RESEARCH ARTICLE

Available Online at http://www.recentscientificcom

CODEN: IJRSFP (USA)

International Journal of Recent Scientific Research

International Journal of Recent Scientific Research
Vol. 16, Issue, 01, pp.017-021, January, 2025

ISSN: 0976-3031

Subject Area : Materials Science

SYNTHESIS OF Cu-DOPED ZnO THIN FILM AND ITS STUDY RELATED TO NO_2 GAS SENSING PROPERTIES

S.S. Dange[1], S.N. Dange[2] and P.S. More[1]

[1]The Institute of Science, Fort, Mumbai-400 032
[2]Jai Hind College, Churchgate, Mumbai- 400 020

DOI: http://dx.doi.org/10.24327/ijrsr.20251601.004

ARTICLE INFO

Article History:

Received 10th December, 2024
Received in revised form 21st December 2024
Accepted 18th January 2025
Published online 28th January, 2025

Key words:

ZnO, Cu-doped ZnO, Gas sensor, Chemical bath deposition method, NO_2 gas.

ABSTRACT

Cu-doped ZnO thin film was synthesized on glass substrate using chemical bath deposition method at room temperature, exhibiting a hexagonal wurtzite structure with a crystallite size of 17.53 nm for 5 wt% Cu doping. The SEM image of the film's crystallites displays a spherical morphology with an average size of approximately 100 nm. Gas sensing studies towards NO_2 gas revealed a linear response up to 50 ppm with sensitivities of 1.64, 2.17, and 3.11 for 10, 25, and 50 ppm, respectively and 3.72 at 100 ppm without full saturation. Response time and recovery time ranged from 30–60 seconds and 25–300 seconds respectively, highlighting the rapid sensing capabilities of the material. Compared to pure ZnO, the Cu-doped ZnO thin film exhibited comparable sensitivity but significantly faster response times, enhancing its suitability for real-time gas detection.

INTRODUCTION

Zinc oxide (ZnO), a II-IV semiconductor with a wide band gap of 3.37 eV at room temperature, has been extensively studied for its multifunctional properties [1]. Its high exciton binding energy supports excitonic emission at room temperature, making it ideal for optoelectronic devices like LEDs, laser diodes and photodetectors [2-6]. Its piezoelectric and pyroelectric properties make it useful for sensors, transducers and actuators [7-9]. ZnO's strong luminescence in the green-white spectrum makes it suitable for phosphor applications. Additionally, ZnO possesses excellent thermal conductivity, making it effective for heat dissipation in devices. Its sensitivity to surface conductivity enables applications in gas sensing [10,11]. ZnO is non-toxic, abundant, easy to synthesize, cost-effective and can be easily doped, making it a versatile and attractive semiconductor material [12-14]. Copper (Cu) as a dopant in ZnO has a significant influence on its electrical, chemical and optical properties [15]. With an ionic radius (0.074 nm) similar to Zn^2, Cu ions substitute Zn^2 in the ZnO lattice, reducing electron concentration and increasing electrical resistivity. This enhanced resistivity improves the sensitivity of metal oxide gas sensors, making Cu-doped ZnO a promising material for resistivity-controlled gas sensing applications [16- 20]. Cu doped ZnO films were synthesized by various deposition methods and used to sense various gases [21-23]. In this work, Cu doped ZnO thin film synthesized by chemical bath deposition method.

*Corresponding author: **S.S. Dange**

The Institute of Science, Fort, Mumbai-400 032

MATERIALS AND METHOD

Copper-doped Zinc Oxide (Cu-doped ZnO) thin film, with an average thickness of 4-6 μm, was successfully synthesized on glass substrates using the chemical bath deposition (CBD) method. The precursor solution was prepared by dissolving zinc nitrate [$Zn(NO_3)_2 \cdot H_2O$] and Copper nitrate $Cu(NO3)_2 \cdot 3H_2O$ in double-distilled water. A 25% AR ammonia solution (NH_4OH, sp.gr. 0.91) was added dropwise into the precursor solution as described in our earlier research work [24]. The obtained film was subsequently annealed at 500°C for 2 hours. Structural characterization and morphology were carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM) with E-DAX. Further, this obtained film was used to investigate its gas sensing properties towards Nitrogen dioxide (NO_2) gas.

