Sol –gel derived WO_3 thin films by spin coating technique and their wettability

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Abstract

Preparation of tungsten trioxide, WO_3, thin films on c-Si substrates using sol-gel method from a precursor based on non-alkoxide materials has been done in this study. Differential scanning calorimetry, DSC, thermogravimetry, TGA, and differential thermal analysis, DTA, have been used to monitor structural changes during heating. Thermal analysis of the xerogel gives a clear idea about water evolving and phase change. X-ray diffraction, XRD, studies revealed that the film dried at 120 ˚C for 1h is non-crystalline. After heating at 700˚C for 2h, a monoclinic phase of WO_3 with preferred orientation along (200) direction appeared. Chemical bonding has been explored by Fourier transform infrared spectroscopy, FTIR. Surface roughness has been found to increase with the increase of annealing temperature as revealed from AFM measurements. At temperatures equal and above 700 ˚C, contact angle decreased due to surface roughness increase. Correlation between the characteristic properties and the contact angle measurements has been discussed.

Keywords
WO_3; sol-gel technique; thin films; surface roughness; contact angle.

1. Introduction

$WO_{3,}$ like many other transition metal oxides, has a number of interesting optical and electrical properties. Its thin films are the best known electrochromic candidates up tell now [1]. They show photochromism [2,3], gasochromism [4], photocatalysis [5], water splitting [6] and gas sensing [7]. Many of the WO_3 thin films applications involve contact with liquids. Contact angle is one of the important macroscopic properties of thin films. It is a direct measure of the wettability of a given surface. Many methods have been used to deposit WO_3 thin films, and their corresponding wettability and its effect on other properties have been studied. For example, contact angle of WO_3 have been measured for films deposited by thermal evaporation [8], pulsed laser deposition [9] and sol-gel techniques [2,4, 8]. Some studies have been carried out to correlate between gasochromism and contact angle [9, 10]. Another one linked between photochromism and contact angle [11]. In the same trend correlation between contact angle and gas sensing property has been investigated [12]. Relationship between photocatalytic activity and wettability has been explored in depth for metal oxides [13]. Wettability effect on the electrochromic properties of WO_3 thin films has been explored by Bertus et al [14]. Two parameters control contact angle, namely surface energy and surface roughness. According to Wenzel equation surface roughness tune the degree not the type of wetting [8];

$$\cos \theta_W = r \cos \theta_Y \qquad (1)$$

where θ_W is the measured contact angle, r is the surface roughness, and θ_Y is the ideal contact angle of a flat surface.

The electric field has been found to reverse the degree of wettability of a polymer [15], and WO_3 thin films covered with polymers [16]. Switching between hydrophilicity and hydrophobicity has been found to depend on many stimulators. Electric polarization, pH and temperature have been found to cause switching between hydrophobicity and hydrophilicity and their super states [17-21]. It has been monitored in polymers [17-21], transition metal oxides [22], and transition metal oxides covered with polymers [16]. It is well known that polymer surfaces conform in response to stimuli such as electric field, electromagnetic waves, pH, and temperature

[17-21]. In many cases switching between super states of wetting has been amplified by surface roughness. In fact, these effects result from surface chemistry and roughness.

Many advantages such as cost and energy reduction, deposition of high-quality films on a large area, and precise control of the microstructure and the water content of the deposited films offered by non-alkoxides routes of sol-gel technique [23-30]. Alkoxide route is expensive and needs special precautions [31, 32]. One of the inexpensive methods, which have been used to deposit tungsten trioxide thin films by sol-gel technique based on non-alkoxides is the ion exchange method [23-26]. Another non-alkoxide precursor for coating WO_3 thin films based on the peroxotungstic acid has been explored [27-30].

Many techniques have been used to measure the contact angle [33, 34]. A very simple and effective method has been developed and tested to measure it using a smart phone camera [34].

