Karaj branch

Journal of Applied Chemical Research

jacr.kiau.ac.ir

Journal of Applied Chemical Research, 12, 1, 58-67 (2018)

Investigation of Structural, Morphological and Optical Properties of Chromium Oxide Thin Films Prepared at Different Annealing Times

Fatemeh Hajakbari[*], Alireza Hojabri

Department of Physics, Karaj Branch, Islamic Azad University, Karaj, Iran

(Received 12 Mar. 2017; Final version received 15 Jun. 2017)

Abstract

Chromium oxide (α-Cr_2O_3) thin films were prepared using thermal annealing of chromium (Cr) films deposited on quartz substrates by direct current (DC) magnetron sputtering. The annealing process of the films was performed for different times of 60, 120,180 and 240 min. The influence of annealing time on structural, morphological and optical properties of the prepared films was investigated by different analysis including X-ray diffraction (XRD), atomic force microscopy (AFM) and spectrophotometry. The XRD patterns showed that upon thermal annealing the Cr films transformed to (α-Cr_2O_3) and the annealing time has a profound effect on crystalline structure of chromium oxide films. According to AFM results, the films surface morphologies were strongly dependent on annealing time and an increase in annealing time led to an increase in the grain size as well as in the surface roughness. The transmittance of the as deposited film was found very low and it improved after annealing.

Keywords: *Sputtering, Chromium oxide, Annealing time, Atomic force microscopy, Transmittance.*

****Corresponding author**: Fatemeh Hajakbari, Department of Physics, Karaj Branch, Islamic Azad University, Karaj, Iran. E-mail: fatemeh.hajakbari@kiau.ac.ir.*

Introduction

Chromium oxide thin films exhibit very good properties such as chemical inertness, mechanical strength and stability, high hardness and optical characteristics [1-8]. Chromium oxide is an important catalyst and a major constituent in many ceramics. There are many crystalline phases of the chromium oxide, including Cr_2O_3, CrO_2, Cr_3O_4, Cr_5O_{12}, Cr_2O_5 and CrO_3 [1]. Among the various chromium oxides, Cr_2O_3 is the most stable under ambient conditions. Cr_2O_3 films can present either p-type or n-type semiconductor behavior, depending on the growth conditions [2]. The Cr_2O_3 films have a wide range of applications, such as corrosion protection [1, 2], wear resistance [1, 2], gas sensor [3], rechargeable lithium ion batteries [4] and optics [5]. Optical applications of Cr_2O_3 thin films include electrochromic coatings and infrared (IR) transmitting coatings [5].

On the other hand, the surface morphology, chemical composition, structure, optical properties and applications of Cr_2O_3 films depend critically on the growth parameters and deposition technique [1-8]. Various chemical and physical techniques have been used for the growth of chromium oxide thin films on different substrates. P. M. Sousa et al [2] reported the synthesis of Cr_2O_3 thin films onto sapphire substrates at room temperature by low pressure laser chemical vapor deposition. X. Pang et al [6] studied the preparation of chromium oxide coatings by reactive radio frequency (RF) magnetron sputtering and investigate the effects of annealing temperatures and times on microstructure and mechanical properties of prepared films. They observed that the coating adhesion was improved by annealing.

S. Punugupati et al [7] reported the epitaxial growth of Cr_2O_3 thin films on sapphire substrates by pulsed laser deposition method. Synthesis of nanocrystalline Cr_2O_3 films on silicon wafers using arc ion plating was investigated by T. G. Wang et al [1]. The results of their investigations showed that the highest thermal stability was obtained for the films prepared at the bias voltage of −100 V due to its most compact structure and the lowest defect density. After the heat treatments, all the films cracked due to the big difference in thermal expansion coefficient between the Cr_2O_3 film and silicon wafer, which caused large thermal stresses. Furthermore, the heat treatment also had a strong influence on the grain size of the Cr_2O_3 films.

