Materials Physics and Mechanics 48 (2022) 106-113
Research article

Received: June 28, 2021
Accepted: February 21, 2022

STUDY OF STRUCTURAL AND OPTICAL PROPERTIES OF IRON, COBALT DOPED AND IRON-COBALT CO-DOPED TIN DIOXIDE SnO_2

K. Chedala[1,2,3], A. Benhaoua[2], R. Gheriani[1,3], A. Hima[4]✉, L. Ayachi[2]

[1]Faculty of Mathematics and Material Sciences, Univ. Ouargla, Ouargla 30000, Algeria

[2]Lab. VTRS, Faculty of Science & Technology, Univ. El-Oued, El Oued 39000, Algeria

[3]Lab. LRPPS, UKMOuargla 30000, Algeria

[4]Department of Electrical Engineering, Fac. Technology, University of El Oued, El Oued, 39000, Algeria

✉ abdelkader-hima@univ-eloued.dz:

Abstract. This paper studied undoped tin dioxide (SnO_2), iron doped tin dioxide (FeTO), cobalt doped tin dioxide (CTO), and iron-cobalt co-doped tin dioxide (FeCTO) thin films using spray pyrolysis technique at a temperature of 480°C heated glass. The dopant concentration value was 12wt %. Whilst, the structural and optical characteristics of fabricated thin films were studied. XRD analyses avowed the formation of rutile thin films structure along (211) and (110) as preferred orientations. The obtained crystallite size varies from 31.96 nm to 46.48 nm. SEM analysis of the surface morphology shows that the whole substrates are well covered by SnO_2 uniform material with variant shape upon post doping. UV-visible investigation of optical transmittance spectra showed that the films have transparency ranging in 85-98%, with a direct bandgap in the range 3.65-3.85eV. Found results show that Fe/Co co-doped SnO_2 presents improvement in properties compared to other single dopants.

Keywords: Fe-Co co-doped SnO_2 thin films, spray pyrolysis method, X-ray diffraction, SEM, UV-Vis Spectroscopy

Acknowledgments.*This work was supported in part by VTRS laboratory of El-Oued University. X-ray diffraction was acquired with an instrument supported by "CENTRE DE DEVELOPPEMENT DES TECHNOLOGIES AVANCEES".*

Citation: Chedala K., Benhaoua A., Gheriani R., Hima A., Ayachi L. Study of structural and optical properties of iron, cobalt doped and iron-cobalt co-doped tin dioxide SnO_2 // Materials Physics and Mechanics. 2022, V. 48. N. 1. P. 106-113.DOI: 10.18149/MPM.4812022_9.

1. Introduction

Transparent conducting oxides (TCOs) thin films are very useful materials for many applications thanks to their high optical transparency in the visible region. They have extensive use in solar cells [1]**,** optoelectronics, display systems, catalytic, and smart window heat mirrors [2,3]. Doped tin oxide (SnO_2) has a particular use due to its essential properties, which are strong electrical conductivity and high transparency [4,5]. Several processing methods were developed in order to deposit tin oxide thin films, which can be generally classified as physical, chemical vapor deposition (PVD) [6], pulsed laser ablation [7],

http://dx.doi.org/10.18149/MPM.4812022_9

molecular beam epitaxial [8], spray pyrolysis [9], sol-gel, and dip/spin coating method [10]. Among these deposition techniques, spray pyrolysis is a simple low-cost method for large area coating [10,11]. Using this method, dopants such as antimony (Sb), indium (In), fluorine (F), iron (Fe), and cobalt (Co) are frequently used to improve tin oxide (SnO_2) properties [12,13].

Despite sustained efforts in research, a systematic study including surface and optical properties are desirable requirements. The achievement of Fe and Co-doped SnO_2 thin films with high crystalline quality and transparent conducting films remains a significant challenge. Thus these synthesized possess potent and desirable physical properties for further development in the industries in the future.

