Journal of Applied Chemical Research, 9, 4, 103-111 (2015)

Journal of Applied Chemical Research
www.jacr.kiau.ac.ir

Thermal Oxidation Times Effect on Structural and Morphological Properties of Molybdenum Oxide Thin Films Grown on Quartz Substrates

Alireza Hojabri*, Fatemeh Hajakbari, Yalda Ghodrat *Department of Physics, Karaj Branch, Islamic Azad University, Karaj, Iran (Received 22 Mar. 2015; Final version received 30 Jun. 2015)*

Abstract

Molybdenum oxide (α-MoO_3) thin films were prepared on quartz and silicon substrates by thermal oxidation of Mo thin films deposited using DC magnetron sputtering method. The influence of thermal oxidation times ranging from 60-240 min on the structural and morphological properties of the preparedfilms was investigated using X-ray diffraction, Atomic force microscopy and Fourier transform infrared spectroscopy. The XRDresults revealed that the as-deposited film was amorphous while those formed at thermal oxidation times between 60-180 min exhibited polycrystalline orthorhombic molybdenum oxides. The presence of (0k0) reflections in XRD patterns indicated the layered structure of α-MoO_3 .Also the surface morphology of the films isdependent on the thermal oxidation times. The FTIR spectrumconfirmed the formation of MoO3 and the peak at 992.53 cm-1implythelayered structure of α-MoO_3.

Keywords: *Thermal oxidation, thin film, MoO3, layered structure, structural properties.*

Introduction

Molybdenum oxide (MoO_3) thin films owing to its structural, morphological and optical properties [1-13] has attracted much interest in divers field such as gas sensors[1], electrochormic devices[2], photonic material[3], solar cells[4], lithium secondary batteries[5]temperature sensor material[6]. Recently nanocrystalline MoO_3 thin films have attracted extensive interest for applications in building nanodevices and nanosensors [7]. Several techniques, such as electrodeposition [8], sol-gel[9], chemical vapor deposition [10],electron beam evaporation [11], laser

***Corresponding author:** Dr Alireza Hojabri, Department of Physics, Karaj Branch, Islamic Azad University, Alborz, Iran. Email: hojabri@kiau.ac.ir, Tel:+982634182637.*

assisted deposition[12] and sputtering[13] have been employedfor preparation of molybdenum oxide films on different substrates.

In the present work, the MoO_3 thin films were obtained successfully through the thermal oxidation of molybdenum thin films deposited on quartz substrates by means of DC magnetron sputtering method. The objective of this study is to preparation and characterization of α-MoO_3 films with layered structure by this low cost technique and studying the influence of thermal oxidation times on structural and morphological properties of the prepared films.

Experimental

Molybdenum (99/99% purity) thin films were depositedon quartz and silicon substrates (1cm×1cm) by dc magnetron sputtering (EDS-160) technique at the same deposition conditions. The starting substrate temperature wasroomtemperatureandduringthedeposition, the substrates are not intentionally heated. Before sputtering, the sputtering chamber was evacuated to an ultimate pressure of 5×10^{-5} mbar by using diffusion and rotary pumps. The pure argon gas was admitted into the chamber and the working pressure was maintained at approximately 5×10^{-2} mbar throughout the depositions process. The distance between the target and the substrate was kept 7 cm. The cathode voltage and discharge current were 120V and 35 mA, respectively. Then, thermal oxidation of prepared Mo films, were done in oxygen atmosphere at temperature of 600 ºC for different oxidation times ranging from 60-240 min in an electrical furnace. The crystalline structures of films were determined by the X-ray diffraction (XRD) with Co (λ=0.17890 nm) radiation (Philips, PW 3710). The surface morphology of films was investigated by atomic force microscopy (AFM) (Auto probe cp, Park scientific instrument). For determination of chemical binding configuration of MoO_3 thin films on silicon substrate, the Fourier transform infrared spectrophotometer (FTIR, Perkin Elmer spectrum 100) in the wave number range of 400-1200 cm^{-1} was employed.

