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 fused 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 films have 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 researches on vanadium oxides could vary the properties by anode 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 thermal conductivity 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 the V₂O₅ crystal lattice and substitute the V⁵⁺ position of the crystal because the ionic radius of these transition metals element which are substantially lower than that of V⁵⁺.

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 a required amount 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 the 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 V$_2$O$_5$. It is important to find new appropriate doping substances that do not change much of the structure of the V$_2$O$_5$ crystals to obtain V$_2$O$_5$ 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 V$_2$O$_5$ 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 V$_2$O$_5$ was prepared. By adding V$_2$O$_5$ precursor solutions with magnesium chloride (MgCl$_2$) and Zinc acetate (Zn(CH$_3$COO)$_2$·2H$_2$O) 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.

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

2.2 Characterization techniques

The undoped V$_2$O$_5$ and Zn-Mg co-doped V$_2$O$_5$ thin films thickness have been measured by the gravimetric weight difference method using the microbalance. An approximate 200nm 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 V_2O_5 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 V_2O_5 and Zn-Mg co-doped V_2O_5 thin films.

At 1% co-doping, uniform and evenly distributed V_2O_5 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 V_2O_5 (b) V_2O_5 with 1% Zn-Mg
(c) $\text{V}_2\text{O}_5$ with 3 \% $\text{Zn-Mg}$

![FESEM images](image)

(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

These 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.

![EDAX spectrum](image)

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.
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.

![Graph showing absorbance vs wavelength for V$_2$O$_5$ films with different dopings.]

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 3.77 eV to 4.07 eV 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 of V$_2$O$_5$ films with different dopings.]

- a) Pure
- b) 1% dope of Zn-Mg
- c) 3% dope of Zn-Mg
- d) 5% dope of Zn-Mg
e) 10 % dope of Zn-Mg

Fig. 6: AFM images of a) Undoped V₂O₅ b) 1 c) 3% d) 5% e) 10%Zn-Mgco-doped V₂O₅ thin films

The average surface roughness from the AFM images study (In figure6) shows an increase in approximate roughness from 31.5 nm to 69.4 nm with Zn-Mgco-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-Mgco-doped V₂O₅ films. The Zn-Mgco-doping effect in V₂O₅ 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 compositions 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 V₂O₅ films are suitable for low band energy and gas sensor-based applications.

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