So, this study has been carried out to correlate between the structure, microstructure, chemical bonding, and wettability of WO_3 thin films prepared from the reaction of W metal and hydrogen peroxide only and discuss the obtained results in light of the previous work.

2. Experimental

2.1. Materials

2.1.1. Gel prepration

Excess hydrogen peroxide 30% (Merk) has been used to dissolve tungsten metal of purity 99.999 %. This reaction is exothermic, so the temperature of the baker in which the reaction has been carried out has been maintained at 0˚C by an ice-water system. After some hours tungsten metal powder dissolves. Sometimes vigorous reaction has been taken place ending with the formation of a milky solution. White vapors have been raised during the reaction. A clear colorless solution has been obtained after filtration. The solution has been kept in a water bath at 60 ˚C to remove excess H_2O_2. The time of heating control the properties of the prepared sol. Its color has been turned to yellow. The solution has been cooled to room

temperature and air blowing technique has been applied to give after a period of time a peroxotungstic acid, PTA, yellow xerogel.

2.1.2. Prepration of the films

A precursor solution for depositing films on c-Si substrates has been prepared by dissolving a known concentration of PTA in deionized water. Films have been deposited by spin coating. Film deposition has been carried out at a spinning speed of 4000 rpm for 1 min. The spinning rate has been measured by a tachometer. Then films have been dried at 120˚C for 1h and one of them has been annealed at 700˚C for 2 h in air.

2.2. Characterization techniques

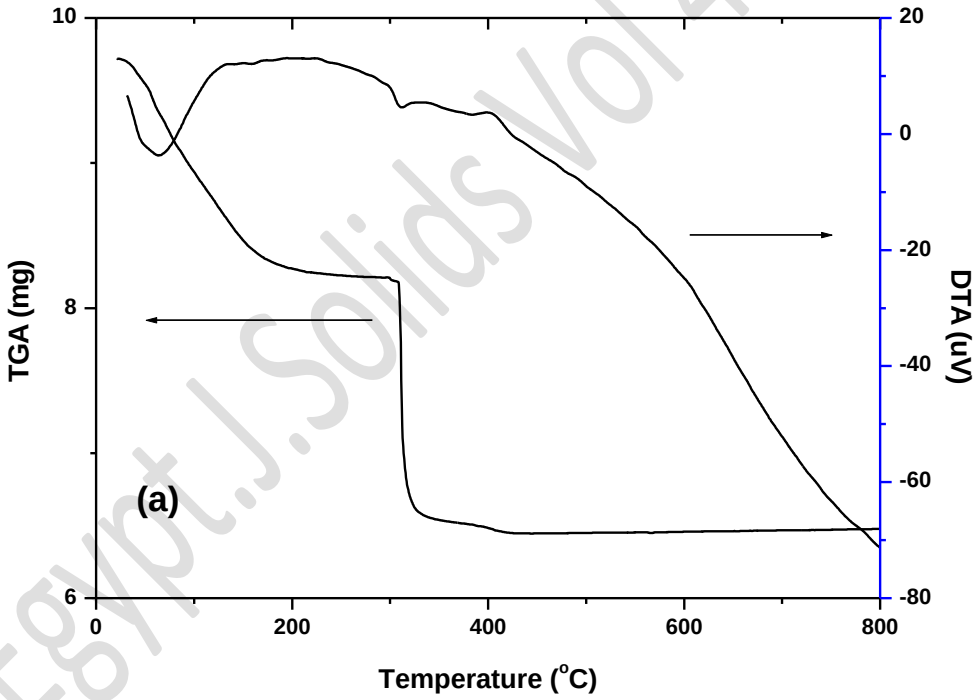
X-ray diffractograms of the deposited films have been recorded in the range of 2θ =10-80˚ by XSPEX x-ray diffractometer with search - match operation version 5.45, using CoKα radiation with an iron filter. The wavelength of the x-rays is 1.79 A˚. The d-values have been calculated using XSPEX software. The morphology of the films has been studied using AFM, PARK SYSTEM, XE-100E. Thermal analysis has been carried out by Shimadzu TGA-50H, Shimadzu DTA-50, and Shimadzu DSC-50, at a constant scan rate of 10 °C/min. The FTIR absorption spectra of specimens have been measured by FTIR-8210 PC Shimadzu spectrophotometer in the range 4000-400 cm^{-1}. First, the absorbance of the substrate has been recorded after that it has been subtracted from the absorbance of the films. Water contact angle has been measured using the sessile drop method.

