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EFFECT OF SILVER DOPING ON THE MICROSTRUCTURAL, OPTICAL, AND MORPHOLOGICAL PROPERTIES OF WO_3 THIN FILMS

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Abstract: Tungsten trioxide (WO_3) thin films (undoped and Ag-doped) were deposited by spin coating on glass substrates. Tungsten hexachloride and silver nitrate were used as the respective tungsten and silver containing precursor solutions containing methanol. The effects of annealing temperature (200°-400°C) on the microstructural, optical, and chemical properties of the thin films were investigated using glancing angle X-ray diffraction (GIXRD), UV-Vis spectro photometry and scanning electron microscopy (SEM). GIXRD results indicated that the recrystallization of WO_3 occurred on annealing at 400°C for 2 h. nevertheless, when doped with silver, the recrystallization was observed to occur at a lower temperature of 300ºC. The optical transmission data revealed that there was a decrease in the optical indirect band gap with increasing annealing temperature for undoped and Ag-doped WO_3 thin films, with the values being lower for the doped films.

Index Terms: ***Tungsten trioxide (WO_3), spin coating, SEM, EDAX, Optical data.***

I. INTRODUCTION

Tungsten oxide (WO_3) is a courier cathodic electro chromic material, whose color turns to blue in its reduced state by inserting a proton or lithium ion when a reverse electrical potential is applied [1, 2] and turns to translucent at its oxidized state by extracting ions when a forward electrical potential is applied. There are many research reports about making tungsten oxide film coatings by a sputtering method, pulsed laser ablation deposition method, sol-gel coating method, electro deposition and spray pyrolysis methods [3-9]. The sol-gel coating method uses tungsten chloride or peroxotungtic acid as a precursor coating solution and synthesizes tungsten oxide thin films by a dip coating or spin coating methods [10-13]. Several research reports have attempted to obtain tungstenoxide thin films using WCl6 precursor solution and ammonium tungstate precursor solution [14-16]. This study aims to synthesize tungsten oxide thin films by the peroxotungstic acid spin coating method. The peroxotugnstic acid is easily synthesized from WCl6 and hydrogen peroxide reactions. In this study, effort was made to obtain the crystalline phase of tungsten oxide by spin coating method and these were characterized.

II. EXPERIMENTAL

Sol–gel method is used to deposit the WO_3 thin films on the glass substrates because sol–gel is simple and low cost technique for deposition. In this research work WCl_6 (Tungsten hexachloride) is used as a precursor to prepare the WO_3 thin film.WCl_6 was purchased from Thermo-Fischer Scientifics of (Reagent grade, 99 wt %). WCl_6 was dissolved in isopropanol at a ratio of 5gm/100ml and freshly prepared sol was used for spin coating. Then the mixture is placed to dry air (in room temperature) for next 5 min.

Undoped: The sol turned yellow immediately after isopropanol is added to WCl_6.The sol was kept in dry air for 3 hrs with constant stirring. The spin coating speed was set at 2000rpm. Multiple depositions of up to 6 layers were carried out to increase the thickness. After every layer annealing was done in air to prepare crack-free films. Each layer was fired for 10 mins at 100^0C before a subsequent coating.

Silver dopant: 2 wt% & 5 wt% of $AgNO_3$ was added to WCl_6 and isopropanol solution. As soon as isopropanol was added the solution became pale yellow. After 24 hrs the solution turned white in color. This colour change can be endorsed to the existence of $AgNO_3$. The obtained thin films are dark brown, homogeneous and adhere well to the substrate.Prior to the deposition the substrate (glass) were cleaned with soap solution, then with acetone and ethanol. Using ultrasonicator the substrates were washed with acetone and ethanol for 5 mins and dried in hot air oven for 30 mins.

The mineralogies of the films were analyzed by glancing Incidence X-ray diffraction (GIXRD, Phillips X'pert Materials Research Diffraction, CuKα, 45 kV, 40 mA. The chemical composition of films was investigated using EDAX. The surface morphologies of the films were assessed using scanning electron microscopy. UV-Visible spectrophotometry was used to measure the optical transmittance of the films in the wavelength range of 300 nm to 800 nm.

