Research Article

Structural, Opticaland Morphological Properties Of Zn And Mg Co-Doped V_2o_5thin Filmnanostructures

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Abstract: The research study reveals metallic co-doping of Zinc(Zn) and Magnesium (Mg) on vanadium pentoxide(V_2O_5) thin film nanostructures by spray pyrolysis deposition technique. The studyfindings 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 showsan orthorhombic crystalline structure with polycrystalline nature.The dopantZn and Mginfused into the V_2O_5 matrixand is confirmed by EDAX images. A field emission scan electron microscope was used to examine surface morphology whichreveals that grain structure has beenmodified by increasing the doping content. It is evident from theatomic force microscopy (AFM) images that the effect of Zn and Mg on V_2O_5 thin filmshave enhanced surface roughness.The transmittance and energy bandgap (Eg) of the film found to be decreased with an increase in doping concentration whereas absorbance varieswith doping levels.The research findings suggest that the Zn-Mg co-doped V_2O_5 thin films could be a potential source for energy,optical and sensor-based device applications.

Keywords: Spray Pyrolysis; Co-doped V_2O_5; XRD;Crystallinity; FESEM;Surface morphology.

1. INTRODUCTION

The advancement in the field of nanomaterialslike transition metal oxides V_2O_5 and their physiochemical properties has attracted the attention of researchers in recent years[1-4].

The area of application of metal oxide-basedV_2O_5 devicesis mainly in storage devices, UV detectors, sensors, electro-optical devices, energy harvesters,transistors, piezoelectric devices etc.TheV_2O_5propertieslike electrical resistivity,n-type conductivity, magnetic susceptibility,high specific power, transmission, high energy density,variable oxidation statesof V_2O_5make the above applications possible [5-14].

Recent researches on various oxides of vanadium ions could vary the properties by anoxide surface formation and chemisorption [15-18]. The electric conductivity of V_2O_5will enhanceduring interaction with reducing gases during which V^{5+}species changes to V^{4+}. The concentration of oxygen nonstoichiometric (V_2O_{5-x}) due to oxygen vacancies are responsible for the semiconducting properties of V_2O_5

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 particularcan be effective in improvingthe solubility of dopant, increasing activation rates by reducing acceptors and donorsionising energies and increasing carrier mobility [19,20].

Zinc and magnesium were added to enhance the optical, structural, electrical and morphological properties of V_2O_5thin film.Both Znand Mg ions easilyenter intothe V_2O_5 crystal lattice and substitute the V^{2+} position of the crystal because the ionic radius of these transition metals element which aresubstantially lower than that of V^{2+}.

The spray pyrolysis thin film deposition method is followed tostudy how a Zn and Mg co-doping allows easy control and replace desired elements within required amountsinthe precursor solution and affects the morphological, microstructuraland optical properties of V_2O_5 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 V_2O_5.
It is important to find new appropriate doping substances that do notchange much of the structure of the V_2O_5 crystals to obtain V_2O_5 thin film which hasa wide optical band gap with improved electrical conductivity.Thework is focused on the fabrication and study ofstructural properties ofZnand Mgco-doped for the development of devices on sensors andenergy-basedapplications.

2. EXPERIMENTAL WORK

2.1 SamplePreparation

The thin films of pure V_2O_5 and Zn-Mg co-dopedwithvarying percentages in equal volumes were fabricated by spray pyrolysismethod on substrate material like glass.[22]. Theconcentrated HCl is added in drops to ammonium metavanadate in 100ml distilled water witha concentration of 0.02 M,the standard solution of $V_2O_5$was prepared.By adding V_2O_5 precursor solutions with magnesium chloride ($MgCl_2$) andZinc acetate($Zn(CH_3COO)_2 2H_2O$) in equal quantities, Zn-Mg co-doped thin films of1%, 3%, 5% and 10 % concentrations were fabricated. The solution is continuously sprayed on the well-purified glass substrate surfaceat 350°C.[23]
Theconditions 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 ° Cfor about one hour in a heated air oven to clear other impure residualsthat exist in the solutions.