Results and discussion

The XRD patterns of Mo films deposited on quartz substrates before and after thermal oxidation at different oxidation times ranging from 60-240 min in temperature of 600 ºC are shown in Figures 1-5. In all figures the wide and broad signal at 22.3ºoriginates from quartz substrate.

The as deposited Mo films are amorphous (Figure 1). After thermal oxidation of the Mo films in temperature of 600 ºC at oxidation times between 60-180 min, the diffraction peaks of (020),(040) and (060)corresponding to the α-MoO_3 phase, were obtained that exhibit the conversion of Mo to MoO_3 (Figures 2-4). The (0k0) reflections indicated the

orthorhombic αphase of molybdenum oxide. The dominant XRD peak corresponds to (040) plane of MoO_3.Also, for oxidation time of 240 min the films is amorphous (fig.5). The width of the diffraction lines are attributed to the size distribution, defects and strain in nano particles. Since the peaks are sharp it is evident that the prepared films are polycrystalline. When the time of oxidation increases from 60-120 min the intensity of MoO_3 diffraction peaks enhance that suggested the films are well crystallized. The XRD results obtained in the present work agree well with the reports by [9, 14,15].

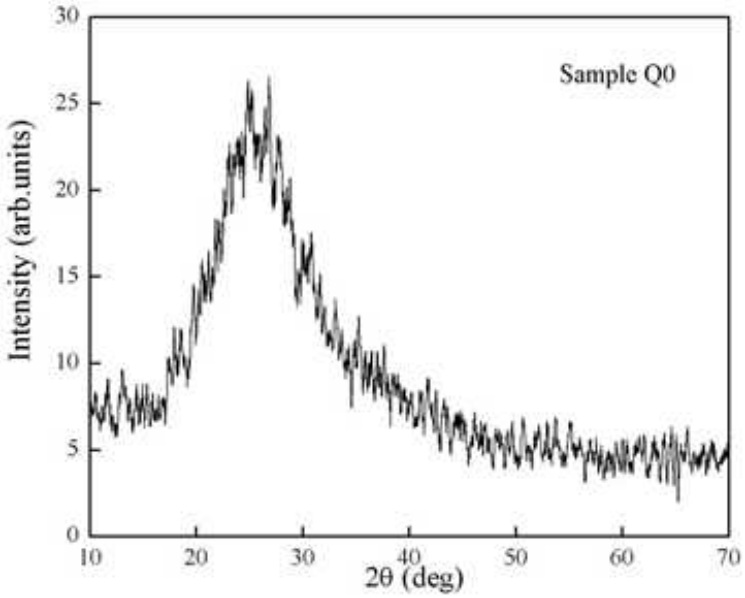


Figure 1. The XRD pattern of the Mo film deposited on quartz substrate.

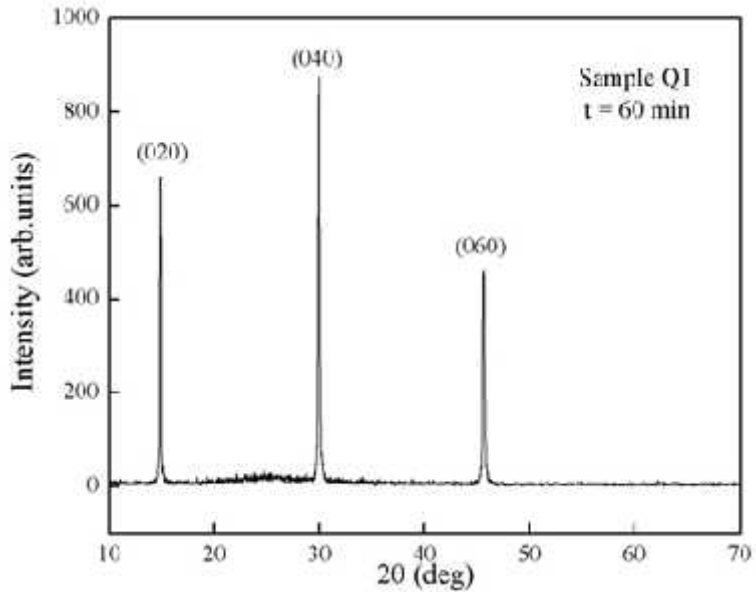


Figure 2. The XRD pattern of the MoO_3 film prepared at thermal oxidation time of 60 min.

