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THE ELECTROCHROMIC PROPERTY OF WO_3 THIN FILM PREPARING BY MAGNETRON SPUTTERING UNDER VARIOUS CRYSTAL STRUCTURES

Haider A. Shukur[1]

[1] **PhD Engineer, Electronic and Communication Department, faculty of engineering, University of Kufa, Najaf, Iraq, Email: haidera.alhattab@uokufa.edu.iq**

ABSTRACT

Tungsten Trioxide (WO_3) thin films with a various crystal structure have been fabricated by a magnetron sputtering method. The effect of changing of crystal structure on the Electrochromic (EC) property was investigated. Atomic force microscopy (AFM) and X-ray diffraction (XRD) have been employed to investigate morphology and structure. For EC measurement, 0.1M $LiClO_4$ aqueous solution was used as electrolyte, and Pt and Ag/AgCl were used for counter and reference electrodes respectively. WO_3 thin film with a various structure has been obtained by changing reactive gas (Ar) gas and O_2 flow rates. Fabricated WO_3 thin films with 002 and 112 crystal structures have a high Electrochromic (EC) response.

KEYWORDS: Thin films, WO3, Electrochromic characteristics, Sputtering Deposition

الخواص الالكتروكروميكية لتراكيب بلورية مختلفة للغشاء الرقيق WO_3المحضر بطريقة الترسيب الماغنترون

حيدر علي شكر

دكتوراه هندسة، قسم الهندسة الالكترونية والاتصالات، كلية الهندسة، جامعة الكوفة، الكوفة، العراق

الملخص

قد تم تكوين غشاء رقيق لاوكسيد التانغستن بتراكيب بلورية مختلفة بواسطة طريقة الترسيب الماكنترونيه وتم دراسة تاثير اختلاف التركيب البلوري للغشاء المصنع على الخاصية الاكتروكروميكية لكل غشاء. شكل السطح الغشاء و مقدار خشونتةتم قياسه بواسط جهاز مجهر القوة الذري(AFM) و التركيب البلوري للاغشية بطريقة حيود الاشعة السينية(XRD). اختبار الخاصية الاكتروكروميكية تم بواسطة جعل المحلول المائي المتوازن 0.1M $LICLO_4$ كقطب و PT كمصدر و AG/AGCL كقطب ثاني. التحكم بالتركيب البلوري لاوكسيد التانغستن تم عن طريق تغيير نسب سريان غازي الاوكسجين و الاركون داخل غرفة صناعة الاغشية .النتائج بينت ان التركيب البلوري له تأثير كبير على الخاصية الاكتروكروميكية بحيث ان الغشاء الذي صنع بتركيب بلوري على الوجوه 002 و 112 كان بمواصفات الاكتروكروميكية عالية.

1. INTRODUCTION

Among transition metal oxides, tungsten trioxide WO_3 thin film is the most hopeful material showing a wide range of novel properties to use in various practical fields. The Electrochromic (EC) property of WO3 thin film anticipated in many fields such as display devices, solar memory devices and windows applications (smart windows) (Gesheva et al. 2012). In smart windows the lighting level inside the room can be controlled by the glass that coated by WO_3 thin film, it is thought to perform energy-saving by reducing the operating time of room air-conditioner and this takes part in the energy-saving revolution (Huang et al. 2015).

EC property of WO_3 thin film has a deep correlation with surface morphology, atomic ratio of tungsten/oxygen and porosity of thin film (Chiu et al. 2014). In this respect, it is possible that EC property also affected by formation method, formation condition subsequently structure of thin film. In other word, the crystal structure of WO_3 thin film has a significant impact on the EC property (Mitsugi et al. 2002). Nevertheless only few works researched about the relation between nanostructure and EC property of WO_3.

