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INFLUENCE OF RUTHENIUM ON STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF V_2O_5 THIN FILMS DEPOSITION AT DIFFERENT PERCENTAGES

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Abstract

Nowadays, semiconducting thin films are efficient candidates for good optical and electrical properties. In this present study, thin films of Ruthenium (Ru) doped V_2O_5 with different weight percentageswere prepared through the method of spray Pyrolysis. The prepared Ru doped thin films were characterized by spectrographic tools such as XRD, SEM with EDAX,FT-IR, UV-vis and Hall effect to study their crystalline nature, functional group, band gap, resistivity, conductivity and mobility of the flow of electrons respectively. The structural morphology of the synthesized thin films was discussed through the micrographic image obtained from Scanning electron microscopy together with their surface occupancy plots. The obtained minimum crystallite size is about 24.8 nm for 8% molarities. The morphological and structural studies show enhanced results for an 8% sample which makes it a viable candidate for optical and electrical applications.

Keywords: Spray Pyrolysis, V_2O_5 Thin films, Surface Morphology, Ruthenium, and Electrical Properties.

1.Introduction

Nowadays, thin films of V_2O_5 have gained noteworthy attention in the microelectronic world [1]. In recent years, vanadium oxides play a vital role due to their sensing activity, selective catalytic and potential applications in electrochemical capacitors [2-5]. And also, vanadium oxide thin film hasa scientific and technological application which includes electrochromic devices (ECD), toxic gas detectors, electronic and optical switches [6-8]. Vanadium oxides have interesting electronic structures is $3d^34s^2$ electrons in their outer shell, which enables them to be in different oxidation states such as V^{2+}, V^{3+}, $V^{4+}$and V^{5+}. This creates complex as well as challenging material. In different vanadium oxides, vanadium pentoxide (V_2O_5) is widely used and is stable. The direct band gap of V_2O_5 makes V_2O_5 thin films lay footprints in photodetection applications which leads to the utilizing V_2O_5 thin films

in optoelectronic devices [9]. However, pure crystalline V_2O_5 generally possess an orthorhombic structure that comprises better chemical property and good specific energy with thermal stability [10]. Because of the mentioned properties of V_2O_5 crystal's orthorhombic structure, these V_2O_5 thin films and their related materials were used for fabricating IR detectors, solar cells and sensors too.

V_2O_5 thin film has been synthesized using various methods such as sputtering [11], sol-gel method [12], hydrothermal [13], pulsed laser deposition [14], chemical vapor deposition [15]and co-precipitation technique [16], etc. Among, these various deposition techniques, the thermal evaporation method is the most predominant. The thermal evaporation technique is the most challenging versatile method for the deposition of V_2O_5 thin films.

However, High surface area V_2O_5 aerogels exhibit a larger lithium intercalation capacity compared to crystalline V_2O_5. Hence, a major difficulty of these electrodes is their limited long-term cycling stability. To overcome the specific rate, intercalation rate and cycling performanceof vanadium oxide metal such as $M_XV_2O_5$ (M= Zr, Ag, Ru, etc.) have been taken to be used as cathode materials due to their unique structure. Moreover, there is no report so far of V_2O_5 particles doped by Ruthenium in lithium-ion batteries at high deposition temperatures. In the present work, pure and Ruthenium doped V_2O_5 thin film in various molar percentages [2, 4, 6and 8%] were deposited. These prepared thin films were synthesized by the spray pyrolysis technique.

The obtained pure and Ruthenium doped V_2O_5 thin filmwere characterized by X-ray diffraction (XRD) for structural analysis, scanning electron microscope (SEM) was used to examine the surface morphology and the electrical studies hall effect were also recorded to find the conductivity of the prepared thin films.