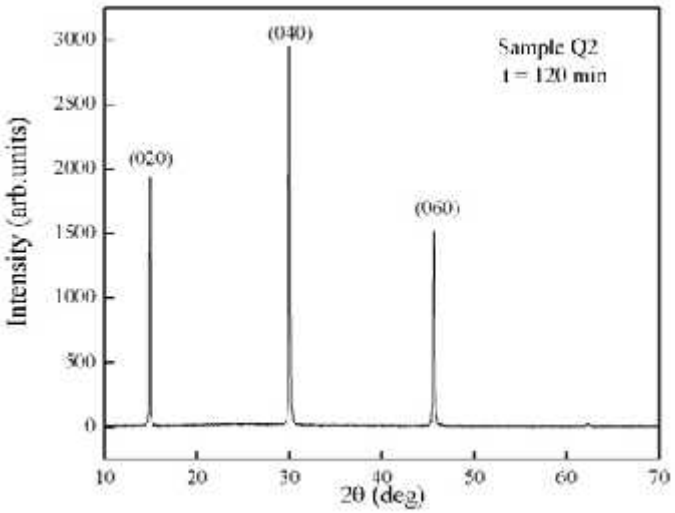


Figure 3. The XRD pattern of the MoO_3 film prepared at thermal oxidation time of 120 min.

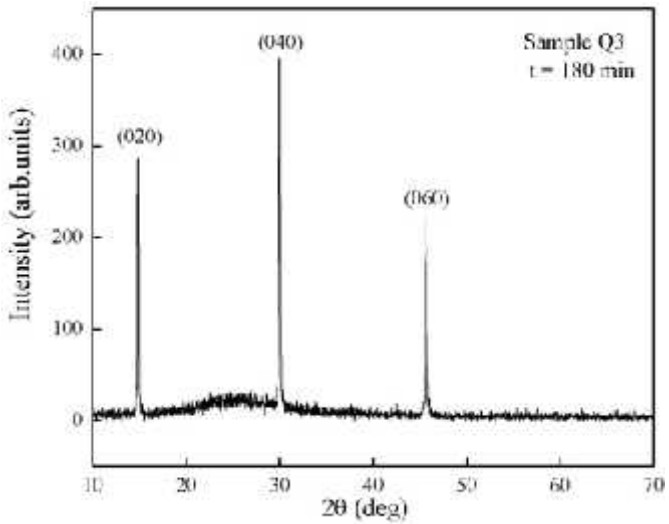


Figure 4. The XRD pattern of the MoO_3 film prepared at thermal oxidation time of 180 min.

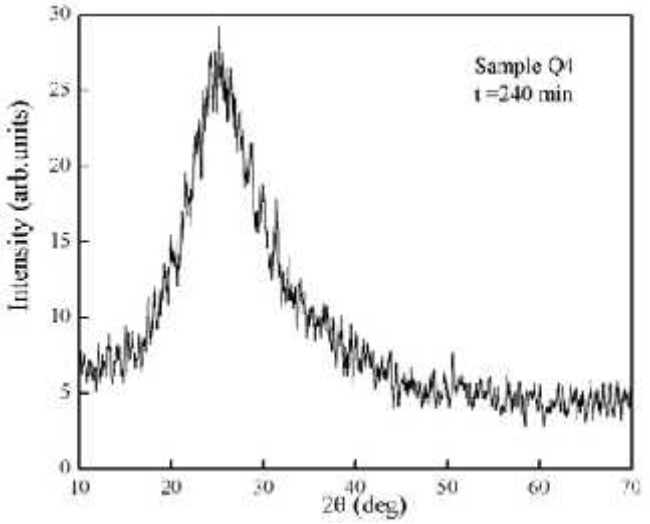


Figure 5. The XRD pattern of the MoO_3 film prepared at thermal oxidation time of 240 min.

