

# Study of structural and antibacterial properties of strontium doped ZnO sprayed thin films

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**Abstract**— A chemical spray pyrolysis method was used to synthesize Sr-doped ZnO (SZO) thin films on glass substrates. The atomic percentages of dopants in the spray solution were [Sr/Zn] = 1, 2, 3, 4, 6 and 8%.

The structural properties of the prepared thin films are characterized by X-ray diffraction (XRD). Both undoped and Sr-doped film show strong preferred c-axis orientation. The unit, a minimum value of the volume cells was obtained at 2% doping level. The texture coefficient (TC) of the film along (002) direction the coefficient changes with the doping level due to Sr incorporation. The antibacterial activity against *S. aureus* is significantly influenced by the strontium incorporation.

**Keywords**—zinc oxide, strontium doping, thin film, spray, antibacterial activity.

## I. INTRODUCTION

Metallic oxides such as SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> have attracted attention as Transparent Conducting Oxide (TCO) because of their large band gap (3.3 eV), low resistivity, abundance, and non-toxicity. Among these binary and despite number of works, zinc oxide (ZnO) is a promising material for many applications such as gas sensor [1-4] light-emitting diodes [5-7], solar cells [8-10] and surface acoustic devices [11-14].

Accordingly, synthesis of polycrystalline ZnO thin films has been widely carried out using different techniques such as ultrasonic chemical vapor deposition [15], pulsed laser deposition [16], DC reactive sputtering [17], RF magnetron sputtering [18], helicon-wave excited plasma (HWP) deposition [19], spin coating [20], sol-gel [21], chemical beam deposition [22] and spray pyrolysis [23-25], among many others.

Although the conventional physical techniques give uniform and compact films with high transparency, they are usually very expensive and difficult to expand to large scale. The desired characteristics of a sensor material need to be balanced with the processing costs for practical applications. Low-temperature chemical techniques involving aqueous route (from solutions) on the other hand are versatile, simple, and cost-effective as compared with vapor-phase techniques. Among the various chemical techniques, one of the used and less studied chemical techniques is spray pyrolysis. This

technique consists in spraying a solution containing the precursor onto heated substrates.

ZnO has been the subject of many research works in terms of doping. Several elements were used as a doping to improve some physical properties of this binary such as indium [26, 27], aluminum [28], tin [29], ytterbium [24, 30], molybdenum [27,31]. Doping by Alkaline earth metal can play an important role and improves some properties of ZnO.

However, Doping in ZnO also play a key role in the possibility of developing effective anti-bacterials credible property choosing a Sr as doping has not yet been studied. To the best of our knowledge, this is the first work on the antibacterial properties of Sr doped ZnO thin films deposited by spray pyrolysis.

In this perspective, the studies on the effect of doping on antibacterial activity of ZnO, have also attracted a lot of attention to the researchers [18-22]. Different elements like Sn, Mn, Mg, Sb, Co and N play a very important role in enhancing the antibacterial efficacy of zinc oxide. It is well established that inhibition and mechanism of antibacterial activity of ZnO have been attributed to the formation of reactive oxygen species, which have reactive hydroxyl radical (OH<sup>•</sup>), toxic superoxide anion radical (O<sub>2</sub><sup>•-</sup>) and hydrogen peroxide with a weaker oxidizer (H<sub>2</sub>O<sub>2</sub>), on the surface which is useful in production of stress and thus inducing death of bacterial cell [23- 25]. Forces of attraction between oppositely charged bacterial cell and nanoparticles prevents growth of bacteria and kill the cell [24].

In this work, the effects of strontium doping with a different concentration on ZnO in terms of structural studies related to properties antibacterial activity of pur ZnO and (ZnO:Sr) thin films against staphylococcus aureus. Also, we presented the elaborating method and doping protocols as well as characterizing techniques.