This paper aims to investigate the structural, optical properties of highly conducting SnO_2, FeTO, CTO, and FeCTO transparent conducting thin films on glass slides with a doping concentration of (12wt.%) on the structure.

2. Experimental details

Preparation of spray solution. SnO_2, FeTO, CTO, and FeCTO thin films were fabricated by means of a chemical spray pyrolysis with the moving nozzle method. As a precursor to tin, Stannous Chloride ($SnCl_2$ $2H_2O$) was used and dissolved in a double-distilled mixture of water and methanol (according to a volume ratio of 1/2:1/2) and then adding a few drops of (HCl). The concentration of the precursor was (0.5 M). Iron chloride ($FeCl_3$) and cobalt chloride dehydrate ($CoCl_2$, $6H_2O$) were used as sources of Fe, and Co elements respectively. In respect of theoretical amounts of doping values of: 12wt.% Fe doped SnO_2; 12wt.% Co doped SnO_2, 12wt.% Fe + 12wt.% Co co-doped SnO_2, the obtained solutions were sprayed onto 480°C heated glass substrates (Ref 217102: having $7.5\times2.5\times0.13cm^3$ as dimensions) with keeping a distance of 5cm between the nozzle and the substrate. Whereas, the deposition time was 5 min with a spray rate of 5ml/min. Once the deposition is made, films were permitted to cool down in room temperature (rt) conditions.

Characterization. The structural properties of studied (undoped SnO_2, FeTO, CTO, and FeCTO thin films are investigated by means of X-ray diffraction (XRD) among an Xray diffractometer (BRUKER – AXS type D8) which is equipped with X'Pert High Score under Cu Kα(λ = 1.5405 Å) radiation in the scanning region between 2θ=20° and 80°. However, the film's grain size was estimated using X'Pert High Score. The surface investigation was done with the scanning electron microscope (SEM). The spectra of the optical transmission were obtained via an UV–VIS–NIR spectrophotometer (Shimadzu, Model 1800) in the spectral area of (200-900 nm). The entire measurements were achieved at room temperature.

3. Results and discussion

X-ray diffraction study. Figure 1 illustrates the XRD patterns of SnO_2 thin films deposited on a glass substrate. Five diffraction peaks were observed at 2θ = 26.609°, 33.792°, 38.011°, 51.683°, and 65.815° which can be attributed respectively to (110), (101), (200), (211), and (301) planes of SnO_2 phase. It is to notice that the obtained XRD spectra have a good agreement with the space group P42/mnm according to JCPDS (No. 41-1445) of the tetragonal, rutile SnO_2 structure [14]. XRD samples spectra show that the preferred trend is (211) peak at 51.683°, the (211) surface exhibits the lowest energy surface. There was a decrease in peak intensity (211) with an increase in Fe and Co doping. The intensity decrease for all the rest amount of doping, When compared to the reported pure SnO_2 [5,15] and owing to this the crystallinity of the Co-doped metal oxides of SnO_2 tends to enhance than that of pure SnO_2 [16].