The average crystalline size and microstrain of the prepared films have been obtained from the following Scherrer relations [16]:

$$D = 0.9\lambda/\beta\cos\theta \quad \text{and} \quad \varepsilon = \beta/4\tan\theta \qquad (1)$$

Where, β is the full-width at half maximum (FWHM) of the diffraction peaks in radians, λ is the wavelength of X-ray (λ=0.17890 nm) and ɵ is the Bragg's angle. The structural parameters of MoO_3 films can be observed in table 1.According to results of table 1, we can observe that all the MoO_3 films are nanocrystalline and the average crystalline size increases varied between 41-78 nm with annealing time. Also, the annealing time augmentation up to 120 min leads to increase of average crystal size and decrease of microstrain. The increase in crystallite size is related to decrease in strain [16].

Table 1. Comparison of α- MoO_3thin films structural parameters (Miller indices, Average crystalline size and Micro strain).

Sample	Phase composition	Miller indices (hkl)	Diffraction Angle 2ϙ (deg.)	Average Crystalline size (nm)	Micro strain (ε)
Sample Q1	MoO_3	(020) (040) (060)	14.90 29.98 45.62	66 53 41	$4.6710\times^{-3}$ 2.93×10^{-3} 2.48×10^{-3}
Sample Q2	MoO_3	(020) (040) (060)	14.89 29.97 45.62	78 63 50	3.98×10^{-3} 2.44×10^{-3} 2.07×10^{-3}
Sample Q3	MoO_3	(020) (040) (060)	14.89 29.98 45.63	66 56 53	4.64×10^{-3} 2.77×10^{-3} 1.97×10^{-3}

The Fourier transform infrared spectrum of MoO_3 thin films formed on silicon substrate at thermal oxidation temperature of 600 ºC for 120 min in the wavenumber ranging from 400-1200 cm^{-1} is shown in fig. 6.In the broad band the band observed at 545.49 cm^{-1} was due to the transverse optical vibration of Mo-O-Mo[15]. Also, the peak observed at992.53cm^{-1} is associated with Mo=O stretching vibration, which is an indicator for layered orthorhombic MoO_3 phase[9]. The bands appeared at 815.46 and 1102.93 cm^{-1}, is related to stretching band of Mo=O and bridging (Mo-O-Mo) respectively. The FTIR studies of the present work are in good agreement with the reports by [9, 15].

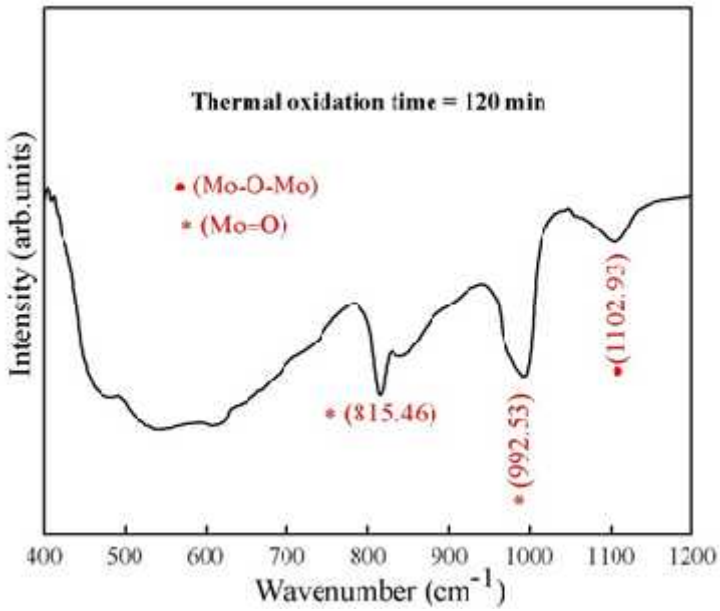


Figure 6. The FTIR spectrum of the MoO_3 thin film on silicon substrate.