3. Results and discussion

3.1. Thermal analysis

The thermal decomposition and/or phase transformation of the dried PTA xerogel studied by TGA, DTA, and DSC techniques are shown in Fig. 1. A gradual weight loss, 14% maximum value, associated with a wide endothermic peak centered at about 73 ºC has been observed as the temperature increased from room temperature to 220 ºC. This is followed by a relatively stable temperature range, where no significant weight loss has been recorded; an almost TGA flat curve up to 310 ºC. Accordingly, no thermal peaks have been recorded with DSC or DTA within that temperature

range. When the temperature reached 316 ºC, a sharp and large drop, 19%, in the sample weight has been recorded. This weight loss is associated with a small endothermic peak observed by both DTA and DSC. At a temperature of 407 ºC, a large exothermic peak, recorded with lower intensity in the DTA, associated with small weight loss has been recorded. Except for the gradual decrease in the DTA recorded signal, no distinct thermal peaks and no weight loss were observed for temperatures higher than 407 ºC, within the investigated temperature range. This observed thermal behavior is similar to those reported for sol-gel derived tungsten oxide xerogels [35-39]. However, small shifts in the onsets and offsets of these transitions and/or obtained values relative to those reported here indeed exist which are mainly due to the difference in the precursor, chemical additives, and/or ambient atmosphere.



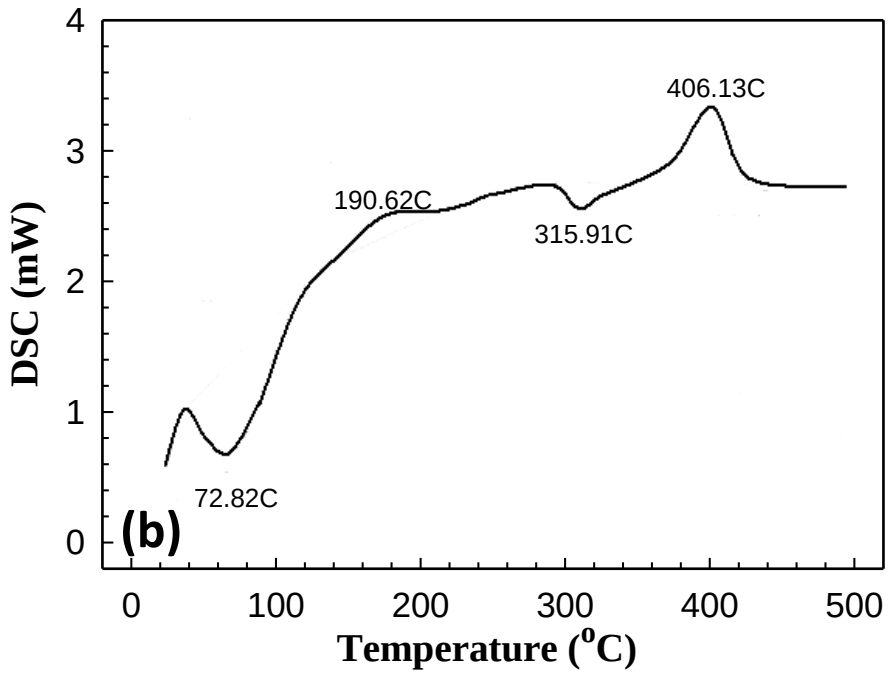


Fig.1. a) TGA and DTA, and b) DSC thermograms of the peroxotungstic acid xerogel.

