td>
<td>0.02M</td>
</tr>
<tr>
<td>Solvent</td>
<td>Deionised water</td>
</tr>
<tr>
<td>Volume % of Zn &amp; Mg in equal quantities</td>
<td>1, 3, 5, 10 and 20</td>
</tr>
<tr>
<td>Air Pressure</td>
<td>2 bars</td>
</tr>
<tr>
<td>Nozzle to substrate distance</td>
<td>24 cm</td>
</tr>
<tr>
<td>Solution spray rate</td>
<td>1 ml/min</td>
</tr>
<tr>
<td>Nozzle diameter</td>
<td>0.8 mm</td>
</tr>
<tr>
<td>Solution spray time</td>
<td>≈ 10 mins</td>
</tr>
</tbody>
</table>

2.2 Characterization techniques
The undoped V₂O₅ and Zn-Mg co-doped V₂O₅ thin films thickness have been measured by the gravimetric weight difference method using the microbalance. An approximate 200 nm uniform thick films were fabricated by spray pyrolysis. The Bruker’s XRD was used for measuring diffraction angle 2θ at a wavelength of 1.5406 Å. The microstructural particle in the film is analysed using FESEM images. The elemental composition is ensured by the EDAX spectrum and AFM images will help in the surface roughness measurement of films. The UV-visible spectrophotometer helps in finding the optical bandgap (Eg), transmittance and absorption coefficient of the films.

3. RESULTS AND DISCUSSIONS
3.1 XRD study
X-ray Diffractometer through the precise range of 10° to 75° having the wavelength of 1.5406 Å help in structural properties study of film and is shown in Figure 1. The XRD associated with the planes (2 0 0) with diffraction angle(2θ)= 12.28° indicate the polycrystallinity nature of films and are crystallized with orthorhombic structure.
3.2 Morphological properties study

Microscopic characteristics of the prepared Zn-Mg co-doped V₂O₅ thin films analyzed by FESEM has a huge impact on the thin film’s structural properties. Figure 2 (a-e) shows images of FESEM for pure V₂O₅ and Zn-Mg co-doped V₂O₅ thin films.

At 1% co-doping, uniform and evenly distributed V₂O₅ was observed with very few doping of Mg and Zn. For 3% of co-doping, a void was observed and the increased void content was found difficult to handle. But with more dopant integration, this structure transforms into a platue-like structure which was visible in 5% and is increased compared to 3% co-dopant. The random distribution with a slight increase in surface roughness is visible here. As co-doping increased to 10%, the size and shape of co-dopants were almost uniform and oriented in the same direction with high surface roughness. However, the concentrations of the dopants (Zn and Mg) increased the grain sizes of the films.

(a) Pure V₂O₅ (b) V₂O₅ with 1% Zn-Mg
(c) $\text{V}_2\text{O}_5$ with 3\%$\text{Zn-Mg}$

e) $\text{V}_2\text{O}_5$ with 10\%$\text{Zn-Mg}$

Fig. 2: FESEM images of a) pure $\text{V}_2\text{O}_5$ b) 1\% c) 3\% d) 5\% and e) 10\% $\text{Zn-Mg}$-doped $\text{V}_2\text{O}_5$ thin films

The spectral peaks in the EDAX images have revealed the elements present in the prepared co-doped films and figure 3 shows the presence of V, O, and co-dopants Zn, and Mg.

Fig 3 (a) EDAX spectrum of (a) pure $\text{V}_2\text{O}_5$ and (b) Zn-Mg co-doped $\text{V}_2\text{O}_5$ thin films

3.3 Optical properties analysis

Electron transitions studies of undoped and Zn-Mg co-doped $\text{V}_2\text{O}_5$ thin films have been analyzed by absorption spectra and exhibits ultraviolet photons with their energy. Wavelengths in the range 300 nm – 800 nm by UV-Visible spectrophotometer is shown in figures 4. The sudden decrease in absorbance with wavelengths while transmittance increases with wavelength were observed especially in the case of 3\% and 5\% co-doping which could be because of a change in crystallinity. It indicates that co-doping at other than these concentrations have little effect on crystal dimensions.
Structural, Optical and Morphological Properties Of Zn And Mg Co-Doped V_{2}O_{5} thin Filmnanostructures

Fig. 4(a): Wavelength Vs Absorbance for the deposited V_{2}O_{5} films and Fig. 4(b): Wavelength Vs Transmittance for the undoped V_{2}O_{5} and Zn-Mg co-doped films.

Fig. 5: Plot of αhv^2 Vs Energy (E_g) for Zn-Mg co-doped V_{2}O_{5} films. The direct energy band-gap (E_g) of the co-doped thin films were calculated by the tauc plot [24]. The E_g value in the range of 3.77eV to 4.07eV in V_{2}O_{5} thin films for different co-doping concentration levels was observed which is shown in figure 5. The E_g for pure V_{2}O_{5} is 3.92 eV however it is observed that the value decreases approximately to 3.80 eV for 1% and 10% concentration. E_g will increase for 3% and 5% co-doping concentration levels. It is clear that concentration levels 3% and 5% will play a major role in optical device applications and is useful in low band energy photovoltaic application.

3.4 Atomic Force Microscopy (AFM) study

![AFM images](image_url)
e) 10 % dope of Zn-Mg

Fig. 6: AFM images of a) Undoped V$_2$O$_5$ b) 1% c) 3% d) 5% e) 10% Zn-Mg co-doped V$_2$O$_5$ thin films

The average surface roughness from the AFM images study (In figure 6) shows an increase in roughness from 31.5 nm to 69.4 nm with Zn-Mg co-doping. The presence of ‘O’ vacancy present in the films is responsible for the high surface roughness. The change in sharp grain shapes to smooth grain size with the increased co-doping is also evident from FESEM images.

4. CONCLUSIONS

The thin films using the spray pyrolysis technique is adopted for fabricating undoped and Zn-Mg co-doped V$_2$O$_5$ films. The Zn-Mg co-doping effect in V$_2$O$_5$ thin films is very much influential on the structural and morphology of thin films and enhancement in linear optical properties have been observed. The XRD indicate the polycrystalline nature of films with orthorhombic phase along the plane (200). The images of FESEM clarify that the undoped film is nonhomogeneous compared to the co-doped films, which is evident from surface roughness values. The prepared composition of the film ensure the expected elements of the films. The Zn-Mg co-doping increases the surface roughness of the films. The bandgap energy found to be varying about 7% with the different co-doping levels of Zn-Mg. The results obtained from these studies suggests that the Zn-Mg co-doped on V$_2$O$_5$ films are suitable for low band energy and gas sensor-based applications.

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