Iman H. Hadi [1]
Doaa Sulaiman [1]
Ban A. Bader [2]

[1] *Department of Applied Science, University of Technology, Baghdad, IRAQ*
[2] *Department of Physics, College of Education, University of Al–Hamdaniya, Nineveh, IRAQ*

Synthesis of Zinc Nanoparticles on Various Substrates Using Direct Current Sputtering Method

Zinc (Zn) thin films were deposited on silicon and glass substrates using DC sputtering. The crystal structure and morphology of the films were characterized by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FESEM), respectively. XRD analysis revealed a dominant Zn (002) peak, indicating a wurtzite crystal structure. FESEM images confirmed a uniform distribution of grains with a granular surface morphology. The grain size of the Zn thin films increased with longer sputtering times on both substrates. Scherrer's equation was employed to calculate the grain size from the XRD patterns. Notably, the Zn thin film deposited on the n-type Si substrate for 10 minutes exhibited the most uniform morphology among all samples. The best result was the formation of ZnNPs on silicon substrate at 5 minute where the particle size was at a peak 9 nm.

Keywords: Nanoparticles; Physical vapor deposition; DC sputtering; Metal NPs/Si
Received: 04 April 2024; **Revised:** 25 April 2024; **Accepted:** 01 May 2024

1. Introduction

Nanomaterials (1-100nm) exhibit distinct characteristics compared to the same material in bulk form to enable them to be used in different fields such as medicine, electronics, energy and environment [1]. Advancements in nanotechnology allow for the complete alteration of chemical as well as physical properties, along with nanoparticles surface-to-volume ratios [2]. This field enables the production of a diverse array of nanoparticles with unique spatial characteristics, facilitating their utilization across various applications and scientific research domains [3]. Zinc nanoparticles (ZnNPs) could be categorized based on the chemical structure into metallic, metal oxides, and semiconductor nanoparticles, zinc metal nanoparticles are good conductors and zinc semiconductors can be used for solar cell applications [4]. Various methods offer control over the structure and size of nanoparticles. While all methods can yield satisfactory nanoparticles, continuous improvement in procedures is essential for enhancing production efficiency and yield, particularly for industrial and commercial applications [5-7]. Deposition of metal thin films onto different substrates, including glass and silicon can be achieved using many techniques such as molecular beam epitaxy, [8], electroplating [9], spray pyrolysis [10], Pulsed Laser Ablation [11], physical vapor deposition (VPD) [12], magnetron, ion beam and DC sputtering [13]. This work aimed to investigate the structural characteristics and surface morphology of zinc thin films placed on two distinct substrates: glass and Si n-type.

2. Experimental Part

Figure (1) illustrates the home-made dc sputtering system schematic diagram. Two types of substrates (glass and n-type Si (111)) were inserted on the anode inside the deposition chamber, Si with resistivity ranging from 5 to 40 Ω.cm and a thickness of 0.45 mm. The dimensions of these substrates were 1x1 cm, after a cleaning process they have being subjected to ethanol in a digital ultrasonic cleaner for fifteen minutes.

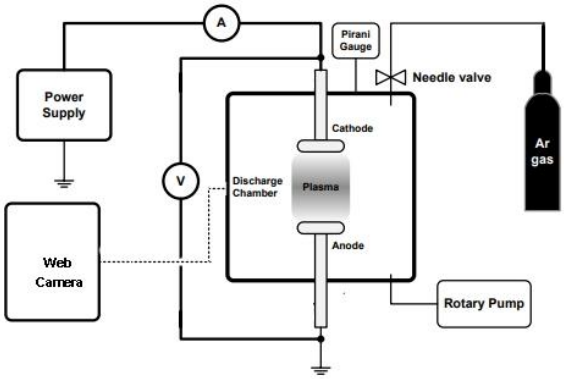


Fig. (1) Schematic diagram of DC sputtering system

A zinc target with 5cm diameter and a 5mm thickness was placed on the sputtering chamber's cathode. Using glow discharge, argon gas in the deposition chamber has been used to create plasma at a flow velocity of 500 sccm and a maximum pressure of 1.5 mbar. The tube discharged to a vacuum below 10^{-2} Torr using a rotary pump and a discharge current of 15 mA. Deposition times of 5 and 10 min were used to achieve various Zn thin film thicknesses, and 30 min were used for the analysis of x-ray diffraction (XRD) patterns obtained using a Phillips Xpert x-ray diffractometer (λ=1.54056Å). A MIRA3 TESCAN field-emission scanning electron microscope (FE-SEM) was used to introduce the structural properties of the prepared thin films.

