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Estimation of Spray deposited ZnO film thickness – A Computational study

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Abstract: The thickness of ZnO thin films synthesized by spray pyrolysis is estimated using artificial neural network. The thickness of spray deposited ZnO film depends on various parameters mainly it depends on concentration of precursor, substrate temperature and time of deposition. In the present work, the three important parameters are estimated in order to obtain a film of particular thickness. Moreover, the characteristics of ZnO film are influenced by the thickness. In order to estimate ZnO film thickness the given data are trained with an accuracy of about 0.002 percent. The film thickness of spray deposited ZnO around 100nm – 500nm can be obtained in lower molar concentration in the range of 0.15M – 0.4M with increasing the temperature and deposition time duration. The desired film thickness of ZnO is reported in the present work to reduce the tedious experimental procedure.
Keyword: ZnO; spray deposition; film thickness; optimization; deposition time.

1. Introduction

Zinc oxide (ZnO) is one of the promising semiconducting metal oxides, which find its wide applications due to its direct band gap of 3.37eV [1] at room temperature and high exiton bonding energy 60meV [2]. ZnO is one of the most attractive transparent conducting oxides [3]. Also it has unique properties such as high transmittance [4] in the visible solar region-high transmittance up to 85% in the visible range. Furthermore, it has high chemical and physical stability, high electrical conductivity and high refractive index [5]. The conductivity of ZnO can be increased by thermal treatment with hydrogen or other doping process. Moreover, ZnO have potential applications in transparent electrode [6], flat panel display [7], organic light emitting diode, solar cell [7] manufacturing as transparent and antireflective coatings, field emission device, sensor, ultrasonic oscillators, transducers, photo protective coatings [8], surface acoustic wave device. They are also used for manufacturing laser diodes [9], piezo-electric devices [10], electronic and optoelectronic devices [11, 12] and field effect devices, schottky diodes [13], UV detectors [14], acoustic resonators [15] and electro-luminescence displays [16].

The synthesis of ZnO thin films and nanoparticles can be prepared by pulsed laser deposition [17], metal organic chemical vapour deposition [18], dc reactive magnetron sputtering-atomic layer deposition [19], sol-gel method [20], radio frequency magnetron sputtering [21], chemical spray pyrolysis [22], ion-beam assisted deposition etc. Few of these techniques provide promising options for large-scale production and a good potential for scale up. Even though there are many method used in the synthesis of ZnO thin films, spray deposition of ZnO thin films are widely used due to its simplicity and the wide range of tunability of band gap, carrier concentration and resistivity of the film. However, the deciding factor of carrier concentration and surface resistance depends on the thickness of the film. Moreover, estimating the thickness of film on different parameters experimentally is a tedious work and also time consuming. Artificial neural network (ANN) gives solution to this problem for optimizing the thickness of the thin film by giving the input parameters. Besides, ANN provides data with higher accuracy within a short duration of time. The thickness of ZnO films prepared using spray pyrolysis technique depends on different deposition and post-deposition conditions such as the concentration of precursor, substrate temperature, spray rate, nozzle to substrate distance, pressure of carrier gas and annealing. In the present work, thickness of spray deposited ZnO thin films are calculated using ANN and the results are reported.

2. Computational details

In the present work, to estimate the thickness of ZnO films by spray pyrolysis method, ANN have been employed to predict the output (thickness of the films) value for the given desired input parameters (concentration, substrate temperature and time of deposition). The thickness of the film is influenced by the precursor solution. Besides, the concentration in molarity, temperature in Kelvin and time in minutes are taken as input parameters. The thickness of the film is predicted based on the given values of concentration, temperature and time of deposition. Moreover, the input data given to ANN for spray pyrolysis method is consolidated from the reported work [23-32]. Initially the data are given as input and they are trained with an accuracy of 0.002 %. Then queries are made to ensure the accuracy of the thickness. Besides, they are found to coincide with that of the given data. Furthermore the unknown parameters are given as input and the corresponding output are recorded.