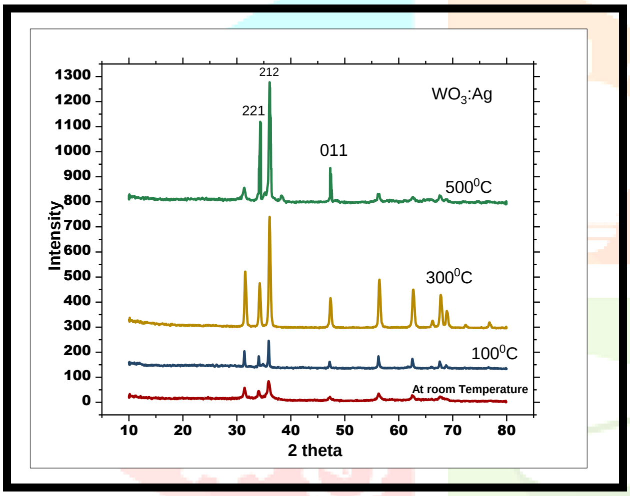
III. Results and Discussions

The XRD pattern of the silver doped sample shows the formation of WO_3 and diffractions matched perfectly with the WO_3monoclinic structure as shown in Fig.1.. The X-ray diffraction (XRD) pattern for synthesized pure and Ag doped (2 wt%, 5 wt %) WO_3. From the figure it has been observed that the Pure WO_{-3} exhibit the diffraction peak at 2θ = 23.123, 23.594 and 24.371 and for Ag doped WO_3 exhibits the diffraction peak at 2θ = 23.024, 23.498 and 24.270 related to (002), (020), (200) reflection of monoclinic phase of WO_3which are in agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) file no. (083-0950).Both Ag doped WO_3 and undoped WO_3 can be well indexed to the standard pattern of monoclinic as shown in Fig. 2.. No additional peaks are found in the XRD pattern which confirms absence of impurities in the synthesized material. It was also noted that the small peak shift was observed for lower angle side for Ag doped samples. Moreover, the intensity of the peak increased with the increase in the Ag concentrations which are annealed at 500^0C. These results clearly indicate that Ag substituted in WO_3 host lattice site.

Scanning electron microscope is a useful technique to determine the morphology and particle size of the samples. Fig. 7 and 8 shows SEM image of Ag doped WO_3 nanoparticles. It is clearly observed that both the samples show plate like morphology with average diameter of 1–1.5 lm and thickness of 80–100 nm. The particle size estimated from XRD results much smaller than the SEM results. This change in size could be due to the larger particles which are composed of many smaller particles. After doping of Ag dopant the plate like morphology decreases when increasing the Ag content. The decrease of crystalline size was also confirmed by XRD results.

The EDAX results confirm the obtained materials which are composed of W and O as shown in Fig 9 and 10. The intensity peak of tungsten was decreased due to the addition of silver ions in the tungsten site and intensity peak of oxygen remains constant for both pure and Ag doped WO3.

The optical property and substitution of silver into WO_3 site, the sample were characterized by UV–Vis transmission spectra analysis. The diffusion reflectance spectra of pure and Ag doped WO3 respectively. It was observed that the optical transparency of the pure WO_3 decreases with increase in the Ag content. The decrease in the transparency of Ag doped WO3 was attributed to the increase in reflectance due to the presence of the metal ion. A considerable red shift was observed in the absorption edges with the increase of Ag content from 2 wt% to 5 wt%, which indicates the decrease in bandgap of WO_3 on doping. The band gap energies (Eg) have been calculated



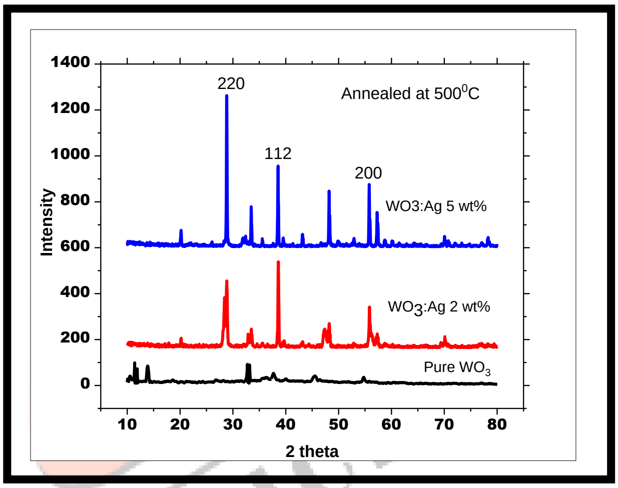
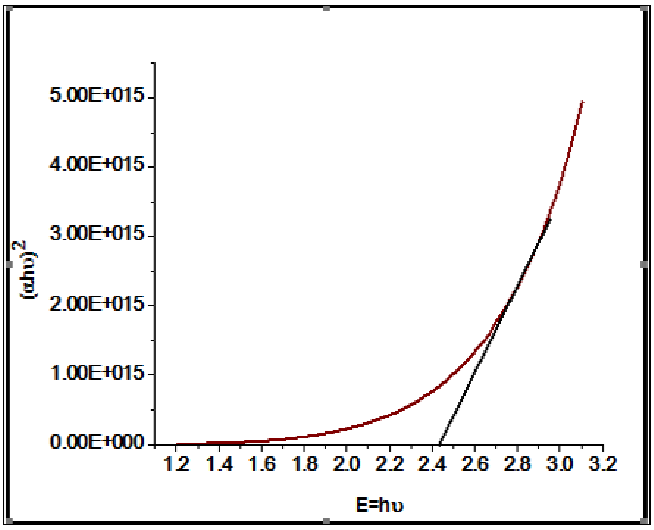


