INTERNATIONAL JOURNAL OF
ARTIFICIAL INTELLIGENCE AND EMERGING TECHNOLOGY

Print ISSN
2735-4792

VOLUME 5, ISSUE 2, 2022, 36 – 48.

Online ISSN
2735-4806

Characterization of ZnS Nano layers produced by pulsed laser deposition

Nehal ALi [1], A. Abou El Magd[1], Y. badr [2]

[1] Department of Engineering Physics and Mathematices, Faculty of Engineering, Tanta University.
[2]National Institute of Laser Enhanced Sciences, Cairo University.

Abstract

Pulsed Laser Deposition, PLD technique was used to fabricate ZnS thin films deposited on crystalline substrate of Al_2O_3 under high vacuum condition. The deposition conditions were optimized. The laser induced plasma LIP, spectroscopic technique was used to diagnose the plasma produced by laser ablation. Elemental analysis by energy dispersive X-ray spectroscopy (EDX) indicates higher S content in ZnS films produced at higher fluence. Interferometery was used to measure the thickness of the films, UV/VIS absorption as will as fluorescence spectroscopy was carried out on both thin layers and bulk samples. Blue shift was obtained in absorption and emission spectra indicating the confinement of the film.

Keywords: ZnS; PLD; thin film; LIP

Print ISSN
2735-4792

VOLUME 5, ISSUE 2, 2022, 36 – 48.

Online ISSN
2735-4806

Introduction

ZnS is interesting materials, not only because they are multicomponent materials with the relatively volatile element sulfur, but also because they are secondary phases in the promising solar cell material which has a band gap of 1.45 eV [1]. ZnS has the largest band gap energy at room temperature among the II-VI compound semiconductors. For this reason, it considered one of the most promising materials for optoelectronic devices and future applications in data storage, data transfer and optically interfaced electronics required semi-conducting thin film which are sensitive in the UV part of the spectrum [2-4].

Extensive efforts have focused on ways to grow high-quality ZnS epitaxial thin films, mainly via molecular beam epitaxy MBE [5], metal-organic chemical vapor deposition MOCVD [6], with the objective of improving optical and electrical properties by obtaining stiochiometric composition of ZnS thin layers, these techniques are difficult to implement with pulsed lased deposition [7-10]. Only few attempts have been made to grow ZnS thin layers by PLD [11-13], although these films that prepared under high vacuum conditions at room temperature show significant differences in structure compared to films produced by conventional deposition methods [14].

Print ISSN
2735-4792
VOLUME 5, ISSUE 2, 2022, 36 – 48.
Online ISSN
2735-4806

These differences are caused by the kinetic energy of the ablated atoms and ions. Advantages of PLD over some other deposition techniques are that it is a pure physical mechanism without the incorporation of carbon and the substrate temperature can be kept relatively low because the kinetic energy of the source particles is sufficiently high enough to provide the required mobility.

In this study, a home made PLD setup is used to produce nano layers of ZnS, deposited on sapphire (Al_2O_3) substrates heated during the deposition. The produced films were characterized using different spectroscopic techniques and the elementary composition of films is determined by EDX results.

Experimental work

Prior to deposition, the sapphire substrates were immersed in dilute NaoH solution for 15 minutes, then washed with distilled water and immersed in a chromic acid for 24 hours, finally, washed with distilled water and isopropyl alcohol and left to dry in vacuum desicator [15].

The growth process was carried out in a vacuum chamber with base pressure of 10^{-5} torr. A Lambda-Physik EMG203 MSE XeCl laser at wavelength 308nm was used for the ablation experiments. The pulse energy was approximately 5 mJ/pulse and the repetition rate 100 Hz, using nearly 900,000 pulses.