RESULTS AND DISCUSSION

- X-ray Diffraction Characterization (XRD)

The X-ray diffraction (XRD) pattern of Cu-doped ZnO thin film is shown in Figure 1. It displays peak positions that confirm the hexagonal wurtzite structure, which is in good agreement with the Joint Committee on Powder Diffraction

Standards (JCPDS) card no. 36-14519. The prominent diffraction peaks of ZnO films correspond to the (100), (002), (101), (102), (110), (103), and (112) crystallographic planes. No additional diffraction peaks corresponding to Cu or copper oxide phases were detected, indicating the absence of secondary phases. The average crystallite size 'D' was determined from the XRD data using the Scherrer equation [23]. The crystallite size was estimated individually from the FWHM of each plane and average of all the planes was taken to obtain the average crystallite size. The average crystallite size for 5wt% Cu doped ZnO was determined to be 17.53 nm.

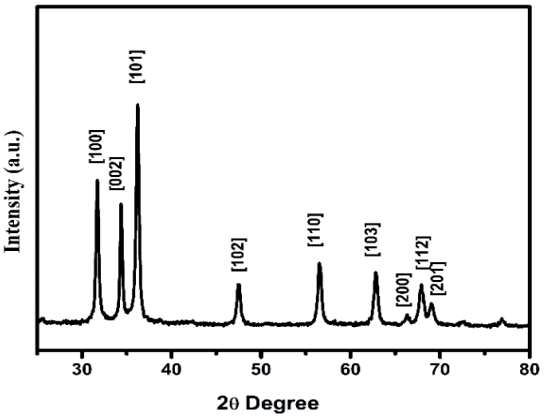

Figure 1. XRD pattern of Cu-doped ZnO Thin Film

(ii) Scanning Electron Microscopy

The surface morphology of Cu-doped ZnO film is shown in figure 2. The SEM image reveals a uniform and distinct spherical morphology, with an average size of 100 nm, evenly distributed across the substrate. The spherical-shaped crystallites exhibit large voids or empty spaces.

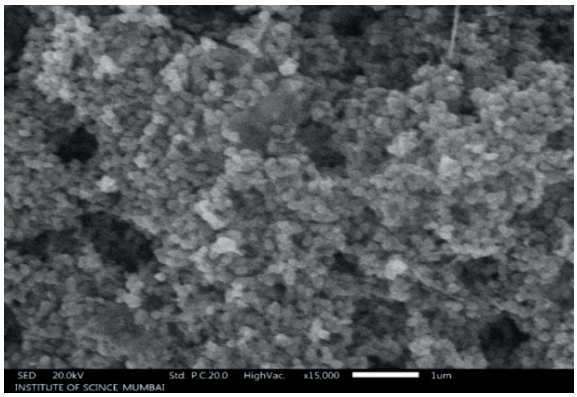

Figure 2. SEM image of Cu doped ZnO thin film

(iii) E-DAX

The EDAX spectrum of Cu doped film is shown in figure 3. It reveals the presence of Zn, O, Cu element and no impurity element are clearly observed.

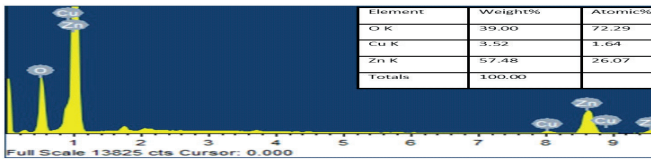

Figure 3. E-DAX of Cu-doped ZnO thin film

(iv) Gas Sensing Studies of Cu-doped ZnO towards NO_2

The Cu doped ZnO film was investigated for its response towards an oxidizing NO_2 gas using using our Static Gas Sensing Measurement System [25]. The corresponding gas response was observed for 10ppm, 25ppm, 50ppm and 100 ppm gas concentrations at 250ºC operating temperature as shown in figure 4. The film demonstrated a good response and complete recovery to various NO_2 gas concentrations.