M. F. Al-Kuhaili et al [5] studied the effects of substrate temperature on optical properties of chromium oxide thin films deposited by electron beam evaporation method. They observed that the optical characteristics of films such as the refractive index, the extinction coefficient and the

optical band gap increased with substrate temperature. In addition to these deposition techniques, metal oxide thin films can be produced by two-step method using sputtering followed by thermal oxidation process [9-13]. This technique compared to other methods is efficient, low-cost and convenient, and has the following advantages. A sputtering process with a pure metal target followed by thermal oxidation is preferable because the metal oxide film and interfacial layer can be controlled during the thermal oxidation process and the stoichiometric metal oxide film can be formed. Also, it avoids the additional introduction of reactive gas (O_2) during reactive sputtering deposition and achieves a high growth rate. However, to the best of our knowledge, few works are available on the preparation of chromium oxide thin films by this method [12]. Therefore in this investigation, Cr_2O_3 thin films were obtained using sputtering followed by annealing and the main purpose of this article is to study the influence of annealing time on structural, morphological and optical properties of the prepared films.

Experimental

In the present experiment, chromium oxide (Cr_2O_3) thin films were prepared by two-step method. Firstly, the chromium (Cr) thin films were grown on quartz substrates by DC magnetron sputtering from a chromium target (purity 99.999%). Before the deposition process, the quartz substrates were cleaned with acetone and ethanol in ultrasonic bath for 15 minutes. The distance between target and substrate was 7 cm and the deposition chamber was initially evacuated to achieve a base pressure of 5×10^{-5} torr by means of a rotary and diffusion pumps. After introducing argon gas as working gas, the total pressure was kept constant at 4×10^{-2} torr and deposition process for all films was performed for 10 minutes. After that, the deposited Cr films were transferred to a tubular furnace for thermal oxidation. The annealing process of the films was performed at 800 ˚C under a flow of high purity oxygen for various times of 60, 120,180, 240 min and then the films denoted as Q1, Q2, Q3 and Q4 respectively. The effect of annealing time on structural, morphological and optical properties of Cr_2O_3 thin films were studied by different analyzing methods. The crystal structure of the films were characterized by X-ray diffraction (XRD, Philips, pw 1800) using Cu Kα radiation (λ=0.1506 nm) at 40 kV and 30 mA in the 2θ scan range from 10 to 70. The morphology of prepared films was studied by atomic force microscopic (AFM, Park Scientific Instrument, Auto probe cp USA) and the transmittance spectra of the films were recorded using a spectrophotometer (CARY 500 Scan).

Results and discussion

The structural analysis of prepared films is carried out using XRD to find out their structure and phases. The XRD patterns of chromium films deposited on quartz substrates indicated that there was no peak except a peak in $2\theta=21^{\circ}$ relating to a quartz substrate (the figure not shown here), that means the as deposited chromium thin films were amorphous before thermal annealing. The XRD patterns of the annealed films on quartz substrate at different annealing times are shown in Figure 1. From the figure, it is observed that after annealing, the Cr_2O_3 phases can be observed in all annealing times due to an oxidation of chromium films. The film formed at annealing time of 60 min shows three weak diffraction peaks. The peak located at 21° is due to the quartz substrate and two other peaks are related to (110) plane of chromium oxide and (110) plane of unoxidized chromium respectively.

The existence of mixed phases of chromium and chromium oxide confirmed that this annealing time is insufficient for oxidation of all chromium films. With increasing the annealing time to 120 min only one intense peak identified and indexed to the (110) plane of the Cr_2O_3. Further increase of annealing time to 180 min leads to change in crystallography direction from (110) to (024). The high intense and sharp peaks observed in the XRD patterns of the films at annealing time of 120 and 180 min confirms the highly oriented and good crystallinity of the films [13]. In addition the films crystallinity is improved by augmentation of annealing time from 60 min to 180 min. These results indicate that the crystalline quality of the Cr_2O_3 films improved with annealing time within 180 min. However, when the annealing time is increased to 240 min, the intensity of the Cr_2O_3 peaks in the XRD pattern obviously decreased. This suggests that the crystalline quality of the film annealed for 240 min has been degraded. Similar results were obtained in our earlier works for CuO and MoO_3 thin films [10, 13]. Moreover for sample prepared at annealing time of 240 min, in addition to peaks corresponding to (110) and (024) orientations, a new weak diffraction peak is observed belonging to (300) orientation. The XRD results show that the annealing time has a profound effect on crystallinity and crystallographic orientation of Cr_2O_3 thin films. These factors can affect the performance and application of devices.