2.Experimental Procedure

V_2O_5 thin films were prepared onto ITO substrates by spray pyrolysisof pure V_2O_5Powder from an electrically heated molybdenum boat kept at ~ 1823 K in a vacuum very good than 8 x 10^{-6}Torr. A Hind High Vacuum 12A4Coating was used for the deposition of the experimental thin films. A diffusion pump backed by a rotary pump was carried to produce the pressure of 3 x 10^{-6}Torr. Well-Polished ITO substrates were mounted on a copper holder which was fixed on a tripod in the bell jar. After getting the ultimate vacuum of 5 x 10^{-6}Torr and the desired substrate temperature in the chamber, the glow discharge was initiated further ionically polished the substrates in the vacuum chamber. This process was done for two minutes. The system was allowed to reach the ultimate vacuum so that the crystalline nature of Ru doped V_2O_5 thin films can be enhanced. When the power was fed to the boat, the material in the boat evaporated and the vapors reacted with the oxygen gas leading to film deposition on the substrate. The temperature of the boat during deposition was monitored using an optical pyrometer [17]. The substrates were sustained at the required deposition temperature and the molybdenum boat in which Ruthenium (Ru) doped V_2O_5 powder with different weight percentages kept. The shutter covering the substrates was opened when therequired temperature of the boat reached about 1823 K and it was maintained during the deposition of

the films.

2.1 Characterization

The well-adherent V_2O_5 films underwent structural, morphological and optical studies. The structural properties characterization by X-ray diffraction is carried out using X'Pert High Scorer-Panalytical Diffractometer with Cu-K radiation of wavelength (1=5406Å). The morphology was analyzed by Scanning Electron Microscope (Hitachi S-4500 SEM machine). Thespectroscopic vibration studies of Ru doped V_2O_5 thin films have been performed on FT-IR (PerkinElmer L1600) between the wavenumber range of 400–4000 cm^{-1}.The optical studiesevolved using UV spectrophotometer, and the wavelength was prescribed from 200 to 800 nm. And the Electrical studies were carried out using the Hall Effect.

3. Result and Discussion

3.1 Structural Analysis

XRD patterns of pure and Ruthenium doped V_2O_5 thin films with different weight percentages (2%, 4%, 6% and 8%) are shown in Fig. 1. The obtained thin films reveal characteristic peaks related to orthorhombic phase crystal structure. The noticed peaks are gently matched with standard patterns of JCPDS card No. 89-2482 and the peaks 20.85, 30.00, 34.97, 50.27,55.02, and 59.80 at crystal plane (101), (012) and (312) respectively [18]. The crystallite size of the prepared Ru doped thin films was calculated using Debye's Scherrer formula [19],

$$D = \frac{K\lambda}{\beta Cos\theta} \qquad \text{---------[1]}$$

Where K is a Scherrer constant, λ is the wavelength of the beam, $\beta$is (FWHM) and θ is Bragg's diffraction angle. The average crystallite size of the prepared thin films decreases from 29.5 to 22.2nm with the increase in weight percentage, which is due to the different ionic radii of Ru and V_2O_5. Compared with the pure V_2O_5, the minute peaks disappeared, when increasing the weight percentage [20]. However, the average dislocation density and Average micro strain of the prepared thin filmsare increased linearly with the increase of weight percentages.