3. Results and Discussion

The XRD patterns are presented in Fig. (2) in the scanning range of 10°-80°. For zinc thin films on glass substrates, the XRD peak is observed at approximately 2θ=36° along the (002) plane. Conversely, for zinc thin films on n-type Si substrates, peaks appear at angles approximately 38°, 54°, and 75° corresponding to the (002), (102), and (004) planes, respectively. Figure (2b) displays the polycrystalline and hexagonal wurtzite structures of the prepared thin films [14]. According to this figure, it's clear that all thin films have maximum intensity along the (002) plane which is the preferred plane for the growth of Zn thin films. Figure (2) clearly shows the influence of substrate type on the XRD pattern of Zn thin film. Thin film growth on Si n-type substrate has larger grain size than that of film deposited on glass substrate. The thin film parameters derived from the XRD results are summarized in table (1).

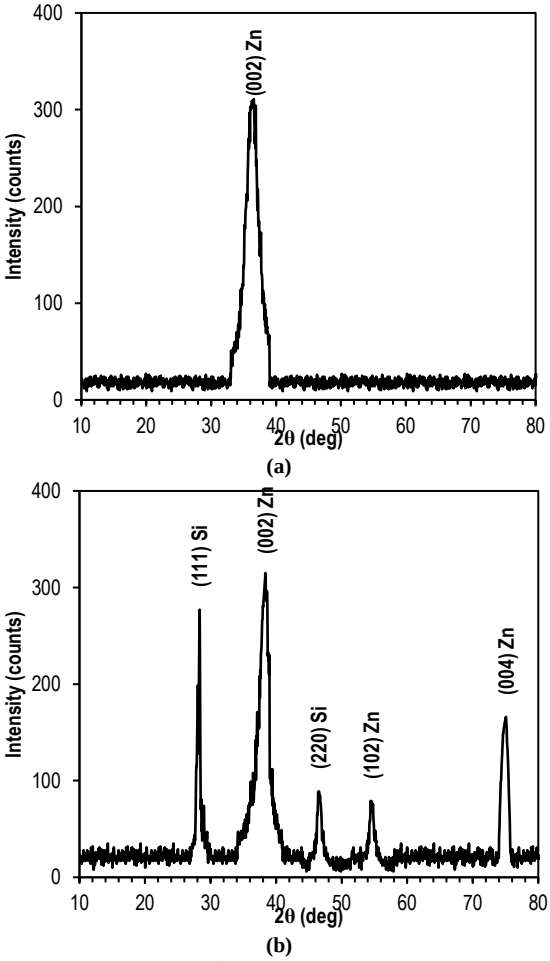


Fig. (2) XRD patterns of Zn nanoparticles on (a) glass, (b) Si (n-type)

Scherrer's equation has been utilized to obtain the grain size (x) within zinc thin film as

$$x = K.\frac{\lambda}{\beta.cos\theta} \qquad (1)$$

In this equation, the average grain shape factor represented by K (0.9), the x-ray wavelength (0.154056nm) denoted by λ, the full-width at half maximum (FWHM) of the peak diffraction signified by β in rad, and the diffraction peak angle represented by θ. Equation (2) emphasizes an inverse relationship between the grain size of nanoparticles and the FWHM of the diffraction peak. As the grain size increases, there will be sharpness in the diffraction peak.

Table (1) Zinc thin film parameters obtained from XRD measurements

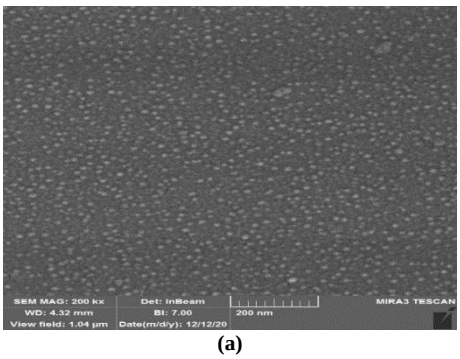
Substrate type	(hkl)	2θ (deg)	FWHM (β) (rad)	x (nm) =0.9λ/βcosθ	δ=1/x² (cm⁻²)
Glass	(002)	36.025	0.046	3.16	1.00E+13
Si n-type	(002)	38.275	0.035	4.23	5.59E+12
	(102)	54.425	0.011	14.64	4.67E+11
	(004)	74.725	0.017	10.06	9.88E+11

