

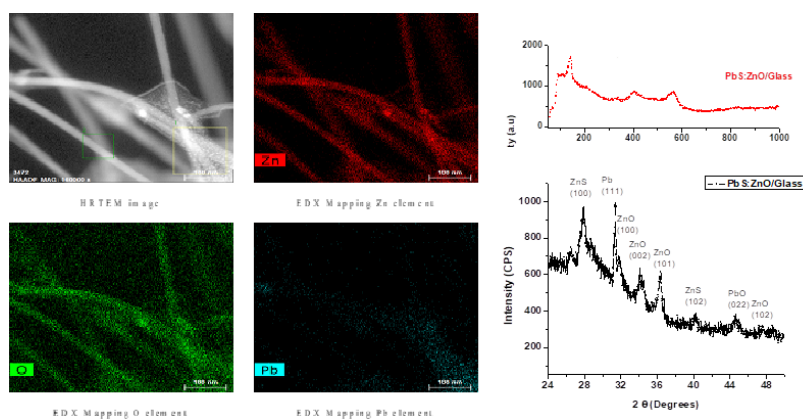
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# Structural and Morphological Study of PbS:ZnO Nanowires Films Deposited Using Thermal Evaporation Method

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We obtained ZnO Nanowires films deposited on two types of substrate (Si (100) and glass) with 12 wt % PbS as dopant by simple thermal evaporation technique. High Resolution Transmission Electron Microscopy (HRTEM) and Energy-dispersive X-ray spectroscopy (EDX) images have confirmed the formation of ZnO Nanowires (NWs). EDX technique was used to investigate the elements content (standard analysis and mapping modes). Morphology and thickness of the films were investigated from surface and cross section of the films via Scanning Electron Microscopy (SEM) images. The Raman, photoluminescence (PL) and X-ray Diffraction (XRD) have confirmed the hexagonal phase structure of the ZnO Nanowires, which appeared to be very fine and their diameters were less than 40 nm and their lengths were of several micrometers using SEM and HRTEM. The effect of PbS as dopant on the growth of ZnO Nanowires as well as on the morphology for two substrates was investigated and compared. These Nanowires films could be applied in several fields. Mapping -EDX has confirmed the stoichiometry of prepared films. Finally, the structure (phase) was verified by different characterization techniques. The optoelectronic application of Nanostructures film will be study later.

## Graphical abstract



## Keywords

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## 1. Introduction

ZnO is prominent semiconductor material. It is commonly used as bio-sensors photo voltaic solar cells [1], nano-generators, biosensor, and LED (light emitting diode) [2]. As well as, ZnO is not harmful to nature, environmental properties

[2], with optical band gap of 3.3 eV.

Nanowires, core-shell and nanotubes were emerged as potential candidates for diverse applications. In general, doping with many metals would improve semiconductor

properties like: ZnO, WO<sub>3</sub> [3], ZnS, PbS [4] and SnO<sub>2</sub> [5], LIS (La(OH)<sub>3</sub>@In<sub>2</sub>S<sub>3</sub>) [6]. The doping procedures would induce some change in electronic properties like band gap and transparency [7, 8]. The electrical properties are related with the crystallography quality (grain size and orientation) [9]. These ZnO and/or ZnS Nanostructures allow to potential optical application in optoelectronic field [10, 11].

Various techniques have been utilized to create semiconductor (ZnO and/or ZnS) thin films like CBD(chemical bath deposition) [12, 13], pulsed laser deposition (PLD) technique [14], magnetron sputtering (RF or DC) [15],ultrasonic spray, sol-gel [16] and thermal evaporation [17, 18]. The last method is simple and low cost. It is usually used for film production. The morphological, structural and optical properties of ZnS and ZnO films are influenced by several factors as variation of grain size, the thickness and percentage of the dopant element [13, 19].

The formation of nanotubes or nanowires as well as the reducing size of nanostructure [20] lead to modification of the chemical, electrical and physical characterization of films comparing to the bulk material behaviors especially in semiconducting films [21]. Nanostructured ZnO was formed as nanobelts, nanocombs, and the core-shell ZnO on silicon Nanowires [22]. Nanohelices and nanowires were synthesized using many depositing methods [23, 24]. Each of these properties creates one-dimensional ZnO nanostructured with attractive applicants for used in devices and technologies. There are both growth mechanisms that explain nucleation and growth, the first one is the vapor-solid and the second is vapor-liquid-solid (VLS) [25].