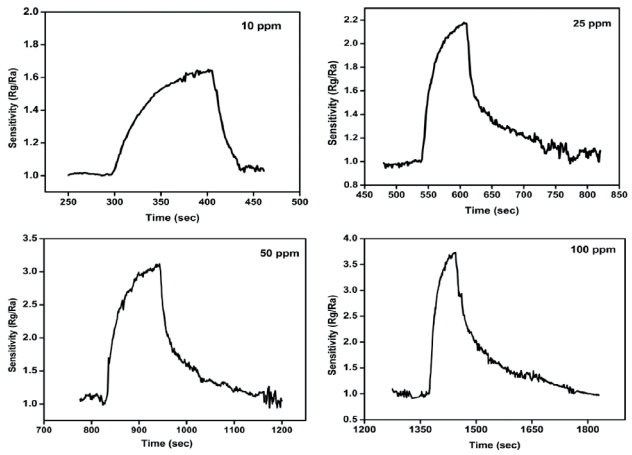

Figure 4. Response Curves of Cu-doped ZnO towards 10 ppm, 25 ppm, 50 ppm and 100 ppm of NO_2

Figure 5 shows the maximum sensitivity of response curves versus NO_2 gas concentration It is seen that the gas response increased linearly up to 50ppm gas concentration with maximum sensitivity as 1.64, 2.17 and 3.11 for 10, 25 and 50 ppm gas concentration respectively and then moves towards saturation, but does not saturate up to 100ppm with maximum sensitivity as 3.72 for 100 ppm gas concentration. The response time and recovery time obtained from the response curves for different concentrations are plotted in figure 6. It is seen that the response time decreases from 46sec for 10ppm gas to 32sec for 25ppm gas and then increases again for 50ppm gas to 61sec and further decreases to 45sec for 100ppm. The response time does not show any particular trend and seems to be in the range of 30 to 60sec for 10-100 ppm gas concentration. The recovery time shows rapid increase from 26 sec to 143 sec as concentration increased from 10ppm to 25ppm. The recovery time further increases almost linearly but comparatively slowly with 202 sec for 50ppm and 300 sec for 100ppm gas concentration respectively. The 10ppm response curve shows faster recovery than response time.

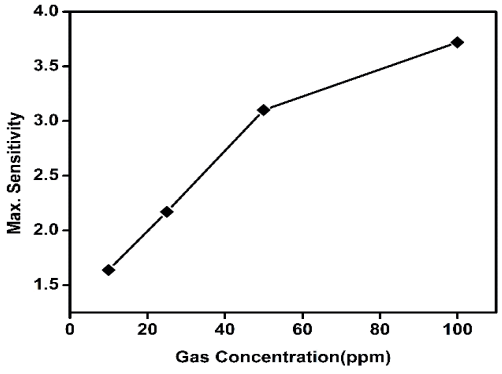

Figure 5. The graph of maximum sensitivity of Cu-doped ZnO film versus NO_2 gas concentration

