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A study of morphological, optical, and photoluminescence properties of ZnS thin films doped Mn and ca

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HIGHLIGHTS

- Fabricated thin films XS (X = Mn, Ca) By using PVD.
- The morphological properties have been influenced by the doping.
- Optical band gap values decrease by increasing the incorporation of Ca^{2+} in the film.
- ZnS films doped with Mn/Ca exhibit PL emissions at various wavelengths.

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ABSTRACT

In this study, zinc sulfide (ZnS) thin films were deposited via physical vapor deposition (PVD) under high vacuum conditions, incorporating dual dopants manganese (Mn^{2+}) and calcium (Ca^{2+}). Morphological examination by AFM revealed that Mn^{2+} promoted a uniform and smooth film structure, whereas Ca^{2+} induced surface roughness. Optical characterization using ultraviolet–visible spectroscopy showed high transparency in the visible range, with doping leading to significant alterations in the bandgap energy. Photoluminescence investigations displayed prominent emission peaks at 385 nm, 448 nm, and 560 nm, characteristic of ZnS bandgap emissions, as well as an additional peak at 600 nm due to the novel dopant's influence. X-ray fluorescence (XRF) and Fourier transform infrared (FTIR) analyses verified the presence of ZnS and other constituents. Doping improved the optical and luminescent characteristics, offering potential for use in optoelectronics, light-emitting diodes (LEDs), and advanced technology development. This customizable approach to ZnS thin films presents innovative opportunities within material science and device manufacturing.

1. Introduction

Zinc sulfide (ZnS) is a semiconductor material that has been widely studied in recent decades [1–4]. it belongs to the group II-VI compound semiconductors. ZnS is a direct bandgap semiconductor, which requires a minimum of energy to excite an electron from the valence band to the conduction band relatively low, this property makes it a good candidate for light-emitting diodes (LEDs) and photovoltaic cells [2,5–7]. It has n-type semiconductor properties with high refractive index and absorption coefficient, wide band gap in the range of 3.2 eV and 3.9 eV at room temperature, and high optical transmittance in the visible region of the electromagnetic spectrum, making it useful for transparent conductive coatings in solar cells [8–12]. ZnS has two common crystal structures: zinc blende and wurtzite [13]. The zinc blende structure is cubic, while the wurtzite structure is hexagonal. Both crystal structures have different properties and are used for different applications.

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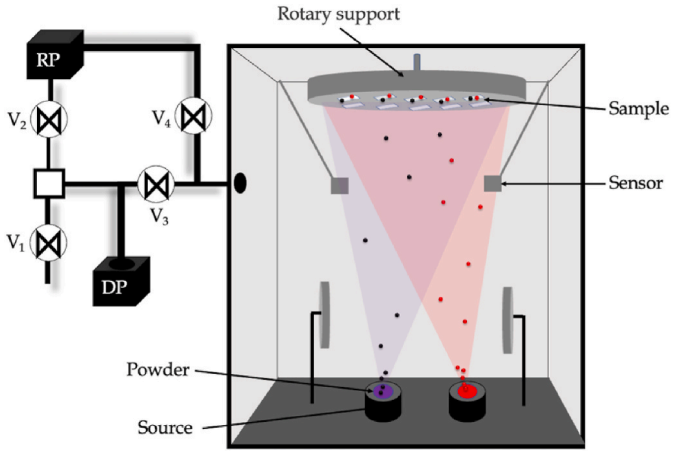


Fig. 1. Diagram of the physical vapor deposition process: DP_Diffusion pump; RP_Rotary vacuum pump; $V_{1,2,3,}$4_valves.

Table 1
Compositions of deposited thin films.

	Composition
Sample 1	ZnS pure
Sample 2	50% ZnS_50%Mn
Sample 3	90% ZnS_10%Mn
Sample 4	95% ZnS_05%Mn
Sample 5	50% ZnS_50%Mn
Sample 6	90% ZnS_10%Ca
Sample 7	95% ZnS_05%Ca

Moreover, it is non-toxic and chemically stable [14–16]. Because of these excellent physical properties, it has become a material of great potential in several optoelectronic devices including photo-catalysis, gas sensors, flat panel displays, light emitting diodes, thin film solar cells, infrared transparencies, photoelectrodes [17–20].

To improve device performance, doping with different elements has been used to modify the structural, electrical, and optical properties of pure ZnS. Several research teams have been working on the modification of the properties of ZnS thin films using doping with: Ni, Fe, Pb, Mn, Cu and F, Cl, and others [21–26].

ZnS material has been widely studied in the form of nanoparticles, single crystals, and thin films. Thin films have represented very good properties and have attracted attention in the last few years. They have been developed using different methods, chemical and physical methods including; pulsed laser deposition (PLD) [27], magnetron Rf sputtering [28], pyrolysis spray [29], chemical bath deposition (CBD) [30], sol-gel [31], ultrasonic spray [32], and thermal vacuum evaporation [33–35]. The Physical vapor deposition (PVD) technology, including techniques such as vacuum evaporation, offers several advantages over other deposition methods in terms of film quality and cost-effectiveness. Unlike chemical vapor deposition (CVD) and shallow chemical bath deposition (SCBD) [36], PVD processes occur in a high vacuum environment, ensuring the purity of the deposited films and precise control over film thickness. In comparison to magnetron sputtering, PVD techniques typically result in lower equipment and maintenance costs, making them more cost-effective for thin film fabrication. Additionally, PVD methods such as vacuum evaporation are well-suited for depositing films on complex geometries and have been shown to produce high-quality thin films with enhanced structural and optical properties. These advantages position PVD as a superior choice for the deposition of ZnS thin films, particularly when compared to techniques such as CBD, SCBD, spin coating, and spray pyrolysis.