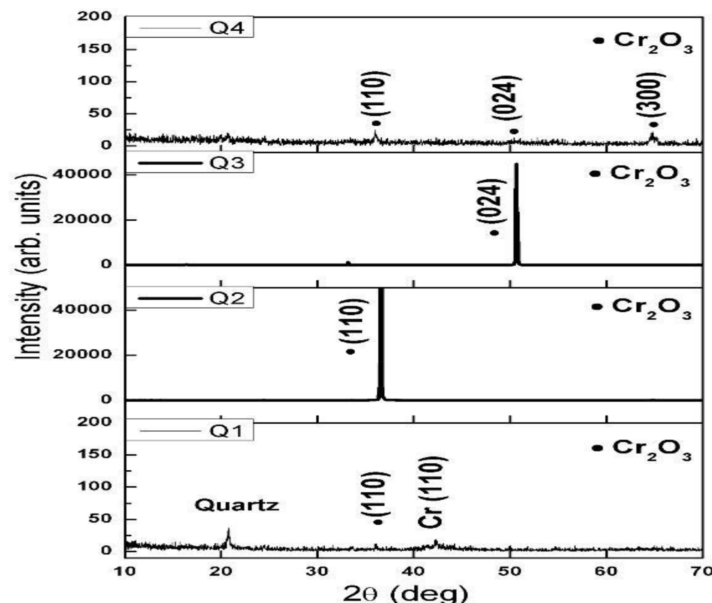


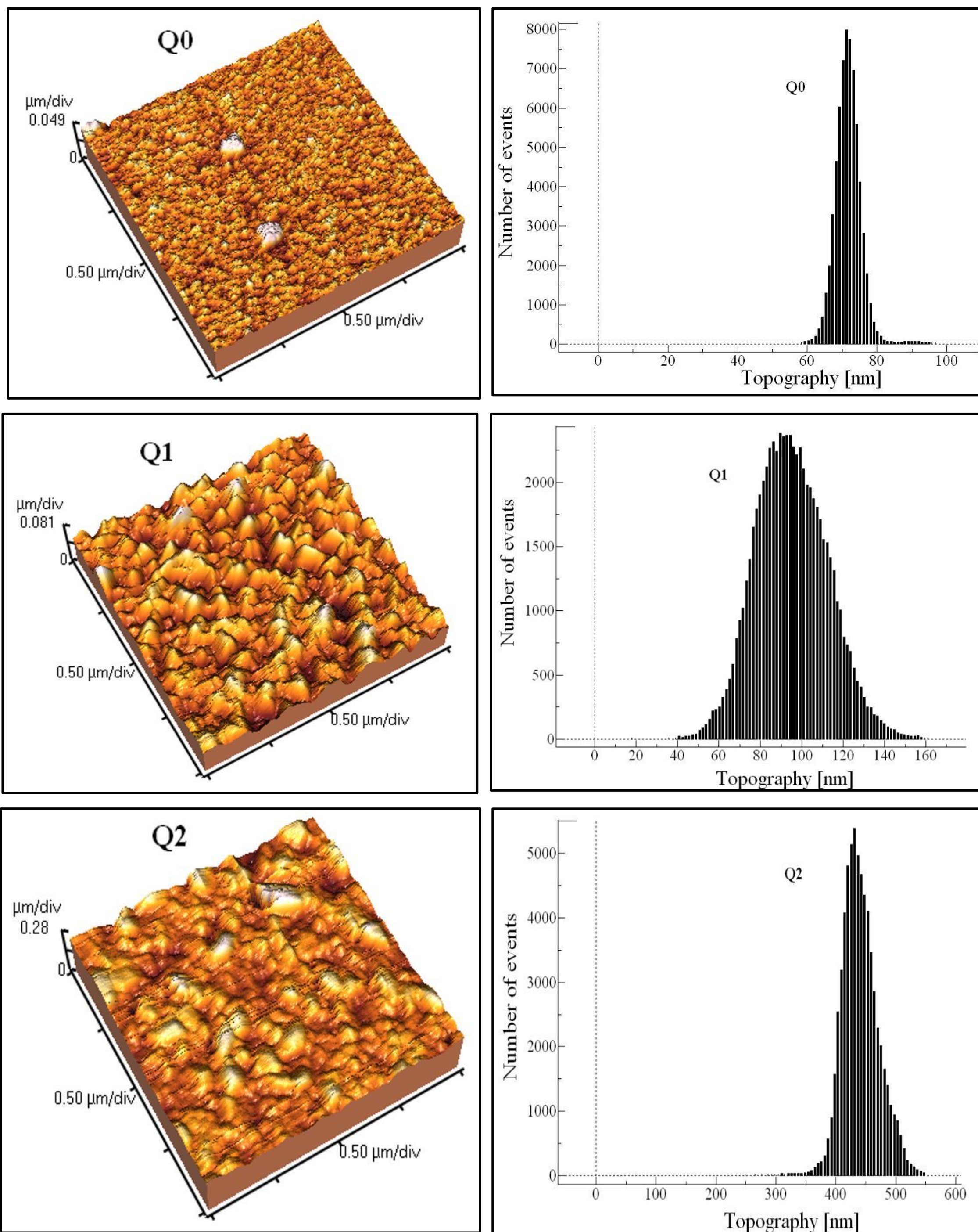
Figure 1. The XRD patterns of the Cr_2O_3 films prepared at different annealing times: Q1: 60 min, Q2: 120 min, Q3: 180 min and Q4: 240 min.

