XRD and SEM Results of WO_3 Thin Films Deposited on Quartz Glasses

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Abstract

Tungsten oxide (WO_3) films are of critical importance for electrochromic device technology, such as for smart windows capable of varying the throughput of visible light and solar energy. In this paper, the evolution of structural and morphological changes of spray-deposited WO_3 thin films was studied. WO_3 thin films were made on quartz glasses using precursor solution of Ammonium Tungstate ($(NH_4)_2WO_4$) by using Chemical Spray Pyrolysis Deposition Technique. The samples were annealed at 500 °C. The structural and surface properties of WO_3 thin films were studied by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The films (have orthorhombic crystal structure and a filamentous like network surface.

Keywords: Thin films, Chemical Spray Pyrolysis, Tungsten Oxide

Introduction

EC is a phenomenon which involves persistent and reversible change of color in an electrochromic material by simultaneous injection of electrons and small ions (such as H^+, Li^+, Na^+). EC materials have been attracting sustained interest during the last few years and show a great potential for the future in the window applications. Among various transition metal oxides, Tungsten Trioxide (WO_3) has been predominantly exploited owing to its cyclic stability and transmission in the bleached state combined with its high coloration efficiency occurring in the visible and infrared regions. EC devices based on WO_3 offer advantages such as low power consumption, open circuit memory effect, and a full angle display and consequently find applications in smart windows, reflectance variable mirrors, and information displays. WO_3 is a n-type semiconductor transparent semiconductor material that has been extensively studied for electrochromic windows applications **[1]** and gas sensing applications such as NO_2, H_2S **[2-4]**. Moreover, WO_3 has been extensively studied for applications including photocatalysis **[5]**, photochromisim **[6]** and supercapasitor **[7]**, etc.

WO_3 thin films were prepared by various methods such as Solvothermal **[4]**, Hydrothermal Reaction **[5,6,8]**, Chemical Vapor Deposition **[9-12]**, Sputtering **[13,14]**, PLD **[3,15,16]**, Sol- gel **[2,17-19]** and Spray Pyrolysis Deposition **[20-29]**. Among them, we employed a Spray Pyrolysis Deposition (SPD) technique for a thin film preparation method. Because the thin film formation is carried out in the air by a simple apparatus in SPD, the technique is one of the most attractive film preparation methods. SPD is essentially the same film processing technique as the so-called pyrosol technique, in which a source solution is sprayed on the heated substrate to be deposited as a film. In other words, when a source solution is atomized, small droplets splash, vaporize on the substrate and leave a dry precipitate in which thermal decomposition occurs. It is reported that WO_3 thin films deposited on FTO, ITO, and glass substrate by SPD Technique was usually usable EC applications **[20-29]**.

In this study, we reported, WO_3 thin films were deposited on quartz glasses by using SPD technique. Quartz glass has unique properties, such as light transmission characteristics, high heat-radiation resistance characteristics. Thus, quartz glass is a material used in many optical applications. After deposition and annealed process, the films were investigated in order to determine structural and surface characteristics with XRD, SEM.

2. Experimental

In the experiment, WO_3 thin films were deposited on to quartz glasses. The schematic representation of SPD apparatus (in our study; L=30cm, α=45°) is shown in Fig. 1**[30]**. The quartz substrates were cleaned prior to deposition by immersing in acetone in an ultrasonic cleaner than washed with methanol and deionize water and then dried in an oven, respectively.