Recent studies have demonstrated the potential of ZnS in the fabrication of Schottky diodes and photodetectors, highlighting its versatility in optoelectronic applications [37]. The unique properties of ZnS, including its wide band gap, high optical transmittance, and excellent photoluminescence characteristics, make it an attractive material for the development of efficient photodetectors and Schottky diodes [38]. By leveraging the inherent properties of ZnS and further enhancing them through techniques such as doping, the material shows promise for realizing high-performance devices for light detection and energy conversion. These advancements underscore the growing interest in utilizing ZnS for the fabrication of Schottky diodes and photodetectors, paving the way for continued research and development in this area.

Zinc sulfide doped thin films have the potential to enhance the performance of optoelectronic devices, expand the visible spectrum range, improve stability and reliability, reduce fabrication costs, and contribute to environmental sustainability [39]. The unique properties of these materials can enable the development of novel optoelectronic devices and technologies, challenge the dominance of existing materials, and attract more researchers and funding to the field of optoelectronics [40]. motivated by the presented properties ZnS thin films doped with different percentages of Ca and Mn were deposited on glass substrates using a vacuum evaporation technique under a high vacuum. The morphological, optical, and photoluminescence properties of the samples were examined. The results showed that doping influences the properties of ZnS. The films showed that the incorporation of Ca^{2+} and Mn^{2+} influences the morphological and bandgap energy and presents high transparency in the visible region. The addition of Ca and Mn elements to ZnS thin films resulted in an enhancement of the photoluminescence properties. These properties make ZnS thin films doped Ca and Mn a potential candidate for optoelectronic applications such as light-emitting diodes (LEDs) and photovoltaic cells.

2. Experimental methods

2.1. Preparation of thin films

The deposition process was carried out on glass substrates using the vacuum evaporation technique. The powder employed consists of ZnS with a purity greater than 99.99%, Ca with a purity exceeding 97%, and Mn with a purity surpassing 98%. The depositions were performed under high vacuum $5*10^{-5}$ torr using System-NANO 36™ (Kurt J. Lesker Company) apparatus [41–43]. Fig. 1 illustrates the schematic representation of the deposition vacuum evaporation process employed in this study. To reach the optimal conditions for the deposition conducted in this experiment, powders (ZnS: Mn for the first deposition and ZnS: Ca for the second deposition) were individually placed in two tungsten boats. The deposition temperatures were manually controlled. The primary objective of this analysis is to deposit thin films with variable compositions as it is presented in Table 1, making the adjustment of deposition rates a crucial aspect. To ensure the deposition of the desired percentages, the boats were covered until rate of each material was control. All parameters, including density, Z-factor, and thickness of each element, were meticulously adjusted [44]. The thickness of the deposited layers will be affected by several parameters: evaporation rate, source geometry, substrate evaporation time, and distance between the substrates and the source. A system of pumping made up of two pumps was used to create the primary vacuum and then the secondary vacuum, afterwards, the materials were heated in a vacuum chamber, causing the evaporation of two of them according to the desired rate and then deposited simultaneously and condense on the substrate. During the whole deposition process, the substrates were spinning at a speed of 20 rpm, and the film thicknesses and deposition rates were adjusted by piezoelectric sensors. The final thickness of the films was 100 nm.

2.2. Characterization of thin films

Atomic force microscopy (AFM) was used to examine the morphological properties of the samples. The AFM imaging was performed at