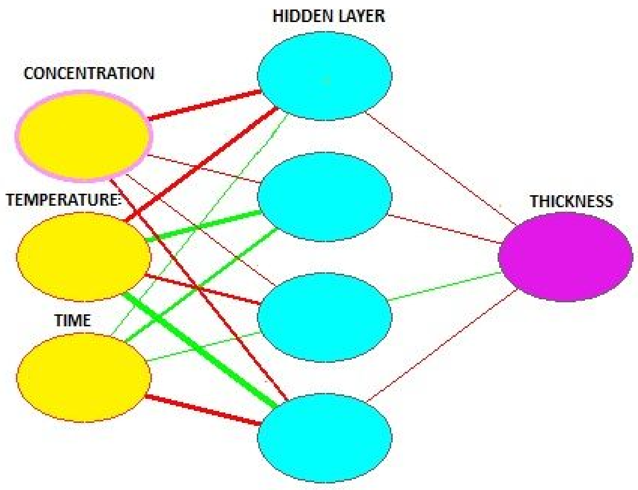

Fig 1 . Architecture of ANN to estimate ZnO film thickness

The architecture, learning algorithm, which is used in the transfer function and the number of neurons influences the computation of the artificial neural network. Back propagation algorithm (BPA) neural network have been used to estimate the thickness of the ZnO film. In this work, Figure 1 represents the simple architecture of ANN for the determination of ZnO film thickness, it has three input parameters in the input layer, four neurons in the hidden layer and one neuron in the output layer thus, constituting a simple architecture. Generally BPA is a supervised learning algorithm, which reduces over all systems to minimum and it uses the sigmoid activation function $f(x)=1/1+e^{-x}$. In general, an interconnection between the input, hidden and output layers are established during the learning and training process. The signal transfer between the layers is enabled because of the interconnection between the layers. Furthermore to add, the determination of intensity of the signals is achieved with the help of the weights of the corresponding signals. This can be done by iteratively changing the weights of the corresponding signals between the neurons and the sum of the squared errors between the calculated weights and expected weights can be minimized by the model selected.

During the learning process, the initial weight vectors W_0 are updated using the following equation,

$$W_i(k+1)=W_i(k)+\mu(T_i-O_i)f'(W_ix_i)x_i$$

where W_i is the weight matrix associated with i^{th} neuron , x_i is the input of i^{th} neuron, O_i is the actual output of the i^{th} neuron, T_i is the target output of the i^{th} neuron and μ is the learning rate parameter.

Training process

For growing the network the results obtained from the experiments [23-32] were used. The concentration of the solution, substrate temperature and time of deposition are given as the input parameters in the three input nodes and the thickness of ZnO film is obtained as output.

Testing process

After back propagation training of the neural network with the data obtained from the spray pyrolysis, test rows are generated, then the accuracy of the neural network is tested by giving input and trained once again. The results obtained have been found to have an error of 0.02968 percent and the accuracy of the results is validated.

3. Results and discussion

The thin film deposition using the spray pyrolysis technique involves spraying a precursor salt solution onto the preheated substrate. The morphology of the film depends on the precursor solution, substrate temperature and the geometry of the atomizer. The atomized droplets strike the substrate surface, spread into substrate surface and undergo thermal decomposition. The morphology of the spray deposited film depends on the momentum and volume of the droplet, as well as the substrate temperature. Besides, the film with different morphology is influenced by metal salt being converted into oxides on the preheated substrate. The schematic diagram is shown in Fig 2. The chemical reactants are selected such that the products other than the desired compound are volatile at that temperature of deposition. The precursor solution is the second important process variable. Solvent, type of salt, concentration of solute in the solvent and additives influence the physical and chemical properties of the precursor solution. Therefore, structure and properties of a deposited film can be tailored by changing composition of precursor solution. Initially to estimate the film thickness of ZnO about 50 data were given and trained.