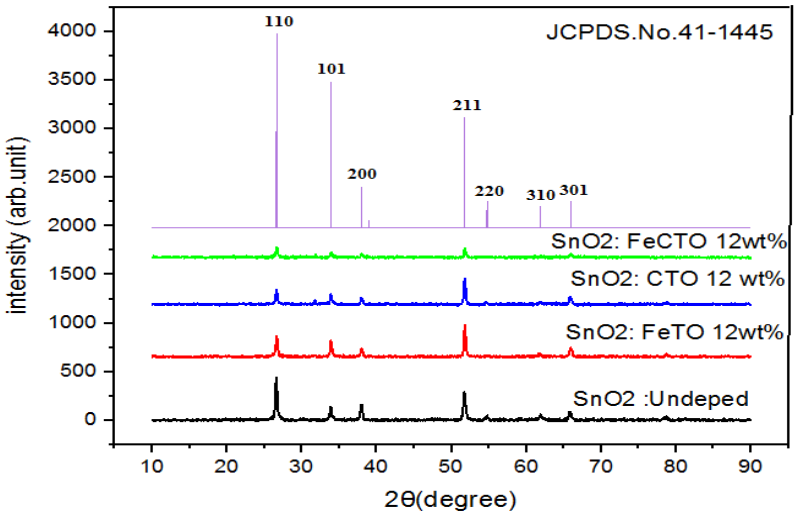

Fig. 1.XRD patterns images of SnO_2, FeTO, CTO, and FeCTO thin films

To get more information concerning the favorite growth directions, different texture coefficient TC(hkl) have been calculated from the X-ray data using the well-known equation (1) [17]:

$$T(hkl) = \frac{I(hkl)/I_0(hkl)}{N^{-1}\sum_n^N I(hkl)/I_0(hkl)}, \quad (1)$$

where $I(hkl)$ and $I_0(hkl)$ are the measured intensity and the standard intensity of the same (hkl)plane according to the JCPDS data, respectively. Whereas, N and n are the reflection and the diffraction peaks number, respectively. TC(hkl) values for (110), (101), (111), (211), and (301) at different vaccinations are illustrated in Fig. 2 and summarized in Table 1. The polycrystalline nature of the films was confirmed by the peaks that are less than the unity.

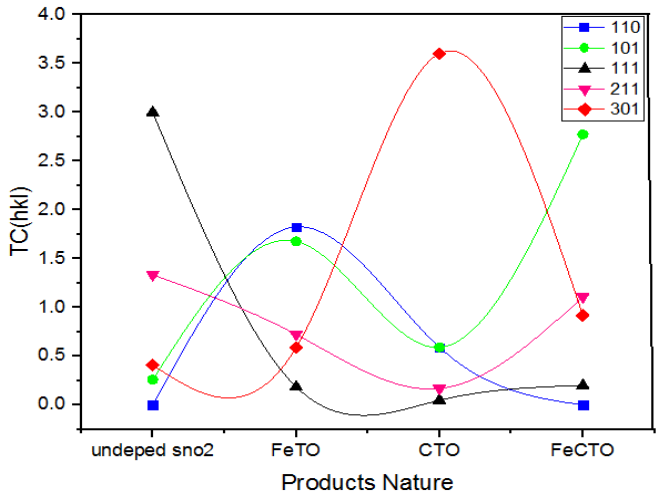

Fig. 2. TC (hkl) variation of SnO_2, FeTO, CTO, and FeCTO thin films

Both lattice constants (a) and (c), for the tetragonal phase structure, were calculated from XRD results via equations (2,3) [18]:

$$2d_{hkl}\sin\theta = n\lambda, \quad (2)$$

$$\frac{1}{d_{hkl}^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}, \quad (3)$$

where d_{hkl}, and (hkl) are the inter-planar space and Miller indices (a) and (c). The values of lattice parameters, 'a' and 'c' are listed in Table 1. It was noted that the lattice parameters (a)

and (c) of SnO_2 thin film are a = b = 4.733 Å and c = 3.198 Å and decrease after Fe, Co and Fe-Co doping.

Table 1. Lattice parameters a, and c, crystallite size D and Tc(hkl)of the products

Materail	Crystallite Size (nm)	Lattice constants (A°)				TC(hkl) of plane		
		a	$\Delta a = a - a_0$	c	$\Delta a = c - c_0$	(110)	(101)	(211)
SnO_2	46.48	4.733	-0.005	3.198	0.011	0	2.59063	0.745692
FeTO	44.36	4.727	-0.011	3.188	0.001-	1.2554	1.15337	0.497295
CTO	31.96	4.728	-0.01	3.188	0.001	1.9612	1.96024	0.560913
FeCTO	40.82	4.729	-0.0092	3.172	0.0151-	0.9828	0.58187	1.427167

In order to calculate the crystallite size D of the SnO_2 films from the XRD patterns, we used Scherer's formula (4) [19]:

$$D = \frac{0.9\lambda}{\beta \cos\theta}, \quad (4)$$

where D is the crystallite size, β is the full width at half-maximum (FWHM) of the most intense diffraction peak, λ is the X-ray wavelength (1.54056 Å), and θ is Bragg angle. As presented in Fig. 3, The crystallite size D(nm) along different orientations, but in Table 1 there is average crystallite size ranged from 46.48 nm to 31.96 nm. This decrease in crystallite size can be crystal defects as a result of the presence of cobalt and iron ions.