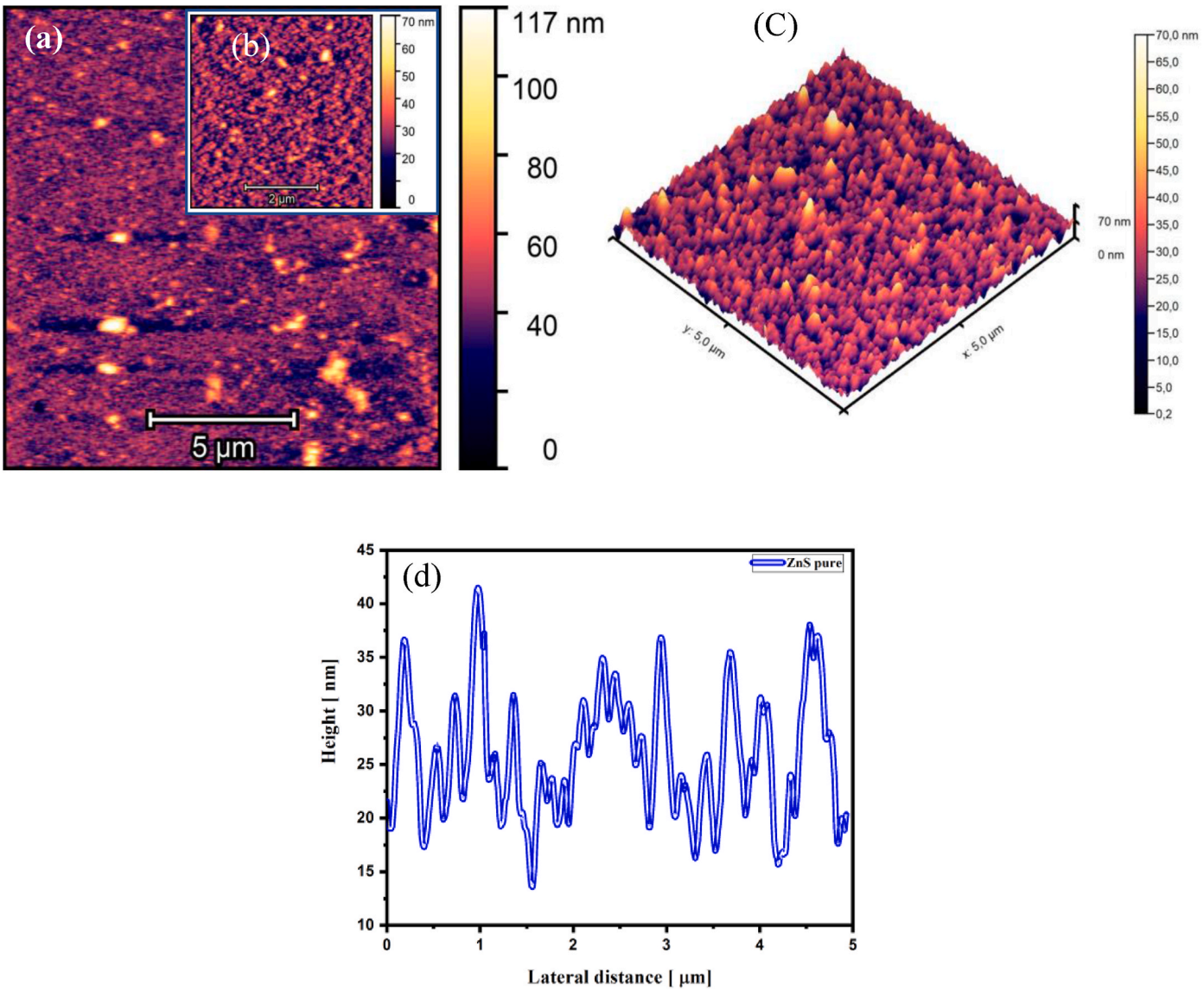


Fig. 2. (a) 2D AFM image (15 µm × 15 µm), (b) 2D AFM image (5 µm × 5 µm), (c) 3D AFM image (5 µm × 5 µm) and (d) Profile of pure ZnS thin film.

