

## Silver Doped Zinc Oxide Thin Film Production by Thermionic Vacuum Arc (TVA) Technique

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**Summary:** In this paper, silver (Ag)doped Zinc Oxide(ZnO) thin films were prepared on glass and silicon substrate by using a thermionic vacuum arc technique. The surface, structural, optical characteristics of silver doped thin films have been examined by X-Ray diffractometer (XRD), field emission scanning emission electron microscopy (FESEM), atomic force microscopy (AFM), and UV-Visible spectrophotometer. As a result of these measurements, Ag, Zn and ZnO reflection planes were determined for thin films formed on Si and glass substrate. Nano crystallites have emerged in FESEM and AFM images. The produced films have low transparency. The optical band gap values were measured by photoluminescence devices at room temperature for thin films produced on silicon and glass substrate. The band gap values are very close to 3.10 eV for Ag doped ZnO thin films. The band gap of un-doped ZnO thin film is approximately 3.3 eV. It was identified that Ag doped changes the properties of the ZnO thin film.

**Keywords;** Ag doped ZnO; Thin Film, TVA, Nanocrystal.

### Introduction

In recent years, Zinc Oxide (ZnO) thin film is a member of the II-VI group semiconductor and it is quite popular with its diversity and antitoxic property in the applications. ZnO is natural material and it is preferred for technological applications with wide band gap (3.3 eV) [1], higher binding energy, wide resistance and high permeability at room temperature. ZnO is widely used in optoelectronic and photonic materials [2-5]. After the doped ZnO material, the characteristics of the ZnO thin film could be modified not only doping element, but also depend on the ratio of the element.

ZnO thin films can be produced in techniques. They are radio frequency magnetron sputtering [6], spray pyrolysis [7], chemical vapor deposition (CVD) [8], pulse laser deposition (PLD) [9], molecular beam epitaxy (MBE) [10], electrochemical deposition [11], and thermionic vacuum arc (TVA) [12]. Compared to these techniques, The TVA technique provides a fast production for thin films made of doped elements. These technique operates as an anodic material plasma generator, the under high vacuum condition [12-16]. The TVA technique is generally an advantageous technique because it does not require the use of an inert gas such as argon during thin film production. The doped ZnO thin film is still being studied to improve the optical and other properties of the material. Doped ZnO thin films are frequently used in semiconductor and photonic applications. Therefore, Fe, Cu, Sn, Co, Sg, etc. studies related to ZnO thin films is very much in the literature [17-21].

Ag doping changes the optoelectronic, photocatalytic characteristics of the ZnO material [22-23]. Ag atoms prefers the occupy Zn zone in ZnO crystal network [24]. In addition to, Ag atom improves the electrical properties, but decreases the optical transmittance of the material [25]. In this work, Ag doped ZnO thin films have been produced by a thermionic vacuum arc (TVA) technique on glass and silicon substrates. The characteristics of the produced Ag doped ZnO films have been determined by XRD, FSEM, AFM, UV-Vis spectrophotometer andinterferometer. It was found that Ag doping has been affecting the surface, microstructure characteristics of the ZnO. Used thin film production technology is a proper technique for the desired ratio doping of ZnO.

### Experimental

In this study, we have obtained ZnO thin films produced on glass and Si substrate by using TVA technique. TVA is a coating technology under the high vacuum conditions with working pressure is approximately  $10^{-5}$  torr. In fact the TVA technique was created to obtain the plasma of any material. Thanks to the material plasma obtained by this technique, the substrate is placed in a suitable place in the vacuum chamber and the material is coated with the formed material. Plasma of many materials can be produced by this method (such as metal, ceramic and semiconductor). The thin films developed by TVA have low roughness, compact, high adhesion, and nanostructures [10, 13, 14].

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A thin film can be produced at different operational parameters in TVA technique. The electron gun configuration can be changed depending on the melting temperature of the material. Higher electrical current may be required for high melting temperature material. In addition, these parameters may be different in the material to be produced in each substrate. The TVA contains two electrodes, one of which is anode and the other is a cathode. The electron gun acts as a cathode, while the plasma acts as an anode in the tungsten crucible where the material to be produced is placed. First, the material on the tungsten crucible with the electron gun is heated and vaporized by bombardment with the aid of the Wehnelt cylinder placed on the electron gun. When the voltage value reaches the value of arc ignition voltage, a plasma of the material creates in the between anode and cathode. A simple schematic

representation of the TVA system is given in Fig .1. In this study, Ag and ZnO materials were placed into the tungsten crucible at the same rate. Glass and silicon substrates were coated with the Ag doped ZnO plasma. The electrodes distance during plasma was fitted to 4mm. The deposition pressure was measured as  $2 \times 10^{-4}$  torr during the experiment. The operating parameters are shown in Table-1.