Additionally, there are many researchers have been used various methods to prepare WO_3 thin film such as pulsed leaser deposition, Sol-gel preparation, vacuum evaporation (Subramanian & Karuppasamy 2007), while only a few researchers used sputtering method with DC sputtering source. Sputtering method has a superior features such as, the ability to form a homogenous thin film, sputtered particles have a kinetic energy of several tens of eV which enhance the quality of film (Henini 2000), also it can provide a precisely control of deposition parameters such that it is possible to control the structure of the deposited WO_3 thin film (Lin et al. 2016) and (Beering et al., 1998)

The aim of this study is to control the structures of WO_3 thin film and investigate the mechanism of thin film structure creation under different fabrication condition, also to investigate the EC property under different structure.

2. EXPERIMENTAL

2.1. Preparation of WO_3 thin film

Fig. 1 shows the multi-process coating system with three different target. In this study Tungsten (W) target with DC magnetron sputtering source was used to fabricate the WO_3 thin film. Cleaning process of substrate was carried out in a separated chamber (not shown in Fig.1) before fabrication process when the coating glass (number 1737) substrate and indium Tin oxide (ITO) glass (For EC property measurement) were sputtered by Ar^+ ion for 10 min to remove the carbon contaminant layer. Deposition chamber was pumped up by a turbo molecular and a rotary pump to reach pressure less than 1.3×10^{-5} Pa. The film fabrication process was carried out under conditions shown in Table 1, reactive Ar gas was inlet near the W target under flow rate of 5 and 10 sccm and input power of 100 W to induce a required plasma to sputter W. simultaneously, O_2 gas was inlet to chamber at a flow rate from 10,12,15 and 20 sccm. The pressure of the film deposition chamber was kept at 8×10^{-2} Pa and at 473 K in a substrate temperature through deposition process. The deposition rates of W thin film were measured by using a quartz crystal microbalance (QCM), which showed 0.027nm/s under 10 sccm and 0.03nm/s under 20 sccm in an O_2 gas flow rate, respectively. The variation in deposition rates due to the surface oxidation of a W target, however the sputtering time was calculated to fix 100 nm in film thickness under each formation condition.