The surface morphological studies of the prepared Mo and MoO_3 thin films are examined by using atomic force microscopy in contact mode. Scans $5 - 5\propto m^2$ were recorded for all samples. The AFM results of Mo films before oxidation is obtained in figure 7.

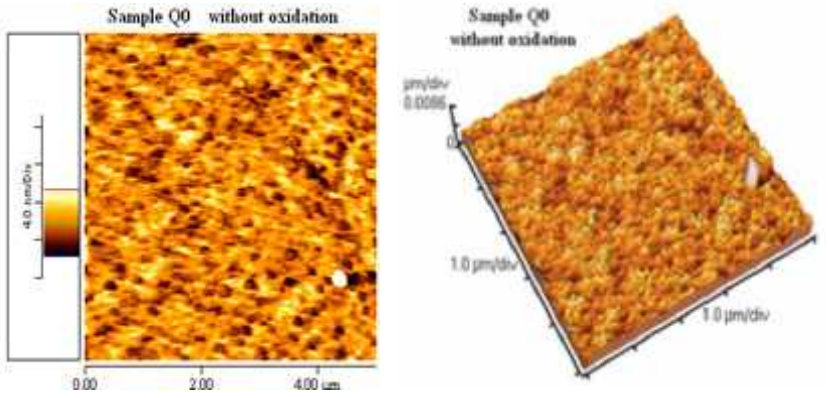
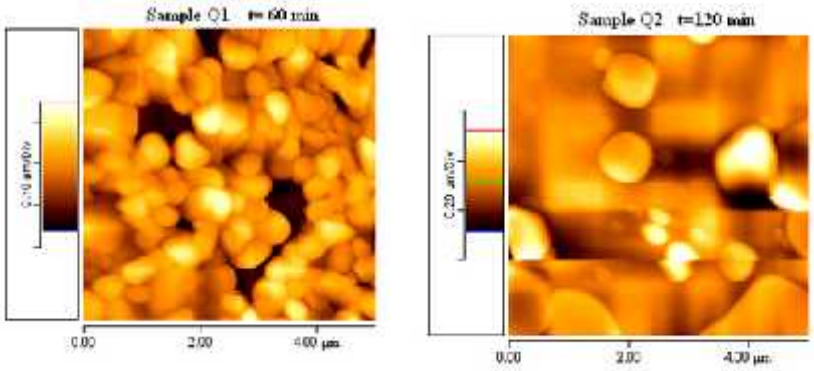


Figure 7. 2D and 3D AFM images of the Mo film on quartz substrate, without oxidation.



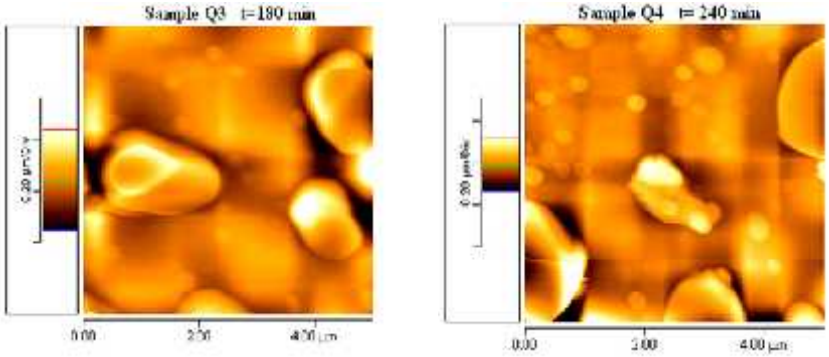


Figure 8. 2D AFM images of the MoO_3 films prepared at different oxidation times.