INTERNATIONAL JOURNAL OF
ARTIFICIAL INTELLIGENCE AND EMERGING TECHNOLOGY
Print ISSN
2735-4792
VOLUME 5, ISSUE 2, 2022, 36 – 48.
Online ISSN
2735-4806

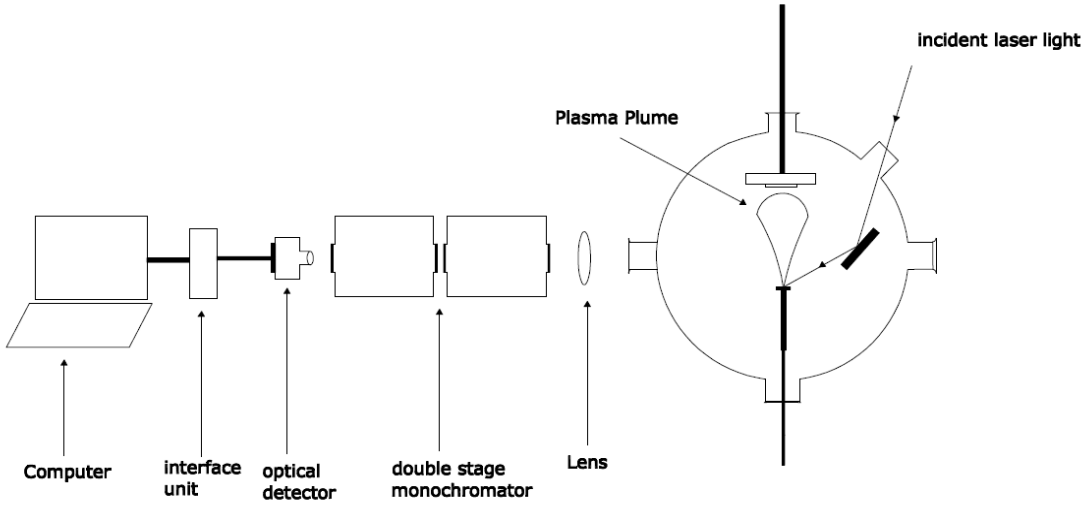

Fig 1 Schematic diagram of plasma diagnosis technique

The target and substrate were placed plane parallel at a distance about 3cm. a calibrated thermocouple was attached to the substrate; which temperature was varied by substrate heater connected to feedthrough to be adjusted by temperature controller fixed outside the chamber. The deposition was performed at 150-230 ˚C.

The film thickness was controlled by varying the number of laser pulses and be measured using interferometric technique.

Laser-induced fluorescence spectroscopy was employed to measure to the atomic spectrum in the plasma plumes generated by pulsed laser deposition. As shown in figure 1, the spectral collected from outside the vacuum chamber perpendicular to the direction of laser beam by collimating lens into the double monochromator setup SpectraPro 500i of ACTON Spectrograph, coupled with photon counter controlled by computer program.

Print ISSN
2735-4792

VOLUME 5, ISSUE 2, 2022, 36 – 48.

Online ISSN
2735-4806

The optical absorption spectra of the films were measured with a dual beam spectrometer computer controlled SHIMADZU (uv-3101pc- UV-VIS-NIR Scanning Spectrophotometer) . The emission spectrum of the resulting films was carried out using fluorescence spectrometer model (Perkin Elmer – LS55). The thickness of the films was measured with interferometric technique. To complete the morphology characterization of the fabricated mats, Energy-dispersive X-ray spectroscopy (EDS) with elemental mapping were conducted.

Results and discussion

Fig (2) shows the absorption spectra of the bulk ZnS and the deposited film. The optical absorption spectrum of both sample have low absorbance in the visible and near infrared regions. However, absorbance in the ultraviolet region is high. Note that the absorption peaks of the film is shifted toward the blue region of the spectrum due to the confinement. Absorption edges of bulk ZnS crystals are 337 nm, while the absorption edge of ZnS thin film is dramatically shifted toward the UV and become 296 nm. We think the band at 310 nm for thin film sample was caused by a large concentration of vacancies and interstitial ions in this samples. The enhanced absorption of the film observed in the neighbourhood of 296 nm is attributed to the $1S_{3/2}$–$1S_e$ transition. The corresponding band gap energy of 4.2 eV is larger than the one observed in bulk ZnS (3.66 eV) [16]. This can be explained as a quantum size effect, due to electron–hole confinement in a small volume.