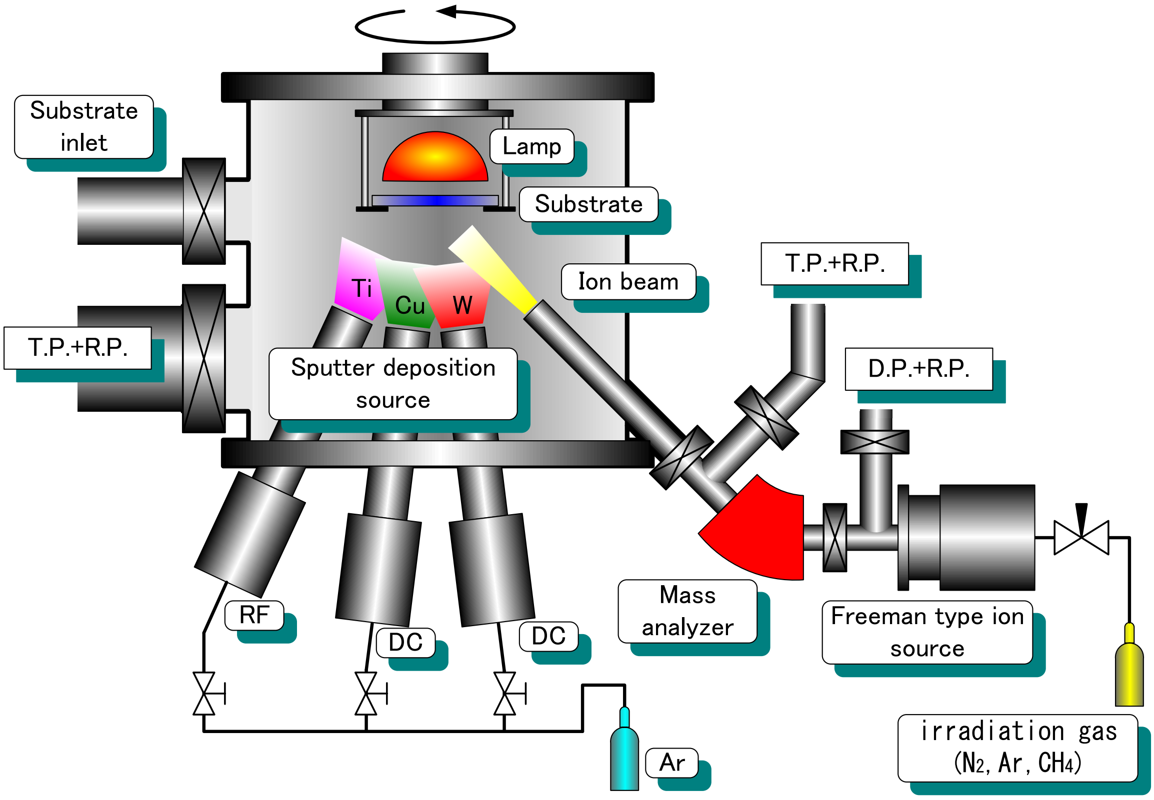

Fig. 1. Multi-process coating system

Table 1. Fabrication conditions

Ar flow rate (sccm)	O_2 flow rate (sccm)				Power (W)	Thickness(nm)
5	10	12	15	20	100	100
10	10	12	15	20		

2.2. Film characterization measurement

The film structure was determined by X-ray diffraction (XRD: MAC science High quality XG M18XCE) with CuKα (0.154 nm) radiation at an incident angle of 0.3°. The surface morphology of samples was observed by an atomic force microscopy (AFM: Shimadzu SPM-9500). For EC measurement, 0.1M $LiClO_4$ aqueous solution was used as electrolyte, and Pt and Ag/AgCl were used for counter and reference electrodes respectively. Coloration and bleaching of the EC cells were carried out by applying DC voltages of -0.5V and +0.2V, respectively, with respect to the reference electrode.

3. RESULTS AND DISCUSSION

3.1. Structure and surface morphology

Figs. 2a and 2b shows XRD patterns of films that sputtered under Ar flow rate of 5 and 10 sccm respectively. O_2 flow rate has been changed from 10 sccm to 20 sccm under each Ar flow rate. In Fig. 2a, the films that formed under O_2 flow rate of 10, 12 and 20 sccm showed a strong peak of 112 phase and weak peak of 022. While the film prepared with O_2 flow rate of 15 sccm showed a 112 single peak of WO_3 structure. In Fig. 2b, the sample prepared at 10 sccm showed a strong 112 phase peak and a weak 002 and 022 phases peak. But the sample prepared at 15 sccm O_2 flow rate showed a strong peak for all 112, 002 and 022 peaks and the film was changed from single phase to mixed structure. With increasing O_2 flow rate more than 15 sccm, the film showed only the 112 peak, which mean a single phase WO_3 structure.