Figure1: Silver doped WO_3 at different annealing temperatures

Figure 2: XRD of silver doped and undoped WO_3 thin films at 500^0C



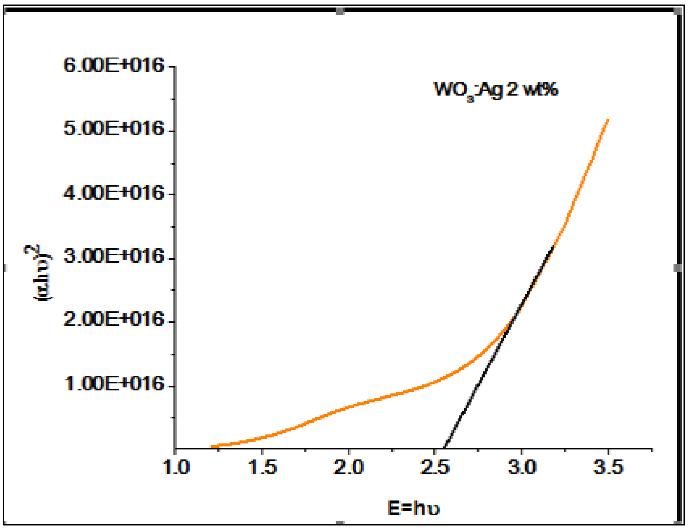
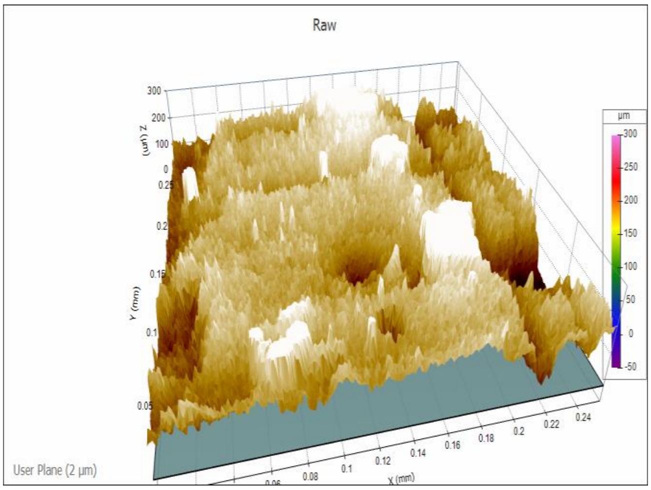