It is reported that physically and chemically adsorbed water molecules are present in PTA xerogels along with structural water arising from the coordination of hydroxyl groups (W-OH) in the hydrated tungsten trioxide xerogel using NMR combined with FTIR [37,38,40,41]. The coordinated hydroxyl-groups are thermally decomposed into tungsten oxide elaborating water molecules that escape into the gas phase. Thus, the observed two-weight losses and two-endothermic peaks suggested a two-step dehydration process; loss of physically trapped water and loss of the structural water. The rather strong bonded OH groups in hydrated tungsten oxide xerogel are responsible for the higher desorption temperature of the structure water than that due to trapped/adsorbed molecules. On the other hand, water molecules adsorbed within the bulk of the sample, which cannot find its way easily to the gas phase, is responsible for the gradual weight loss observed in the TGA and the first broad endothermic peak. Finally, the small exothermic peak observed in the DSC at ~190 ºC between the two endothermic peaks could be attributed to the condensation of the W-OH groups and/or initiation

of crystallization. Similar exothermic peaks between the two endothermic peaks were previously reported for tungsten oxide precursor powders [39].

Although its intensity is lower in DTA than in DSC, an exothermal peak centered at 407 ºC is confirmed using both techniques. This peak is a typical crystallization peak of tungsten oxide into its monoclinic phase [40]. For a PTA xerogel prepared by ion exchange method, two exothermic peaks were previously reported [40]. These peaks were attributed to the formation of hexagonal WO_3 phase at the lower temperature and transformation into the monoclinic phase at the second peak. Some samples were reported to form monoclinic WO_3 phase directly showing single exothermal peak as evidenced by XRD [40]. In our experiment, we observed only a single exothermic peak, up to the maximum investigated temperature. This indicates the direct formation of a single phase tungsten oxide with powder an onset crystallization temperature to be as low as 365 ºC and complete crystallization at ~ 425 ºC. These results are consistent with that obtained for heat-treated PTA xerogels using XRD, and FTIR, not shown here.

3.2. Structure and morphology

XRD patterns of the c-Si substrate, the film dried at 120˚C for 1h, and the film annealed at 700˚C for 2h are shown in Fig.2. It is clear that the film dried at 120˚C is amorphous and crystallizes upon heating at 700˚C. The d-values of some of the XRD peaks of the crystalline film are 3.65703, 3.84728 and 1.82697. They agree with the d-values of monoclinic WO_3, JCPDS card NO: 83-0951, with a preferred orientation along (200) direction. The (200) peak has been used to calculate the crystallite size using Sheerer equation [28];

$$L = \frac{0.89\lambda}{\beta cos\theta} \qquad (2)$$

where λ equals 1.79 A˚, β is the full-width half maximum of the peak, and θ is the diffraction angle. The obtained value is 49 nm.