Table-1: Experimental parameters for the deposition in TVA system.

Parameter (Unit)	Value
Discharge Current (A)	0.2
Duration (s)	60
Working Pressure (torr)	$2 \times 10^{-4}$
Voltage (V)	500
Filament Current (A)	20

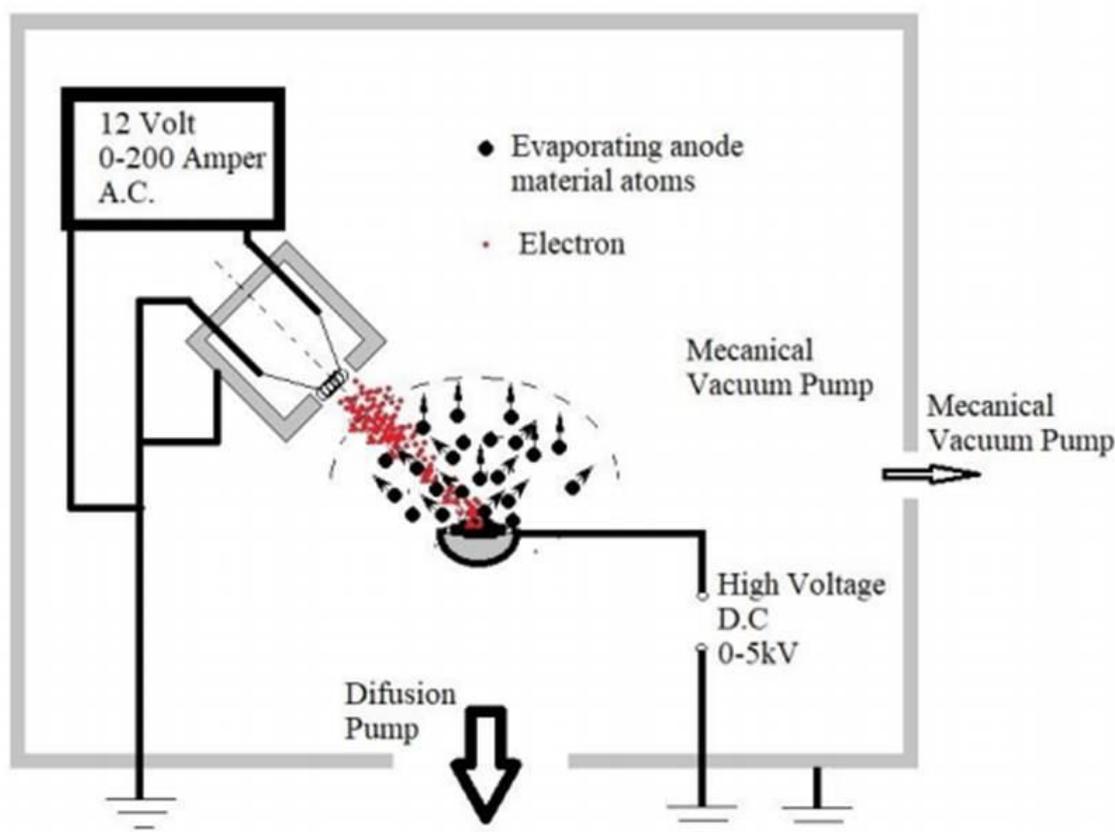


Fig. 1: A simple schematic representation of the TVA system.