Table 1: Thin film depositionparameters pure $V_2O_5$and Zn-Mg co-dopedthin films by spray pyrolysis

Spray Parameters	**Optimum Values**
Glass substrate temperature	350ºC
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

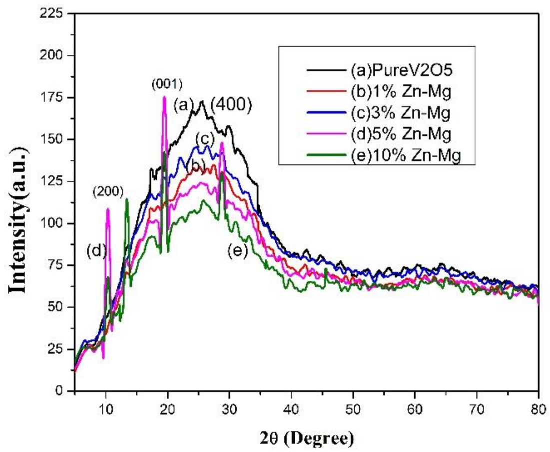
The undoped V_2O_5 and Zn-Mg co-doped V_2O_5 thin films thickness have beenmeasured bythe gravimetric weight differencemethod using the microbalance.An approximate 200nm uniform thick films were fabricated by spray pyrolysis. The Bruker's XRD was used for measuring diffraction angle 2θat a wavelength 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 spectrophotometerhelps in finding the optical bandgap (Eg),transmittance and absorption coefficient of the films.

3. RESULTS AND DISCUSSIONS

3.1XRD study

X-ray Diffractometer through the precise range of 10º to 75º having the wavelength of 1.5406 Å help in structural propertiesstudy of film and is shown in Figure 1. The XRDassociated with the planes (2 0 0)with diffraction angle(2θ)= 12.28° indicate the polycrystallinity natureof films and are crystallized with orthorhombic structure.