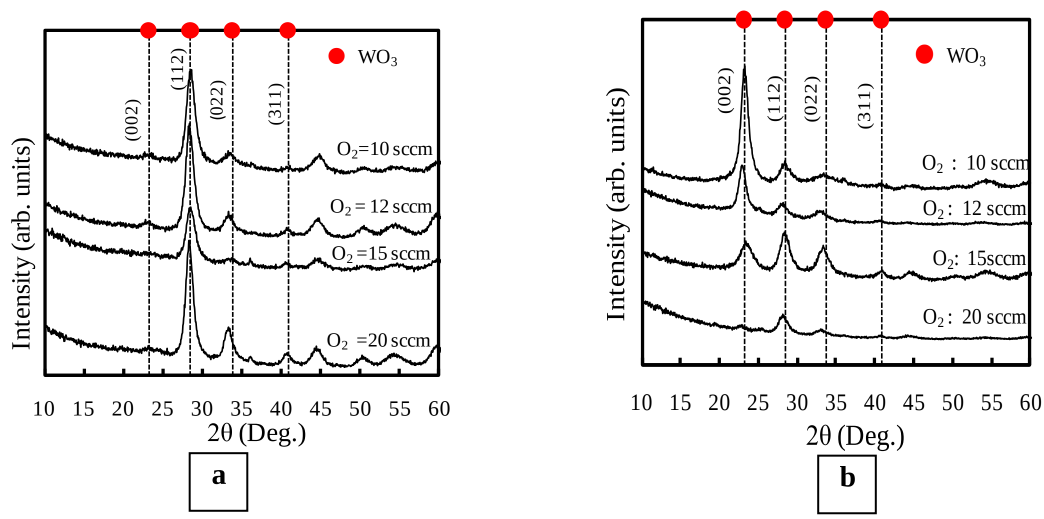

Fig. 2. XRD patterns under various O_2 flow rates and a) reactive gas Ar=5 sccm, b) reactive gas Ar= 10 sccm.

Generally, higher O_2 or O_2^+ Ar gas flow rate ratio reduces the incident Ar ion on the W target. Further, in sputtering method, a high O_2 flow rate increases the impedance of the plasma and reducing the voltage difference between the substrate and the target. Thus, the number of incident Ar ion on the target is reduced (Subrahmanyam & Karuppasamy 2007). Furthermore, it is possible that the increasing of O_2 flow rate oxidized the molecular of the target surface.

Therefore, it can be considered that the atoms of W target surface blown in W or W-O form and deposited on the substrate with a various shapes, and this can mainly influence the crystal structure of the deposited samples (Avellaneda 2007). From XRD pattern results, by using the reactive magnetron sputtering, with changing O_2 flow rate (Atmosphere gas) and Ar gas (reactive gas), it is well know that a WO_3 thin film with a different crystal structure can be produced.

Surface morphology of WO_3 prepared at Ar 5 sccm and 10 sccm is shown in Fig. 3a and 3b respectively with a measured area of 1x1 μm for all samples. For each value of Ar gas flow rate the O_2 flow rate was changed from 10 sccm to 20 sccm. In Fig. 3a, at 10 sccm O_2 flow rate the surface roughness (Ra) was 0.574nm, by increasing O_2 flow rate the no large difference has been observed. In Fig. 3b, the samples prepared at 12 and 15 sccm showed a large surface morphology comparing with the other two samples. The samples that showed a mixed crystal structure in XRD pattern showed also a high surface roughness, it can be considered that the results of both of the measurements are compatible.