INTERNATIONAL JOURNAL OF
ARTIFICIAL INTELLIGENCE AND EMERGING TECHNOLOGY
Print ISSN
2735-4792
VOLUME 5, ISSUE 2, 2022, 36 – 48.
Online ISSN
2735-4806

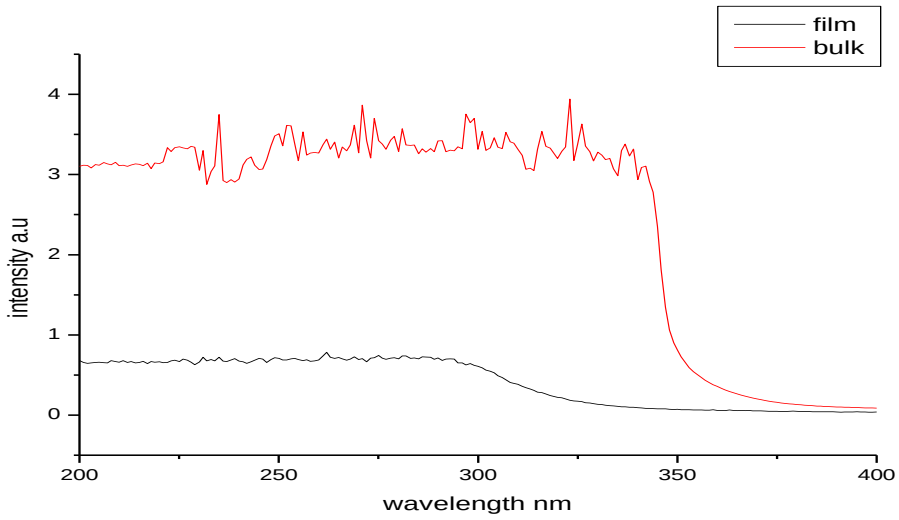

Fig. 2 Optical absorption of ZnS bulk and deposited film samples

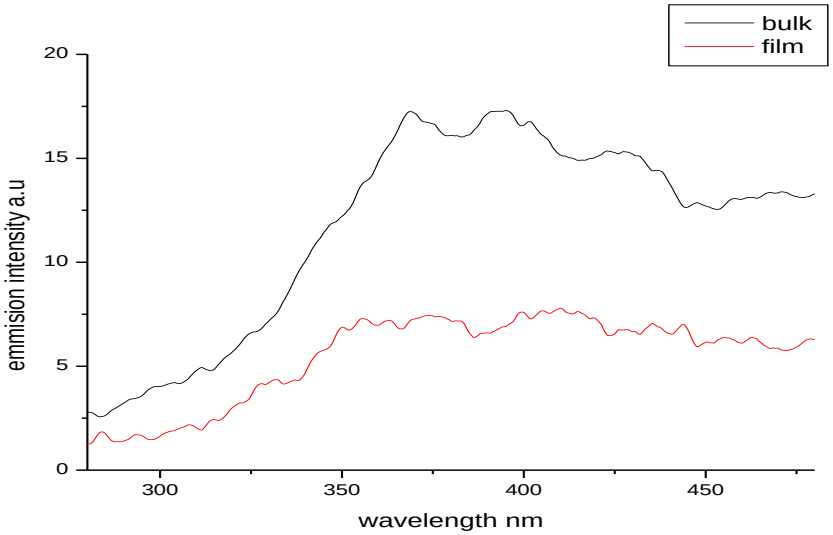

Fig. 3. the fluorescence spectra of ZnS bulk and deposited film samples

INTERNATIONAL JOURNAL OF
ARTIFICIAL INTELLIGENCE AND EMERGING TECHNOLOGY
Print ISSN 2735-4792
VOLUME 5, ISSUE 2, 2022, 36 – 48.
Online ISSN 2735-4806

Figure 3 represents the fluorescence spectra of the ZnS bulk and deposited film using an excitation wavelength of 280 nm. emissions of bulk and thin film samples present show the same emission trend as a broad band centered at 370 nm for the bulk sample while centered at 405 nm for the thin film which is associated with excitonic emission of ZnO. For the thin film, a broader emission band and a remarkable redshift of emission is observed. This may be due to the disorder that enhances defect levels near electronic bands, which capture the photocarriers efficiently. Thus, we attribute the redshift and decrease of excitonic recombination to the crystallinity loss.