The density of dislocation (δ), indicating the dislocation length per unit volume of the crystal, could be calculated using the equation below:

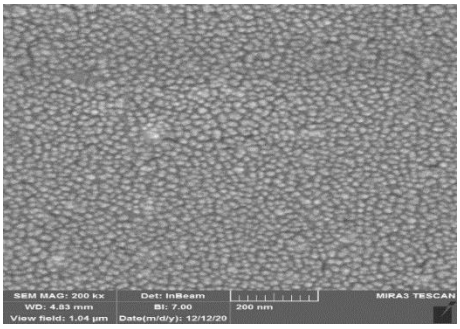
$$\delta = 1/x^2 \qquad (2)$$

Surface morphology was studied depending on FE-SEM results. Figure (3) depicts a consistent and distinguishable granular surface morphology characterized by an identical distribution of the ZnNPs synthesized in this investigation. The nanoparticles exhibit uniform dispersion across the entirety of the substrate's surface. However, for samples prepared after 10 minutes of sputtering, the surfaces of both glass and silicon (Si) could not be observed.

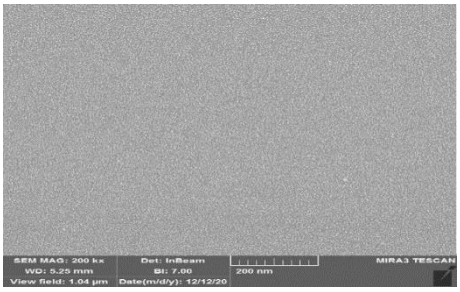
Figure (4) illustrates the energy-dispersive x-ray (EDX) spectroscopy analysis of zinc nanoparticles synthesized after different sputtering times on different substrates. These data indicate that the EDX spectra of elements is largely similar with differing element weights according to the variation in sputtering time. Specifically, for ZnNPs deposited on glass substrates, about 23.6% and 30.2% of the total weight zinc consisted in the resulted nanoparticles after 5 and 10 minutes, respectively. Conversely, for ZnNPs deposited on n-type Si substrates, about 27.6% and 34.8% of the weight was attributed to zinc.



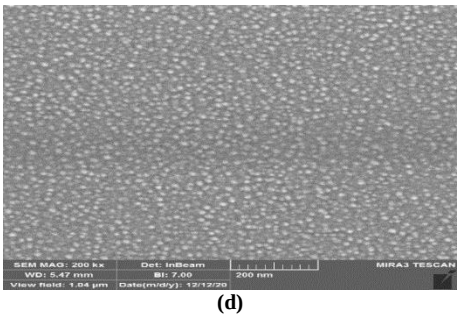
(a)



(b)

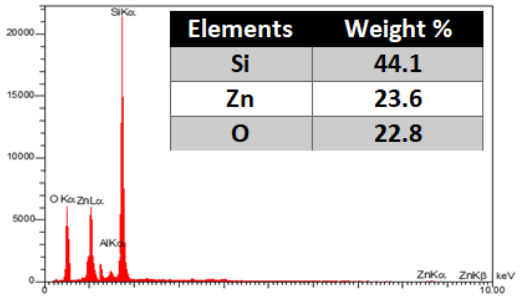


(c)



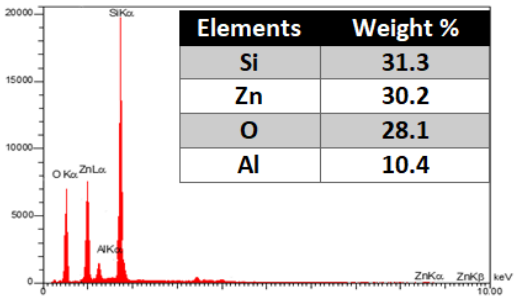
(d)

Fig. (3) SEM images of Zn nanoparticles (a), (b) glass (c), (d) Si (n-type) at 5 and 10 minutes, respectively



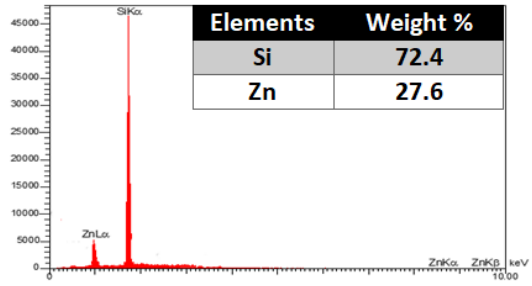
Elements	Weight %
Si	44.1
Zn	23.6
O	22.8