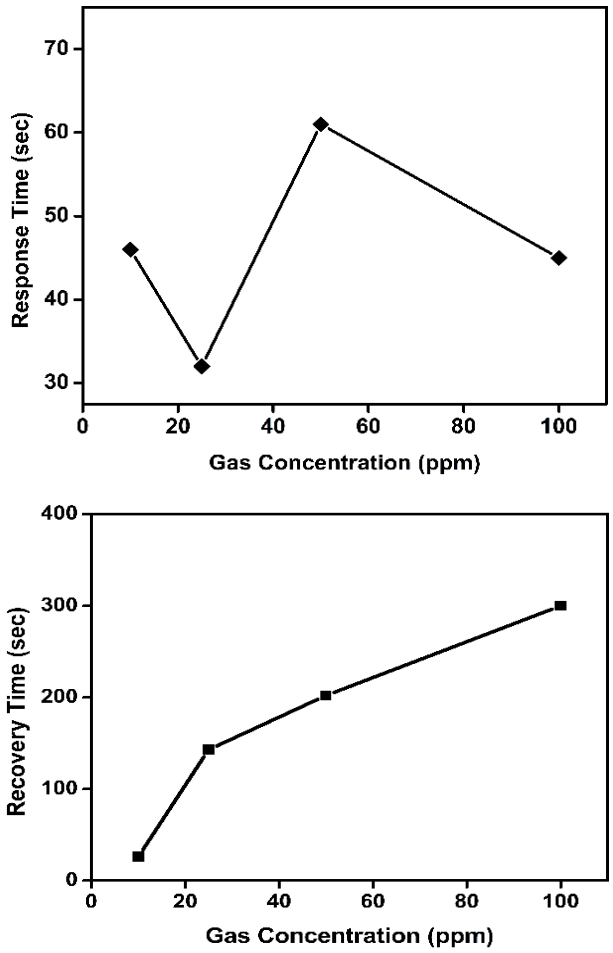

Figure 6 Response Time and Recovery Time of Cu-doped ZnO film versus NO_2 concentration

Figure 7 shows the response of Cu-doped ZnO towards NO_2 gas at 250ºC operating temperature for different gas concentrations over continuous measurement. The sensor has shown good response with complete recovery in continuous measurement and the maximum response is linearly increased with increase in gas concentration.

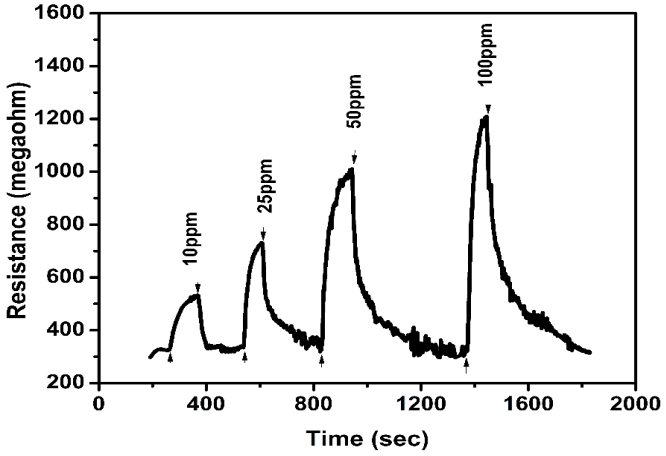

Figure 7 Continuous measurement of response of 5wt% Cu doped ZnO towards NO_2

Figure 8 (a) and 8 (b) shows the comparison of maximum sensitivity and the response time of Cu doped ZnO with pure ZnO as reported in our earlier work, respectively [26].

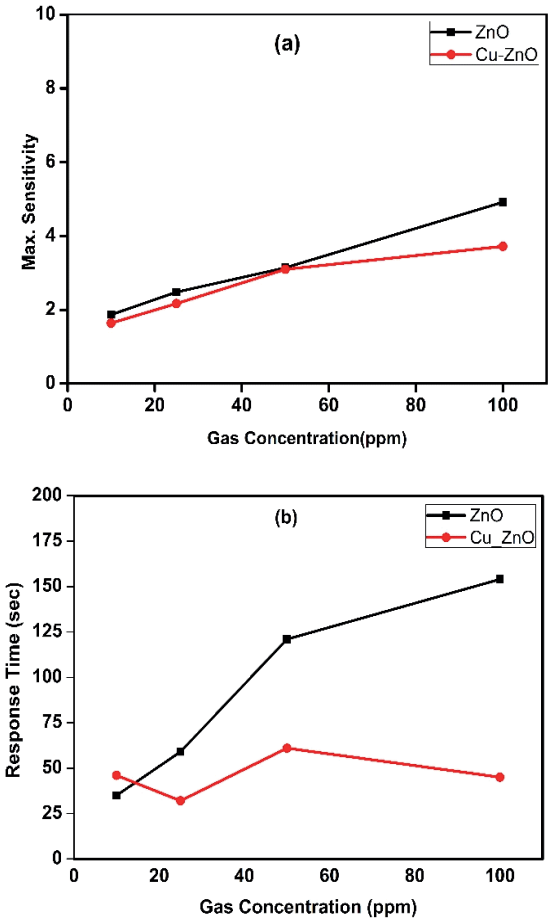

Figure 8 (a) Comparison of maximum sensitivity of Cu doped ZnO with pure ZnO and (b) Comparison of the Response Time of Cu doped ZnO with pure ZnO

This study compares the performance of Cu-doped ZnO and pure ZnO sensors in terms of maximum sensitivity and response time. The results show that the maximum sensitivity of Cu-doped ZnO is nearly identical to that of pure ZnO. However, the Cu-doped ZnO sensor demonstrates a significantly lower response time, ranging from 30 to 60 seconds, which is much faster than that of pure ZnO.