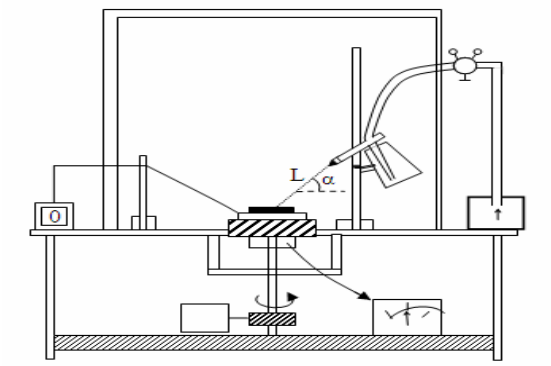

Figure 1. The schematic representation of SPD apparatus (in our study; L=30 cm, α=45°) (Güven Turgut et al., 2013)

Ammonium Tungstate ($(NH_4)_2WO_4$) was pyrolytically decomposed into WO_3 and deposited on substrates according to the following endothermic reaction **[28-29].**

$$\mathbf{WO_3+2NH_4OH \rightarrow (NH_4)_2WO_4+H_2O \quad (60\ °C) \quad (1)}$$
$$\mathbf{(NH_4)_2WO_4 \rightarrow WO_3+H_2O \uparrow + 2NH_3 \uparrow \quad (350\ °C) \quad (2)}$$

The precursor $(NH_4)_2WO_4$ was obtained by mixing WO_3 powder (99.9 %) with ammonium solution (25%) at an average temperature of 60°C (see reaction 1). The thin films were obtained by performing deposition using a freshly prepared 0.01M solution (different *V*L: 50, 75 ml, 100 ml) with a spray rate of 5 ml/min. Forced air was used as a carrier gas. The substrate temperature was maintained at 350°C during deposition (see reaction 2). Post-annealing process was performed at 500°C in air for improving the quality and crystalline structure of the thin films. The films were uniform, and well adherent to the substrates whose adherence was checked by a scotch tape test.

The structural properties were studied using X-ray diffractometer (Panalytical Empyrean) operated at 30 kV, 40 mA with CuKα radiation (λ = 1.5406 Å). The morphologies of the films were studied using a Scanning Electron Microscopy (FEI Inspect 550).

Result and Discussion

XRD patterns of the as-deposited and annealed WO_3 thin films (using different solution *V*L: 50 ml, 75 ml, 100 ml) are shown in Fig.2. All of annealed WO_3 thin films showed high intensity crystalline peaks corresponding to orthorhombic WO_3 structure. The highest intensity peaks are observed at (020) reflection for each samples. The lower intensity peaks corresponding to (212), (410), (240) reflections are observed for each sample too. However, two peaks with very low intensity are observed for as-deposited film using 75 ml, 100 ml solutions, that may be (200), (121) reflection peaks of orthorhombic phase. It is seen that as the amount of solution increases, intensity of the peaks increases too because of increasing thickness of the crystal structure. It is obvious that the film deposited at 350°C using the solution of 100 ml volume has best crystalline structure whit a very sharp major peak.

The crystallize sizes were calculated using The Scherer law **[31]**;

$$D = k\lambda/(\beta \cos\theta) \quad (1)$$

Where λ is the X-Ray wavelength, k is the constant (0.9)**,** θ is the Bragg angle, β is the full width at half maximum (see equation 1). This law is valid for crystallizes mean D (grain size) less than 200 nm **[32]**. Using XRD patterns of the thin films, it was calculated grain sizes (*D*) and *d* values. The results are gathered in Table 1 **[33]**.