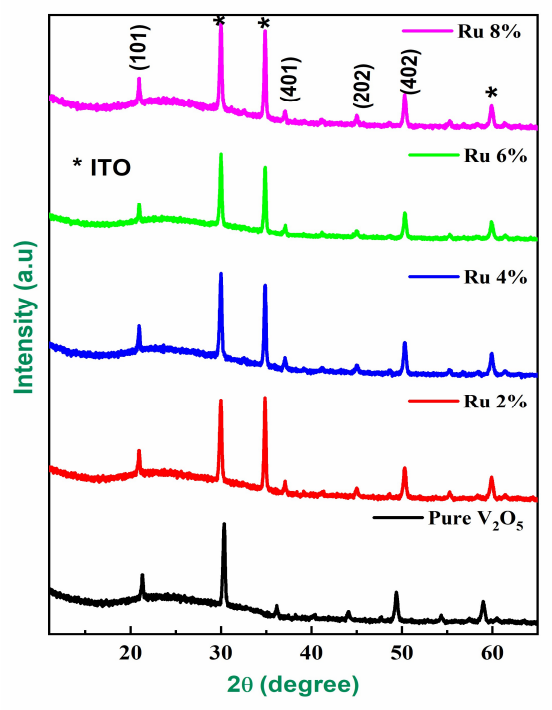

Fig. 1 XRD patterns of pure V_2O_5 with different weight percentages

Table1. Structural parameters of pure V_2O_5 with different weight percentages

S.No	Sample	Averagecrystallite size $X10^{-9}m$	AverageDislocationdensity$X10^{14}$ m	Average Microstrain, $\varepsilon X10^{-3}m$
1	V_2O_5	29.5	1.14061E+15	0.00122
2	2%	28.3	1.2461E+15	0.00138
3	4%	26.8	1.38471E+15	0.00154
4	6%	24.6	1.52471E+15	0.00184
5	8%	22.2	1.65471E+15	0.00213

3.2 Morphology Studies

3.2.1 SEM Micrographs

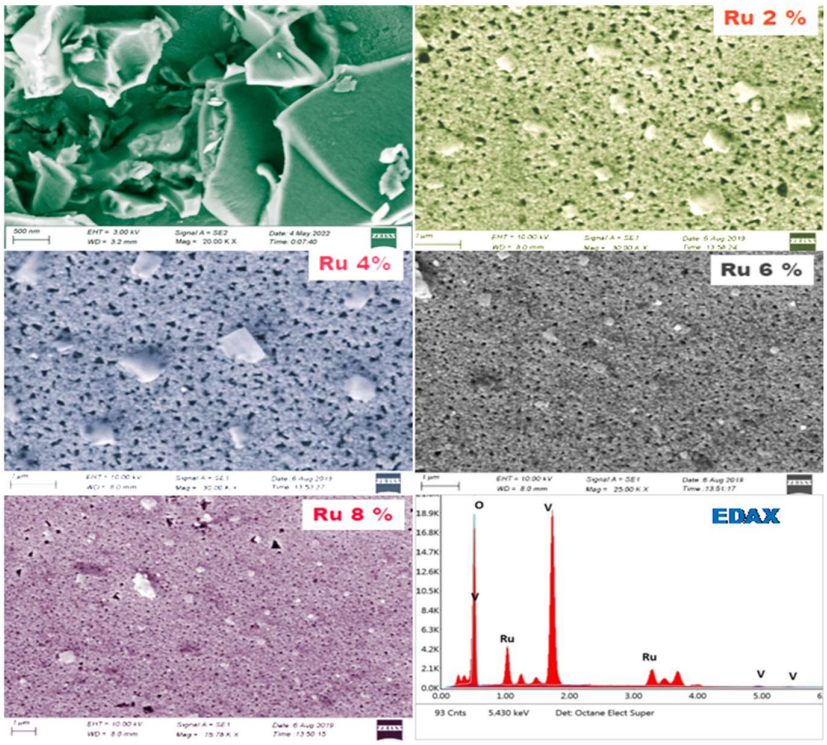

Fig 2. SEM with EDAX images of Ru-doped V_2O_5 with different weight percentages

SEM images of Rudoped V_2O_5 with different weights percentages (2, 4, 6and 8%) thin films are shown in Fig2. From the Figure the prepared thin films were spongy in shape with few agglomerations. The noticed spongy-like shape gets reduced in the increase of Ruthenium dopant percentage. The 8% Ru doped V_2O_5 thin film shows a smooth surface with plateless scattered on its Surface. In Fig 2, EDAX shows the confirmation of occurred elements such as Ruthenium, vanadium, and oxide with their appropriate atomic ratio. There is no secondary phase of impurity.