The object of the work is to examine the growth of doping PbS: ZnO Nanowires (morphology and structural properties) behavior using thermal evaporation method. XRD and PL techniques were used to explore crystallographic and optical properties. We used EDX (classic and mapping modes) to determine the composition of films. The morphology evolution was achieved via HRTEM and SEM characterization

of the surface. Up to our comprehension there are few works where ZnO (using PbS as dopant) was prepared by simple thermal evaporation in order to obtain Nanowires ZnO films [26, 27].

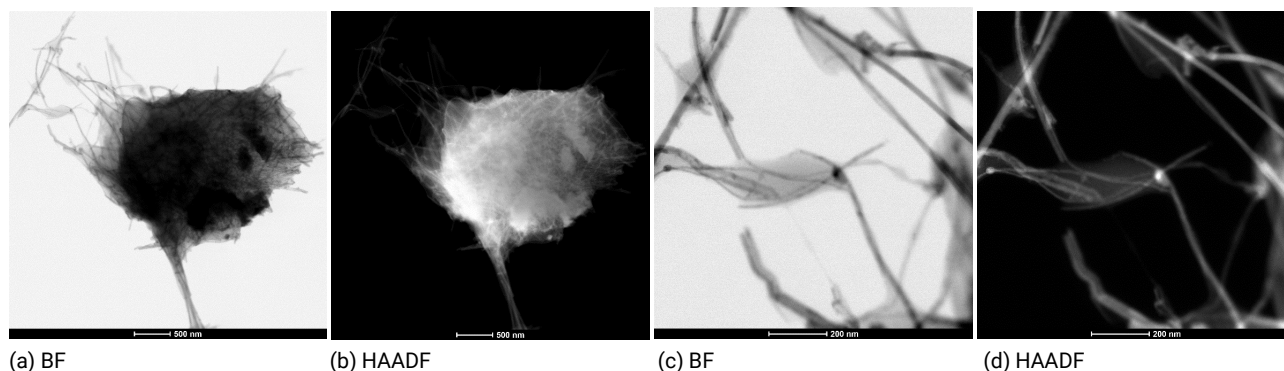
## 2. Materials and Methods

Zinc oxide was doped with PbS to obtain PbS:ZnO thin films. Where, PbS:ZnO Nanostructures were synthesized on two types of substrate (glass and Si (100)) using simple thermal evaporation set-up [28]. ZnO(88 wt %) and PbS (12 wt %) powders were mixed and placed in the once crucible as source material, under a vacuum of the chamber(about 10<sup>-5</sup> Torr). The holder of the substrate was heated before deposition to 200°C. Turbomolecular pump was used at low speed (pumping speed 25000 rpm) to obtain the high vacuum to eliminate the humidity as well as the undesirable elements. Morphology (thickness and surface) and elements composition were approximated of the deposited films by SEM and EDX, respectively. Structural [20] and optical properties were examined using XRD and PL using Laser He-Cd (A 325 nm).We were recorded the FTIR spectra of the films utilize Jasco 300 E [4]. We were used HRTEM image HAADF (High-angle annular dark-field) and BF (bright field), also with EDX mapping and classic modes to get the elements composition.

## 3. Results and Discussion

### 3.1 TEM and EDX mapping study

Figure 1 presents TEM images (a) BF and (b) HAADF big scale, (c) BF (filed) small scale, (d) HAADF (dark filed) black, big scale for PbS:ZnO film. For the additional examination of the microstructure of the produce, the TEM measurements were achieved over above selected region and for Pb-doped ZnO Nanowires (NWs)as shown in Figure 2-a.