## Results and Discussion

In the present study, the morphological, structural, optical characteristics of the Ag doped ZnO thin films by TVA were investigated. The microstructural properties of the films characterized by Panalytical Empyrean X-Ray diffractometer. The using XRD pattern was performed with  $\text{CuK}_\alpha$  radiation ( $\lambda=1.54056 \text{ \AA}$ ) in the  $2\theta$  range from  $10^\circ$  to  $80^\circ$  degrees and Panalytical PIXcel3D was used as an X-Ray detector. The XRD patterns are presented in Fig. 2a and 2b. As can be seen in Fig. 2, Ag and Zn reflections planes were assigned. The XRD patterns were assigned with the related diffractions planes. All assigned peaks are related with the ZnO reflections (JCPDS card no: 36-1451). The peak located at  $38.37^\circ$  was indexed as to be Ag plane reflection (JCPDS card no: 04-0783) [26-28]. The thickness of the films deposited onto glass and Si substrate are 60 and 25 nm, respectively. For Si substrate, the sample thickness is bigger than the film thickness. So, Si wafer XRD reflection was also shown in Fig 2b. For the film deposition onto glass substrate, (102), (110), (103), and (202) reflections were assigned as to be ZnO crystal phases. For the film deposition onto Si wafer, (111), (102), and (110) reflections were assigned as to be ZnO crystal phases, too. The observed reflections for the Ag doped ZnO show the good adherence with the literature [26-28]. Si wafer is n-type p-doped in  $\langle 111 \rangle$  orient. Resistivity is 0.009-0.012  $\Omega\cdot\text{cm}$ . (111) Miller indices were not detected in the XRD pattern of the Ag doped ZnO onto glass substrate, but it is not so for Si substrate.

The morphological and surface properties of Ag doped ZnO thin films formed on glass and silicon substrates were determined by Ambios Q-scope atomic force microscopy. Surface characteristics of the produced Ag doped ZnO thin films were analyzed on  $10\mu\text{m} \times 10\mu\text{m}$  scanning areas in non-contact mode. The AFM images of Ag doped ZnO thin films formed on glass and silicon substrates are shown in Fig. 3a and 3b, respectively.

According to the results given in Fig. 3a and 3b, substrate materials changed the crystal orientations and grain size dimensions for the Ag doped ZnO. The smallest grains were observed in the Ag doped ZnO thin films onto Si substrate.

FESEM images of the Ag doped ZnO thin films produced on glass and silicon substrates were obtained by Carl Zeiss Supra VP40 FESEM at 100.000 X magnification. FESEM images are given in Fig 4a and 4b. From the images one can see that the regular crystallized layers formed on Si and glass substrate are agreeable with AFM images. It was concluded from the FESEM images, the Ag doped ZnO thin films are in colony structures.

The thickness, refractive index ( $n$ ), and reflectance of the produced thin films were determined by Filmmetrics F20 interferometer. The thickness of the Ag doped ZnO thin films onto glass and Si wafer are 62 nm and 25 nm respectively. Refractive index ( $n$ ) and reflection curves depend on wavelength are shown in Fig 5. The transmittance values of the Ag doped ZnO thin films have been measured with the UV-Vis Spectrophotometer in the range of 300-1100 nm. The graphs are shown in Fig 5c.

The optical properties gives more important and key properties of the electronic band structures of the doping mechanism of the produced films. Photoluminescence spectra ( $PL$ ) are given in Fig 6. Un-doped ZnO thin film has the optical band gap of 3.3 eV. After the doping of the Ag element, optical band gap values decrease to lower value approximately 3.10 eV [22-24].

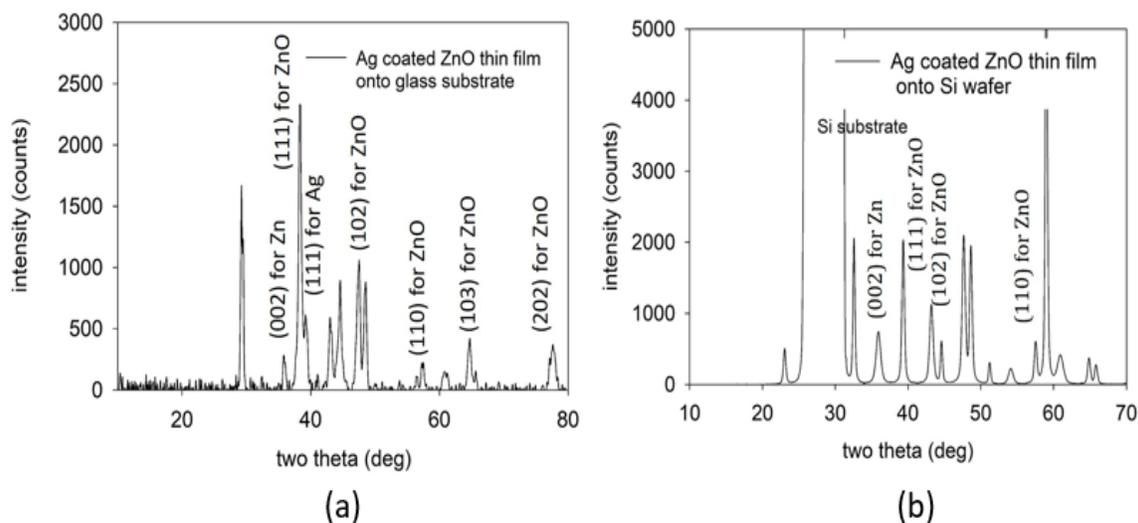


Fig. 2: XRD patterns of Ag doped ZnO thin films deposited onto a) glass and b) Si substrate.