3.2.2 Surface Occupancy plots

We intended to illustrate the surface micro structural condition of pure and varied percentages of Ruthenium iondoped V_2O_5films, as seen in the previous SEM photographs. Here, the surface condition was demonstrated with the aid of a surface occupancy plot through image J. Thin film samples have been shown in Fig 3(a-e) to illustrate the surface occupancy state. To begin, to compare the outcomes of the SEM compared with those of the SOP, in the case of pure V_2O_5 thin film, the SEM reveals a peeled micro structural condition along with crippled and aggregated conditions, as shown in Fig. 3. The SOP reveals that the signals must be intensified in certain regions due to the microstructures' clumping. However, after incorporating 2%, 4% and 6% of Ru-ions into the V_2O_5, the surface morphology was radically transformed, as depicted in Fig.3(b-d), exhibiting pinholes – (micro channels) appearing in the scanning region. The mild, consistent signals with some strong signals due to minor agglomerations are visible in their SOP. After that, in the case of 8% of Ru-ion doped V_2O_5

SOP having very smooth and well-distributed signals with a reduction in micro structural sizes, as seen in Fig. 3e. So, we infer that the current SOP study has appropriate evidence for the Ru-ions implications in host thin film. We suggest the vital thing about the pin-hole and void formations, which are acquired due to defects arising in crystalline V_2O_5while interrupting with dopant ions. As a result of the exterior diffusion of Ru-ions during specimen meets calcination in thin films, multiple stoichiometry vacancies can be created in this kind of cavity. The microstructural parameters in this instance of pin-holes are more advantageous for charge transfers, suggesting that they may operate as channels, resulting in improved electrical conductivity [21]. Ultimately based on the outcomes, it was found that various Ru-ions doped V_2O_5thin films were more useful for solar cell-based applications.

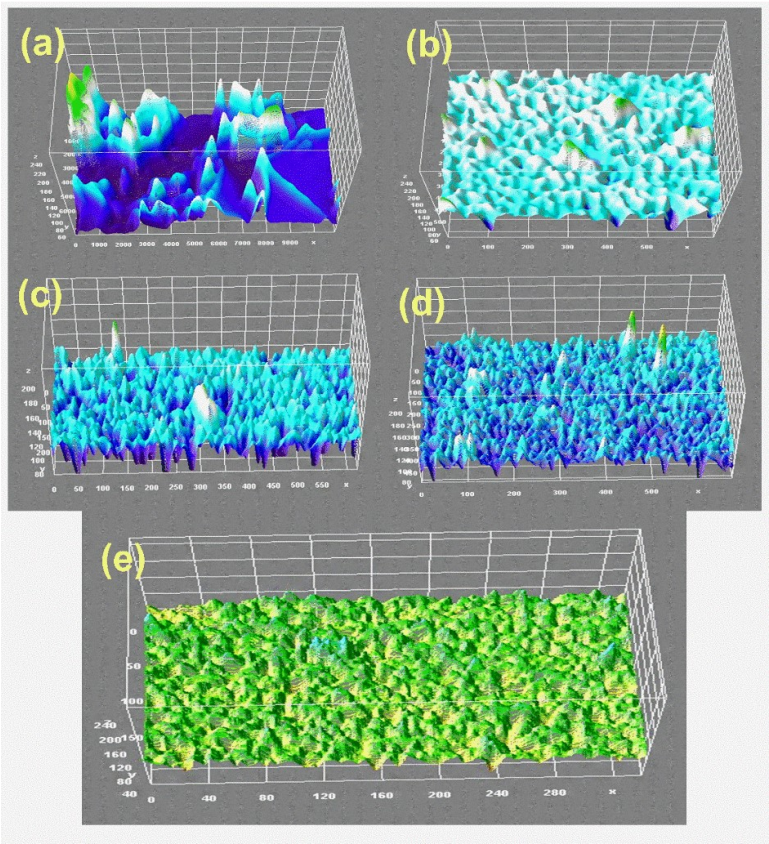

Fig. 3(a-e) Surface Occupancy plots of Ru-doped V_2O_5 with different weight percentages

3.3 Functional Studies

Fig.4 depicts the FT-IR spectra of pure and varied percentages of Ruthenium ion-doped V_2O_5 films. The presence of functional groups in the produced thin films are further confirmed by the absorption of IR in molecular vibrations. The stretching vibration of the metal-oxide bond is represented by the vibrational frequency at 621cm^{-1}. Water molecules stretching vibration O-H bonds are responsible for the strong, intense peak at 3250 cm^{-1}. O-H bending

vibration is responsible for the peak at 1310 cm^{-1}, which is caused by the calcinated thermal interfaces, on the other hand, theexperimental reaction may be a factor for O-H molecule incorporation[22].