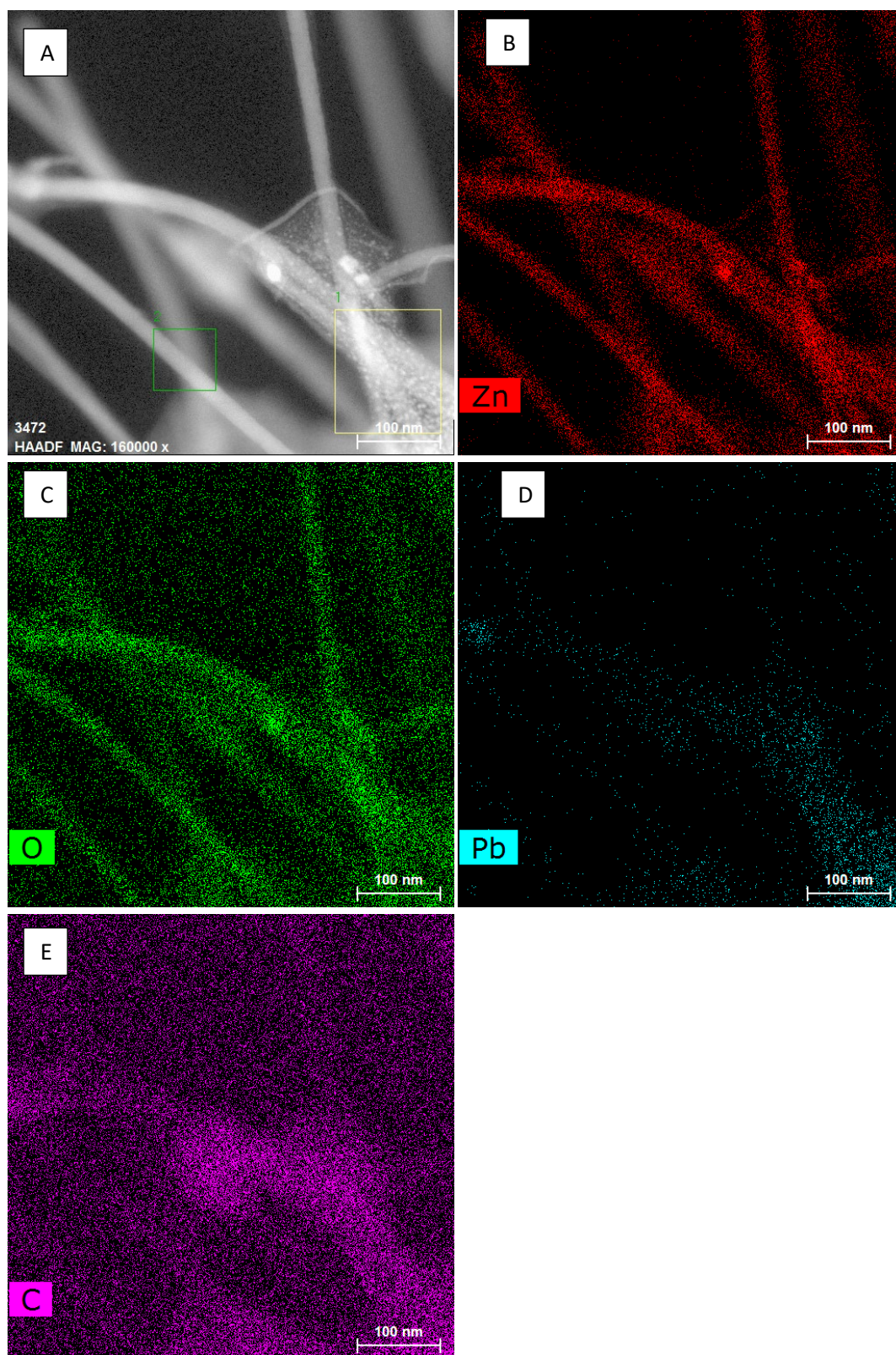
**Fig. 1.** TEM images (a) BF (bright filed) big scale, (b) HAADF ( dark filed) black, big scale,(c) BF (bright filed) at small scale, (d) HAADF at big scale for PbS:ZnS film.

TEM study shows the structure of ZnO. It is like Nanowires or Nanotubes structure. The diameters of the nanowires are in the range of 25 nm. And, the length of some micrometers (examined by SEM method and the length are more the measurement of TEM images).

The EDX mapping for each elements are analyzed, where the zone studied was the Figure 2-a which presents TEM mapping images and it conforms the nanowires structure. The Figure 2-b presents Zn element mapping, similarly Figure 2-c for O element are the mainly components of the nanowires films, where the Pb (Figure 2-d) is in very low percentage and

it is in the base of nanowires (down or bottom).The C element is very low (2-e) due to the grid of TEM (it used the C amorphous for catch the nanostructure like nanowires and nanotubes)

Very thin ZnO nanowires have not often described in the literatures [29-32]. However, the synthesizing procedure must engage more than one step in order to get the wished thin NW's. In our case, the preparation of the NWs was achieved via the thermal deposition method (simple as well as inexpensive).



**Fig. 2.** TEM image, (a) images of EDX mapping (b) Zn, (c) O, (d) Pb and (e) C elements.

The Table 1 presents a few Pb quantity in the two nanowires (about 1.78 at %), and the film is stoichiometry with low Si percentage due to the TEM preparation.

The Table 2 shows that there is not a Pb in the two nanowires (for intersection zone where the Pb is about 0.07 at %), and the film is stoichiometry with low Si percentage due to the TEM preparation.