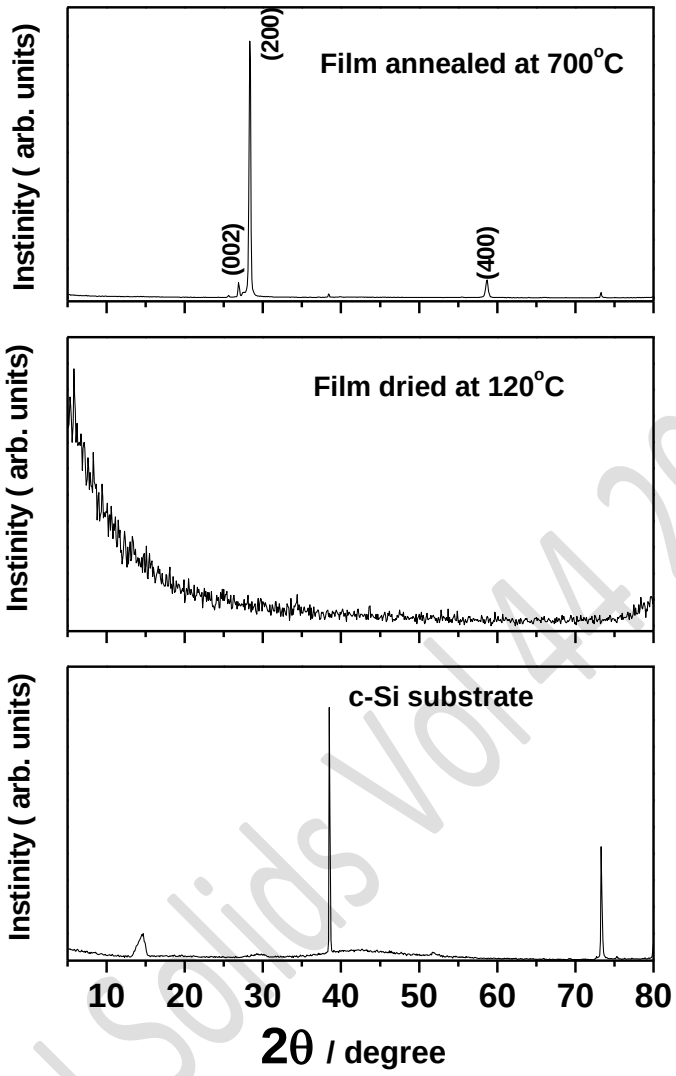


Fig.2. XRD patterns of the c-Si substrate, film dried at 120 °C and film annealed at 700 °C.

The morphology of the films has been monitored by AFM as shown in Fig. 3. Surface roughness increased with the increase of annealing temperature. The root mean square, RMS, values of roughness increased from 55 to 105 nm for samples annealed at 800°C and, 900°C, respectively. At 800 °C annealing temperature for 1h, Usta et al [42] found that the value of RMS roughness of a WO_3 thin film equals 24 nm for films deposited by thermal evaporation. By the same method, Kumar et.al [43] found it equals

23 nm after annealing at 600°C for 1h, and Jafari et al [37] found it equals 48 nm for a film annealed at 500°C for 1h.