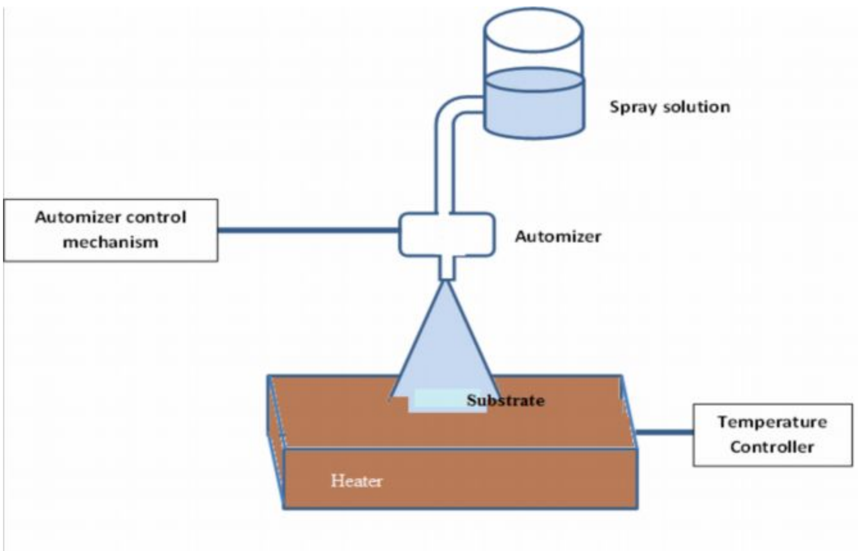

Fig 2. Schematic diagram of spray deposition

The data extracted have been trained with an accuracy of 0.002 percent. Initially the queries were made with the existing data. Considering a particular thickness value, the same input parameter values as that of the given data say, the concentration was 0.05 M, temperature as 600 K and time of deposition was 40 minutes.

In the present work, zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$] is taken as precursor salt and precursor solution is prepared in the deionized water. Initially to optimize the film thickness of ZnO about 50 data were given and trained. The data extracted have been trained with an accuracy of 0.002 percent. Furthermore the queries were made with the existing data. Then the values of the input parameters were taken for the concentration of 0.15 M, temperature of 623 K and time of 30 minutes and the thickness was found to be 310.7 nm. We observed the change in the value of the thickness of the film according to the changes made in the input parameter values as shown in Fig 3. Moreover, the morphology of ZnO film depends on deposition time and substrate temperature.