Table 1 the absorption, fluorescence and the stoke shift of bulk and thin film samples

Bulk sample			Thin film sample		
Absorption Wavelength	Emission wavelength	Stoke shift	Absorption wavelength	Emission wavelength	Stoke shift
337 nm	368 nm	31 nm	296 nm	356 nm	60 nm
	394 nm	57 nm		375 nm	79 nm
	427 nm	90 nm		410 nm	114 nm
	447 nm	110 nm		435 nm	139 nm

The color of the ZnS plasma was bright purple. The plasma color depends on materials. The spectrophotometer device was used for optical emission spectroscopy (OES) of ZnS plasma as discussed in the material and methods.

INTERNATIONAL JOURNAL OF
ARTIFICIAL INTELLIGENCE AND EMERGING TECHNOLOGY
Print ISSN
2735-4792
VOLUME 5, ISSUE 2, 2022, 36 – 48.
Online ISSN
2735-4806

The optical emission spectrum of ZnS was shown in Figure 4. The atomic line spectrum of Zn and S atoms was assigned in Optical emission plasma spectrum.

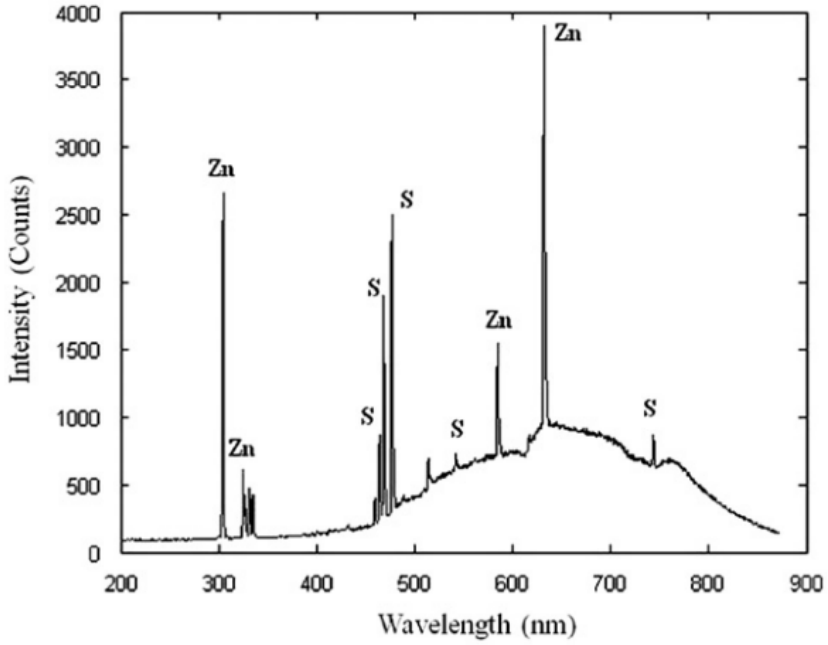

Fig.4 Optical emission plasma spectrum of ZnS during the deposition

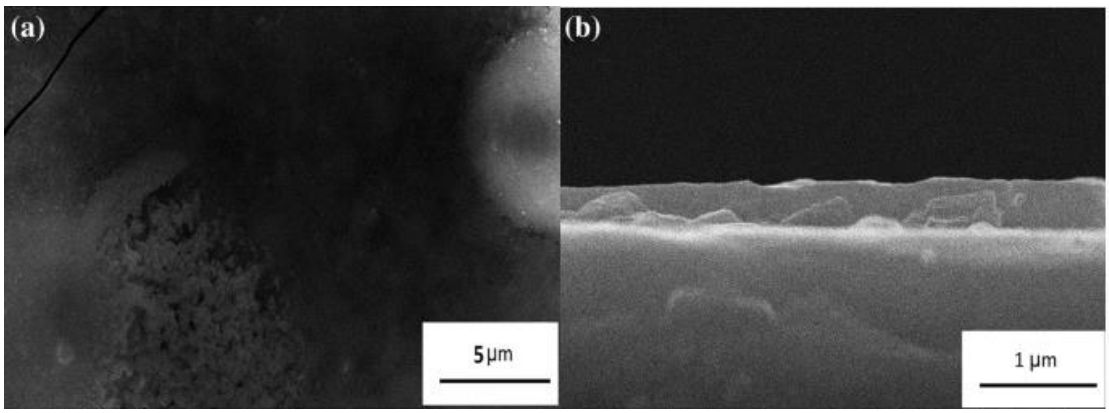

Fig 5 (a) Top-view SEM image, (b) Cross-sectional view of ZnS layer deposited on glass substrate at 300 °C

INTERNATIONAL JOURNAL OF
ARTIFICIAL INTELLIGENCE AND EMERGING TECHNOLOGY