The gas sensing mechanism of metal oxide semiconductor-based gas sensors is mainly based on changes in electrical resistance caused by interactions between oxygen and target gas molecules adsorbed or desorbed on the surface of the sensing material as well as the catalytic activity of dopants. Oxygen molecules adsorbed on the sensor surface extract electrons from the conduction band, forming oxygen ion species (,. This process reduces the carrier concentration near the surface, thereby increasing the sensor's electrical resistance. Gas molecules interacting with the Cu-doped ZnO surface preferentially react at Cu sites, trapping conduction electrons and forming negatively charged oxygen species, depending on the operating temperature [27-28]. This electron trapping increases the surface electrical resistance, which constitutes the gas sensing response of the material.

When Cu-doped ZnO exposed to an oxidizing gas such as NO_2, the gas detection process involves the consumption of conduction electrons, leading to an increased the potential barrier height and reduced surface conductance [29-30]. The response to NO_2 gas is described by the following reaction:

+

The active sites of sensor available for the adsorption upto 100 ppm of gas concentration So, It is observed that as the gas concentration increases the sensing response is also increases.

The fast response of the sensor might be due to the nanostructures with voids of Cu-ZnO sensor as it possesses a high surface to volume ratio. So the surface of sensor become highly active due to adsorbed oxygen species and is more influenced by the near surface and surface defects, these nanostructures facilitates the fast transfer of gas molecules to and from the interaction region [31, 32].