**Table 1.** EDX- Zone 1 (in the bottom of nanowires)

Element	Weight %	Atomic %
O K	22.87	53.48
Zn K	59.03	33.77
Si K	8.24	10.97
Pb L	9.87	1.78



**Table 2.** EDX-Zone 2 (intersection of two nanowires)

Element	Weight %	Atomic %
O K	24.26	54.43
Zn K	69.63	38.23
Si K	5.69	7.27
Pb L	0.42	0.073

Figures 1 and 2 present TEM images and EDX mapping, respectively; verified that the growth was as Nanowires, also the films were mainly composed of Zn and O elements, in

accordance with XRD study (see last paragraph).

### 3.1.1 HRTEM study

Similarly, Figure 3 presents TEM images (a) and (b) at large scale in BF mode (bright field), and HRTEM images at very small scale (c) BF and (d) HAADF (dark filed). This high resolution images (c and d) confirm Nanowires structural growth; where, the diameters of nanowires are less than 50 nm. We can conclude that the thermal evaporation method is interesting method to get ZnO nanostructure (Nanowires) in these selected parameters.



**Fig. 3.** (a) and (b) TEM images at medium in BF mode (Bright Field), and HRTEM images very small scale (c) BF and (d) HAADF (dark filed).

### 3.2. SEM and EDX study

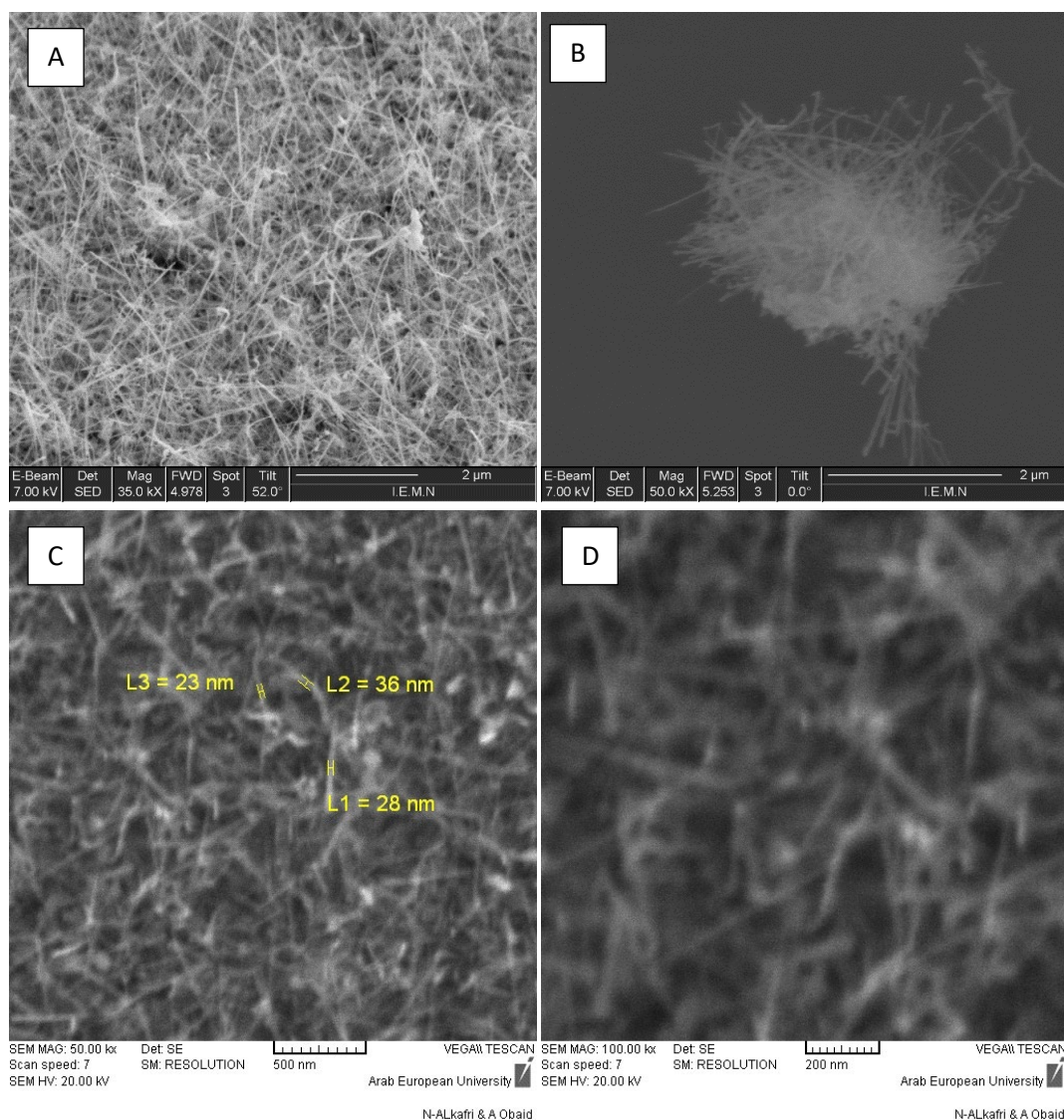
SEM technique was employed to explore the structural morphology of the prepared samples. Figures 4a,b shows the surface morphology of doped ZnO NWs sample with two magnifications (at 35k and 50 k mag using E-Beam 7 KV). It is clear that the sample corresponds of ultra-thin arbitrarily oriented NWs with uniform diameter that varied from ~23 nm to 36 nm and with length of some micrometers as shown in Figure 4-c (at 50 k magnification). For additional investigations, cross-sectional SEM images were carried out for the same doped product on top of, where front view of the NW sidewall was get and shown in Figure 4. The morphology of the doped product signifies the formation of the cantilever-as NWs above another thin layer (Figure 4-b).