Fig. 1: V_2O_5 and Zn-Mg co-dopedthin films XRD patterns

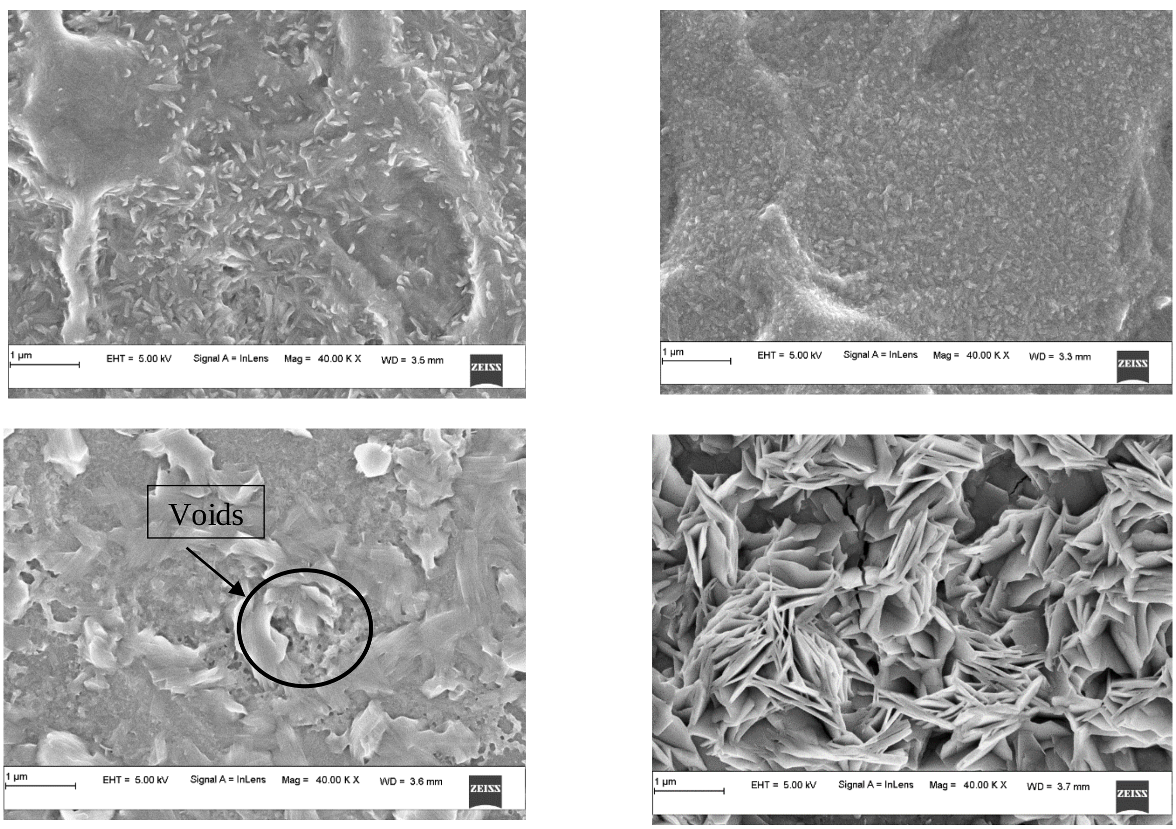


3.2 Morphological properties study

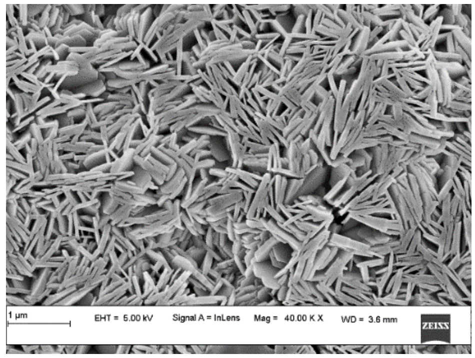
Microscopic characteristics of the prepared Zn-Mg co-doped V_2O_5 thin films analyzed by FESEM has a huge impact on the thin film'sstructural properties.Figure. 2 (a-e) shows images of FESEMfor pure V_2O_5 and Zn-Mg co-doped V_2O_5 thin films.

At 1% co-dopinguniform 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 founddifficult to handle.But with moredopantintegration, 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%, thesize and shape of co-dopantswere 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



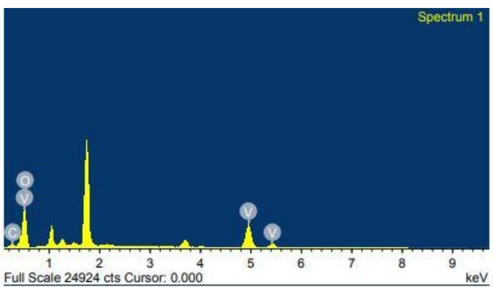
(c) V_2O_5 with 3 %Zn-Mgd)V_2O_5 with 5 %Zn-Mg



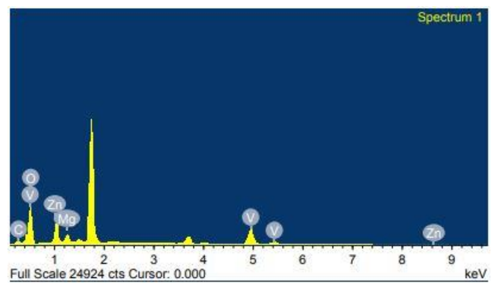
e) V_2O_5 with 10%Zn-Mg

Fig. 2: FESEM images of a) pure V_2O_5 b) 1% c) 3% d) 5% and e) 10% Zn-Mgco-doped V_2O_5 thin films