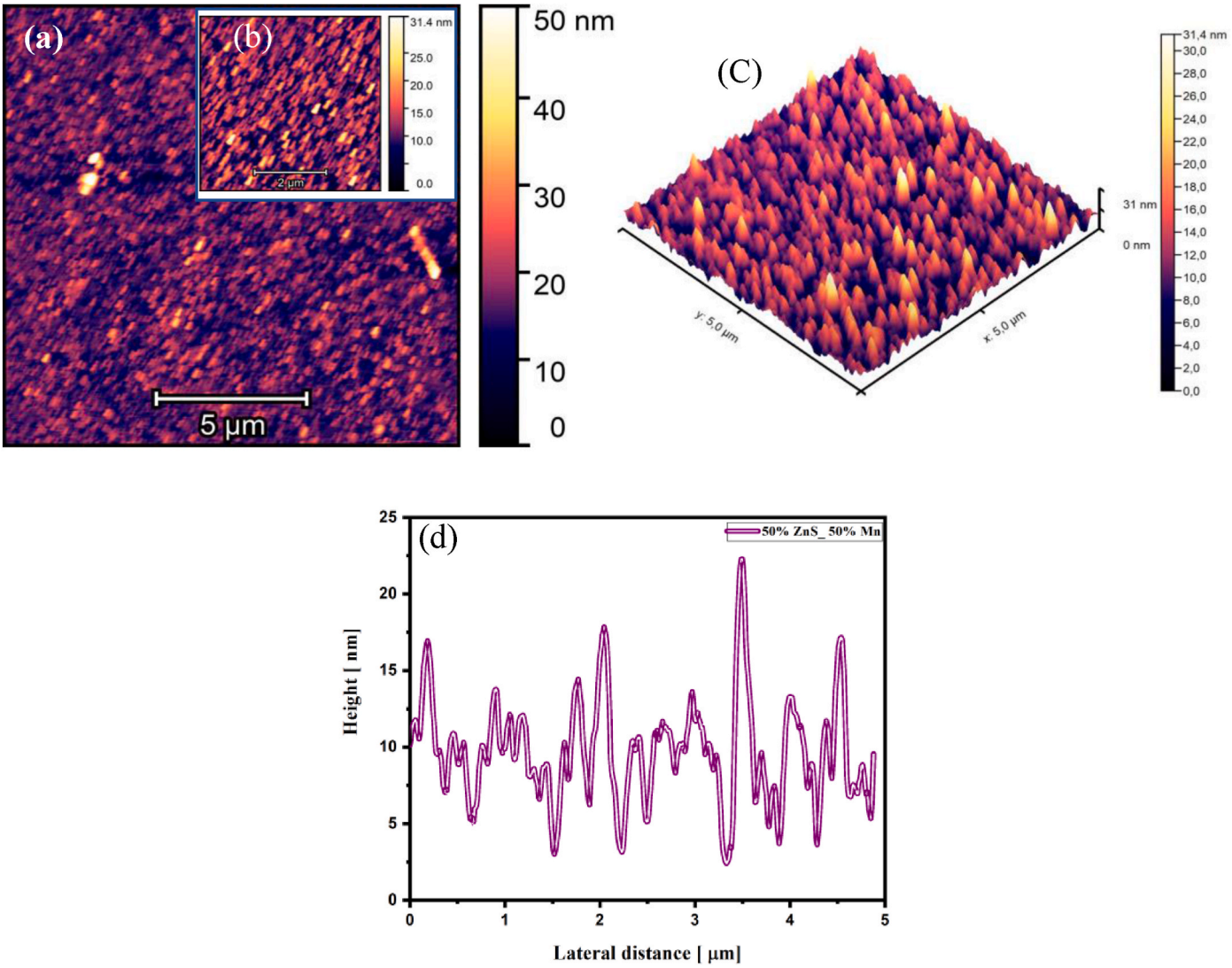


Fig. 3. (a) 2D AFM image (15 µm × 15 µm), (b) 2D AFM image (5 µm × 5 µm), (c) 3D AFM image (5 µm × 5 µm) and (d) Profile of 50%ZnS_50%Mn thin film.

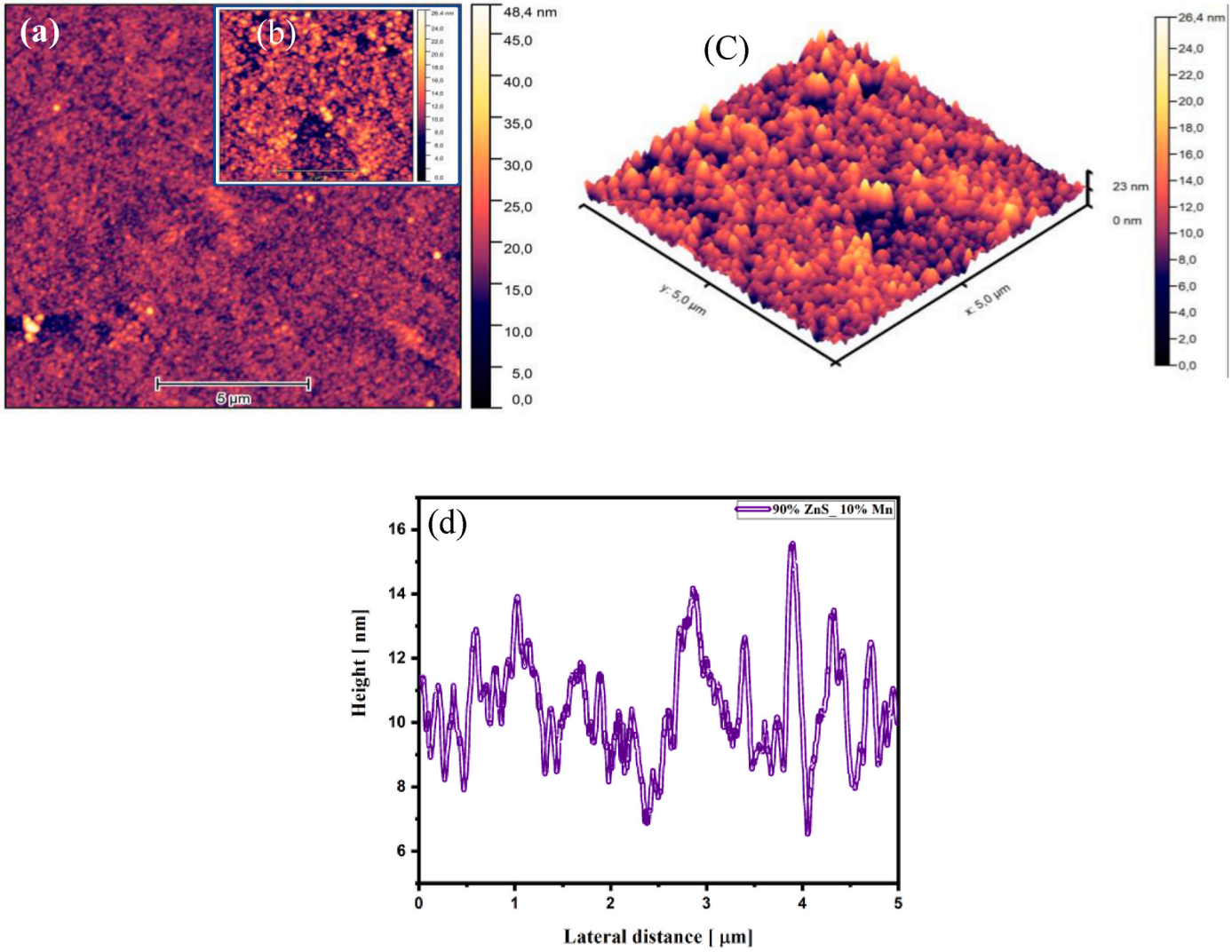


Fig. 4. (a) 2D AFM image (15 µm × 15 µm), (b) 2D AFM image (5 µm × 5 µm), (c) 3D AFM image (5 µm × 5 µm) and (d) Profile of 90%ZnS_10%Mn thin film.