Print ISSN 2735-4792
VOLUME 5, ISSUE 2, 2022, 36 – 48.
Online ISSN 2735-4806

Figure 5 (a) shows a top-view image of the ZnS film showing only a small crack and limited amounts of defects on the surface due to the low synthesizing temperature. Figure 5 (b) shows a cross-section view of the ZnS film prepared at 300 °C, the cross-section view shows a good distribution in the thickness of the layer that ranges from 570 to 575 nm.

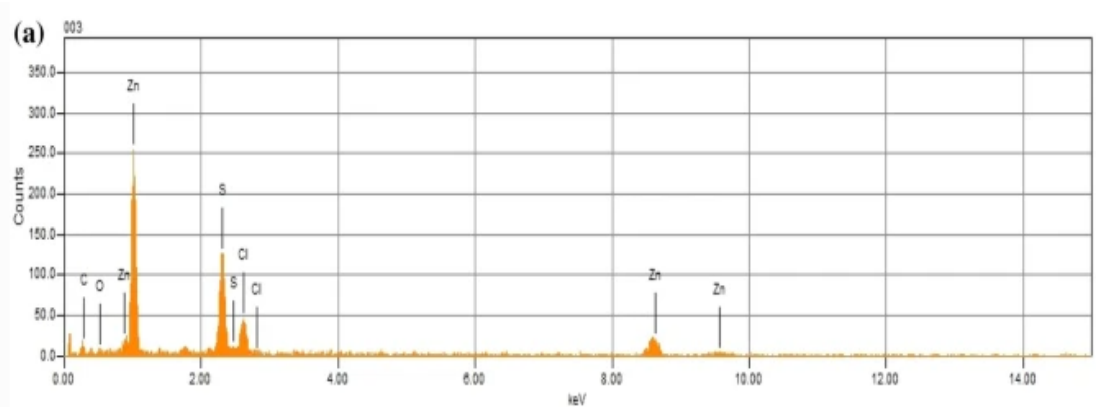

Fig 6 EDX analysis of ZnS thin film on Al_2O_3 substrates

Figure 6 presents the EDX spectra for ZnS thin films deposited on sappier. The results confirm the presence of Zinc, Sulfur. The high signals of Zn and S indicate the formation of the Zinc Sulfide element. Al atoms are due to the glass substrate while Ca and C signals are attributed to the sample holder and the microscope grid respectively, while the Cl peaks are found because of the chlorine associated in the utilized precursors while O is resulted from reacting with the atmosphere.

INTERNATIONAL JOURNAL OF
ARTIFICIAL INTELLIGENCE AND EMERGING TECHNOLOGY
Print ISSN
2735-4792
VOLUME 5, ISSUE 2, 2022, 36 – 48.
Online ISSN
2735-4806