## II. EXPERIMENTAL DETAILS

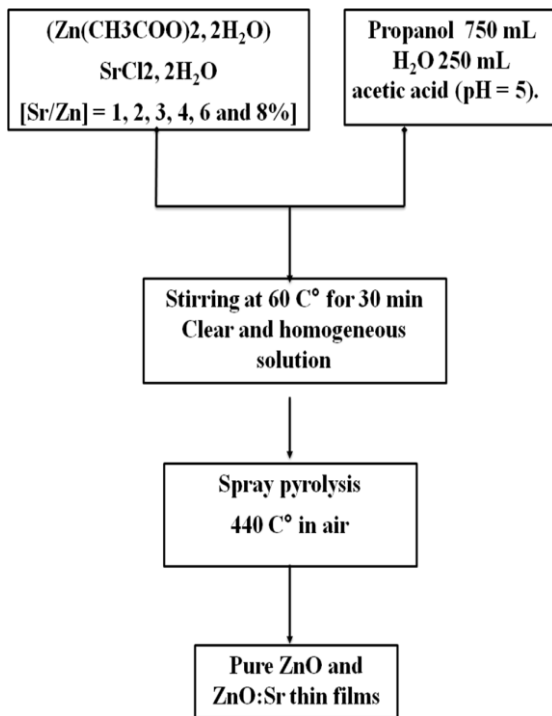
### A. Sr-doped ZnO films preparation

ZnO thin films have been first prepared on glass substrates by the spray process at 440°C in air, using propanol and zinc acetate Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> : 10<sup>-1</sup> M. The

solution contained a mixture of water and propanol with fraction volumes of 1/4 and 3/4 respectively. The precursor mixture was acidified using acetic acid (pH = 5). The mixture is magnetically stirred at 60°C for 30 minutes to get homogeneous. The carrier gas was nitrogen through a 0.5 mm diameter nozzle. The nozzle-to-substrate plane distance was fixed at the optimal value of 25 cm. During the whole deposition process, precursor mixture flow rate was approximately 20 mL/min.

Under similar experimental conditions, strontium-doped ZnO thin films solutions have been fabricated by adding hydrated strontium chloride (SrCl<sub>2</sub>, 2H<sub>2</sub>O, 99.9% purity) to the precursor solution while maintaining acidity level. The strontium-to-zinc molar ratios [Sr<sup>2+</sup>]/[Zn<sup>2+</sup>] were 0.01, 0.02, 0.04, 0.06 and 0.08. In the three elaborated samples, the strontium-to-zinc molar ratios [Sr<sup>2+</sup>]/[Zn<sup>2+</sup>] were 0.01, 0.02, 0.04, 0.06 and 0.08. After deposition, the coated substrates were allowed to cool down naturally to room temperature.

The flow chart of the entire process for preparing ZnO and strontium-doped ZnO films is schematically drawn in Figure 1.



**Figure 1 :The flow chart for preparation of ZnO:Sr thin films**

### B. Cracterisation techniques

The crystal structures of all prepared thin films were analyzed by means of X-ray apparatus (Philips PW 1729 system) using Cuka $\alpha$  monochromatic radiation ( $\lambda = 1.54059$  Å).

For antibacterial susceptibility test against *Staphylococcus aureus* ATCC 25923 was determined by agar well diffusion method [26]. *S. aureus* is a Gram positive bacterium that causes skin and food poisoning and

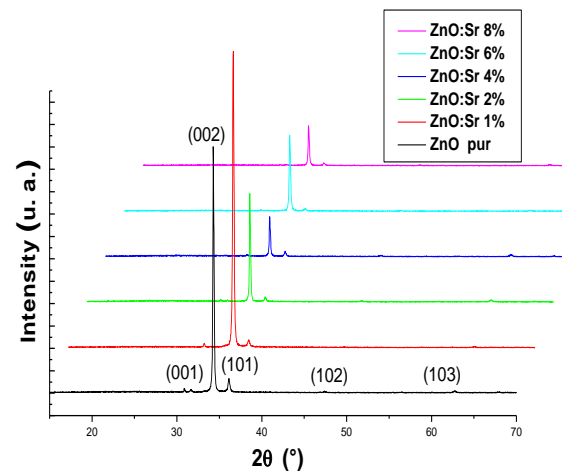
respiratory infections [27, 28], was purchased from CHU El-Oued (Centre Hospitalier et Universitaire ,El-Oued, Algeria).