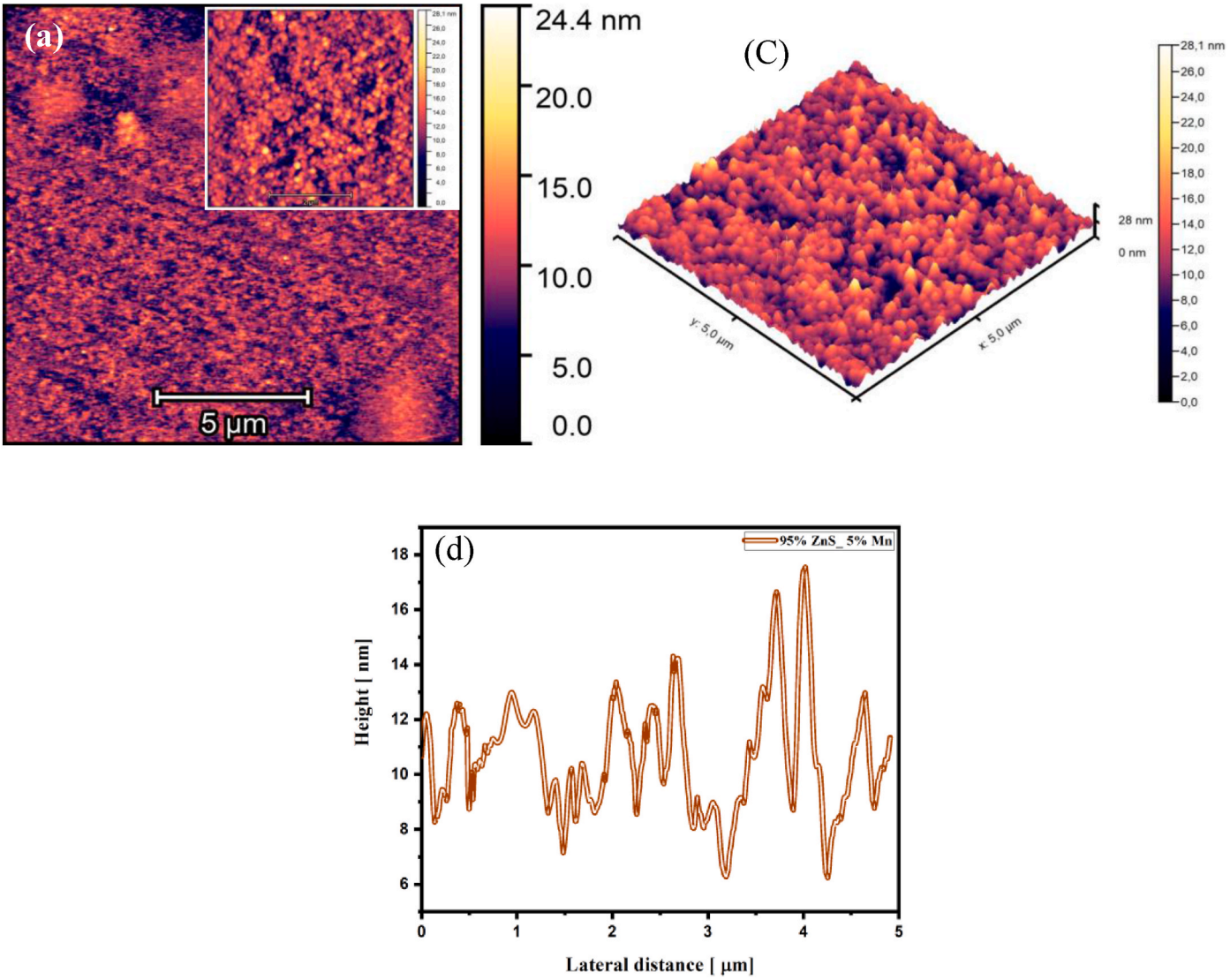


Fig. 5. (a) 2D AFM image (15 µm × 15 µm), **(b)** 2D AFM image (5 µm × 5 µm), **(c)** 3D AFM image (5 µm × 5 µm) and **(d)** Profile of 95%ZnS_10%Mn thin film.