Next, the surface morphology of the films was analyzed by AFM. The three dimensional (3D) AFM images and their corresponding topographic histogram profiles of the prepared samples are displayed in Figure 2. As shown in Figure 2, the unannealed film (sample Q0) depicts a smooth surface morphology with a very small number of islands distributed sparsely on the surface while the annealed films at different annealing times depict a disturbed surface with oriented grains and rough surface.

The plot of root mean square (RMS) roughness and average roughness of the films are shown in Figure 3. The plot reveals that the RMS and average roughness values follow the similar trends and first increases with the increase in annealing time from 60 to 180 min due to the Cr_2O_3 crystallite growth and then decreases with the increase in annealing time from 180 to 240 min, which proves that the sample after annealing for 180 min has the highest crystalline quality. Similar results have been reported earlier [13, 14]. The average grains sizes were obtained by means of the WSxM 5.0 Develop 7.0 software from 2D AFM images [15]. The results show that an increase in annealing time leads to agglomeration of grains and the mean grain size increases from 76 to 200 nm. Also the roughness values exhibit a similar tendency to that of grain sizes observed from AFM analysis [16 - 20]. This can be due to the fact that at longer annealing time, atoms can move more and fill the defects, hence larger grains may form. In addition, by formation of larger grains usually the valleys between the grains become wider and deeper,

hence surface roughness increases. Similar changes in gain size and roughness of chromium oxide thin films with annealing temperatures was reported by K. Khojier et al [12]. They observed that the films annealed at lower temperatures (200 and 300 ◦C) contain smaller grains with lower surface roughness, whereas larger grains with higher surface roughness were obtained at higher annealing temperatures of 500 ◦C and 600 ◦C. The roughness, grain size and grain distributions are important factors that can strongly affect the mechanical, chemical and optical properties of chromium oxide thin films. It is also reported that film hardness and surface roughness have an inverse relation [12], so that the films with more surface roughness may have a lower hardness. The histogram of the surface height distribution profiles (The right figures in Figure 2.) show a shape of Gaussian distribution that confirmed the homogenity of the films and the surface roughness is increased by peak broadening in the height distribution profiles. From the AFM images we can observe that annealing times have significant impact on surface morphology as well as surface roughness.