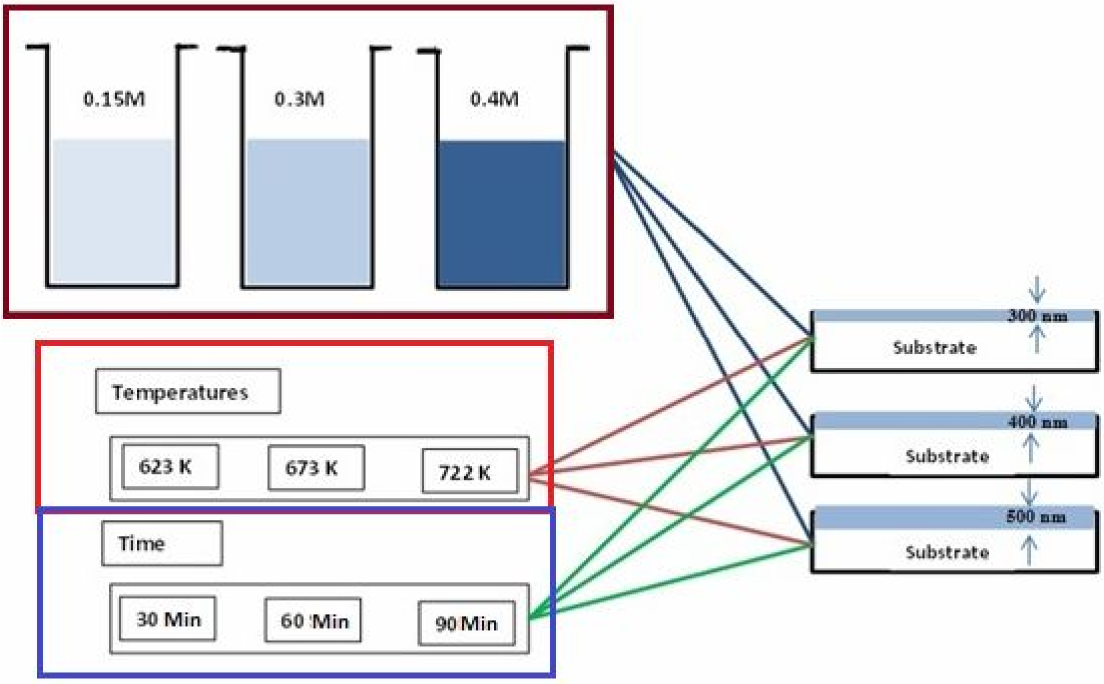

Fig 3. Flow chart of various ZnO film thickness using spray deposition

O:0	I:1	I:2	I:3	O:0	I:1	I:2	I:3	O:0	I:1	I:2	I:3
320.0000	0.3000	673.0000	45.0000	264.6728	0.0500	400.0000	60.0000	160.0000	0.0100	400.0000	60.0000
440.0000	0.3700	523.0000	30.0000	310.7651	0.1500	623.0000	30.0000	140.0000	0.0100	400.0000	60.0000
220.0000	0.0200	680.0000	40.0000	575.8785	0.3500	423.0000	90.0000	230.0000	0.0100	400.0000	60.0000
260.0000	0.0100	673.0000	60.0000	234.7618	0.2500	623.0000	60.0000	225.0000	0.0100	400.0000	60.0000
160.0000	0.0100	400.0000	60.0000	426.6872	0.1700	423.0000	30.0000	150.0000	0.0100	400.0000	60.0000
140.0000	0.0100	400.0000	60.0000	262.2747	0.1164	589.4076	56.3557	182.0000	0.0100	400.0000	60.0000
230.0000	0.0100	400.0000	60.0000	370.0000	0.1700	563.0000	50.0000	161.3666	0.0100	400.0000	60.0000
225.0000	0.0100	400.0000	60.0000	265.0000	0.2800	473.0000	30.0000	160.0000	0.0100	400.0000	60.0000
150.0000	0.0100	400.0000	60.0000	410.0000	0.3300	683.0000	40.0000	145.0000	0.0100	673.0000	60.0000
182.0000	0.0100	400.0000	60.0000	120.0000	0.0100	400.0000	30.0000	140.0000	0.0100	673.0000	60.0000
160.0000	0.0100	400.0000	60.0000	300.0000	0.1800	573.0000	40.0000	140.0000	0.1500	673.0000	60.0000
145.0000	0.0100	673.0000	60.0000	290.0000	0.1300	620.0000	50.0000	142.0000	0.1500	673.0000	60.0000
140.0000	0.0100	673.0000	60.0000	257.6985	0.1081	594.5087	58.8133	132.9859	0.1500	673.0000	60.0000
140.0000	0.1500	673.0000	60.0000	350.0000	0.2050	563.0000	60.0000	145.0000	0.1500	673.0000	60.0000
142.0000	0.1500	673.0000	60.0000	310.0000	0.0700	683.0000	35.0000	150.0000	0.0100	673.0000	60.0000
145.0000	0.1500	673.0000	60.0000	350.0000	0.2050	563.0000	60.0000	120.0000	0.0100	673.0000	60.0000
150.0000	0.0100	673.0000	60.0000	231.6667	0.0780	583.4545	59.3939	176.5971	0.3000	673.0000	60.0000
120.0000	0.0100	673.0000	60.0000	120.0000	0.0100	400.0000	30.0000	182.0000	0.3000	673.0000	60.0000
182.0000	0.3000	673.0000	60.0000	580.0000	0.4000	726.0000	90.0000	174.0000	0.1000	723.0000	90.0000
174.0000	0.1000	723.0000	90.0000	320.0000	0.2700	723.0000	70.0000	300.0000	0.2000	726.0000	90.0000
300.0000	0.2000	726.0000	90.0000	245.0000	0.0500	420.0000	50.0000	490.7697	0.4000	722.0000	90.0000
450.0000	0.4000	722.0000	90.0000	430.0000	0.3500	723.0000	45.0000	450.0000	0.4000	722.0000	90.0000
340.0000	0.1000	473.0000	40.0000	249.3694	0.0986	592.4177	59.5782	340.0000	0.1000	473.0000	40.0000
380.0000	0.1000	473.0000	40.0000	400.0000	0.2500	623.0000	55.0000	380.0000	0.1000	473.0000	40.0000
190.0000	0.0100	673.0000	30.0000	350.0000	0.2050	563.0000	60.0000	190.0000	0.0100	673.0000	30.0000
210.0000	0.0100	673.0000	60.0000	299.5012	0.3000	673.0000	45.0000	210.0000	0.0100	673.0000	60.0000
245.0000	0.0100	673.0000	90.0000	320.0000	0.3000	673.0000	45.0000	245.0000	0.0100	673.0000	90.0000
580.0000	0.1000	473.0000	40.0000	440.0000	0.3700	523.0000	30.0000	580.0000	0.1000	473.0000	40.0000
370.0000	0.0100	673.0000	90.0000	220.0000	0.0200	680.0000	40.0000	370.0000	0.0100	673.0000	90.0000
190.0000	0.0100	673.0000	60.0000	260.0000	0.0100	673.0000	60.0000	190.0000	0.0100	673.0000	60.0000
155.0000	0.0100	673.0000	30.0000	161.3666	0.0100	400.0000	60.0000	155.0000	0.0100	673.0000	30.0000