The test solution was prepared with known weight of fractions in 10 mg/mL, dissolved in 5 percent dimethyl sulphoxide (DMSO) and cultured overnight. The agar Petri plates were prepared by pouring 20 mL of Mueller Hinton Agar. After drying and solidifying, 0.1 mL of test solution was poured and uniformly spread in plates. The excess inoculums were drained and the plates were allowed to dry for 5 minutes. Later than, ZnO and (ZnO:Sr) coated glass slides were cut into squares (10 x 10 sq. cm) were placed on the petriplates with gently pressed to ensure contact with the agar surface. Gentamycin (30 mg/disc) were used as the positive controls and 5 per cent DMSO was used as blind control in these assays. Lastly, the agar plates were incubated at 37°C for 24h. The zones of inhibition were measured for each tested sample in millimeters.

## III. RESULTS AND DISCUSSION

### A. Structural properties

Figure 2, shows the XRD patterns of ZnO :Sr thin films deposited on microscope glass in air at 440°C.



**Figure 2 : XRD patterns of ZnO :Sr thin films**

X-ray diffraction show well-defined peaks of (001), (002), (101), (102) and (103), corresponding to hexagonal würtzite phase according to JCPDS 036-1451 card.

As ZnO crystallizes in the hexagonal structure, the interplanar spacing (d) of given Miller indices h, k and l, dhkl values of ZnO:Sr thin films were also calculated by using Bragg equation (eq 1) [27, 28] :

$$2d_{hkl} \sin \theta = n\lambda \quad (1)$$

where n is the order of diffraction (usually n = 1) and  $\lambda$  is the X-ray wavelength. Table I summarizes the calculated values of dhkl of the prepared ZnO:Sr thin films.

**TABLE I.** CALCULATE INTERPLANAR SPACING DHKL OF ZNO:SR PREPARED FILMS.

	$d_{(100)}$ (Å)	$d_{(002)}$ (Å)	$d_{(101)}$ (Å)	$d_{(102)}$ (Å)	$d_{(103)}$ (Å)
<b>ZnO</b>	2,8221	2,6138	2,4847	1,9179	1,4789
<b>ZnO :Sr 1%</b>	2,8825	2,6020	2,4741	0,0000	0,0000
<b>ZnO :Sr 2%</b>	2,8326	2,6197	2,4927	1,9164	1,4819
<b>ZnO :Sr 4%</b>	2,8239	2,6094	2,4794	1,9149	1,4802
<b>ZnO :Sr 6%</b>	2,8752	2,5976	2,4755	1,9103	1,4755
<b>ZnO :Sr 8%</b>	2,8117	2,5976	2,4715	1,9081	1,4793

It can be seen that the interplanar spacing dhkl values are strongly depend on Sr content.

We have calculated the lattice parameters by using the following formula (eq 2):

[31]:

$$d_{hkl} = \frac{1}{\sqrt{\frac{4(h^2 + k^2 + hk)}{3a^2} + \frac{l^2}{c^2}}} \quad (2)$$

Where a, c are the lattice parameters and  $d_{hkl}$  is the crystalline surface distance for (hkl) indices.

From calculated value of lattices parameters listed in table 2, it is found that this parameter reaches a high value for 2% Sr doping level. This value seems an appropriate value for possibly incorporation of this doping inside the zinc oxide thin film. Also, when Sr content increases, these parameters decrease too showing a possibly escape of this doping element to form oxides with high index. The latest has a crystalline phase different to hexagonal structure and goes with the structural and optical finding described above. Indeed, the compactness of the host material decreases at this special doping and pave the way for high interaction of this 2% Sr-doped ZnO oxide against photon light and electric response as well as sensitivity applications.

Moreover, the texture coefficient (TC) which indicates the maximum preferred orientation of the films along the diffraction plane means that the increase in preferred orientation is associated with increase in the number of grains along that plane.  $TC_{(hkl)}$  values have been calculated from X-ray data, using the following formula [31,33]:

$$TC_{(hkl)} = \frac{I(hkl) / I_0(hkl)}{N^{-1} \sum I(hkl) / I_0(hkl)} \quad (3)$$

where  $I(hkl)$  is the measured relative intensity of (hkl) plane,  $I_0(hkl)$  is the standard intensity of the same plane taken from the JCPDS 036-1451 card, and N is the reflection number.  $TC_{(hkl)}$  calculated values of the ZnS prepared thin films are gathered in Table II.