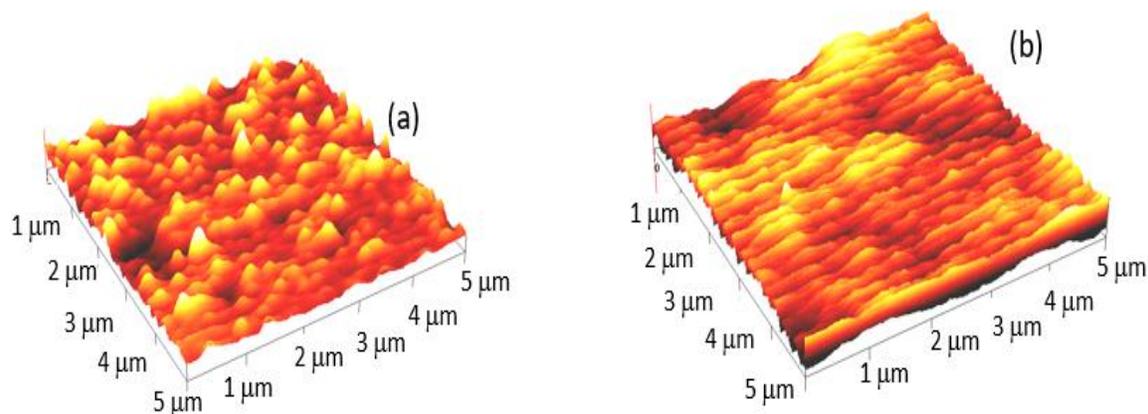


Fig. 3: AFM images of Ag doped ZnO thin films deposited onto a) glass and b) Si substrate.

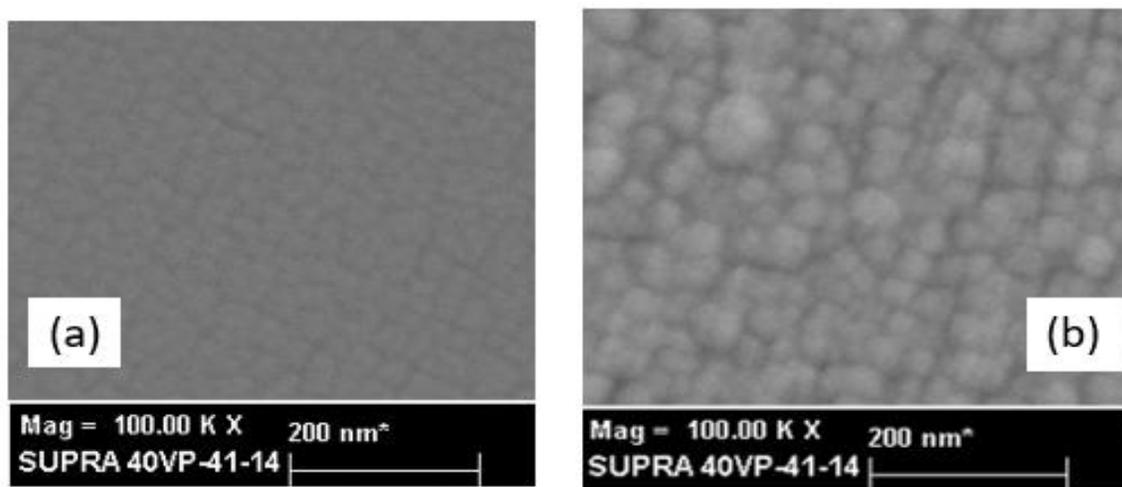


Fig. 4: FESEM images of Ag doped ZnO thin films deposited onto a) glass and b) Si substrate.