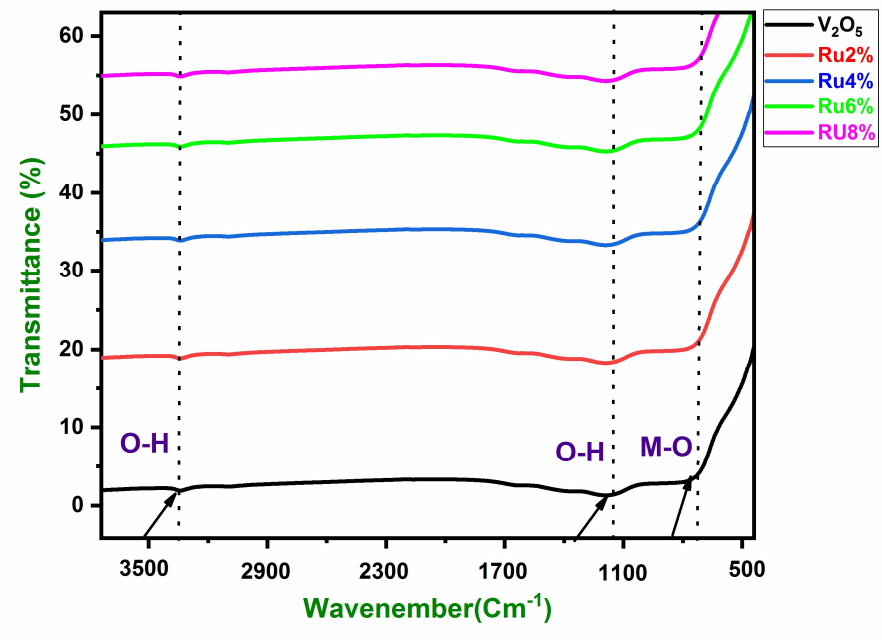

Fig.4 FTIR Spectra of Ru doped V_2O_5 with different weight percentages

Table.2 FT-IR Spectra of Ru doped V_2O_5 with different percentages

S.NO	Vibrational assignments	Experimental absorption (cm^{-1})				
		V_2O_5	2%	4%	6%	8%
1	Metal - oxide	621	621	621	621	621
2	O - H bending vibration	1310	1310	1310	1310	1310
3	O - H stretching vibration	3250	3250	3250	3250	3250

3.4 Optical Studies

Figure 5 depicts the UV-Vis spectra of Ruthenium ion-doped V_2O_5 films with different weight percentages (2% to 8%). As the doping percentage rises, the absorbance decreases monotonously. The abrupt drops in transmittance are caused by the absorption of the majority of incoming photons with wavelengths between 300 nm and 800 nm. The region of fundamental absorption edge for ITO coated Ru doped V_2O_5 thin films with absorbance values of 325.6, 320.8,317.4, 311.1 and 305.4at 2% to 8% are depicted in Fig.5. The spectra show that the absorption edge indicates a red shift in wavelength as crystallite size decreases, which suggests a shift on the lower energy side. The microstructure and growth conditions of the films have an impact

on the optical characteristics of ITO-coated Ru-doped V_2O_5 thin films with various weight percentages.