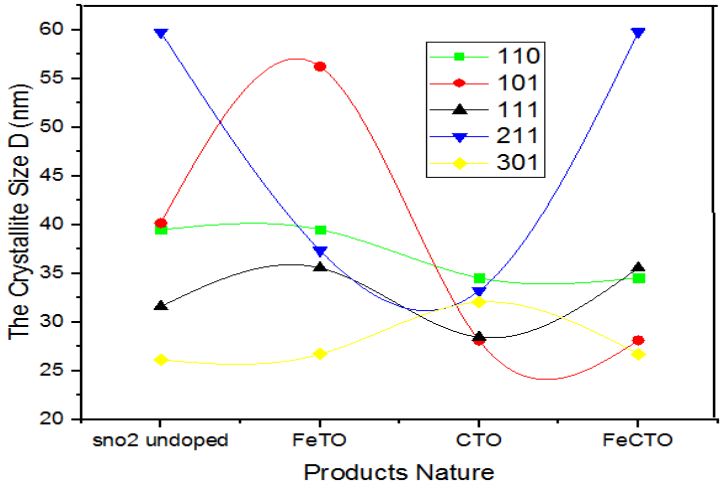

Fig.3. The crystallite size D(nm) along different orientations of SnO_2, FeTO, CTO, and FeCTO thin films

Surface morphology. The surface morphology of as-deposited SnO_2, FeTO, CTO, and FeCTO thin films is studied using field scanning electron microscopy (SEM). As shown in Fig. 4, the surface morphology shows a homogeneous surface structure for the undoped sample. But for the doped films, it was observed the presence of agglomerations revealst he co-existence of cobalt and iron as doping elements substituting the tin atoms and oxygen ones.