We expect that, PbS formed a thin monolayer on top of the

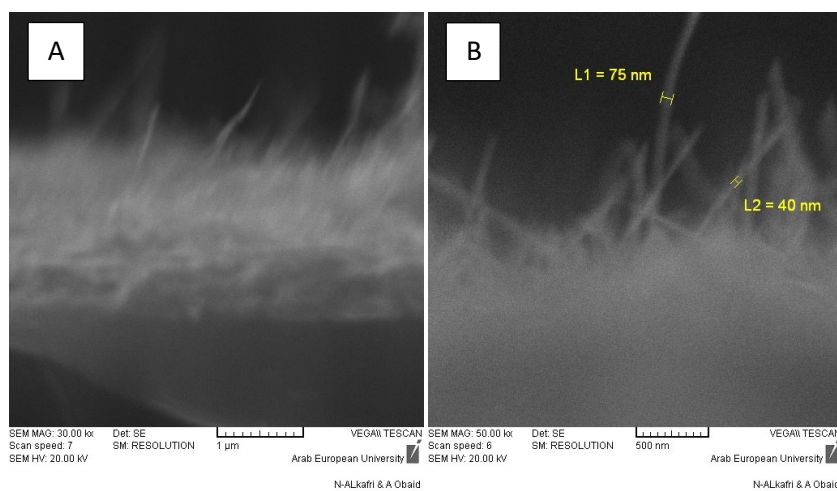
substrate and on down of the nanowires. The PbS was a catalyst during the deposition process, and it played the essential role for nonstructural growth [33].

Figure 5 shows morphology cross section images by SEM for ZnO nanowire samples deposited on Si(100) substrate at two magnifications 30 k and 50 k corresponding to figures 5-a and 5-b, respectively. Where the images confirm nanowires growth with diameter varied from 40 nm to 70 nm as shown in Figure 5-b.

The SEM images figures 4 and 5) verify that the growth is as Nanowires in accordance with TEM observation. The composition of the PbS:ZnO films was checked firstly via EDX (EDX-SEM), where the Figure 6 shows spectra of PbS:ZnO/Si(100) film. Also, the element percentage was reported in Table 4.



**Fig. 4.** SEM top view for surface morphology of ZnO nanowires film, (a) at 35 k magnification and (b) at 50 k magnification using E-Beam 7 kV and (c) at 50 k magnification and (d) at 100 k magnification using High Voltage 20 kV.



**Fig. 5.** SEM cross section morphology of ZnO nanowires film deposited on Si(100) substrate. (a) 30k and (b) at 50 k magnifications.

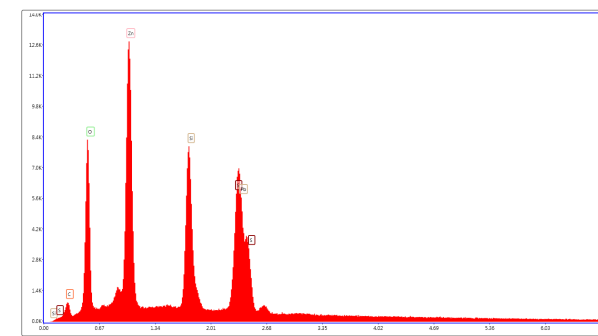


Fig. 6. EDX spectra for PbS:ZnO/Si(100) film.