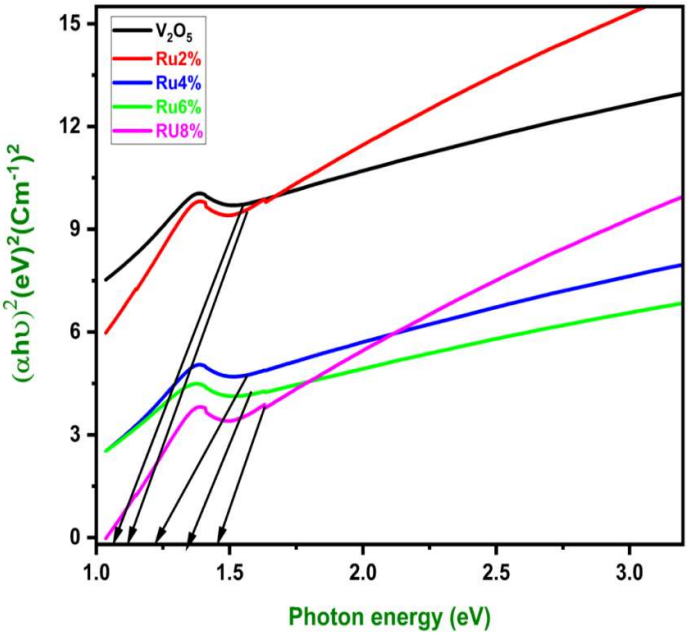

Fig. 5 Optical absorption spectra of Ru-doped V_2O_5 with different percentages

The optical band gap energies are 2.06, 2.11, 2.16, 2.28, and 2.39 eV. The band gap energies are increases with the increase in doping percentage which is agreed with the Brus equation [23]. Furthermore, the widening of bandgap in the prepared Rudoped V_2O_5 thin films is due to the phenomenon of quantum size effects, which is higher for films at low growth temperatures, where the size of grains is relatively low (≤50nm). In addition, the mean crystal dimension becomes small; therefore, the quantum size effects lead to increase in the band gap. The defects in the lattice of Ru-doped V_2O_5 thin films are due to the oxygen vacancy between two V-O layers that create lower absorption bands in optical spectra. This oxygen vacancy is raised due to the disorders inatomic arrangement.

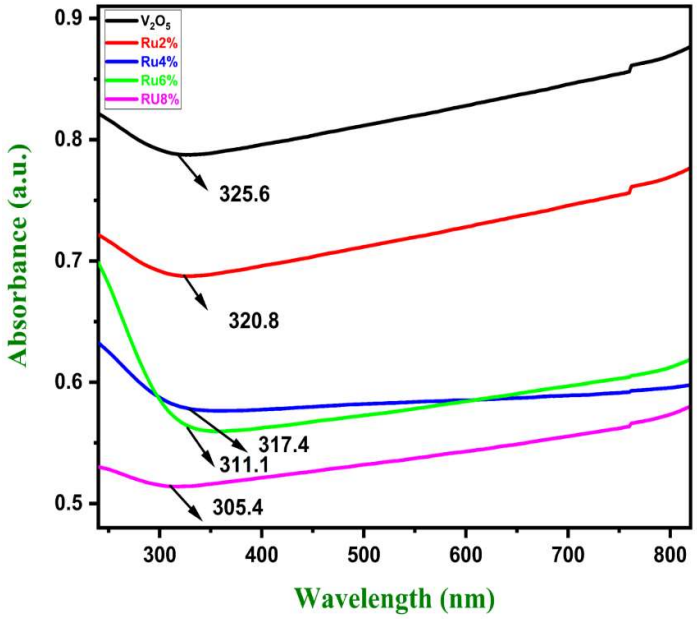

Fig. 6 Bandgap energy of Ru-doped V_2O_5 with different percentages

Table.3 Optical properties of Rudoped V_2O_5 with different percentages

Composition	Absorbance	Bandgap (eV)
V_2O_5	325.6	2.06
2%	320.8	2.11
4%	317.4	2.16
6%	311.1	228
8%	305.4	2.39

3.5 Electrical Studies

3.5.1 Hall Effect

The transport parameters of the prepared samples were studied by using the Hall Effectat room temperature. The changes in the electrical transport because of increasing the dopant amount of Ruthenium in V_2O_5 thin films are summarized in the Table.4. The ions of vanadium show semiconducting features because of their different oxidation states due to the bouncing of 3d unpaired electrons. Fig. 7(a) shows the mobility and carrier concentration of the pure V_2O_5 thin films and V_2O_5 thin films doped with (2,4,6 and 8%) of ruthenium. It shows that the mobility and carrier concentration increases for 2% of dopants and then it gradually decreases for 4,6 and 8% of dopants.