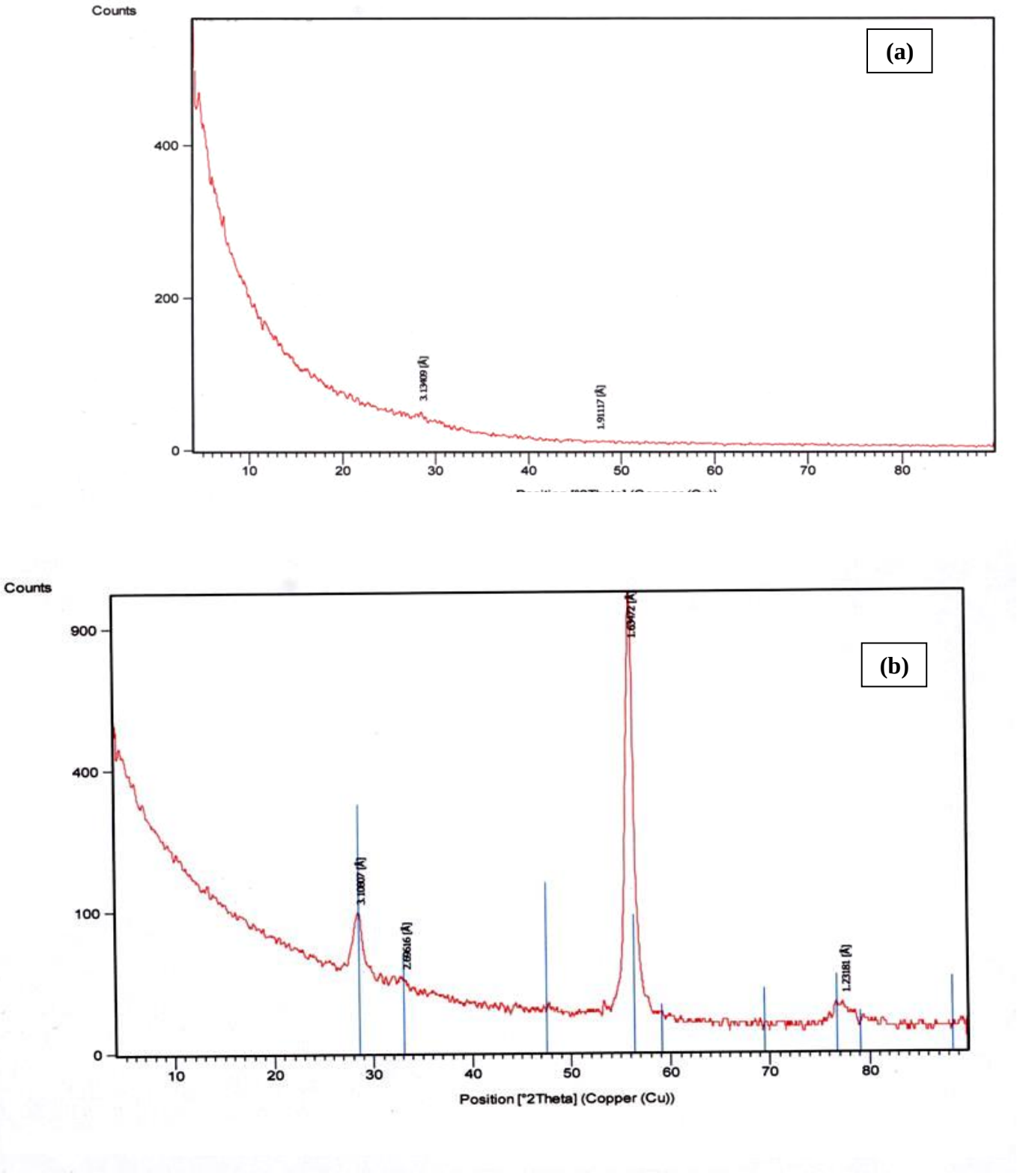

Fig. 7 XRD spectra of (a) Al2O3 substrate and (b) ZnS thin films.