Fig. 4 Data set given for training of ANN collected from various literatures Ref. [22-33]

Furthermore, to obtain a film of thickness of 200-300 nm, the concentration should be 0.01-0.03 M and temperature should be around 550 K with time duration of 30-60 min. In order to obtain a film of thickness 300-500 nm, the concentration should be 0.2-0.35 M and the temperature should be around 600 K for time duration of 45-60 min. Besides for a film of thickness of 500-600 nm, the concentration should be 0.35-0.4 M and the temperature should be around 723 K with the time duration of 90 min. It is possible to achieve the film thickness of 300-400 nm in low molar concentration with 600-700 K temperature. Moreover, the thickness of the film increases with increasing the solution concentration and deposition duration. After training ANN the queries were made with the existing data. For instance, the thickness of the film when the concentration was 0.05 M, temperature 520 K and time of deposition 60 minutes was found to be 264.67 nm. Then the values of the input parameters were taken as 0.15 M, 623 K, 30 minutes as concentration, temperature and time of deposition respectively and the thickness was found to be 310 nm. Thus by varying the input parameter values namely concentration, temperature and time of deposition the thickness of the films can be obtained. We observed the change in the value of the thickness of the film according to the changes made in the input parameter values. They are estimated so as to get accurate values. After optimization the following results were found. To obtain a film of thickness 200-300 nm, the concentration should be 0.01-0.15 M and temperature should be around 550 K with spraying time of 60 minutes. In order to obtain a film of thickness 300-500 nm, the concentration should be 0.2-0.35 M and the temperature should be around 600 K is required with time duration of 45 minutes. To obtain a film of thickness 500-600 nm, the concentration should be 0.35-0.4 M and the temperature should be around 723 K with the deposition time of 40 minutes.

Conclusion

In summary, the thickness of spray deposited ZnO thin film is estimated using artificial neural network. In order to prepare the film thickness of 300 nm, the concentration of precursor solution should be around 0.2 M, substrate temperature should be maintained at 550 K and the time of deposition should be 30 minutes. Furthermore, for the film thickness of 400 nm, the concentration of the solution is around 0.25-0.35 M, temperature is kept at 600 K and the time of deposition should be 45 minutes. A film of thickness of 500 nm can be obtained when the concentration of the solution is around 0.35-0.4 M, temperature is maintained at 700 K and the time of deposition is nearly 60 minutes. Besides, thickness of ZnO film can be controlled over a wide range. Film of thickness ranging from 100-500 nm can be obtained with the concentration of the solution being 0.15-0.4 M and the substrate temperature should be in the range of 500-600 K and time of deposition is in the interval of 45-60 minutes. Thus, artificial neural network eliminates the tedious experimental procedures and characterization to obtain a definite ZnO film thickness. Moreover, it also reduces the time and cost to synthesize a particular thickness of ZnO film.