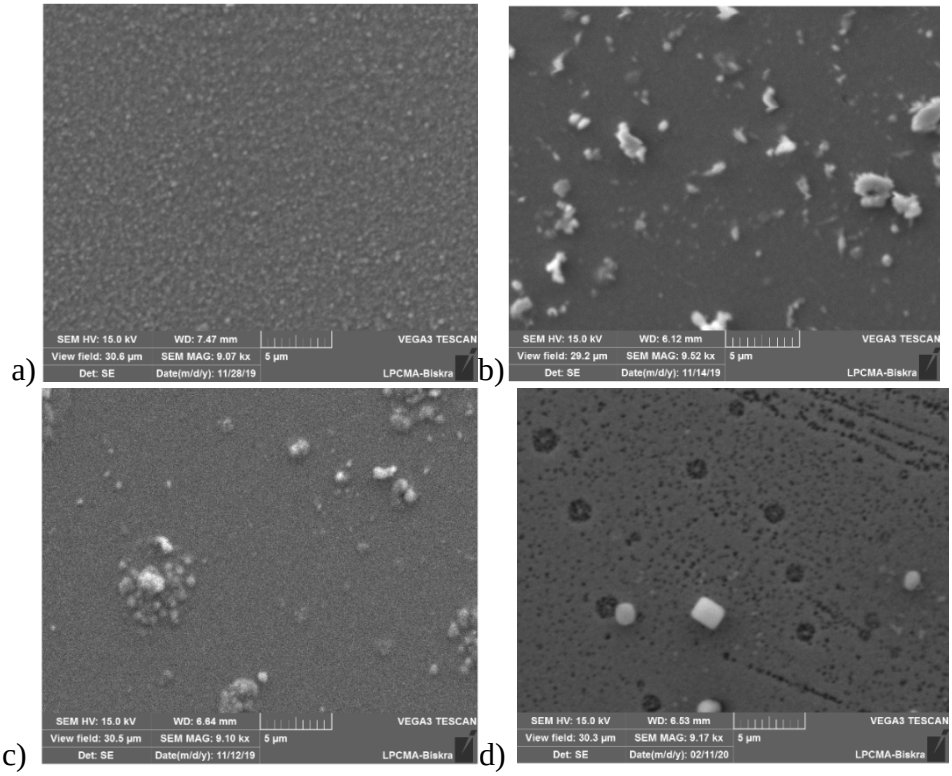

Fig. 4. SEM images of a) undoped, b) FeTO, c) CTO, and d) FeCTO thin films

EDX analysis.EDX spectra of the un-doped and FeCTO thin films on glass substrates are shown in Fig. 3. EDX results confirmed the presence of the constituents Cobalt (Co), oxygen, (O), Iron (Fe), and tin (Sn) in the grown films. It is clear from Fig. 3 that Co and Fe ions are successfully incorporated in the host SnO_2 material. The consistent and sharp peaks with tin oxide and cobalt and Iron demonstrated that both synthesized were crystalline in nature [20].

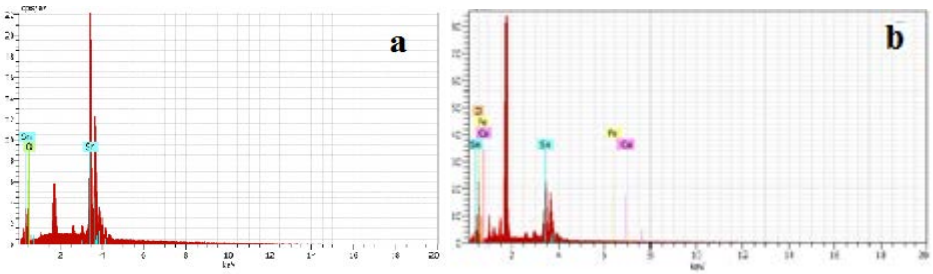

Fig.5. EDX images of a) undoped, b) Fe/Co co-doped SnO_2 (FeCTO12wt %) thin films

Optical properties. Figure 5 shows the transmittance spectrum for all of the samples. The average transmittance spectra of thin films were found to be about 90% in the visible range. The transmittance of the films exhibits an increase in their values after doping (FeTO, CTO) and is more enhanced for the co-doped (FeCTO) reaching 98%.

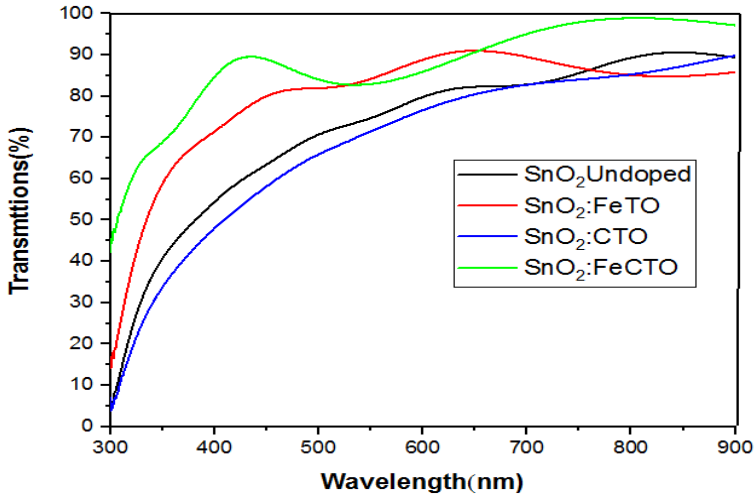

Fig. 5. Transmittance spectra of SnO_2, FeTO, CTO, and FeCTO thin films

The direct optical band gap energy of SnO_2 films was obtained from the transmission spectra using Tauc's relation (5) [6]:

$$(\alpha h\upsilon)^2 = A(h\upsilon - Eg)^2, \quad (5)$$

where α is the absorption coefficient, h is the Planck constant, υ is the frequency, and Eg is the bandgap energy. Whereas, A is a constant independent on $h\upsilon$. According to Fig 6, the measurement of bandgap plays a vital role in semiconductors. The bandgap energy of an insulator is large (> 4 eV), but is lower for a semiconductor (< 3 eV) [19]. The direct optical band gap (Eg) has augmented from 3.65 eV to 3.85 eV with doping increasement. This increase in the energy bandgap was already observed in Co and Fe-doped SnO_2 [5], which may be due to the defects decreament.This increase in optical bandgap may be due to two effects: the decrease in defects; also it may be related to the increase in the grain size which is inverted to Eg.

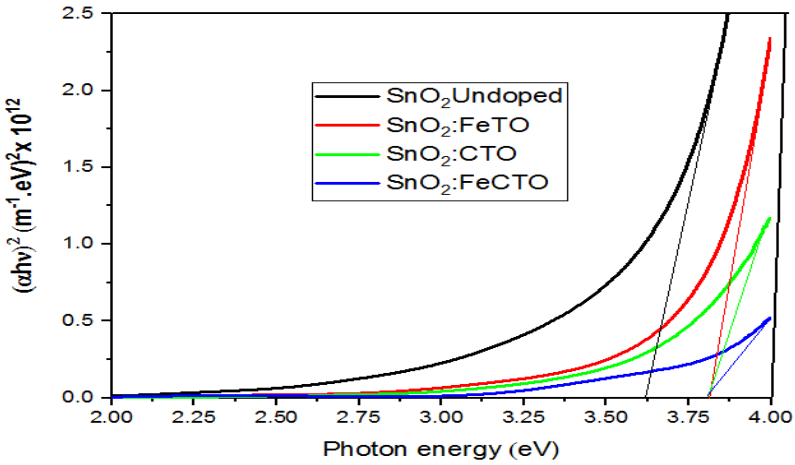

Fig. 6. Bandgap (Eg) of SnO_2, FeTO, CTO, and FeCTO thin films

4. Conclusions

In this study SnO_2, FeTO, CTO, and FeCTO thin films were successfully synthesized using the spray pyrolysis with moving nozzle method (SPMN). Structural and optical properties of SnO_2 thin films have been studied. XRD analyses showed the presence of polycrystalline structure with the tetragonal crystal structure. Both the undoped and doped tin oxide films grew along (211) as favorite orientation. The values of crystallite size decrease from 46.48 to 31.96 nm. Optical transmittance spectra of the thin films are more than 85% in the visible spectrum, with a direct bandgap in the range of 3.65-3.85eV. Results of SEM, XRD, EDX

and gap energy data were found supportive of each other. A close agreement of our results was observed with the previously reported data [15].

References

[1] Qian J, Liu P, Xiao Y, Jiang Y, Cao Y, Ai X, Yang H. TiO_2-coated multilayered SnO_2 hollow microspheres for dye-sensitized solar cells. *Advanced Materials.* 2009;21(36): 3663-3667.

[2] Ma H, Zhang D, Win S, Li S, Chen Y. Electrical and optical properties of F-doped textured SnO_2 films deposited by APCVD. *Solar Energy Materials and Solar Cells.* 1996;40(4): 371-380.

[3] Mokaripoor E, Bagheri-Mohagheghi M-M. Study of structural, electrical and photoconductive properties of F and P co-doped SnO_2 transparent semiconducting thin film deposited by spray pyrolysis. *Materials Science in Semiconductor Processing.* 2015;30: 400-405.

[4] Rahal A, Benhaoua A, Jlassi M, Benhaoua B. Structural, optical and electrical properties studies of ultrasonically deposited tin oxide (SnO_2) thin films with different substrate temperatures. *Superlattices and Microstructures.* 2015;86: 403-411.