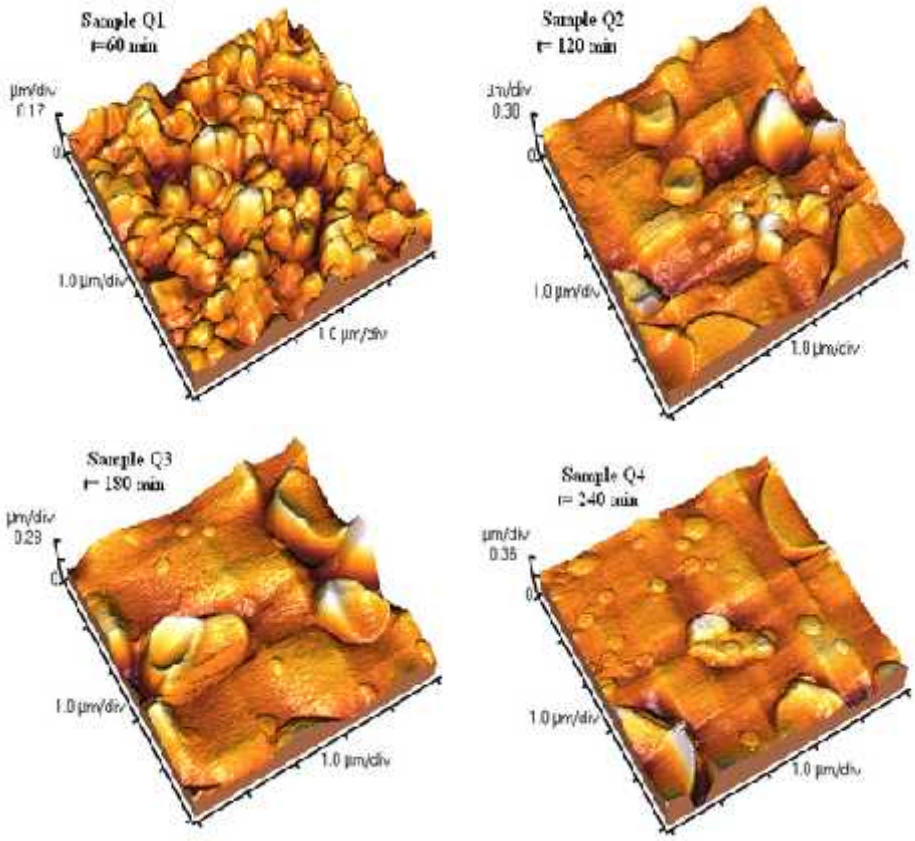


Figure 9. 3D AFM images of the MoO_3 films prepared at different oxidation times.

The surface of Mo film (Sample Q0) is smooth with an rms roughness of 1.18 nm that can be due to the amorphous structure of this film. After thermal oxidation of Mo films the surface morphology was varied and the roughness of films increased due to the conversion of amorphous to crystalline structure(figs 8 -10). The layered structure is clearly observed in AFM images and confirmed the XRD and FTIR results. The dependence of film surface roughness to thermal oxidation times is obtained in fig 10. It is observed that the root mean square (RMS) roughness and average roughness have similar trends and varies by oxidation times.