References

1. Lokhande, B. J., Patil, P. S. and Uplane, M. D. Deposition of highly oriented ZnO films by spray pyrolysis and their structural , optical and electrical characterization, *Materials letter*, 2002,57, 573–579.
2. Zhao, J.-L., Li, X.-M., Bian, J.-M., Yu, W.-D. and Zhang, C.-Y. Comparison of structural and photoluminescence properties of ZnO thin films grown by pulsed laser deposition and ultrasonic spray pyrolysis, *Thin Solid Films,* 2006, 515, 1763–1766.
3. Wienke, J. andBooij, S. ZnO:In deposition by spray pyrolysis — Influence of the growth conditions on the electrical and optical properties, *Thin Solid Films* 2008, 516, 4508–4512.
4. Taskin, M. and Podder, J. Structural, Optical and Electrical Properties of Pure and Co- Doped ZnO Nano Fiber Thin Films Prepared by Spray Pyrolysis, *App. Sci. Report*, 2015, 9(1), 1–6.
5. Zahedi, F., Dariani, R. S. and Rozati, S. M. Effect of substrate temperature on the properties of ZnO thin films prepared by spray pyrolysis, *Mater. Sci. Semicond. Process,* 2013,16, 245–249.
6. Mahajan, C. M. and Takwale, M. G. Intermittent spray pyrolytic growth of nanocrystalline and highly oriented transparent conducting ZnO thin films: Effect of solution spray rate, *J. Alloys Compd.,.* 2014, 584, 128–135.
7. Sadananda Kumar, N., Bangera, K. V. and Shivakumar, G. K. Effect of annealing on the properties of Bi doped ZnO thin films grown by spray pyrolysis technique, *Superlattices Microstruct.,* 2014, 75, 303–310.
8. Gokulakrishnan, V., Parthiban, S., Jeganathan, K. and Ramamurthi, K. Investigation on the effect of Zr doping in ZnO thin films by spray pyrolysis, *Appl. Surf. Sci,* 2011, 257, 9068–9072.
9. PrasadaRao, T. and Santhoshkumar, M. C. Highly oriented (100) ZnO thin films by spray pyrolysis, *Appl. Surf. Sci.,* 2009, 255, 7212–7215.
10. Abed, S. Aida, M.S,Bouchouit, K, Arbaoui, A, Iliopoulos, K, and Sahraoui, B, Non-linear optical and electrical properties of ZnO doped Ni Thin Films obtained using spray ultrasonic technique, *Opt. Mater. (Amst).,* 2011, 33, 968–972.