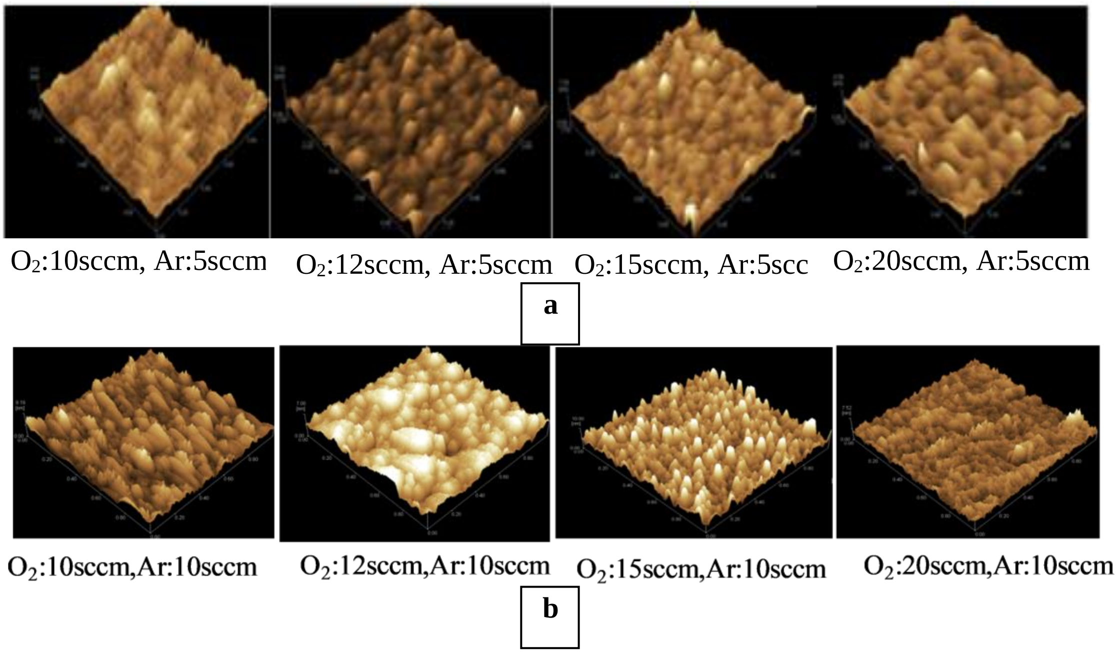

Fig. 3. Surface morphology of fabricated WO_3 thin film under various O_2 flow rates and a) reactive gas Ar=5 sccm, b) reactive gas Ar=10sccm with a measured area of 1x1 μm.

3.2. Electrochromic property

Fig. 4a and 4b show the cyclic potentiometer properties of the sampled prepared at O_2 flow rate from 10~20 sccm and 5 and 10 sccm of Ar flow rate. In this measurement, the current was measured when a Dc voltage from -1 to +1.5 V has been applied between each sample and the Ag/AgCl electrode (Yamamoto et al. 2002). Fig. 5 and 6 show the visible light (VL) transmittance through the samples prepared at O_2 flow rate from 10~20 sccm and 5 and 10 sccm of Ar flow rate respectively. In this measurement, the coloration efficiency was measured by measure the area between the two transmittance curves in blanches and coloured state of each sample. In Fig. 4a, for the sample prepared at 10 sccm of O_2, A current of -0.5mA was flow when a -1.0V voltage was applied through the WO_3 electrode while the current decreased to -0.35mA for the sample prepared 15 sccm of O_2 for the same value of applied voltage. Furthermore, with increasing of O_2 flow rate the current was decreased with a wide range value until it reached to -0.025mA at 20sccm of O_2 flow rate. With increasing of O_2 flow rate the coloration area was decreased as it shown in Fig. 5. In figure 6, for the sample prepared at 10sccm of O_2 flow rate the follow current was -0.9mA at -1.0V of applied voltage, while the current has been decreased to -0.75mA at 15sccm O_2 flow rate. Additionally, the current decreased to -0.5mA for the sample prepared with maximum O_2 flow rate of 20sccm. In figure 6, for the sample prepared at 10sccm of O_2 flow rate it is clear that area between the curves is the most widely, this area was narrowed by increasing O_2 flow rate gradually. In this case, according to the results of XRD, for the samples prepared at 10sccm of Ar flow rate the crystal structure has changed from 002 single to 002,112 and 022 mixed crystal structure with increasing of O_2 flow rate until it became 112 approximately amorphous crystal structure with increasing O_2 flow rate. Here, it was noticed that the samples with a single crystal structure shown an excellent coloration efficiency more than the samples with a mixed crystal structure. From the above results, the sample with 002 crystal structures observed excellent EC properties, while the EC performance has been declined for the samples with 112 crystal structures. The WO_3 with 002 and 112 crystal structure exhibits the best EC properties.