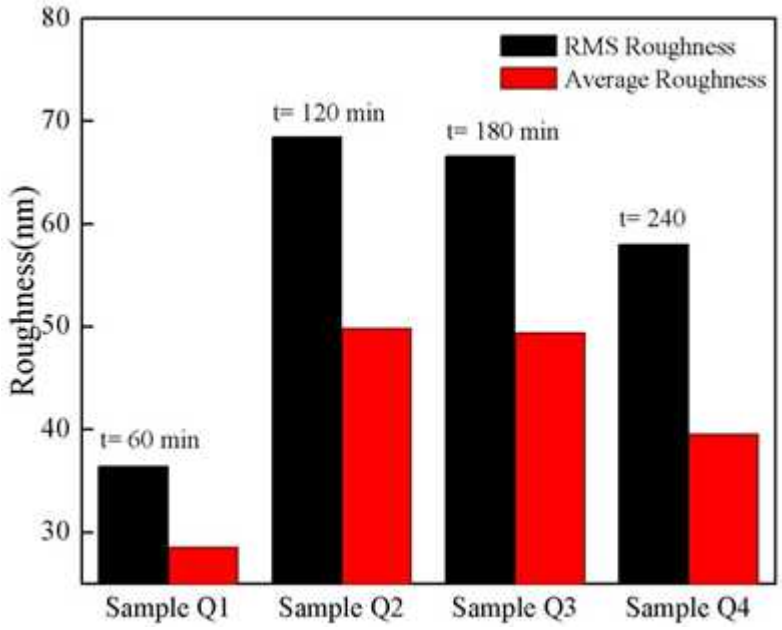


Figure 10. The MoO_3 thin films roughness versusthermaloxidation times.

Conclusion

Thin films of α-MoO3 were prepared by thermal oxidation of Mo films deposited on quartz and silicon substrate using dc magnetron sputtering method. The as-deposited amorphous Mo films converted to crystalline α-MoO3 thin films by thermal oxidation at temperature of 600°C for oxidation times of 60-180 min. The layered structure of the MoO3 films is clearly seen in AFM images. Also, the AFM and FTIR results are in good agreement with the results obtained by the X-ray analysis. The average crystalline size and surface roughness of films was influenced by oxidation time.

Acknowledgements

This work was supported by Islamic Azad University, Karaj Branch, Alborz, Iran.

References

[1] M.B. Rahmani, S.H. Keshmiri, J. Yu, A.Z. Sadek, L. Al-Mashat, A. Moafi,K. Latham, Y.X. Li ,W. Wlodarski, K. Kalantar-zadeh, *Sens. Actuators B.*,145, 13 (2010).

[2] C-S.Hsu, C-C.Chan, H-T.Huang, C-H. Peng, W-C. Hsu, *Thin Solid Films*, 516, 4839 (2008).

[3]T. He, J.*Yao,J.Photochem and Photobio C: Photochem.Rev.*, 4, 125 (2003).

[4] X. Fan, G. Fang, P. Qin, N. Sun, N. Liu, Q. Zheng, F. Cheng, L.Yuan, X. Zhao, *J. Phys. D: Appl. Phys*., 44, 045101 (2011).

[5] Y. Li, Y. Bando, *Chem. Phys. Lett.*, 364, 484 (2002).

[6] W-Q. Yang, Z-R.Wei, X-H.Zhu, D-Y. Yang,*Phys. Lett.A*.,373, 3965 (2009).

[7] E. D.B. Santos, F.A.Sigoli,I.O.Mazali, *J.Solid. State .Chem.*, 190, 80 (2012).

[8] D. Sinkeviciute,J.Baltrusaitis,N.Dukstiene, *J. Solid. State.Electrochem.*, 15, 711 (2011).

[9] M. Dhanasankar, K.K. Purushothaman, G. Muralidharan, *Solid.State*. Sci.,12, 246 (2010).

[10] R. Martinez Guerrero, J.R. Vargas Garcia, V. Santes, E. Gomez,*J. Alloys. Compd*., 701, 434 (2007).

[11] S.Y. Lin, Y.C. Chen, C.M. Wang, P.T. Hsieh, S.C. Shih, *Appl. Surf. Sci*. 255, 3868 (2009)

[12]A. Pardo, J. Torres, *Thin Solid Films*, 520, 1709 (2012).

[13] S.H. Mohamed, S. Venkataraj, *Vacuum*, 81, 636 (2007) .

[14] V. Nirupama,P. S, Reddy, O. M. Hussain, S. Uthanna,*Ionics*.,13, 451(2007).

[15] S. Uthanna, V. Nirupama, J.F. Pierson, *Appl. Surf. Sci*., 256, 3133 (2010).

[16]A.Hojabri, F. Hajakbari, N. Soltanpoor, M.S. Hedayati.,*J. Theor. Appl. Phys*., 8, 132 (2014).