**TABLE II.** CALCULATE TEXTURE COEFFICIENT  $TC_{(hkl)}$  VALUES OF ZNO:SR PREPARED FILMS.

	$TC_{(100)}$	$TC_{(002)}$	$TC_{(101)}$	$TC_{(102)}$	$TC_{(103)}$
<b>ZnO</b>	0,070	4,566	0,276	0,040	0,048
<b>ZnO :Sr 1%</b>	0,073	4,794	0,132	-	-
<b>ZnO :Sr 2%</b>	0,103	4,487	0,231	0,076	0,103
<b>ZnO :Sr 4%</b>	0,228	3,881	0,460	0,168	0,262
<b>ZnO :Sr 6%</b>	0,116	4,565	0,180	0,065	0,075
<b>ZnO :Sr 8%</b>	0,179	4,227	0,320	0,118	0,156

From these results, it is observed that  $TC_{(002)}$  is so high, showing that the crystallites are mainly perpendicular to substrate plane (parallel to C axis).

XRD spectra were used to study the effect of incorporation of the element Sr in the ZnO matrix respectively on the crystallite size, using the formula Debye-Scherrer (eq 4) [27, 30]:

$$D = \frac{k \cdot \lambda}{\beta_{\frac{1}{2}} \cos(\theta)} \quad (4)$$

where  $k=0.90$  is the Scherrer constant,  $\beta_{1/2}$ = corrected half width of the peak and  $\lambda=1.54 \text{ \AA}$  is the wavelength of CuK $\alpha$  radiation.

The calculated values of crystallite size are gathered in tables III.

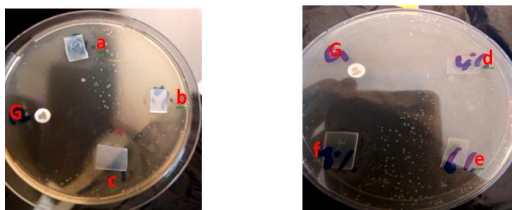
**TABLE III.** CALCULATE CRYSTALLITE SIZE  $D_{(hkl)}$  VALUES OF ZNO:SR PREPARED FILMS

	$D_{(100)}$ (nm)	$D_{(002)}$ (nm)	$D_{(101)}$ (nm)	$D_{(102)}$ (nm)	$D_{(103)}$ (nm)
<b>ZnO</b>	83,92	168,97	106,18	55,10	59,10
<b>ZnO :Sr 1%</b>	209,51	120,71	70,78	-	-
<b>ZnO :Sr 2%</b>	137,59	230,94	116,01	45,18	64,59
<b>ZnO :Sr 4%</b>	69,92	168,99	84,92	73,48	59,10
<b>ZnO :Sr 6%</b>	17,47	169,06	84,96	36,76	38,80
<b>ZnO :Sr 8%</b>	80,22	169,08	141,57	35,79	48,50

From this structural study, it is found a particular effect for 1% [Sr]/[Zn] ratio. Indeed, for low doping, the minimum of lattice parameter c of the hexagonal structure was obtained for the 1% doping level. This same doping level gives the best orientation of crystallites according to (002) perpendicular to the plane of the substrate. Also, it is found the less crystallite size. These doping level appear specific in terms of structural properties of the deposited thin films.

## B. Anti-bacterials properties

Figure 8, shows the antibacterial activity of the pure ZnO and Sr-doped thin films were evaluated by agar well diffusion method against *S. aureus*.



**Fig. 3: Antibacterial activity of Staphylococcus aureus ATCC 25923 for: G) positive control, a) ZnO, b) 1% Sr, c) 2% Sr, d) 4% Sr, e) 6% Sr and f) 8% Sr**

The observed zone of inhibition value of ZnO, Sr(1%)ZnO, Sr(2%)ZnO, Sr(4%)ZnO, Sr(6%)ZnO, Sr(8%)ZnO reached 26, 29, 24.5, 18, 20, 20 and 20 mm respectively. Gentamycin is a positive control, for which the zone of inhibition is 33 mm. The increase in Sr content from 0 to 2% effectively promotes yield the high antibacterial activity against *S. aureus*, however, a further increase in Sr doping levels has an adverse effect. This result indicating that the highest value for zone of inhibition is considered for 2% Sr-doped ZnO oxide.