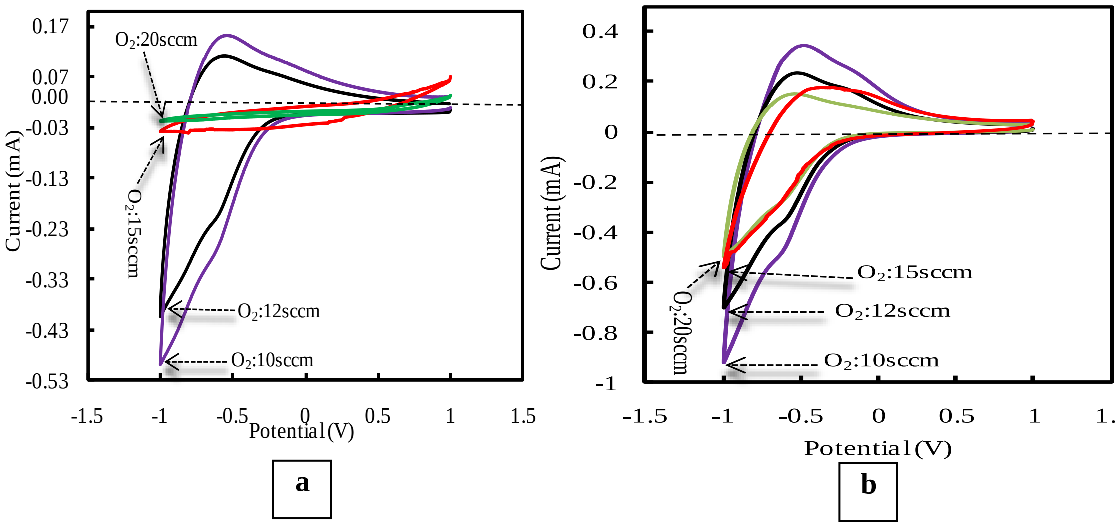

Fig. 4. Cyclic potentiometer of fabricated WO_3 under various O_2 flow rates and a) reactive gas Ar =5 sccm, b) reactive gas Ar =10 sccm.