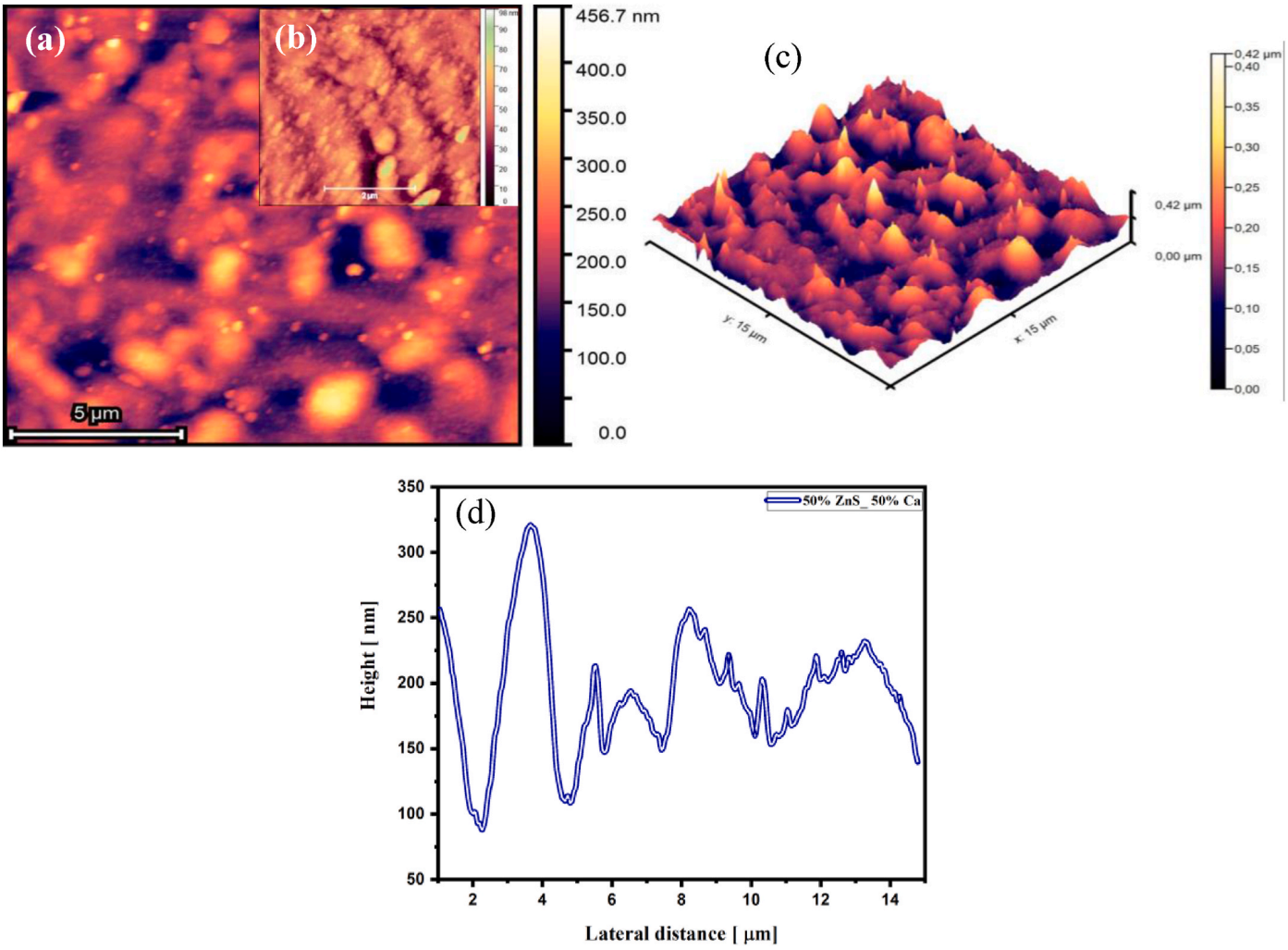


Fig. 6. (a) 2D AFM image (15 µm × 15 µm), **(b)** 2D AFM image (5 µm × 5 µm), **(c)** 3D AFM image (5 µm × 5 µm) and **(d)** Profile of 50%ZnS_50%Mn thin film.