CONCLUSION

Cu-doped ZnO thin film synthesized using chemical bath deposition method exhibit a potential for NO_2 gas sensing applications. Structural analysis confirmed the hexagonal wurtzite structure with a crystallite size of 17.53 nm at 5 wt% Cu doping in ZnO, while SEM analysis revealed a uniform sphere-like morphology of an average size 100 nm. Gas sensing studies demonstrated a linear and consistent response to NO_2 concentrations up to 50 ppm, with response and recovery times ranging between 30–60 seconds and 26–300 seconds, respectively. These results underscore the rapid and reliable sensing capabilities of the material. Furthermore, the significant reduction in response times compared to pure ZnO highlights an important role of Cu doping in ZnO. These findings establish Cu-doped ZnO as a promising material for real-time NO_2 gas detection, with significant potential in environmental monitoring and industrial applications.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. U. Ozgur, Y. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho, H. Morkoc, 'A comprehensive review of ZnO materials and devices,' Journal of Applied Physics, vol. 98, p. 041301, 2005.
2. S. J. Pearton and F. Ren, "Advances in ZnO-based materials for light emitting diodes," Current Opinion in Chemical Engineering, vol. 3, pp. 51-55, 2014.
3. A. Furukawa, N. Ogasawara, R. Yokozawa, A. Tokunaga, 'Electron trap level of Cu-doped ZnO,' Japanese Journal of Applied Physics, vol. 47, p. 8799, 2008.
4. X. B. Wang, C. Song, K. W. Geng, F. Zeng, F. Pan, 'Photoluminescence and Raman scattering of Cu-doped ZnO films prepared by magnetron sputtering,' Applied Surface Science, vol. 253, no. 16, pp. 6905-6909, 2007.
5. N. Al-Hardan, M. J. Abdullah, A. AbdulAziz, 'The gas response enhancement from ZnO film for H gas detection,' Applied Surface Science, vol. 255, pp. 7794-7797, 2009.
6. A. D. Qasem, G. R. Saleem, H. Y. Zain, A. G. Mohammed, 'Crystalline nanostructured Cu doped ZnO thin films grown at room temperature by pulsed laser deposition technique and their characterization,' Applied Surface Science, vol. 270, pp. 104-108, 2013.
7. Y. M. Tao, S. Y. Ma, H. X. Chen, J. X. Meng, L. L. Hou, Y. F. Jia, X. R. Shang, 'Effect of the oxygen partial pressure on the microstructure and optical properties of ZnO:Cu films,' Vacuum, vol. 85, pp. 744-748, 2011.
8. S. D. Shinde, G. E. Patil, D. D. Kajale, V. B. Gaikwad, G. H. Jain, 'Synthesis of ZnO nanorods by spray pyrolysis for HS gas sensor,' Journal of Alloys and Compounds, vol. 528, pp. 109–114, 2012.
9. S.Sureshkumar, B. Venkatachalapathy, T. M. Sridhar, "Enhanced H_2S gas sensing properties of Mn doped ZnO nanoparticles—an impedance spectroscopic investigation," Mater. Res. Express, vol. 6, pp. 075009, 2019.V. L. Patil, S. A. Vanalakar, N. L. Tarwal, A. P. Patil, T. D. Dongale, J. H. Kim, P. S. Patil, 'Construction of Cu doped ZnO nanorods by chemical method for low-temperature detection of NO gas,' Sensors and Actuators A: Physical, vol. 299, p. 111611, 2019.
10. S. S. Bharadwaj, B. W. Shivaraj, H. N. N. M. Krishna, M. Ganiger, M. Idris, P. Anawal, V. S. Angadi, 'Synthesis and characterization of Copper doped Zinc oxide thin films for CO gas sensing,' Materials Today: Proceedings, vol. 5, pp. 20904-20911, 2018.
11. L. Chow, O. Lupan, G. Chai, H. Khallaf, L. K. Ono, B. Roldan-Cuenya, I. M. Tiginyanu, V. V. Ursaki, V. Sontea, A. Schulte, 'Synthesis and characterization of Cu-doped ZnO one-dimensional structures for miniaturized sensor applications with faster response,' Sensors and Actuators A: Physical, vol. 189, pp. 399-408, 2013.
12. A. Ghosh, A. Ghule, R. Sharma, 'Effect of Cu doping on LPG sensing properties of soft chemically grown nano-structured ZnO thin film,' Journal of Physics: Conference Series, vol. 365, p. 012022, 2012.
13. B.R. Sankpal, S.D.Saratale, C.D Lokhande., A.Ennaoui., "Sol. Energy Mater. Solar Cells," vol. 83, p. 447, 2004.
14. M. Zhao, X. Wang, L. Ning, J. Jia, X. Li, L. Cao, 'Electrospun Cu-doped ZnO nanofibres for HS sensing,' Sensors and Actuators B, vol. 156, pp. 588-59, 2011.
15. G. H. Kim, D. L. Kim, B. D. Ahn, S. Y. Lee, H. J. Kim, 'Investigation on doping behavior of copper in ZnO thin film,' Microelectronics Journal, vol. 40, pp. 272-275, 2009.
16. H. Gómez-Pozos, E. J. Luna Arredondo, A. M. Álvarez, R. Biswal, Y. Kudriavtsev, J. V. Pérez, Y. L. Casallas-Moreno, M. de la L. Olvera Amador, 'Cu-Doped ZnO Thin Films Deposited by a Sol-Gel Process Using Two Copper Precursors: Gas-Sensing Performance in a Propane Atmosphere,' Materials, vol. 9, pp. 84-87, 2016.
17. T. Ivanova, A. Harizanova, T. Koutzarova, B. Vertruyen, 'Facile deposition of ZnO:Cu films: Structural and optical characterization,' Materials Science in Semiconductor Processing, vol. 30, pp. 561–570, 2015.
18. A. Hartmann, M. K. Puchert, R. N. Lamb, 'Influence of copper dopants on the resistivity of ZnO films,' Surface and Interface Analysis, vol. 24, pp. 671–674, 1996.
19. R. Shukla, A. Srivastava, N. Kumar, A. Pandey, M. Pandey, 'Optical and sensing properties of Cu doped ZnO nanocrystalline thin films,' Journal of Nanomaterials, pp. 1–10, 2015.
20. A. Furukawa, N. Ogasawara, R. Yokozawa, A. Tokun-

aga, 'Electron trap level of Cu-doped ZnO,' Japanese Journal of Applied Physics, vol. 47, p. 8799, 2008.