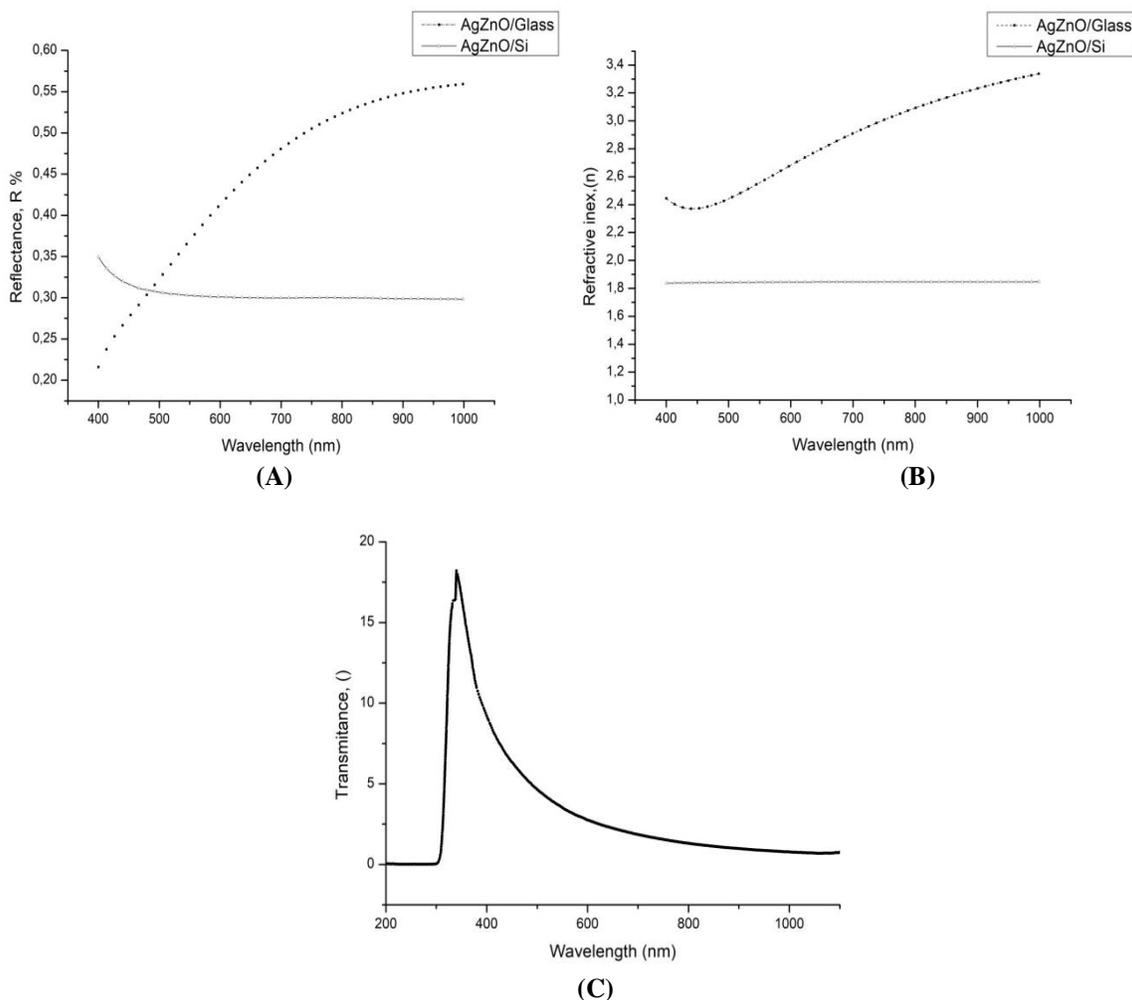


Fig. 5: Refractive index ( $n$ ) and reflection curves depend on wavelength of Ag doped ZnO thin films deposited onto a) glass and b) silicon substrate. c) Transmittance spectra of the Ag doped ZnO thin film onto glass substrate.

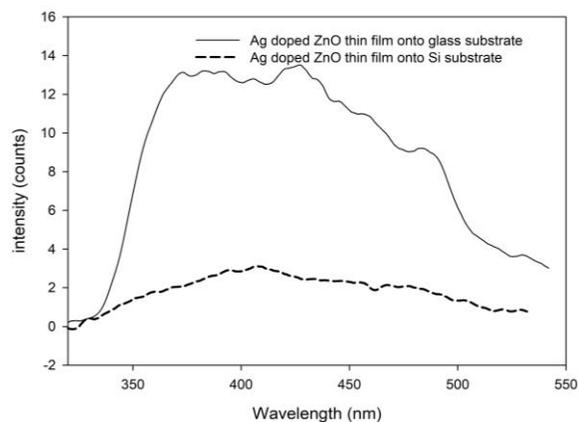


Fig. 6: Photoluminescence spectra image of Ag doped ZnO thin films.