Figure 3: Energy gap of WO_3:Ag 5wt%

Figure 4: Energy gap of WO_3:Ag 2 wt%



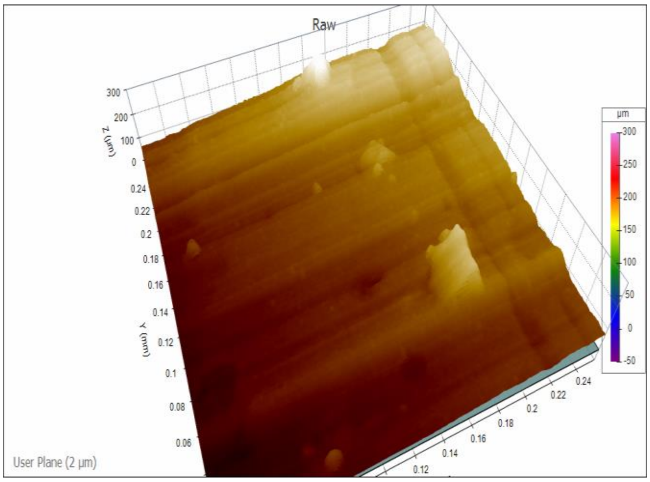
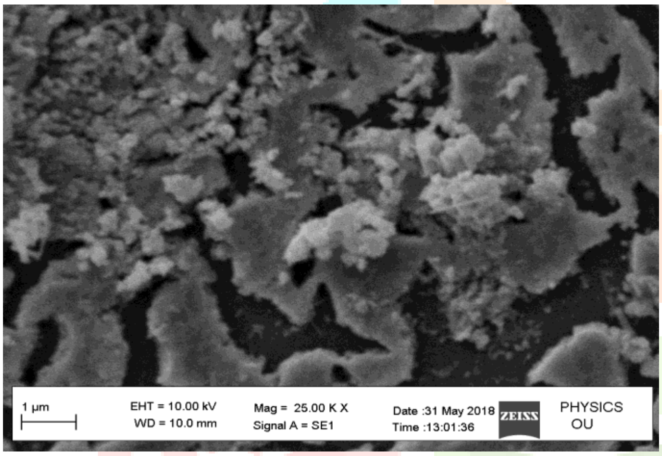


Figure 5: AFM images of WO_3:Ag 5wt%

Figure 6: AFM images of WO_3:Ag 2 wt%



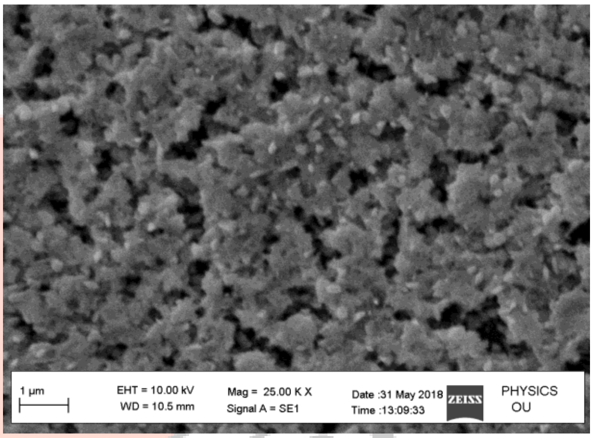
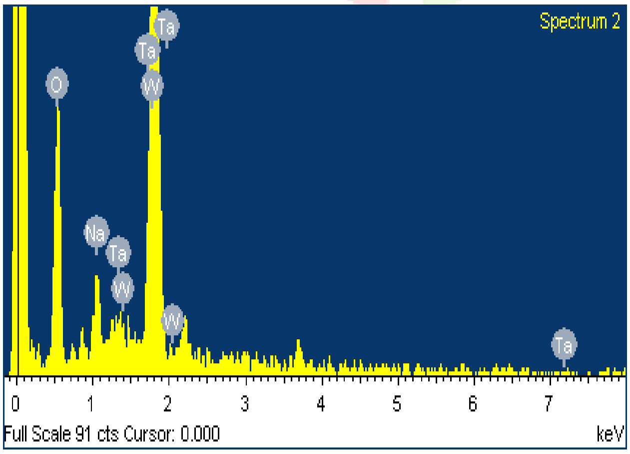


Figure 7: SEM images of WO_3:Ag 5wt%

Figure 8: SEM images of WO_3:Ag 2 wt%



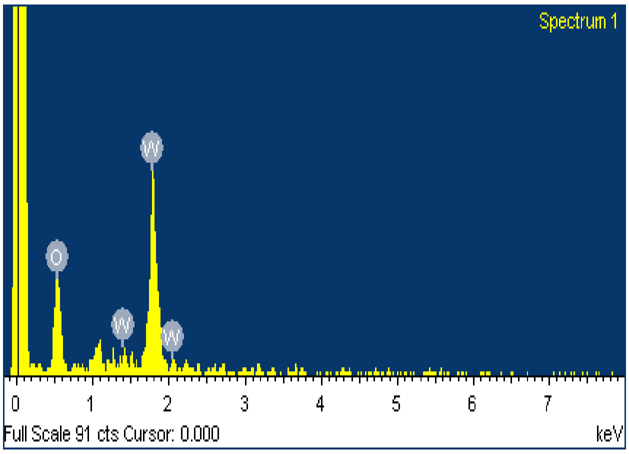


Figure 9: EDAX images of WO_3:Ag 5wt%

Figure 10: EDAX images of WO_3:Ag 2 wt%

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