According to previous work [31-33], the mechanism of the antibacterial activity of ZnO nano-particles can be attributed as oxidative stress induced by the formation of hydrogen peroxide ( $H_2O_2$ ), hydroxyl radical ( $OH^\cdot$ ) and superoxide ( $O_2^\cdot$ ), produced enters the cell membrane of bacteria and kills them. The enhanced in inhibitory activity of ZnO:Sr is also due to the formation of another phase of (SrO).

## IV. CONCLUSION

In summary, the structural properties and anti-bacterials activity of ZnO and strontium doped ZnO thin films deposited on glass substrates by spray pyrolysis method in the temperature of 440 °C were investigated. XRD pattern of prepared samples showed polycrystalline wurtzite with a preferential (0 0 2) orientation. Anti-bacterial studies against *S. aureus* show a high dependency to Sr incorporation in ZnO matrix.

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## REFERENCES

- [1] K. Ravichandran et al. / Enhancement in the antibacterial efficiency of ZnO nanopowders by tuning the shape of the nanograins through fluorine doping, *Superlattices and Microstructures* 69 (2014) 17–28, <http://dx.doi.org/10.1016/j.spmi.2014.01.020>
- [2] M Shoeb1 , Braj R Singh1 , Javed A Khan1 , Wasi Khan1 , Brahma N Singh2 , Harikesh B Singh3 and Alim H Naqvil , ROS-dependent anticandidal activity of zinc oxide nanoparticles synthesized by using egg albumen as a biotemplate, *Adv. Nat. Sci.: Nanosci. Nanotechnol.* 4 (2013) 035015 (11pp), doi:10.1088/2043-6262/4/3/035015
- [3] Jun Han, Shuai Yuan, Lina Liu, Xiaofeng Qiu, Haibo Gong, Xiaopeng Yang, Cuncheng Li, Yufeng Haob and Bingqiang Cao, *J. Mater. Chem. A*, 3 (2015) 5375.
- [4] A. Souissi, A. Boukhachem, Y. Ben Taher, A. Ayadi, A. Mefteh, M. Ouesleti, S. Guermazi, M. Amlouk, *Optik* 125 (2014) 3344.
- [5] Dagang Miao , Huawen Hu, Lu Gan, *Journal of Alloys and Compounds* 639 (2015) 400.
- [6] C. Manoharan, G. Pavithra , S. Dhanapandian , P. Dhamodaran, B. Shanthi, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 141 (2015) 292.
- [7] A. Boukhachem, S. Fridjine, A. Amlouk, K. Boubaker, M. Bouhafs, M. Amlouk, *Journal of Alloys and Compounds* 501 (2010) 339.
- [8] A. Amlouk, K. Boubaker, M. Amlouk, M. Bouhafs, *Journal of Alloys and Compounds* 485 (2009) 887.
- [9] A. Boukhachem, B. Ouni, M. Karyaoui, A. Madani, R. Chtourou, M. Amlouk, *Materials Science in Semiconductor Processing* 15 (2012) 282.
- [10] H. Sato, T. Minami, S. Takata, T. Miyata, and M. Ishii, *Thin Solid Films*, 236 (1993) 14.
- [11] S. Tewari and A. Bhattacharjee, *Pramana*, 76 (2011) 153.
- [12] A. Boukhachem, S. Fridjine, A. Amlouk, K. Boubaker, M. Bouhafs, M. Amlouk, *Journal of Alloys and Compounds* 501 (2010) 339.
- [13] J.L. van Heerden, R. Swanepoel, *Thin Solid Films*, 1–2 (1997) 72.
- [14] K. Pradeev raj, K. Sadaiyandi, A. Kennedy, R. Thamizselvi, Structural, optical, photoluminescence and photocatalytic assessment of Sr-doped ZnO nanoparticles, *Materials Chemistr and Physics* (2016), doi: 10.1016/j.matchemphys.2016.07.068.