## Conclusions

Ag doped ZnO thin films were produced onto glass and Si substrate by thermionic vacuum arc (TVA) technology. The surface, microstructural, surface, and optical properties were determined. According to the results, homogeneity, rough and nanostructure Ag doped ZnO thin films were grown onto glass and Si substrate. Transmission spectrum shows the interesting result. Ag doped ZnO thin film is transparent only narrow spectral range and band gap of the film of 3.15 eV are lower than the undoped band gap energy of the ZnO material. Finally, using by TVA, high quality and narrow band Ag doped ZnO thin films were produced. Produced films will be used in semiconductor, optical filter technology and detectors.

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## References

1. L. Vayssieres, Growth of arrayed nanorods and nanowires of ZnO from aqueous solutions, *Advanced Materials*, **15**, 464 (2003).
2. D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, S. Koyama, M.Y. Shen, T. Goto, Optically pumped lasing of ZnO at room temperature, *Applied Physics Letters*, **70**, 2230 (1997).
3. Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, X. L. He, J. P. Li, C. L. Lin, Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors, *Applied Physics Letters*, **84**, 3654 (2004).
4. D. C. Look, Recent advances in ZnO materials and devices, *Materials Science and Engineering: B*, **80**, 383 (2001).
5. K. Ueda, H. Tabata, T. Kawai, Magnetic and electric properties of transition-metal-doped ZnO films, *Applied Physics Letters*, **79**, 988 (2001).
6. J. S. Cho, Y. J. Kim, J. C. Lee, S.H. Park, K.H. Yoon, Structural and optical properties of textured ZnO:Al films on glass substrates prepared by in-line rf magnetron sputtering, *Solar Energy Mater. Sol. Cells*, **190**, 95 (2011).
7. S. Rajeh, A. Barhoumi, A. Mhamdi, G. Leroy, B. Duponchel, M. Amlouk, S. Guermazi, Structural, morphological, optical and opto-thermal properties of Ni-doped ZnO thin films using spray pyrolysis chemical technique, *Bull. Mater. Sci.*, **39**, 177e186, (2016).
8. K. Tang, S.L. Gu, S.Z. Li, J.D. Ye, S.M. Zhu, H. Chen, J.G. Liu, R. Zhang, Y. Shi, Y.D. Zheng, Influence of thermally diffused aluminum atoms from sapphire substrate on the properties of ZnO epilayers grown by metal-organic chemical vapor deposition, *J. Vac. Sci. Technol. A*, **29**, 03A106, (2011).
9. M. G. Tsoutsouva, C.N. Panagopoulos, D. Papadimitriou, I. Fasaki, M. Kompitsas, ZnO thin films prepared by pulsed laser deposition, *Mater.Sci. Eng., B*, **176**, 480e483 (2011).
10. A.S.H. Hussein, Z. Hassan, S.M. Thahab, S.S. Ng, H. Abu Hassan, C.W. Chin, Effect of Al mole fraction on structural and electrical properties of Al<sub>x</sub>Ga<sub>1-x</sub>N/GaN heterostructures grown by plasma-assisted molecular beam epitaxy, *Appl. Surf. Sci.*, **257**, 4159 (2011).
11. D.Q. Gao, D.S. Xue, Y. Xu, Z.J. Yan, Z.H. Zhang, Synthesis and magnetic properties of Cu-doped ZnO nanowire arrays, *Electrochim. Acta*, **54**, 2392 (2009).
12. M. Özgür, S. Pat, R. Mohammadigharehbagh, C. Musaoğlu, U. Demirkol, S. Elmas, S. Ozen, S. Korkmaz, *Journal of Alloys and Compounds*, **774**, 1017e1023 (2019).
13. S. Pat, S. Temel, N. Ekem, S. Korkmaz, M. Ozkan, M.Z. Balbag, Diamond-like carbon coated on polyethylene terephthalate by thermionic vacuum arc, *J. Plastic Film Sheeting*, **27**, 127e137 (2011).
14. S. Pat, S. Korkmaz, S. Ozen, V. Senay, Optical, surface and magnetic properties of the Ti-doped GaN nanosheets on glass and PET substrates by thermionic vacuum arc (TVA) method, *Part. Sci. Technol.*, **1e6** (2018).
15. S. Elmas, S. Pat, R. Mohammadigharehbagh, C. Musaoğlu, M. Özgür, U. Demirkol, U. S. Özen, Ş. Korkmaz, Determination of physical properties of graphene doped ZnO (ZnO: Gr) nanocomposite thin films deposited by a thermionic vacuum arc technique. *Physica B: Condensed Matter*, **557**, 27 (2019).
16. U. Demirkol, S. Pat, R. Mohammadigharehbagh, C. Musaoğlu, M. Özgür, S. Elmas, S. Özen, Ş. Korkmaz, Investigation of the substrate effect for Zr doped ZnO thin film deposition by thermionic vacuum arc technique, *J. Mater. Sci. Mater. Electron.*, **29**, 18098 (2018).
17. M. Wang, G. Liu, H. Yu, S.H. Lee, L. Wang, J. Zheng, T. Wang, Y. Yun, J.K. Lee, ZnO Nanorod Array Modified PVDF Membrane with Superhydrophobic Surface for Vacuum Membrane Distillation Application, *ACS. Appl. Mater. Interfaces.*, **10**, 13452 (2018).
18. K. Rahimi, A. Yazdani, Improving photocatalytic activity of ZnO nanorods: A comparison between thermal decomposition of zinc acetate under vacuum and in ambient air, *Mater. Sci. Semicond. Process.*, **80**, 38 (2018).
19. F. C. Correia, P.B. Salvador, J. M. Ribeiro, A. Mendes, C. J. Tavares, Corrigendum to Effect on the electrical and morphological properties of Bi incorporation into ZnO: Ga and ZnO: Al thin films deposited by confocal magnetron sputtering, *Vacuum*, **154**, 340 (2018).
20. W. Khan, F. Khan, H.M.S. Ajmal, N. U. Huda, J. H. Kim, S. D. Kim, Evolution of Structural and Optical Properties of ZnO Nanorods Grown on Vacuum Annealed Seed Crystallites, *Nanomaterials*, **8**, 68 (2018).
21. D. Acosta, A. López-Suárez, C. Magaña, F. Hernández, Structural, electrical and optical properties of ZnO thin films produced by