Print ISSN
2735-4792
VOLUME 5, ISSUE 2, 2022, 36 – 48.
Online ISSN
2735-4806

XRD patterns were shown in Figure 7. Crystal orientations and the distance between the two adjacent planes were assigned in the figure. XRD analysis of the produced ZnS thin films on sapphire substrates with PLD technique was recognized using CuKa beam, which has wavelength of 540 nm. According to XRD data in Fig. 7(a), the structure of the sapphire substrate was amorphous without any characteristic crystalline peaks. While the spectrum shown in figure 7(b) is attributed to the deposited ZnS film. The spectrum consists of four distinct peaks located at angles 28.581, 34.561 , 56.381, and 77.3 which corresponds to the (1 1 14), (1 1 3), (1 1 42), (1 1 2) reflections of the ZnS lattice growing in a rhombohedral phase, which has come up in the hexagonal crystal family. These results belong to 04-012-8174 numbered ASTM card.

Conclusion

In this paper, ZnS was deposited as a thin film on Sapphire substrates by PLD technique, successfully. Some physical properties of produced ZnS thin films were introduced and analyzed. The structure of the films has been specified by a SEM microscope capable of magnifying 10 k times, absorption and emission properties, EDX and XRD. According to the results of ZnS thin films Al2O3 substrates, they have high quality and their average surface roughness was very low due to the advantage of PLD technique. The film shoed blue shift emission and a band gap of 4.2 eV. According to XRD data the ZnS thin films is polycrystalline with (0 1 14) preferred orientation.

Print ISSN
2735-4792

VOLUME 5, ISSUE 2, 2022, 36 – 48.

Online ISSN
2735-4806

References

[1] B. Shin, O. Gunawan, Y. Zhu, N.A. Bojarczuk, S.J. Chey, S. Guha, Thin film solar cell with 8.4 % power conversion efficiency using an earth-abundant Cu2ZnSnS4 absorber, Prog. Photovoltaics Res. Appl. 21 (2013) 72–76.

[2] J. Shi, J. Zheng, P. Wu Preparation, characterization and photocatalytic activities of holmium-doped titanium dioxide nanoparticles J. Hazard Mater., 161 (2009), pp. 416-422

[3]B. Poornaprakash, S. Ramu, S.H. Park, R.P. Vijayalakshmi, B.K. Reddy Room temperature ferromagnetism in Nd doped ZnS diluted magnetic semiconductor nanoparticles
Mater. Lett., 164 (2016), pp. 104-107

[4] N. Aggarwal, K. Kaur, A. Vasishth, N.K. Verma Structural, optical and magnetic properties of Gadolinium-doped ZnO nanoparticles J. Mater. Sci. Mater. Electron., 27 (2016), pp. 13006-13011

[5] K. Ichino, T. Onishi, Y. Kawakami, S. Fujita, J. Cryst. Growth, 138(1994)28.

[6] S. Nakamura, S. Takgimoto, T. Ando, H. Kugiyama, Y. yamada, J. Crystal Growth 221 (2000) 388.

[7] Robert Eason, Pulsed Laser Deposition Of Thin Films, Wiley, New York , 2007.

[8] S. Yano, R. Schroeder, B. Ullrich, H. Sakai, J. thin Solid films 423 (2003) 273-276.

[9] G. Reibe, S. Weibmantel and D. Rost, Appl. Phys. A79 (2004) 1275-1278.

Print ISSN
2735-4792

VOLUME 5, ISSUE 2, 2022, 36 – 48.

Online ISSN
2735-4806

[10] D. B. Chrisey, G.K. hubber, Pulsed Laser Deposition of thin Films Wiley, New York, 1994.

[11] Hidenori Hiramatsu, Hiromichi Ohta, Msahiro Hirano, Hideo Hosono, Solid State Communications 124 (2002) 411-415.

[12] Y.Z. Yoo, T. chikyow, P. Ahmet, M. Kawasaki, T. Makino, Y.Segawa, H. Koinuma, Adv. Mater. 13(2001)1624.

[13] K. T. Hillie, C. Curren and H.C. Swart, Applied Surface Science 177(2001) 73-77.

[14] H. U. Krebs. Int. J. Non-Equilib. Process. 10(1997) 3.

[15] M.Y. Nadeem, W. Ahmed, M.F. Wasiq, Journal of Research (Science) 16 (2005) 105–112.

[16] M. Cardona, G. Harbeke Phys. Rev., 137 (1965), p. A