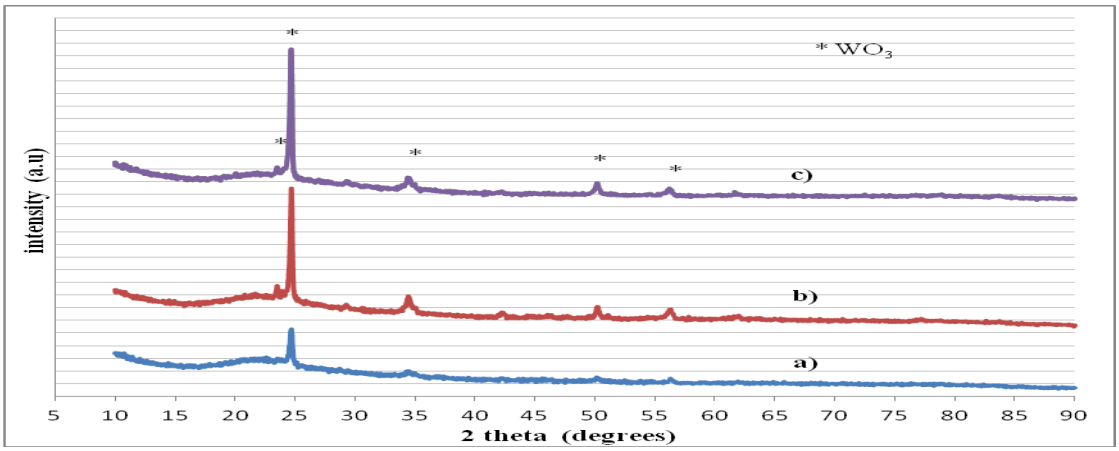

Figure 2. XRD spectra of the WO_3 thin films deposited on quartz glasses at different volumes and annealed at 500°C **[a)** 50 ml, **b)** 75ml, **c)** 100 ml**]**

Table 1. *d* space , 2 theta (degrees), Grain size (D) and (h,k,l) indices (different *VL*:50ml, 75 ml,100 ml)

XRD cards:[PDF-98-000-0836]		**Sample deposited by using 50 ml solution and annealed at 500 ºC**			
d (Å)	**2 theta (degrees)**	**d (Å)**	**2 theta (degrees)**	**D (nm)**	**(h k l)**
3,67	**24,23**	3,60	**24,72**	54,8	**(020)**
2,54	**35,29**	2,60	**34,38**	37,9	**(212)**
1,82	**50,10**	1,82	**50,17**	50,9	**(410)**
1,65	**55,61**	1,63	**56,28**	33,8	**(240)**
XRD cards:[PDF-98-000-0836]		**Sample deposited by using 75 ml solution and annealed at 500 ºC**			
d (Å)	**2 theta (degrees)**	**d (Å)**	**2 theta (degrees)**	**D (nm)**	**(h k l)**
3,76	**23,49**	3,78	**23,52**	114,7	**(200)**
3,67	**24,23**	3,60	**24,72**	65,7	**(020)**
3,04	**29,37**	3,05	**29,27**	30,8	**(121)**
2,54	**35,29**	2,60	**34,45**	37,8	**(212)**
1,82	**50,10**	1,81	**50,22**	59,0	**(410)**
1,65	**55,61**	1,63	**56,26**	41,0	**(240)**
XRD cards:[PDF-98-000-0836]		**Sample deposited by using 100 ml solution and annealed at 500 ºC**			
d (Å)	**2 theta (degrees)**	**d (Å)**	**2 theta (degrees)**	**D (nm)**	**(h k l)**
3,76	**23,49**	3,78	**23,50**	65,6	**(200)**
3,67	**24,23**	3,61	**24,69**	65,7	**(020)**
3,04	**29,37**	3,04	**29,41**	37,4	**(121)**
2,54	**35,29**	2,59	**34,62**	56,0	**(212)**
1,82	**50,10**	1,82	**50,19**	59,1	**(410)**
1,65	**55,61**	1,63	**56,16**	73,0	**(240)**

The SEM was used for morphological analysis of WO_3 thin films. The tungsten atoms distorted from their symmetrically located positions within the oxygen octahedral, to form zigzag chains with alternating short and long W- O bond distances at SEM images of the WO_3 thin films deposited by SPD technique **[29]**. WO_3 thin film showed fibrous-bridge-like network and micro porous surface morphology, deposited by using SPD technique **[21]**.

Fig.3 shows SEM images for WO_3 thin films prepared at 350 °C on quartz glasses substrates for a solution different volume (50 ml, 75 ml, 100 ml). It is shown that the micrographs captured at different magnifications ($8x10^3$- $16x10^3$) for each samples. It is observed that WO_3 thin films have a uniform, filamentous (like chain) surface morphology throughout the film surface and variable length filaments distribute all over the surface. It is clear that intensity of the fibrous structure increase, when volume of the solution increases. Such network structures are usually observed at metal oxide **[28]**.