11. Ashour, , Kaid, M., El-Sayed, N. Z. and Ibrahim, Physical properties of ZnO thin films deposited by spray pyrolysis technique, *Appl. Surf. Sci.,* 2006, 252, 7844–7848.
12. U, J. L. V. H. and Swanepoel, R. XRD analysis of ZnO thin films prepared by spray pyrolysis, *Thin Solid Films*, 2006, 299, 72–77.
13. Bacaksiz, E., Aksu, S., Yılmaz, S., Parlak, M. and Altunbaş, M. Structural, optical and electrical properties of Al-doped ZnOmicrorods prepared by spray pyrolysis, *Thin Solid Films*, 2010, 518, 4076–4080.
14. Silva, T. G.. Structural and optical properties of ZnO films produced by a modified ultrasonic spray pyrolysis technique, 2014, *Thin Solid Films,* 551, 13–18.
15. Miki-Yoshida, M., Paraguay-Delgado, F., Estrada-López, W. and Andrade, E. Structure and morphology of high quality indium-doped ZnO films obtained by spray pyrolysis, *Thin Solid Films,*2000, 376, 99–109.
16. Qian, L. ,Zheng, Y., Choudhury, K.R., Bera, D., So, F., Xue, J., Holloway, P.H., Electroluminescence from light-emitting polymer/ZnO nanoparticle heterojunctions at sub-bandgap voltages. *Nano Today* , 2010, 5, 384–389.
17. Kenanakis, G., Katsarakis, N. and Koudoumas, E. Influence of precursor type, deposition time and doping concentration on the morphological, electrical and optical properties of ZnO and ZnO:Al thin films grown by ultrasonic spray pyrolysis, *Thin Solid Films,* 2014, 555, 62–67.
18. de la L. Olvera, M., Maldonado, a., Asomoza, R., Konagai, M. and Asomoza, M. Growth of textured ZnO:In thin films by chemical spray deposition, *Thin Solid Films,*1993, 229, 196–200.
19. Hwang, K.-S., Jeong, J.-H., Jeon, Y.-S., Jeon, K.-O. and Kim, B.-H. Electrostatic spray deposited ZnO thin films. *Ceram. Int..,* 2007, 33, 505–507.
20. M. Rydzek, M. Reidinger, M. Arduini-Schuster, J. Manara, Low-emitting surfaces prepared by applying transparent aluminum-doped zinc oxide coatings via a sol–gel process, *Thin Solid Films*, 2012, 520, 4114–4118.
21. H.S. Yoon, K.S. Lee, T.S. Lee, B. Cheong, D.K. Choi, D.H. Kim, et al., Properties of fluorine doped ZnO thin films deposited by magnetron sputtering, *Sol. Energy Mater. Sol. Cells,* 2008, 92, 1366–1372.
22. Vimalkumar, T. V., Poornima, N., SudhaKartha, C. and Vijayakumar, K. P. On tuning the orientation of grains of spray pyrolysed ZnO thin films. *Appl. Surf. Sci*., 2010, 256, 6025–6028.
23. Krunks, M., Dedova, T. and OjaAçik, I. Spray pyrolysis deposition of zinc oxide nanostructured layers. *Thin Solid Films,* 2006, 515, 1157–1160.
24. Romero, R., Leinen, D., Dalchiele, E. a., Ramos-Barrado, J. R. and Martín, F. The effects of zinc acetate and zinc chloride precursors on the preferred crystalline orientation of ZnO and Al-doped ZnO thin films obtained by spray pyrolysis. *Thin Solid Films,* 2006, 515, 1942–1949.
25. Tarwal, N. L. and Patil, P. S. Superhydrophobic and transparent ZnO thin films synthesized by spray pyrolysis technique. *Appl. Surf. Sci.,* 2010, 256, 7451–7456.
26. Joseph, B., Manoj, P. K. and Vaidyan, V. K. Studies on the structural, electrical and optical properties of Al-doped ZnO thin films prepared by chemical spray deposition, *Ceram. Int.*, 2006, 32, 487–493.
27. Jayakrishnan, R., Mohanachandran, K., Sreekumar, R., SudhaKartha, C. and Vijayakumar, K. P. ZnO thin Films with blue emission grown using chemical spray pyrolysis, *Mater. Sci. Semicond. Process.,*2013, 16, 326–331.
28. Zahedi, F., SabetDariani, R. and Rozati, S. M. Spray Pyrolysis Deposition of ZnO Thin Films from Zinc Chloride Precursor Solution at Different Substrate Temperatures. *Acta Metall. Sin.English Lett.,* 2014, 28, 110–114.
29. Thilakan, P., Radheep, D. M., Saravanakumar, K. and Sasikala, G. Deposition and characterization of ZnO thin films by modified pulsed-spray pyrolysis, *Semicond. Sci. Technol.,* 2009, 24, 085020.
30. Tewari, S. and Bhattacharjee, a. Structural, electrical and optical studies on spray-depositedaluminium-doped ZnO thin films, *Pramana.,*2011, 76, 153–163.
31. Behera, D., Panigrahi, J. and Acharya, B. S. Probing the effect of nitrogen gas on electrical conduction phenomena of ZnO and Cu-doped ZnO thin films prepared by spray pyrolysis, *Ionics (Kiel).,* 2011, 17, 741–749.
32. Lehraki, N. Aida M,S., Abed S, Attaf N, Attaf A, Poulain M, ZnO thin films deposition by spray pyrolysis: Influence of precursor solution properties. *Curr. Appl. Phys.,* 2012, 12, 1283–1287.

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