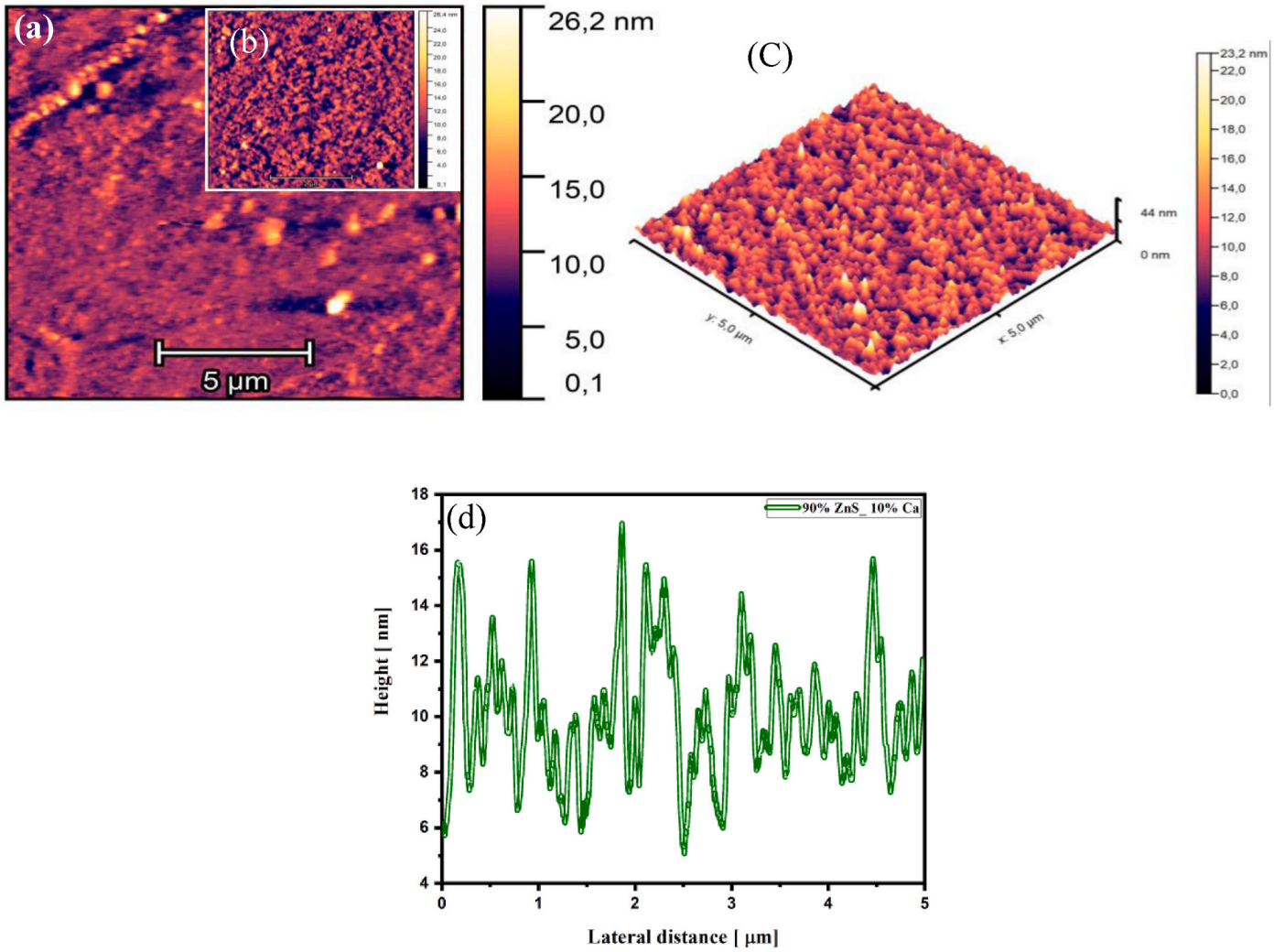


Fig. 7. (a) 2D AFM image (15 µm × 15 µm), (b) 2D AFM image (5 µm × 5 µm), (c) 3D AFM image (5 µm × 5 µm) and (d) Profile of 90%ZnS_10%Ca thin film.