- [15] Ramin Yousefi , FaridJamali-Sheini, Mohsen Cheraghizade c, Sara Khosravi-Gandomani d, Abdolhossein Saaedi e, Nay Ming Huang f, Wan Jeffrey Basirun, Majid Azarang, Enhanced visible-light photocatalytic activity of strontium-doped zinc oxide nanoparticles, *Materials Science in Semiconductor Processing* 32 (2015) 152–159, <http://dx.doi.org/10.1016/j.mssp.2015.01.013>
- [16] Asad Mahmood, Fatih Tezcan, Gülfeza Kardaş, and Faruk Karadağ, Effect of Sr doping on the electronic band structure and optical properties of ZnO: A first principle calculation, *Journal of Applied Physics* 122, 113102 (2017); doi: 10.1063/1.5002075
- [17] T. A. Vijayan, R. Chandramohan, S. Valanarasu, J. Thirumalai, and S. P. Subramanian, *J. Mater. Sci.* 43, 1776 (2008).
- [18] R. Brayner, R. Ferrari-Iliou, N. Brivoivo, S. Djediat, M. F. Benedetti, F. Fievet, *NanoLett.* 6 (2006) 866-870.
- [19] K. H. Tam, A. B. Djurišić, C. M. N. Chan, Y. Y. Xi, C. W. Tse, Y. H. Leung, W. K. Chan, F. C. C. Leung, D. W. T. Au, *Thin Solid Films*, 516 (2008) 6167-6174.
- [20] G. X. Tong, F. F. Du, Y. Liang, Q. Hu, R. N. Wu, J. G. Guan, X. Hu, *J. Mater. Chem. B* 1 (2013) 454-463.
- [21] K. R. Raghupathi, R. T. Koodali, A. C. Manna, *Langmuir* 27 (2011) 4020-4028.
- [22] Mahendra C, Murali M, Manasa G, Pooja P, Abhilash MR, Lakshmeesha TR, Satish A, Amruthesh KN, Sudarshana MS, Antibacterial and antimutagenic potential of bio-fabricated zinc oxide nanoparticles of *Cochlospermum religiosum* (L.), *Microbial Pathogenesis* (2017), doi: 10.1016/j.micpath.2017.07.051
- [23] H. A. Foster, I. B. Ditta, S. Varghese, A. Steele, *Appl. Microbiol. Biotechnol.* 90 (2011) 1847-1868.
- [24] W. W. Wilson, M. M. Wade, S. C. Holman, F. R. Champlin, *J. Microbiol. Methods* 43 (2001) 153-164.
- [25] K.R. Raghupathi, R.T. Koodali, A.C. Manna, Size-dependent bacterial growth inhibition and mechanism of antibacterial activity of zinc oxide nanoparticles *Langmuir*, 27 (2011), pp. 4020-4028.
- [26] P.M. Hall, J.M. Morabito, *Thin. Solid. Films* 33 (1976) 107e134.
- [27] F. Yakuphanoglu, Y. Caglar, S. Ilican, M. Caglar, *Physica B: Condensed Matter* 394 (2007) 86.
- [28] B.D. Cullity, "Elements of X-ray Diffraction", A.W. Pub. Comp. Inc., Boston, 1978.
- [29] Y. Narendar, G. L. Messing, *Catal.Today*, 35 (1997) 247.
- [30] X.Y. Li, H.J. Li, Z.J. Wang, H. Xia, Z.Y. Xiong, J.X. Wang, B.C. Yang, *Opt. Commun.* 282 (2009) 247.
- [31] N. Talebian, M.R. Nilforoushan, E.B. Zargar, *Appl. Surf. Sci.* 258, 547 (2011)..
- [32] C. Manoharan, G. Pavithra, S. Dhanapandian, P. Dhamodaran, B. Shanthi, Properties of spray pyrolysed ZnO:Sn thin films and their Antibacterial activity, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2015).
- [33] J. Panigrahi, D. Behera, I. Mohanty, U. Subudhi, B.B. Nayak, B.S. Acharya, *Appl. Surf. Sci.* 258 (2011) p.304–311.