The optical transmittance spectra of as deposited and annealed Cr_2O_3 films were recorded as a function of wavelength in the range 300-800 nm, and are shown in Figure 4. The transmittance of the as deposited film was found very low and it improved after annealing. The low value of the transmittance of as deposited film is due to scattering of light by the metallic chromium. The transmittance of the films annealed at different annealing times were lower than 50% in the range 300 –800 nm wavelengths, illustrate that oxidation of Cr remains incomplete during oxide formation. Also, the interference fringes in the transmittance spectra of the annealed films indicated that the films have a uniform thickness and the Cr_2O_3 thin films are homogeneous. It is observed that increasing the annealing time reduces the transmittance values. This decrease in optical transmittance is due to crystalline nature and high surface roughness of the annealed films. According to AFM results, the roughness of films increased by annealing time augmentation and the rougher surface of the films leads to a larger scattering [21].


Q0
µm/div
0.049
0
0.50 µm/div
0.50 µm/div
Q0
Number of events
Topography [nm]
Q1
µm/div
0.081
0
0.50 µm/div
0.50 µm/div
Q1
Number of events
Topography [nm]
Q2
µm/div
0.28
0
0.50 µm/div
0.50 µm/div
Q2
Number of events
Topography [nm]

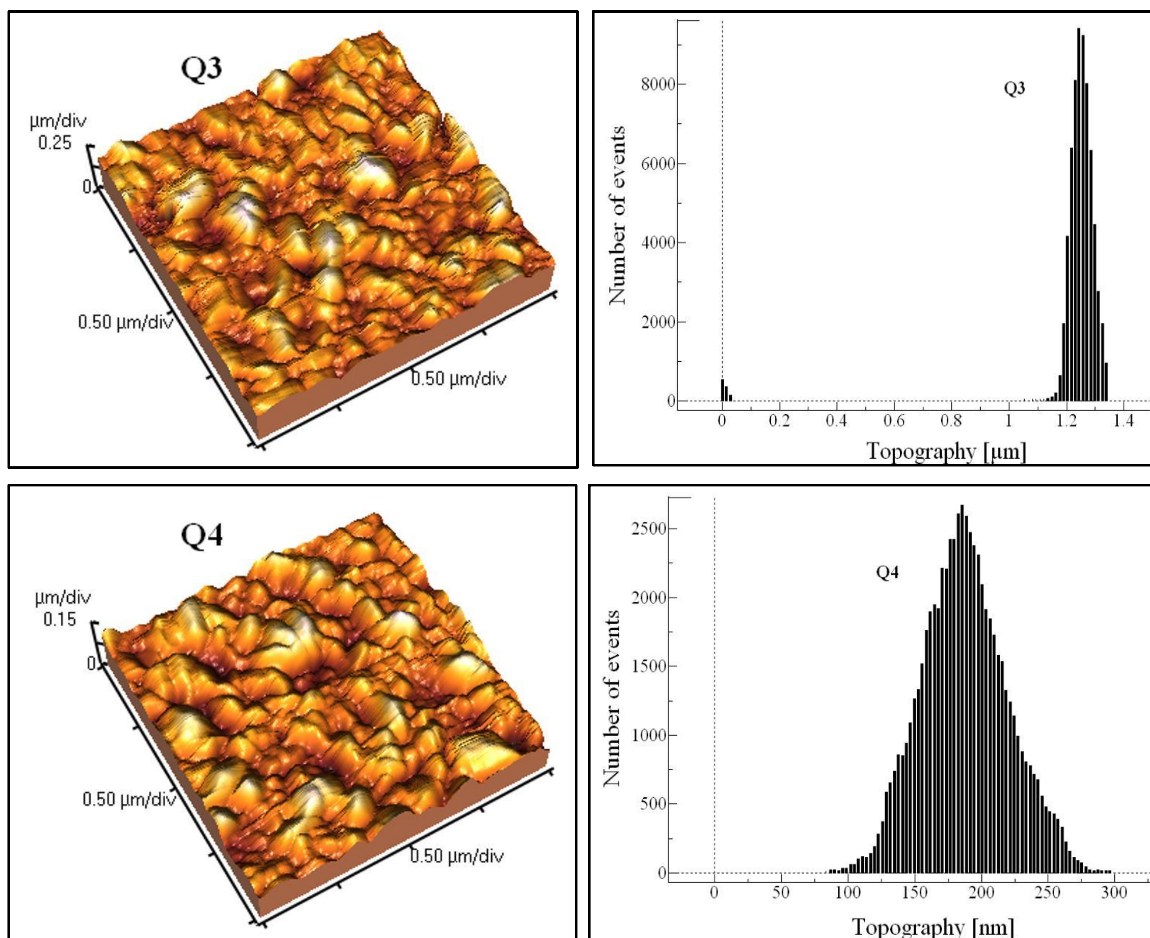


Figure 2. Three dimensional AFM images (left figures) and corresponding topographic histogram (right figures) of the Cr_2O_3 films prepared at different annealing times: Q0: without annealing, Q1: 60 min, Q2: 120 min, Q3: 180 min and Q4: 240 min.

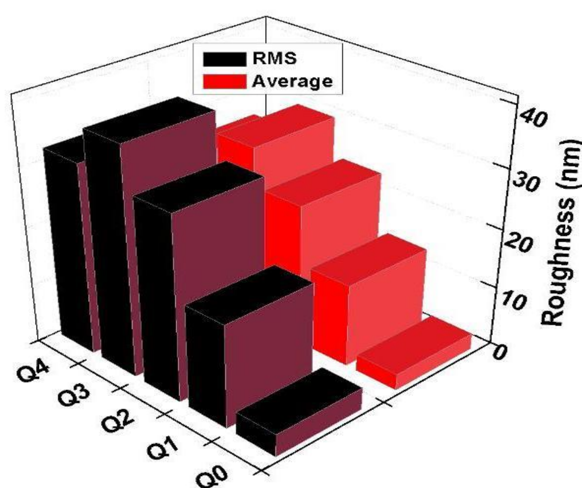


Figure 3. Plot of RMS and average roughness of the Cr_2O_3 films prepared at different annealing times: Q0: without annealing, Q1: 60 min, Q2: 120 min, Q3: 180 min and Q4: 240 min.

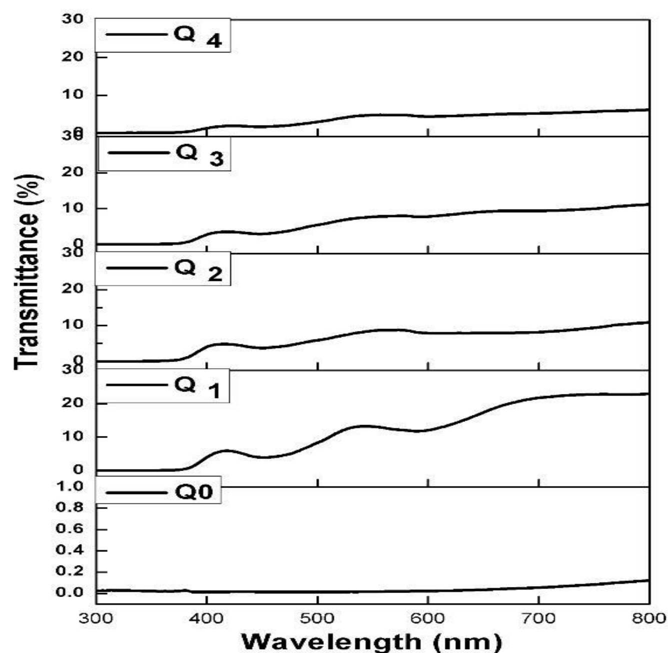


Figure 4. The transmittance spectra of the Cr_2O_3 films prepared at different annealing times: Q0: without annealing, Q1: 60 min, Q2: 120 min, Q3: 180 min and Q4: 240 min.