The film is consisted mainly of Zn and O. Consequently, the film is approximately stoichiometry (Table 3) with considering that the EDX (SEM equipped EDX) is semi quantitative techniques. Also, the atomic percentage for Pb and S are about 8.71 % and 8.58 %, respectively. The results are conformed to EDX-HRTEM results in last paragraph, where the ZnO structure is nanowires film using PbS as dopant.

Table 3. Weight and Atomic percentage for PbS:ZnO film

Element	Weight %	Atomic %
O K	18.54	55.19
Zn L	37.77	27.52
S K	5.78	8.58
Pb M	37.91	8.71

### 3.3. XRD, Photoluminance and Raman study

XRD pattern presents ZnO wurtzite phase (hexagonal structure according to PDF Number: 36-1451) for (PbS doped ZnO/Si(100) film) as shown in Figure 7-a. The peaks at 31.70°, 34.40°, 36.30° and 47.52° have associated to (100), (002), (101) and (102) orientation for ZnO wurtzite material, respectively. The peaks (002) and (102) matching to wurtzite hexagonal structure according to obtained ZnS using spray pyrolysis [34]. The peaks at 31.4° corresponds to a (111) orientation of Pb cubic phase. While, the peak at 31.4° corresponds to a (111) orientation of Pb cubic phase and at 44.6° corresponds to a (022) orientation of PbO cubic phase. This difference in phase (hexagonal or cubic) maybe due to the deposition methods especially (energy of bombardment, chemistry or physics of precursors [35].

Photoluminance (PL) characterization emission spectra of PbS:ZnO film are shown in Figure 7-b. The small peak at 380 nm (3.26 eV) due to optical band gap of ZnO materials in two substrates (Si in black color and glass in red color) [36], The another peak shows at about 525 nm matched to the defects in the film (electrons transition to vacancies of sulfur). It is known that important intensity such as our case could be interesting for optoelectronics devises (nanocrystals, grain size of the crystal and/or doping influence the emission of semiconductors which is beneficial for light in specific range or domains). We have found in recent work, that the variation in value of band gap is as a result of the structural difference (nanowires for doped film and dense for non-doped one) and the dopant element (PbS or Pb) for nanowires film [36].

The Raman scattering spectra of the films (Figure 7-c) have bands at E<sub>2</sub>L structure at 90 cm<sup>-1</sup>, 332 cm<sup>-1</sup>, 406 cm<sup>-1</sup>, 438

cm<sup>-1</sup> (mode E<sub>2</sub>H) and 565 cm<sup>-1</sup> characteristic to the wurtzite phase [37, 38] and confirms the influence of the technique on the structure as well as properties of ZnO films (wurtzite phase in accordance with the XRD study). The two peaks at 145 cm<sup>-1</sup> and 990 cm<sup>-1</sup> correspond to the PbS, by reason of using PbS as dopant which was observed in provirus work [4].

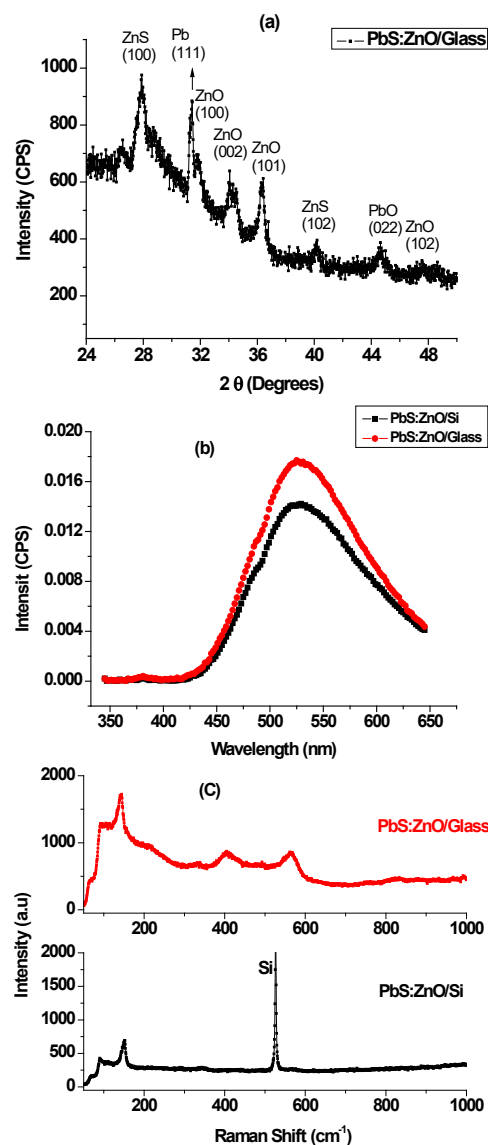


Fig. 7. (a) XRD pattern for PbS:ZnO/glass and (b) PL spectra and (c) Raman spectra for PbS:ZnO nanowires film deposited on glass substrate and Si(100).