(a)



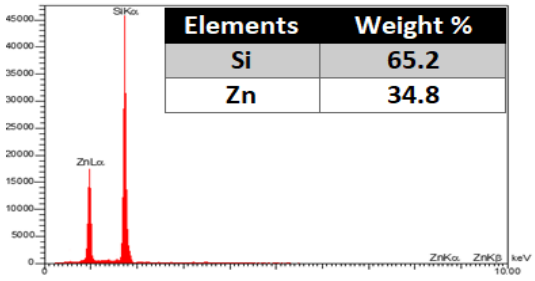
Elements	Weight %
Si	31.3
Zn	30.2
O	28.1
Al	10.4

(b)



Elements	Weight %
Si	72.4
Zn	27.6

(c)

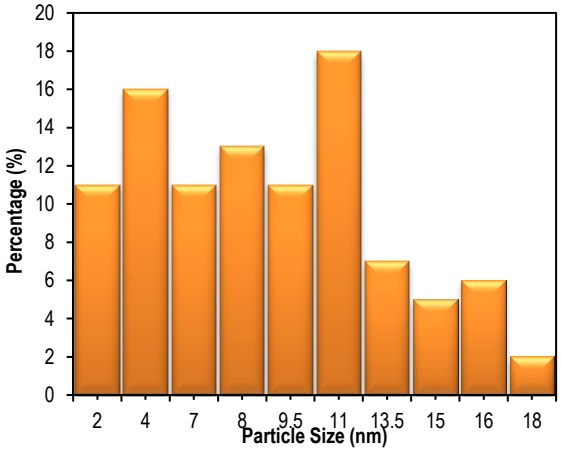


Elements	Weight %
Si	65.2
Zn	34.8

(d)

Fig. (4) EDX results at 5 and 10 minutes of (a), (b) Zn NPs on glass and (c), (d) Zn NPs on Si (n-type)

The histogram of zinc deposition on glass at 5 minutes (Fig. 5a) reveals a range of 2-18 nm, with a peak at 11 nm. Extending the deposition time to 10 minutes (Fig. 5b) leads to ZnNPs ranging from 6 to 28 nm, with a peak at 13 nm. On silicon substrate at 5 minutes (Fig. 5c), ZnNPs sizes vary from 2 to 11 nm, with a peak at 9 nm. At 10 minutes (Fig. 5d), ZnNPs sizes range from 4 to 19 nm, with a peak at 10 nm.



(a)