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



a) Pure V_20_5

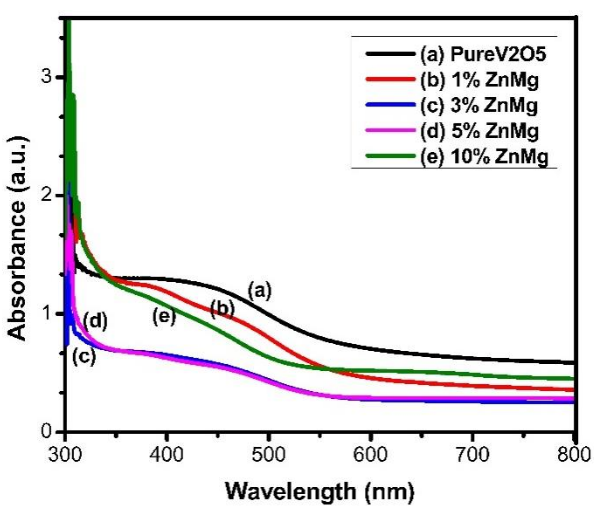


b) 1% Zn-Mgco-doped

Fig 3 (a) EDAX spectrum of (a) pure V_20_5 and (b) Zn-Mgco-doped V_20_5 thin films

3.3 Optical properties analysis

Electron transitions studiesof undopedand Zn-Mg co-doped V_2O_5 thin filmshave 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 withwavelength wereobserved 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.



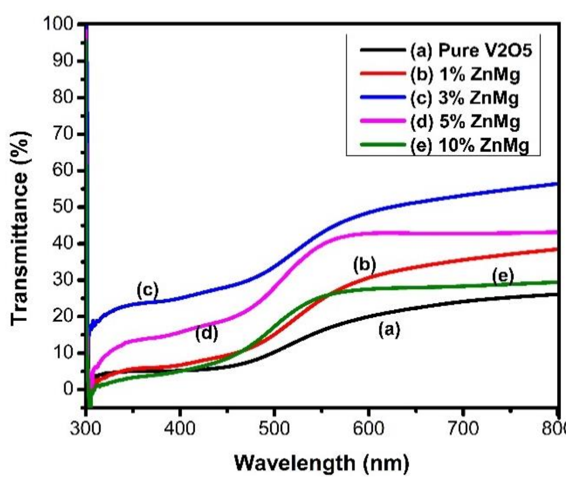


Fig. 4(a):Wavelength VsAbsorbance for the deposited V_2O_5films and Fig. 4 (b):Wavelength Vs Transmittance for the undoped V_2O_5 and Zn-Mgco-doped films.

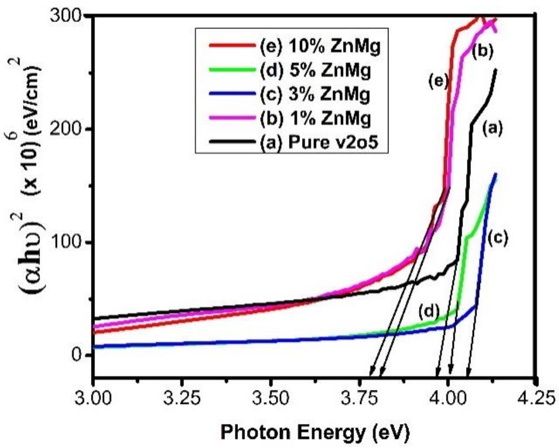
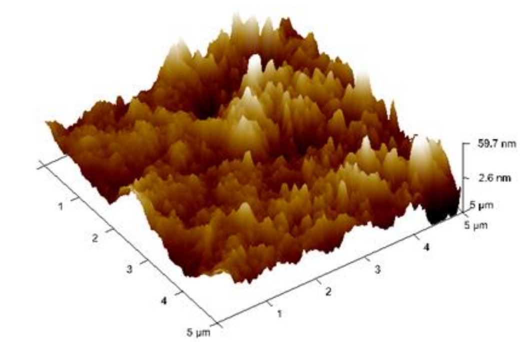


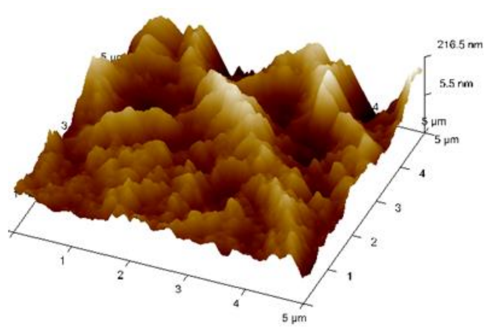
Fig. 5: Plot of $\alpha h\upsilon^2$ Vs Energy (Eg) for Zn-Mgco-doped V_2O_5films.