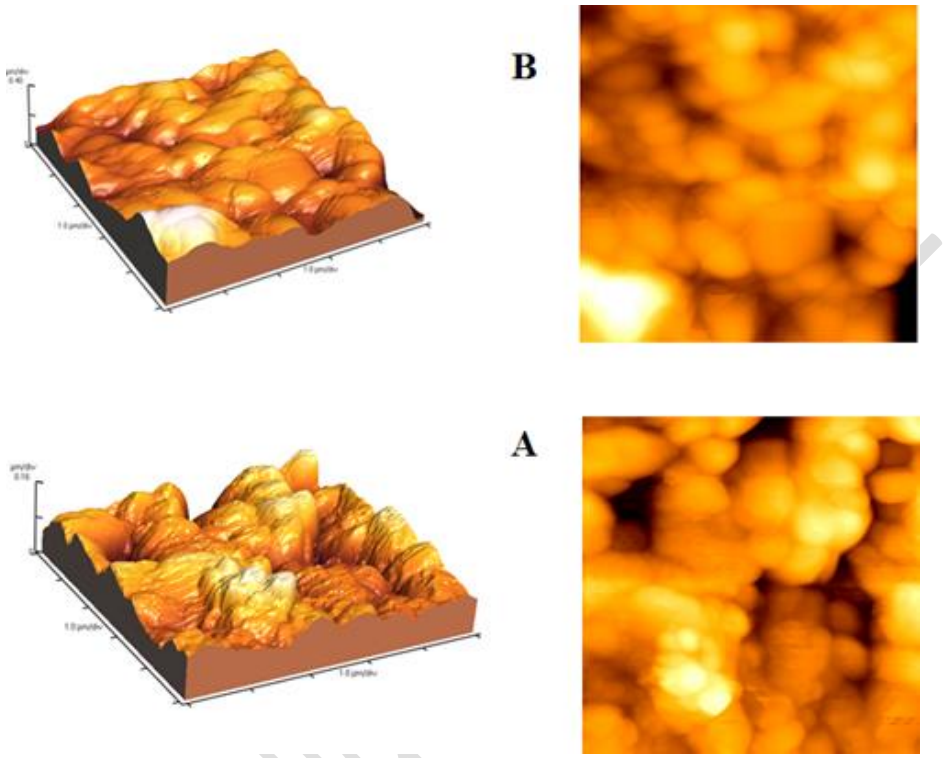


Fig. 3. AFM images of the films annealed at 800°C (A), and that annealed at 900°C (B).

3.3. Chemical bonding

Many studies have been reported for bonding in WO_3 thin films [8-11]. For thin films and bulk samples prepared by sol-gel technique, FTIR spectroscopy gives a clear idea about hydration, hydroxylation, and crystallinity [8-11,40,41]. The spectra of the film dried at 120°C and that annealed at 700°C are shown in Fig. 4. Table 1 assigns the bonds between atoms in the film. It is clear that there is a difference between the amorphous and crystalline structures from the existence of different groups and sharp peaks.

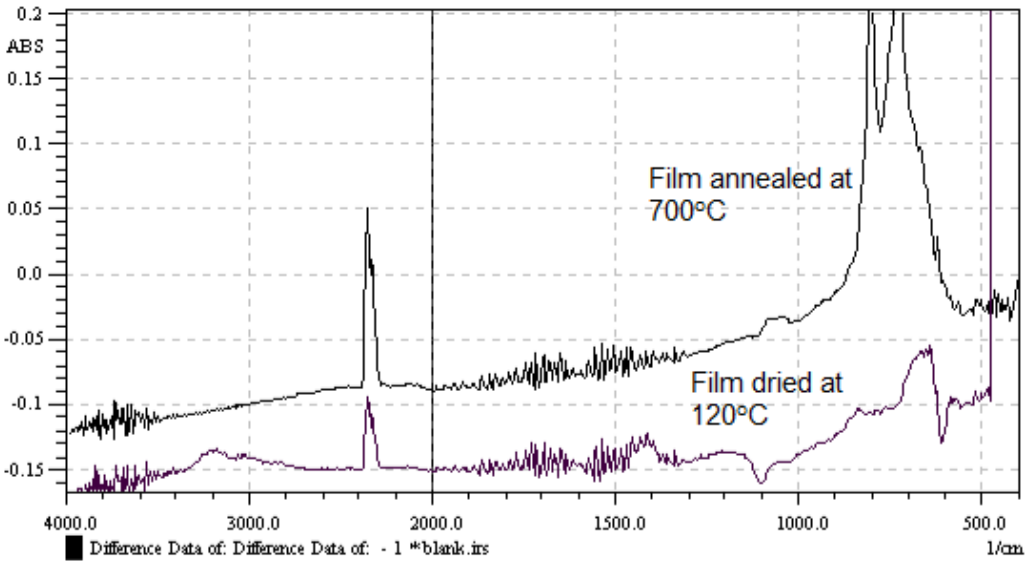


Fig.4. FTIR spectra of the film dried at 120°C, and that annealed at 700°C

Table 1 : Vibrational modes of the films.

Band assignment	Film deposited at 120 °C	Film deposited at 700 °C
ν(W-O-W)	-------	717 cm^{-1}
ν(O-W-O)	-------	790 cm^{-1}
ν(W-O-W)	600-720 cm^{-1}	------
ν(W═O)	------	1020-1100 cm^{-1}
ν(W-OH)	1500-1330 cm^{-1}	------
CO_2	2330 cm^{-1}	2330 cm^{-1}
ν(OH)	3350-2700 cm^{-1}	------

3.4. Contact angle measurments

Fig.5 shows the measured contact angles of the film annealed at 700 ºC, 800ºC and 900ºC, respectively. The associated average contact angles are 50 ± 3°, 35 ± 5°, and 20 ± 1°.