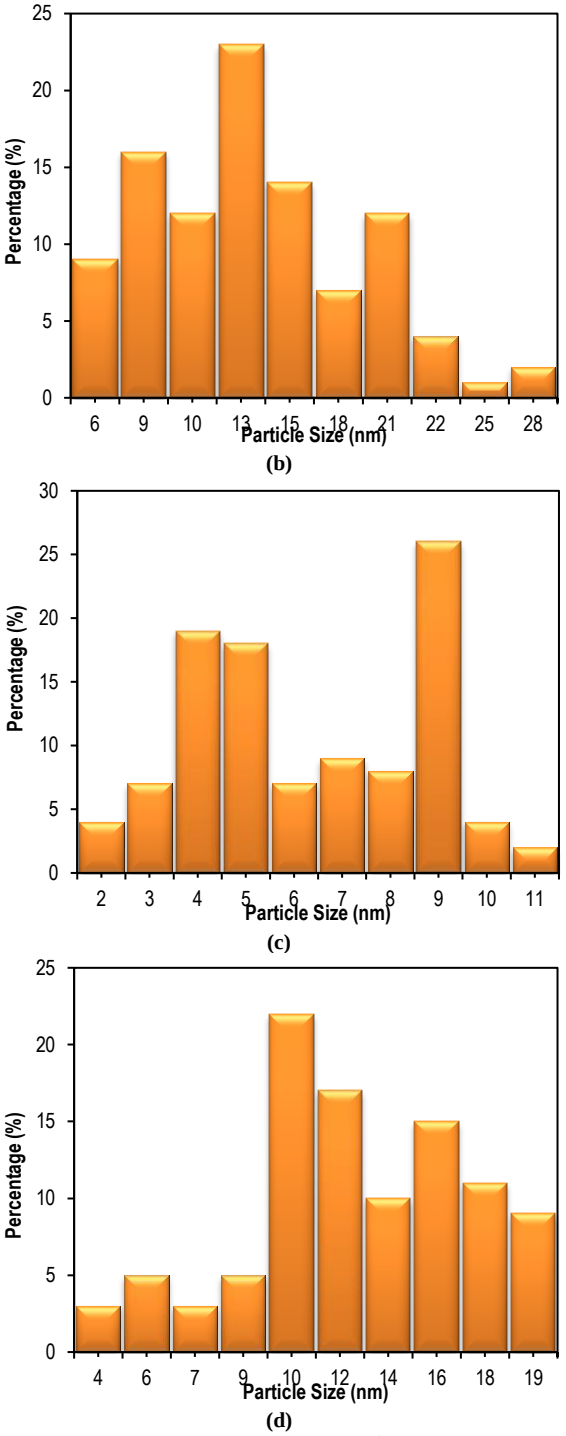


Fig. (5) Histogram at 5 and 10 minutes of (a), (b) Zn NPs on glass and (c), (d) Zn NPs on Si (n-type)

4. Conclusion

This study examines the influence of substrate type and sputtering time on Zn thin film deposition using dc sputtering. The results show a positive correlation between sputtering time and Zn thin film thickness. The successful formation of Zn with a wurtzite structure on both n-Si (111) and glass substrates was confirmed. The ZnNPs deposited on the n-type Si substrate had a larger grain size those deposited on glass. When Zn thin films are deposited on Si or glass substrates, a granular surface forms. The produced thin films have a standard orientation along the (002) plane and a polycrystalline nature with a hexagonal wurtzite structure.

References

[1] A.T. Saleh, "Nanomaterials: Classification, Properties, and Environmental toxicities", *J. Enviro. Technol. Innov.*, 20 (2020) 101067.

[2] P. Szczyglewska, A. Feliczak-Guzik and I. Nowak, "Nanotechnology–General Aspects: A Chemical Reduction Approach to the Synthesis of Nanoparticles", *Molecules*, 28 (2023) 4932.

[3] M. Mohammed et al., "Accurate Synthesis and Performance of SERS Sensing of Au/Ag Nanocomposites Site-Deposited on Apple Surfaces", *Plasmonics*, 18 (2023) 1-6.

[4] I. Khan, K. Saeed and I. Khan, "Nanoparticles: Properties, applications and toxicities", *Arab. J. Chem.*, 12 (2019) 908-931.

[5] G. Dutta and A. Sugumaran, "Bioengineered zinc oxide nanoparticles: Chemical, green, biological fabrication methods and its potential biomedical applications", *J. Drug Deliv. Sci. Technol.*, 66 (2021) 1773-2247.

[6] I.H. Hadi, K.I. Hassoon and M.F. Jawad, "Well-modifying the optical properties of bare Si solar cell by incorporating CuNPs", *Opt. Quant. Electron.*, 54 (2022) 629.

[7] K. Altammar, "A review on nanoparticles: characteristics, synthesis, applications, and challenges", *Front. Microbiol.*, 14 (2023)1155622.

[8] H. Mohamed, "Properties and applications of quantum dot heterostructures grown by molecular beam epitaxy", *Nanoscale Res. Lett.*, 1 (2006) 32-45.

[9] Q. Chen, "Electrodeposition of epitaxial metal thin films on silicon for energy conversion and flexible electronics", PhD thesis, Missouri University of Science and Technology (2019).

[10] P. Dainius and G. Ludwig, "Thin Film Deposition Using Spray Pyrolysis", *J. Electroceram.*, 14 (2005) 103-111.

[11] B.A. Bader et al., "Photodetector Based on Titanium Oxide Nanoparticles Produced via Pulsed Laser Ablation", *Adv. Cond. Matter Phys.*, 2022 (2022) 8066167.

[12] S. Doaa, M. Alwan and K. Walid, "Enhanced pesticides' limit of detection using bimetallic alloys nanoparticles", *J. Mater. Sci. Mater. Electron.*, 32 (2021) 18689-18698.

[13] I.H. Hadi, K.I. Hassoon and M.F. Jawad, "Characterization of Copper Nanostructures Prepared by DC Sputtering on Various Substrates", 1st Samarra Int. Conf., AIP Conf. Proc., 2394 (2022) 090015.

[14] J. Bhavana et al., "Effect of zinc acetate concentration on structural, optical and electrical properties of ZnO thin films deposited by electrostatic spray on ITO substrate", *J. Electrochem. Soc.*, 159 (2012) 716-721.