- chemical spray using ethanol in different amounts of the sprayed solution, *Thin Solid Films*, **653**, 309 (2018).
22. C. A. Gouvêa, F. Wypych, S.G. Moraes, N. Durán, P. Peralta-Zamora, Semiconductor-assisted photodegradation of lignin, dye, and kraft effluent by Ag-doped ZnO, *Chemosphere*, **40**, 427 (2000).
  23. R. S. Zeferino, M.B. Flores, U. Pal, Photoluminescence and Raman scattering in Ag-doped ZnO nanoparticles, *J. Appl. Phys.*, **109**, 014308 (2011).
  24. Q. Wan, Z. Xiong, J. Dai, J. Rao, F. Jiang, First-principles study of Ag-based p-type doping difficulty in ZnO, *Opt. Mater.*, **30**, 817 (2008).
  25. D. R. Sahu, Studies on the properties of sputter-deposited Ag-doped ZnO films, *Microelectronics J.*, **38**, 1252 (2007).
  26. S. S. Patil, M. G. Mali, M.S.Tamboli, D.R.Patil, M.V. Kulkarni, H.Yoon, H.Kim, S.S.Aldeyab, S.S.Yoon, S.S.Kolekar, B.B.Kale, Green approach for hierarchical nanostructured Ag-ZnO and their photocatalytic performance under sunlight, *Catal. Today*, **260**, 126 (2016).
  27. A.N.Kadam, R.S.Dhabbe, M.R.Kokate, N.L.Gavade, P.R.Waghmare, K.M.Garadkar, Template free large scale synthesis of multi-shaped ZnO nanostructures for optical, photocatalytic and antibacterial properties, *J. Mater. Sci. Mater. Electron.*, 26p. 8367, (2015).
  28. A.N.Kadama, D.P.Bhopateb, V. V. .Kondalkarc, S.M.Majhib, C.D.Bathulad, A.-V.Trana, S.-W.Lee, Facile synthesis of Ag-ZnO core-shell nanostructures with enhanced photocatalytic activity, *J. Ind. Eng. Chem.*, **61**, 78 (2018).