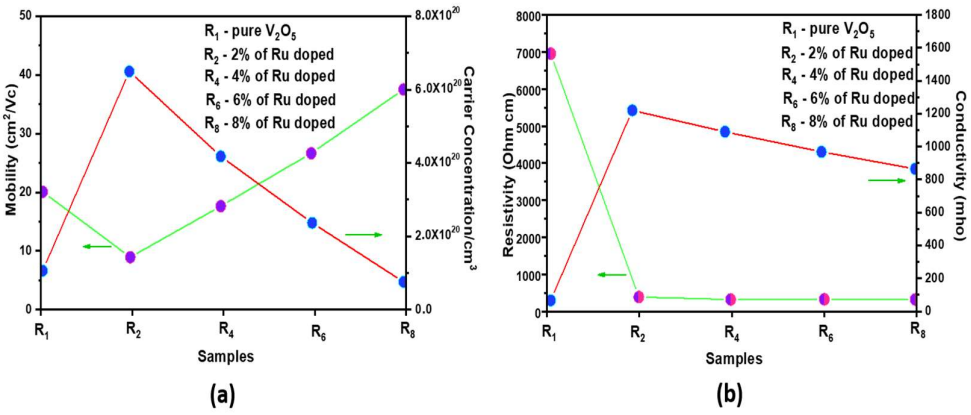

Fig. 7 Electrical studies of V_2O_5 thin filmswith different percentages

However, Fig.7(b) shows the resistivity and conductivity of the pure V_2O_5 thin films and V_2O_5 thin films doped with (2, 4, 6 and 8%) of Ruthenium. which portrays that, the thin film's conductivity rises as a result of the creation of Oxygen vacancies. So, the Ruthenium inclusion on the V_2O_5 thin film matrix leads to a remarkable influence on the mobility of the prepared samples is revealed.

Table.4 Electrical parameters of V_2O_5 thin filmswith different percentages

Sample	Resistivity (ρ)(Ω cm)	Conductivity (σ)(Ω cm)$^{-1}$	Mobility (μ)(cm^2/Vs)	Carrier concentration/C m^3
R_0	2.19x10^3	4.61x10^2	0.8 x10^1	1.7 x10^{20}
R_2	6.45x10^3	1.17 x10^2	4 x10^1	6.8 x10^{20}
R_4	4.89x10^3	1.09 x10^2	2.5 x10^1	4.4X10^{20}
R_6	4.39 x10^3	0.95 x10^2	1.4 x10^1	2.5X10^{20}
R_8	3.97 x10^3	0.88 x10^2	0.45 x10^1	0.8X10^{20}

4. Conclusion

The thin films of Pure V_2O_5 with differentweight percentages (2, 4, 6and 8%) were prepared and coated in the ITO substrate by the method of spray pyrolysis. The XRD pattern shows the respective peaks of the prepared V_2O_5 thin films with orthorhombic structures. The average crystallite size of the Pure V_2O_5 and doped Ruthenium withdifferent weight percentagesare 29.5 to 22.2 nm respectively. It shows that the crystallite size decreases with the increase inweight percentages. The FTIR spectra show the appropriate bands of bonds present in the prepared samples, while the optical spectra show their corresponding absorption spectra with their respective band gaps, which indirectly shows the prepared material is a semiconductor. In addition, the SEM/EDAX micrographs showthat the synthesized thin films were formed in the shape of crumbled paper for 8% of molar concentration. However, surface occupancy plots show that sheet-like particles are uniformly distributed over the scanning

surface area. Hence, this present study suggests that V_2O_5thin films prepared through spray pyrolysis with the increase in thedopant weight percentages enhance its optical and electrical properties, which may lead to use the prepared samples for effective optical and electrical applications.

Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflict of interest

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