The direct energy band-gap (E_g)of the co-doped thinfilms were calculated by the tauc plot [24].The E_g value in the range of 3.77eV to 4.07eV in V_2O_5 thin films for different co-doping concentration levels wasobserved which isshown in figure 5.The E_g for pure V_2O_5 is 3.92 eV however it is observed that the value decreases approximately to 3.80 eV for 1% and 10% concentration.$E_g$willincrease 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.

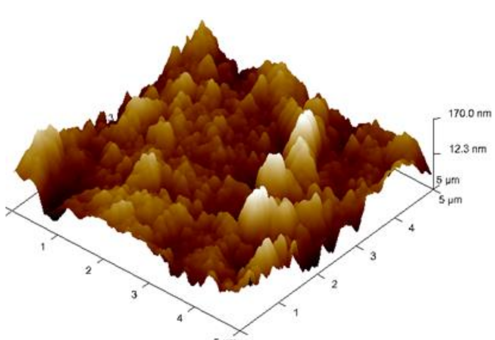
3.4 Atomic Force Microscopy (AFM) study



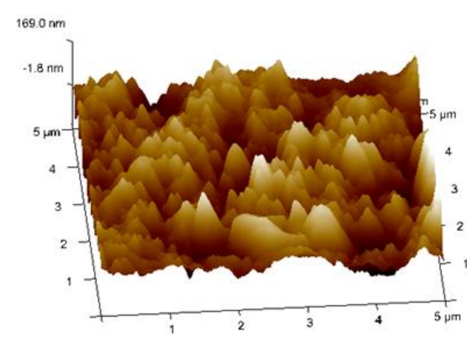
a)Pure



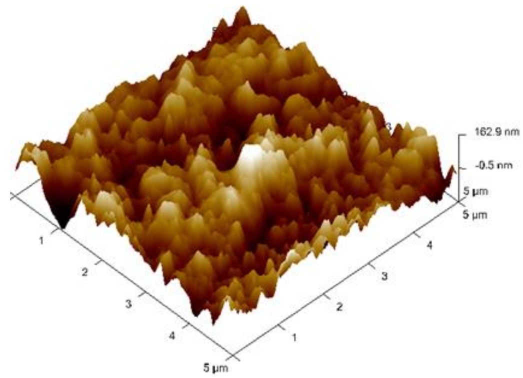
b) 1% dope of Zn-Mg



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 V_2O_5 b) 1 %c) 3%d) 5% e) 10%Zn-Mgco-doped V_2O_5 thin films

The average surface roughness from the AFM images study (In figure6) shows an increasein approximateroughness from 31.5nm to 69.4nm with Zn-Mgco-doping. The presence of 'O' vacancy present in the films is responsible for the high surface roughness. The change insharp grain shapes to smooth grain size with the increased co-doping is also evident from FESEM images.

4. CONCLUSIONS

The thin films usingthe spray pyrolysis technique is adopted for fabricating undoped and Zn-Mgco-doped V_2O_5films. The Zn-Mgco-doping effect in V_2O_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 phasealongthe plane (200). The images of FESEM clarify that the undoped film is nonhomogeneouscompared to the co-doped films,which is evident from surface roughness values. The prepared compositionsof the film ensure theexpected elements of the films. The Zn-Mg co-doping increases the surface roughness of the films. The bandgap energy found to bevarying 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_2O_5 films are suitable for low band energy andgas sensor-basedapplications.

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