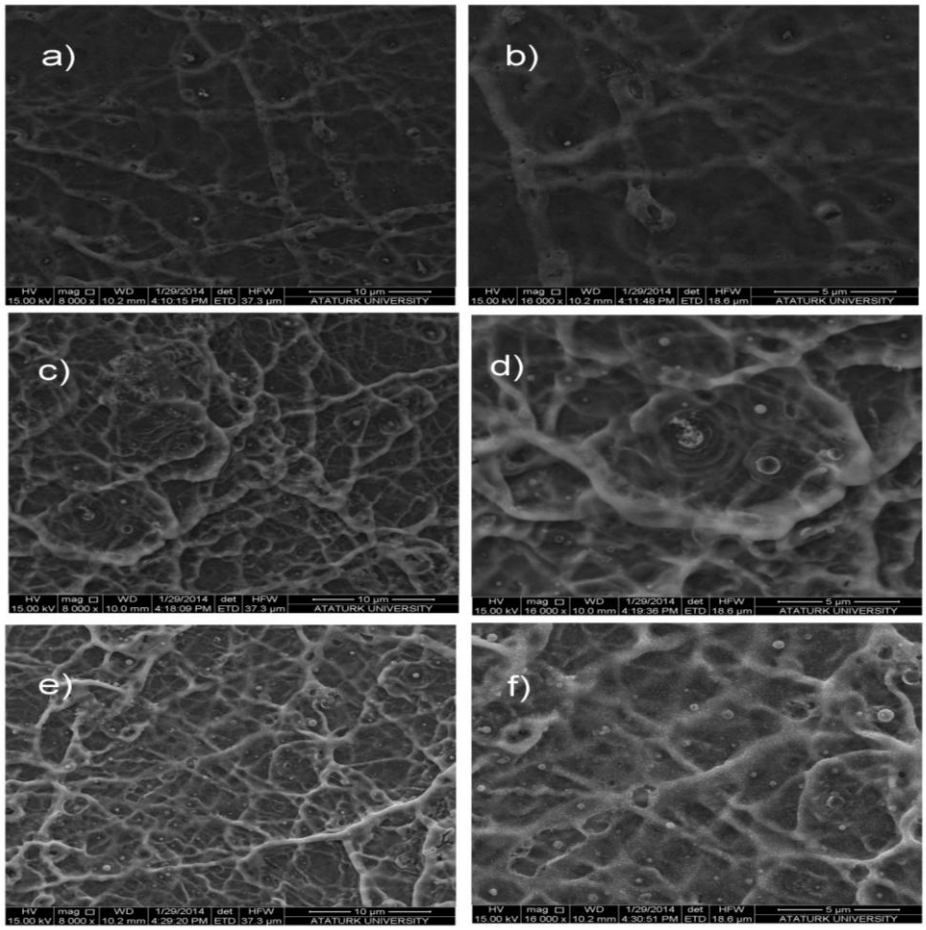

Figure 3. SEM micrographs of WO_3 thin films obtained for different solution volumes **[a)**,**b)** 50 ml; **c)**,**d)** 75ml; **e)**,**f)** 100 ml**]**

Conclusion

In this work, we deposited WO_3 thin films on quartz glasses using Chemical Spray Pyrolysis Method. The thin film was analyzed by XRD and SEM to be observed structure and surface properties. XRD patterns of WO_3 thin films deposited at 350 °C on quartz glasses (annealed samples at 500 °C) have peaks corresponding to the orthorhombic WO_3 structure. A Fibrous structure of WO_3 films was observed at SEM analysis. Such network structures are usually used for chromic application on technology. According to XRD spectra and SEM micrographs, it is obvious that the films will be able to use for electrochromic applications. At Previous studies, electrochromic performance of the films will be experienced and characterized.

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