[5] Segueni L, Rahal A, Benhaoua B, Allag N, Benhaoua A, Aida MS. Iron doping SnO_2 thin films prepared by spray with moving nozzle: structural, morphological, optical, and type conductivities. *Digest Journal of Nanomaterials and Biostructures.* 2019;14(4): 923-934.

[6] Mattox DM. *Handbook of physical vapor deposition (PVD) processing*. William Andrew; 2010.

[7] Benhaoua A, Rahal A, Benhaoua B, Jlassi M. Effect of fluorine doping on the structural, optical and electrical properties of SnO_2 thin films prepared by spray ultrasonic. *Superlattices and Microstructures.* 2014;70: 61-69.

[8] Suja M, Bashar SB, Morshed MM, Liu J. Realization of Cu-doped p-type ZnO thin films by molecular beam epitaxy. *ACS Applied Materials & Interfaces.* 2015;7(16): 8894-8899.

[9] Perednis D, Gauckler LJ. Thin film deposition using spray pyrolysis. *Journal of Electroceramics.* 2005;14(2): 103-111.

[10] Wang X, Shi F, Gao X, Fan C, Huang W, Feng X. A sol–gel dip/spin coating method to prepare titanium oxide films. *Thin Solid Films.* 2013;548: 34-39.

[11] Chandra S, Ravichandran K, George G, Arun T, Rajkumar P. Influence of Fe and Fe+ F doping on the properties of sprayed SnO_2 thin films. *Journal of Materials Science: Materials in Electronics.* 2016;27(9): 9558-9564.

[12] Francioso L, Forleo A, Capone S, Epifani M, Taurino AM, Siciliano P. Nanostructured In_2O_3–SnO_2 sol–gel thin film as material for NO_2 detection. *Sensors and Actuators B: Chemical.* 2006;114(2): 646-655.

[13] Korotcenkov G, Boris I, Brinzari V, Han S, Cho B. The role of doping effect on the response of SnO_2-based thin film gas sensors: Analysis based on the results obtained for Co-doped SnO_2 films deposited by spray pyrolysis. *Sensors and Actuators B: Chemical.* 2013;182: 112-124.

[14] Batzill M, Diebold U. The surface and materials science of tin oxide. *Progress in Surface Science.* 2005;79(2-4): 47-154.

[15] Mahmoudi M, Benhaoua A, Benhaoua B, Segueni L, Gheriani R, Rahal A. study of structural, optical and electrical properties of fluorine, cobalt doped and fluorine-cobalt co-doped tin dioxide SnO_2. *Digest Journal of Nanomaterials and Biostructures.* 2019;14(4): 1079-1086.

[16] Anandan K, Rajendran V. Size controlled synthesis of SnO_2 nanoparticles: facile solvothermal process. *J. Non-Oxide Glasses.* 2010;2(2): 83-89.

[17] Paufler P, Barrett CS, Massalski TB. Structure of Metals.*Crystal Research and Technology*. 1981;16(9): 982.
[18] Dghoughi L, Elidrissi B, Bernede C, Addou M, Lamrani MA, Regragui M, et al. Physico-chemical, optical and electrochemical properties of iron oxide thin films prepared by spray pyrolysis. *Applied Surface Science.* 2006;253(4): 1823-1829.
[19] Scherrer P. *KolloidchemieEinLehrbuch*. Springer; 1912.
[20] Göpel W, Schierbaum KD. SnO_2 sensors: current status and future prospects. *Sensors and Actuators B: Chemical.* 1995;26(1-3): 1-12.

THE AUTHORS

Chedala K.
e-mail: khadidjachedala02@gmail.com
ORCID: -

Benhaoua A.
e-mail: Othman.benhaoua@gmail.com
ORCID: -

Gheriani R.
e-mail: ragheriani@yahoo.fr
ORCID: -

Hima A.
e-mail: abdelkader-hima@univ-eloued.dz
ORCID: 0000-0002-5533-3991

Ayachi L.
e-mail: lakdarayachi2010@gmail.com
ORCID: -