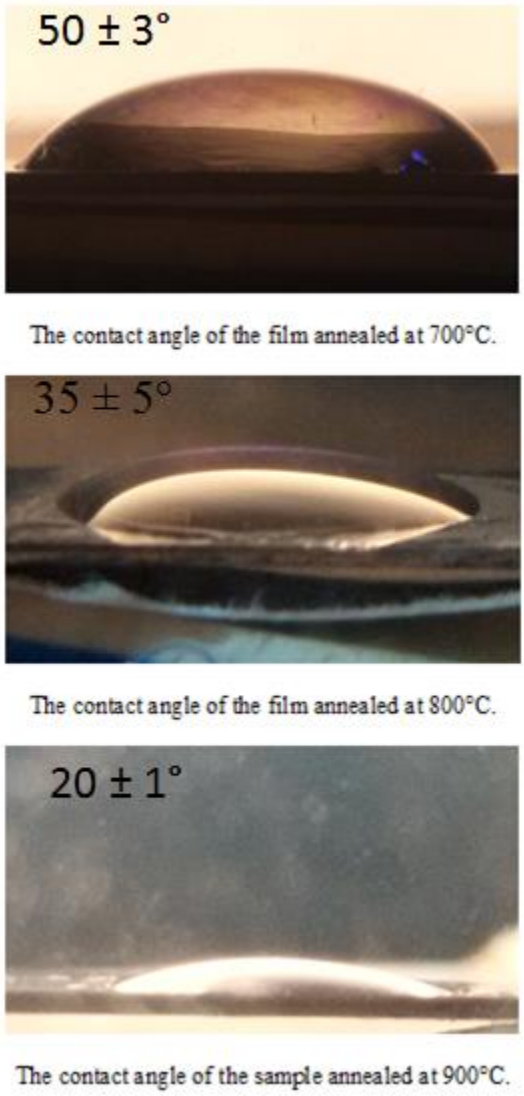


Fig. 5 Contact angle measurments.

A hydrophobic to hydrophilic transition has been recorded for WO3 thin films deposited by spin coating using nearly a method similar to that used in this study. Films have been annealed up to 400°C [10]. Contact angle

decreased with the increase of temperature. This behavior has been attributed to surface desorption of water molecules [10]. A similar chemisorbed water content of the surface has been found to affect the contact angle assisted by surface roughness for WO3 films deposited by dip coating and thermal evaporation and annealed up to 400°C [8]. The high is the concentration of the chemisorbed water the high is the contact angle. Surface roughness causes an opposite effect. In the above study, the contact angle increased at 500°C in spite of the increase of surface roughness and absence of water [8]. An increase in the contact angle with the increase of deposition temperature has been found for films deposited by PLD [9]. The behavior has been attributed to the increase of hydroxylation. But if we look carefully we will find that contact angle increased with the decrease of roughness. So, it can be said that there is more than one factor control the wettability trend that can be correlated to surface energy, which opens this point for further studies. In the studied samples, surface roughness controls the contact angle. It decreases with its increase.

4. Conclusion:

A non-alkoxide sol-gel route has been used to prepare a precursor of the WO_3 powders and thin films. The precursor is a peroctungstic acid, PCA. Amorphous based and monoclinic crystalline WO_3 thin films have been gown on c-Si substrates using the spin coating method. A good correlation between different characterization techniques has been found. DTA and DSC results show that starting from 400ºC, crystallization completes, and moreover, DTA and TGA confirmed that there is no phase change up to 800 º C. FTIR spectra and XRD patterns confirmed the thermal analysis studies. At temperatures equal and above 700°C, surface roughness increased. Consequently, the contact angle decreased.

Declaration of Conflicting Interests

The author(s) declared no potential conflicts of interest concerning the research, authorship, and/or publication of this article.

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