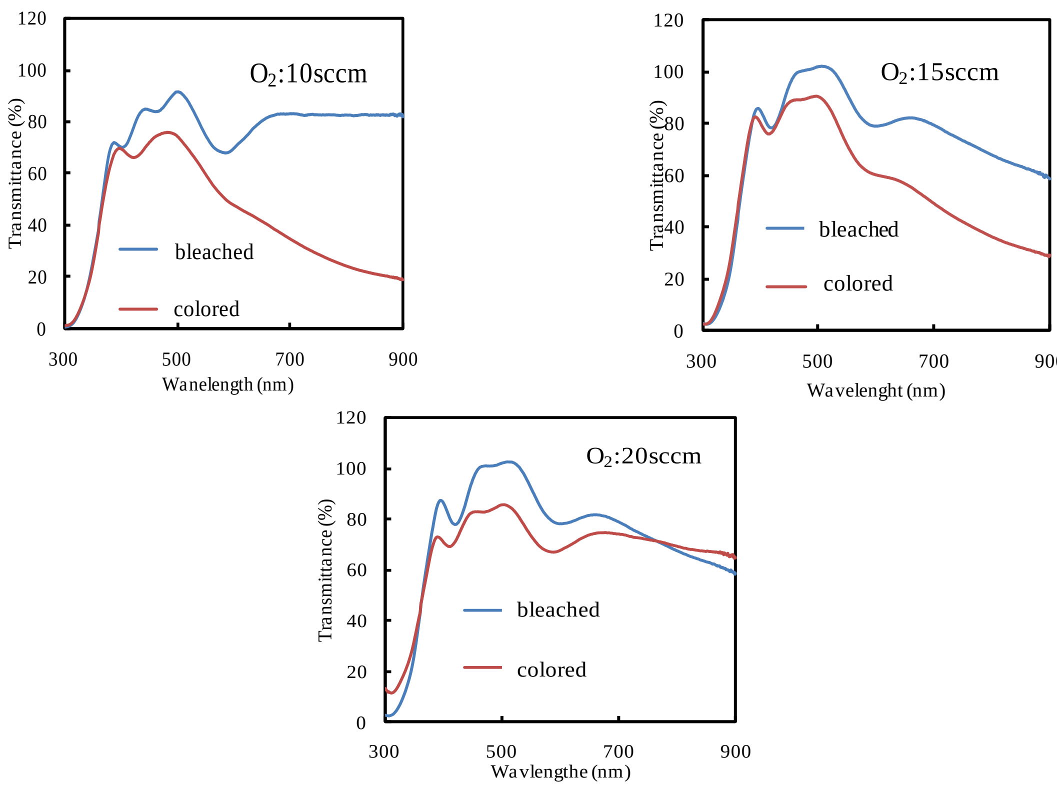

Fig. 5. VL transmittance through WO_3 at Ar=10sccm and various O_2 flow rates

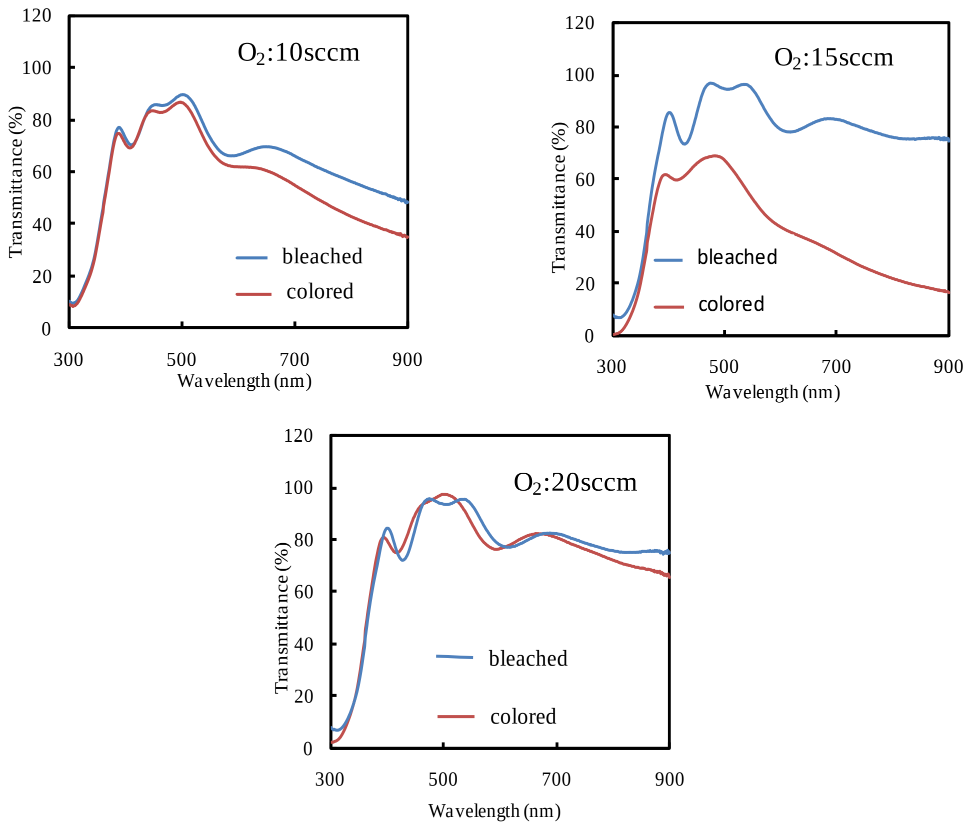

Fig. 6. VL transmittance through WO_3 at Ar=10sccm and variousO_2 flow rates

4. CONCLUSION

WO_3 thin film was prepared by sputtering magnetron deposition method. Structure and EC properties have been studied under various O_2 and reactive Ar gas flow rate.

WO_3 thin film with a mixed structure showed a high surface roughness while the film with same crystal structure showed the same surface roughness. The WO_3 with 002 crystal structure showed an excellent EC behavior, when the crystal structure changes to 112 the EC properties were declined. However, it became clear that the WO_3 thin films with 002 and 112 crystal structures show the best EC property

This study showed that the structure of WO_3 thin film is related to deposition conditions strongly and showed what parameter is important to control structure. This work also phenomenologically analyzed and elucidated phenomenon of EC with change of WO_3 thin film structure.

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