21. S. D. Shinde, G. E. Patil, D. D. Kajale, V. B. Gaikwad, G. H. Jain, 'Synthesis of ZnO nanorods by spray pyrolysis for HS gas sensor,' Journal of Alloys and Compounds, vol. 528, pp. 109–114, 2012.
22. V. L. Patil, S. A. Vanalakar, N. L. Tarwal, A. P. Patil, T. D. Dongale, J. H. Kim, P. S. Patil, 'Construction of Cu doped ZnO nanorods by chemical method for low-temperature detection of NO gas,' Sensors and Actuators A: Physical, vol. 299, p. 111611, 2019.
23. M. B. Rahmani, S. H. Keshmiri, M. Shafiei, K. Latham, W. Wlodarski, J. du Plessis, K. Kalantar-Zadeh, 'Transition from n- to p-type of spray pyrolysis deposited Cu doped ZnO thin films for NO sensing,' Sensor Letters, vol. 7, pp. 621–628, 2009.
24. S. S. Dange, S. N. Dange, P. S. More, 'Synthesis of almond-like ZnO microcrystals by chemical bath deposition method at room temperature,' International Journal of Innovative Research in Science, Engineering and Technology, vol. 4, no. 8, pp. 7827-7832, 2015.
25. S. S. Dange and S. N. Dange, 'Development of low-cost static gas sensing measurement system,' International Journal of Innovative Research in Science, Engineering and Technology, vol. 13, no. 12, pp. 20704-20709, Nov 2024.
26. S. S. Dange, S. N. Dange, P. S. More, 'Cost-effective ZnO thin film using chemical bath deposition for NO gas sensing,' International Journal of Innovative Research in Science, Engineering and Technology, vol. 13, no. 11, pp. 19204-19209, Nov 2024.
27. P. S. Kolhe, S. G. Kulkarni, N. Maiti et al., 'Effect of Cu doping concentration on HS gas-sensing properties of Cu-doped SnO thin films,' Applied Physics A, vol. 125, p. 372, 2019.
28. M. Takata, D. Tsubone, H. Yanagida, 'Dependence of electrical conductivity of ZnO on degree of sensing,' Journal of the American Ceramic Society, vol. 59, pp. 4-8, 1976.
29. C. Xiao, T. Yang, M. Chuai, B. Xiao, M. Zhang, 'Synthesis of ZnO nanosheets arrays with exposed (100) facet for gas sensing applications,' Physical Chemistry Chemical Physics, vol. 18, pp. 325–330, 2016.
30. M. S. Choi, H. G. Na, A. Mirzaei, J. H. Bang, W. Oum, S. Han, S. W. Choi, M. Kim, C. Jin, S. S. Kim, H. W. Kim, 'Synthesis and gas sensing properties of ZnO-CuO nanocomposites prepared by the microwave-assisted combustion method,' Journal of Alloys and Compounds, vol. 811, p. 151975, 2019.
31. A. Kolmakov, M. Moskovits, 'Chemical sensing and catalysis by one-dimensional metal-oxide nanostructures,' Annual Review of Materials Research, vol. 34, pp. 151–180, 2004.
32. Z. Y. Li, H. N. Zhang, W. Zheng, W. Wang, H. M. Huang, C. Wang, A. G. Macdiarmid, Y. Wei, 'Highly sensitive and stable humidity nanosensors based on Li-Cl-doped TiO electrospun nanofibers,' Journal of the American Chemical Society, vol. 130, pp. 5036–5037, 2008.

How to cite this article:

S.S. Dange., S.N. Dange and P.S. More. (2025). Synthesis of Cu-doped ZnO thin film and its study related to NO2 gas sensing properties. *Int J Recent Sci Res*.16(01), pp.017-021.

****