## 4. Conclusions

In this paper, ZnO nanowires (NWs) were synthesized by simple thermal evaporation technology, utilizing PbS powder as dopant, and elaborated on two types of substrate. The optical and structural properties of the samples were studied using HRTEM, SEM, PL, Raman and XRD techniques. TEM and EDX mapping observations were shown that surface of NWs appeared with lengths of few micrometers and the diameter of fewer than 40 nm. Using EDX and TEM techniques, we verified that ZnO nanowires were stoichiometry with little quantity of Pb and S as consequence of little percentage of the dopant. XRD and Raman observations proved the Nanostructural of prepared film on both substrates (glass and Si). PL spectra were used to get optical descriptions (band



gap) of the PbS;ZnO Nanowires, where it could be interesting in potential candidate for new applications (batteries, solar cell and/or sensing of gas devices).

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## Author Contributions

Bassam Abdallah: Conceptualization, Methodology, Writing- Original draft preparation. M. Kakhia: Investigation. W. Zetoun: Formal analysis, Software.

## References and Notes

- [1] Haque, F.; Rahman, K. S.; M. A. Islam, M. J. R.; Akhtaruzzaman, M.; Alam, M. M.; Alothman, Z. A.; Sopian, K.; Amin, N. *Chalcogenide Lett.* **2014**, *11*, 189.
- [2] Shin, S. W.; Pawar, S. M.; Park, C. Y.; Yun, J. H.; Moon, J.-H.; Kim, J. H.; Lee, J. Y. *Sol. Energy Mater. Sol. Cells.* **2011**, *95*, 3202. [\[Crossref\]](#)
- [3] Abdallah, B.; Kakhia, M.; Shaker, S. A. *Compos. Interfaces* **2016**, *23*, 663. [\[Crossref\]](#)
- [4] Abdallah, B.; Ismail, A.; Kashoua, H.; Zetoun, W. *J. Nanomater.* **2018**, *2018*, 1. [\[Crossref\]](#)
- [5] Ao, D.; Ichimura, M. *Solid-State Electron.* **2012**, *69*, 1. [\[Crossref\]](#)
- [6] Hu, S.; He, J.; Chen, F.; Liu, B.; zhai, W.; He, Q. *Appl. Phys. A* **2021**, *127*, 102. [\[Crossref\]](#)
- [7] Chaisitsak, S. *Sensors* **2011**, *11*, 7127. [\[Crossref\]](#)
- [8] Abdelkrim, A.; Rahmane, S.; Abdelouahab, O.; Abdelmalek, N.; Brahim, G. *Optik (Munich, Ger.)* **2016**, *127*, 2653. [\[Crossref\]](#)
- [9] Al-Khawaja, S.; Abdallah, B.; Shaker, S. A.; Kakhia, M. *Compos. Interfaces* **2015**, *22*, 221. [\[Crossref\]](#)
- [10] Abdallah, B.; Zidan, M.; Allahham, A. *Silicon* **2021**, *13*, 4139. [\[Crossref\]](#)
- [11] Assfour, B.; Abadllah, B.; Kakhia, M. *Aerosol Sci. Eng.* **2022**, *1*.
- [12] Lin, Y.-C.; Chao, Y.-T.; Yao, P.-C. *Appl. Surf. Sci.* **2014**, *307*, 724. [\[Crossref\]](#)
- [13] Sinha, T.; Lilhare, D.; Khare, A. *J. Electron. Mater.* **2018**, *47*, 1730. [\[Crossref\]](#)
- [14] Kurnia, F.; Ng, Y. H.; Tang, Y.; Amal, R.; Valanoor, N.; Hart, J. N. *Cryst. Growth Des.* **2016**, *16*, 2461. [\[Crossref\]](#)