Conclusion

In this work, a simple two-step method using DC magnetron sputtering followed by annealing was employed to prepare Cr_2O_3 films**.** The annealing time was varied while the other deposition and annealing conditions were kept constant. The XRD results show that the Cr_2O_3 phases can be observed for all annealing times. Also the films crystallinity is improved by augmentation of annealing time from 60 min to 180 min. According to AFM results, annealing times have significant impact on surface morphology as well as surface roughness and the roughness values exhibit a similar tendency to grain sizes. In this work all films were prepared at the same annealing temperature for different times. For future work we can change the annealing temperatures to study the effect of annealing temperature on the chemical composition, surface morphology and optical properties of prepared films.

Acknowledgement

The authors gratefully acknowledge the financial support of Islamic Azad University of Karaj Branch.

References

[1] T. G. Wang, Y. Liu, H. Sina, C. Shi, S. Iyengar, S. Melin, K. H. Kim, *Surf. Coat. Technol.,* 228, 140 (2013).

[2] P. M. Sousa, A. J. Silvestre, O. Conde, *Thin Solid Films.,* 519, 3653 (2011).

[3] V. Balouria, A. Kumar, A. Singha, S. Samanta, A.K. Debnath, A. Mahajan, R. K. Bedi, D. K. Aswal, S.K. Gupta, J. V. Yakhmi, *Sens. Actuators, B.,* 157, 466 (2011).

[4] Y. I. Boldyrev, N. D. Ivanova, G. V. Sokolsky, S. V. Ivanov, O. A. Stadnik, *J. Solid State. Electrochem.,* 17 , 2213 (2013).

[5] M.F. Al-Kuhaili, S. M. A. Durrani, *Opt. Mater.,* 29, 709 (2007).

[6] X. Pang, K. Gao, F.Luo, H. Yang, L. Qiao, Y. Wang, A. A. Volinsky, *Thin Solid Films.,* 516, 4685 (2008).

[7] S. Punugupati, J. Narayan, F. Hunte, *J. Appl. Phys.,* 117, 193907 (2015).

[8] N. He, H.Li, L. Ji, X.Liu, H. Zhou, J. Chen, *Ceram. Intl.,* 41, 9534 (2015).

[9] F. Hajakbari, M. Ensandoust, *Acta. Phys. Pol. A.*, 129, 680 (2016).

[10] A. Hojabri, F. Hajakbari, M. Najarsadeghi, *J. Appl. Chem. Res.,* 9, 73 (2015).

[11]S. Y. Jeong, J. B. Lee, H. Na, T. Y. Seong, *Thin Solid Films.,* 518, 4813 (2010).

[12] K. Khojier, H. Savaloni, Z. Ashkabusi, N. Z. Dehnavi, *Appl. Surf. Sci*., 284, 489 (2013).

[13] A. Hojabri, F. Hajakbari, Y, Ghodrat, *J. Appl. Chem. Res.,* 9, 103 (2015).

[14] F. Shi, *J. Mater. Sci. Mater. Electron.,* 22, 596 (2011).

[15]I. Horcas, J. M. Fernandez, j. G. Roderiguez, J. Colchero, J. G. Herrero, A. M. Baro, *Rev. Sci. Instru.,* 78, 013705 (2007).

[16] U. Akgul. K. Yildiz, Y. Atici, *J. Mater. Sci. Mater. Electron.,* 28, 4758 (2017).

[17] Y. Fadhli, A. Rabhi, M. Kanzar, *J. Mater. Sci. Mater. Electron.,* 25, 4767 (2014).

[18] L. S. Cavalcante, M. A. Santos , F. M. Pontes, I.A. Souza, L. P. S. Santos, I.L.V. Rosa, M. R. M. C. Santos, L.S. S. Junior, E. R. Leite, E. Longo, *J. Alloys Compd.,* 437, 269 (2007).

[19] F. Hajakbari, F. Shafienejad, *Jpn. J. Appl. Phys*., 55 ,035503 (2016).

[20] Y. C. Teh, A. A. Saif, *J. Alloys Compd.,* 703, 407 (2017).

[21] R. R. Krishnan, K. G. Gopchandran, V. P. Mahadevanpillia, V. Ganesan, V. Sathe, *Appl. Surf. Sci.,* 255, 7126 (2009).