- [15] Abdallah, B.; Zidan, M. D.; Allahham, A. *Int. J. Mod. Phys. B* **2019**, *33*, 1950348. [\[Crossref\]](#)
- [16] Alnama, K.; Abdallah, B.; Kanaan, S. *Compos. Interfaces* **2016**, *24*, 499. [\[Crossref\]](#)
- [17] Vishwakarma, R. *J. Theor. Appl. Phys.* **2015**, *9*, 185. [\[Crossref\]](#)
- [18] Jeyachitra, R.; Senthilnathan, V.; Kathirvel, D. *Int. J. ChemTech Res.* **2014**, *6*, 3152.
- [19] Al-Douri, A. A. J.; Heavens, O. S. *Thin Solid Films* **1983**, *100*, 273. [\[Crossref\]](#)
- [20] Abdallah, B.; Kakhia, M.; Abou Shaker, S. *Compos. Interfaces* **2016**, *23*, 663. [\[Crossref\]](#)
- [21] Vaishnav, V. S.; Patel, P. D.; Patel, N. G. *Thin Solid Films* **2005**, *490*, 94. [\[Crossref\]](#)
- [22] Hazra, P.; Singh, S. K.; Jit, S. *J. Vac. Sci. Technol., A.* **2015**, *33*, 01A114. [\[Crossref\]](#)
- [23] Moore, D.; Ding, Y.; Wang, Z. L. *Angew. Chem. Int. Ed.* **2006**, *45*, 5150. [\[Crossref\]](#)
- [24] Yu, J. H.; Joo, J.; Park, H. M.; Baik, S.-I.; Kim, Y. W.; Kim, S. C.; Hyeon, T. *J. Am. Chem. Soc.* **2005**, *127*, 5662. [\[Crossref\]](#)
- [25] Malyarevich, A. M.; Gaponenko, M. S.; Savitski, V. G.; Yumashev, K. V.; Rachkovskaya, G. E.; Zakharevich, G. B. *J. Non-Cryst. Solids.* **2007**, *353*, 1195. [\[Crossref\]](#)
- [26] Ahmad, M.; Pan, C.; Yan, W.; Zhu, J. *Mater. Sci. Eng.* **2010**, *174*, 55. [\[Crossref\]](#)
- [27] Abdallah, B.; Mahmoud, K.; Walaa, Z.; Alkafri, M. N. *Mate. Res. Express.* **2019**. [\[Crossref\]](#)
- [28] Abdallah, B.; Kakhia, M.; Zetoun, W.; Alkafri, N. *Microelectron. J.* **2021**, *111*, 105045. [\[Crossref\]](#)
- [29] Lin, Y.-R.; Yang, S.-S.; Tsai, S.-Y.; Hsu, H.-C.; Wu, S.-T.; Chen, I. C. *Cryst. Growth Des.* **2006**, *6*, 1951. [\[Crossref\]](#)
- [30] Gokarna, A.; Parize, R.; Kadiri, H.; Nomenyo, K.; Patriarche, G.; Miska, P.; Lerondel, G. *RSC Advances* **2014**, *4*, 47234. [\[Crossref\]](#)
- [31] Sun, Y.; George Ndifor-Angwafor, N.; Jason Riley, D.; Ashfold, M. N. R. *Chem. Phys. Lett.* **2006**, *431*, 352. [\[Crossref\]](#)
- [32] Shkurmanov, A.; Sturm, C.; Franke, H.; Lenzner, J.; Grundmann, M. *Nanoscale Res. Lett.* **2017**, *12*, 134. [\[Crossref\]](#)
- [33] Abdallah, B.; B.Assfour; Kakhia, M.; Bumajdad, A. *Nanosyst.: Phys., Chem., Math.* **2020**, *11*, 537. [\[Link\]](#)
- [34] Alnama, K.; Abdallah, B.; Kanaan, S. *Compos. Interfaces* **2017**, *24*, 499. [\[Crossref\]](#)
- [35] Jazmati, A.; Abdallah, B.; Lahlah, F.; Abou Shaker, S. *Mate. Res. Express.* **2019**, *6*, 086401.
- [36] Abdallah, B.; Kakhia, M.; Alssadat, W.; Zetoun, W. *Prot. Met. Phys. Chem. Surf.* **2021**, *57*, 80. [\[Crossref\]](#)
- [37] Jamal, R. K.; Suhail, A. M.; Hussein, M. T.; Khashi, H. J. *Int. J. Thin Film Sci. Tec.* **2012**, *1*, 61.
- [38] Exarhos, G. J.; Sharma, S. K. *Thin Solid Films* **1995**, *270*, 27. [\[Crossref\]](#)

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