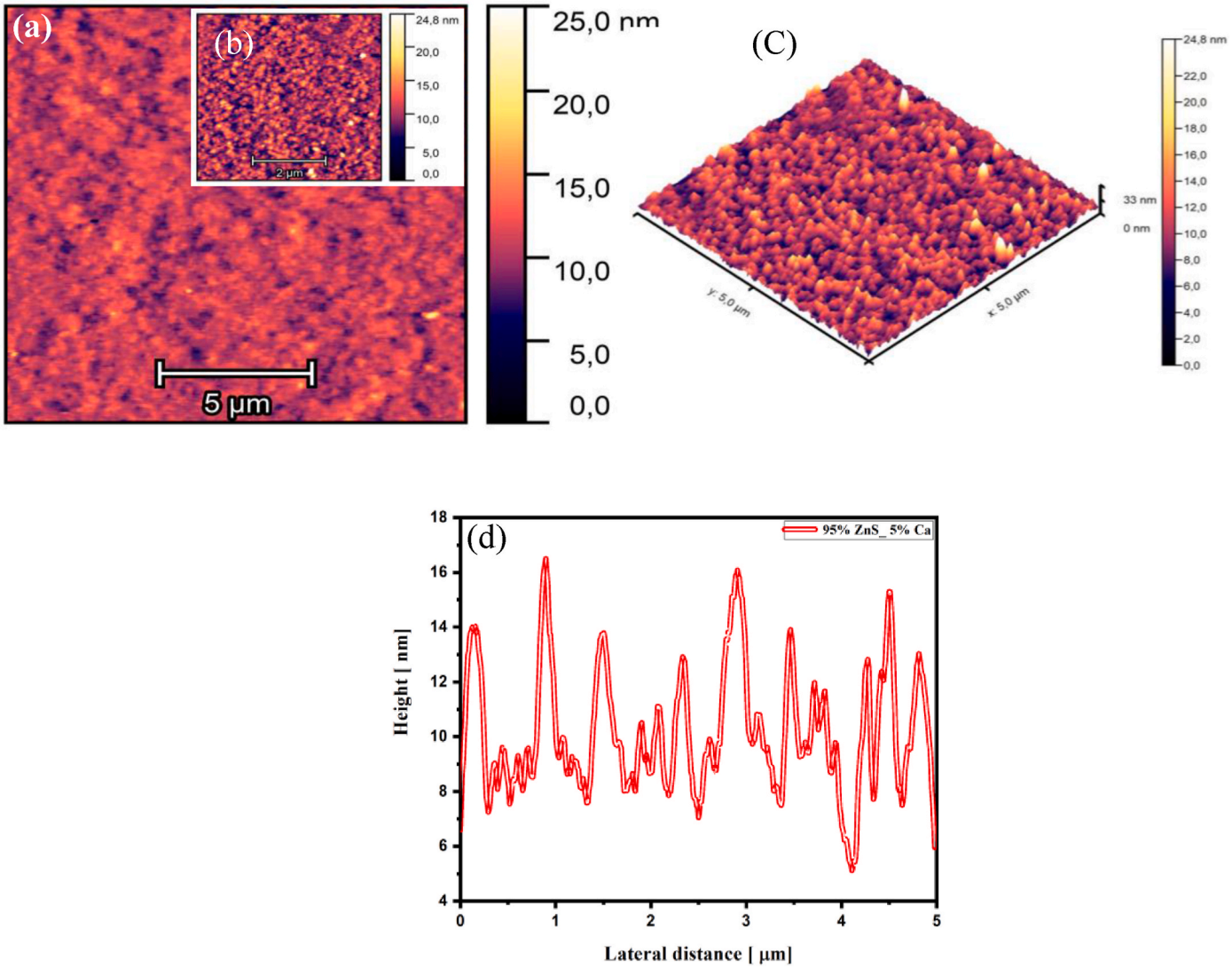


Fig. 8. (a) 2D AFM image (15 µm × 15 µm), **(b)** 2D AFM image (5 µm × 5 µm), **(c)** 3D AFM image (5 µm × 5 µm) and **(d)** Profile of 95%ZnS_05%Ca thin film.

Table 2
The values of roughness values of all the studied samples.

	Pure ZnS	5% of Mn	10% of Mn	50% of Mn	5% of Ca	10% of Ca	50% of Ca
Sq (nm)	6.32	3.6	3.2	3.1	3.2	3.2	44

room temperature in contact mode by using Nanosurf easy Scan 2 AFM with a SICON-A cantilever microscope.

The Transmission and the absorbance of the samples were measured in the spectral range 200–1100 nm at normal incidence using a double beam spectrophotometer (SPECORD 250 PLUS). Whereas the Tauc plot method was used to examine the optical band gap of the samples.

The emission and excitation spectrum of the samples were investigated by using the FluoroMax-4 apparatus and the FluorEssence software at room temperature.

The optical images were investigated by using Cascade Microtech MPS 150.

Fourier transform infrared (FTIR) spectrum in region 500–4000 cm^{-1} was obtained using NICOLET FT-IR 8700 Spectrometer.

XRF measurement was done by using M6 JETSTREAM BRUKER.

3. Results and discussion

3.1. Morphological properties

Atomic force microscopy (AFM) plays a pivotal role across various domains of thin film investigation and applications. It promotes a profound comprehension of surface characteristics, allowing the enhancement of device performance and the customization of materials for specific functionalities [45]. AFM operates as a crucial tool in assessing morphological attributes like surface topography, grain size, and roughness. Therefore, thin films exhibit varied roughness levels, influenced by deposition methods and substrates, which in turn can impact optical, electrical, and mechanical properties. Through detailed examination of surface properties and optimization of film deposition techniques, AFM aids in the advancement of optoelectronic devices [46].

In order to evaluate the influence of doping on the morphological properties of the films the roughness (Sq) and the profiles of the films

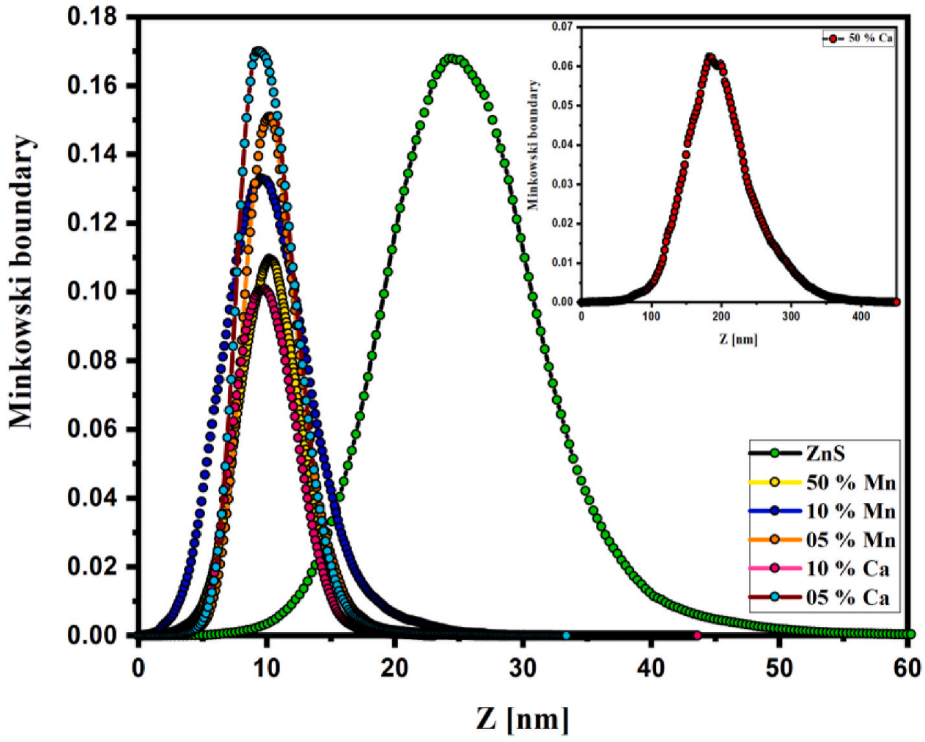


Fig. 9. The Minkowski surface S(z) [no unit] for the scanning areas of 15 μm × 15 μm for 50% ZnS_ 50%Ca and 5 μm × 5 μm for all the sample.

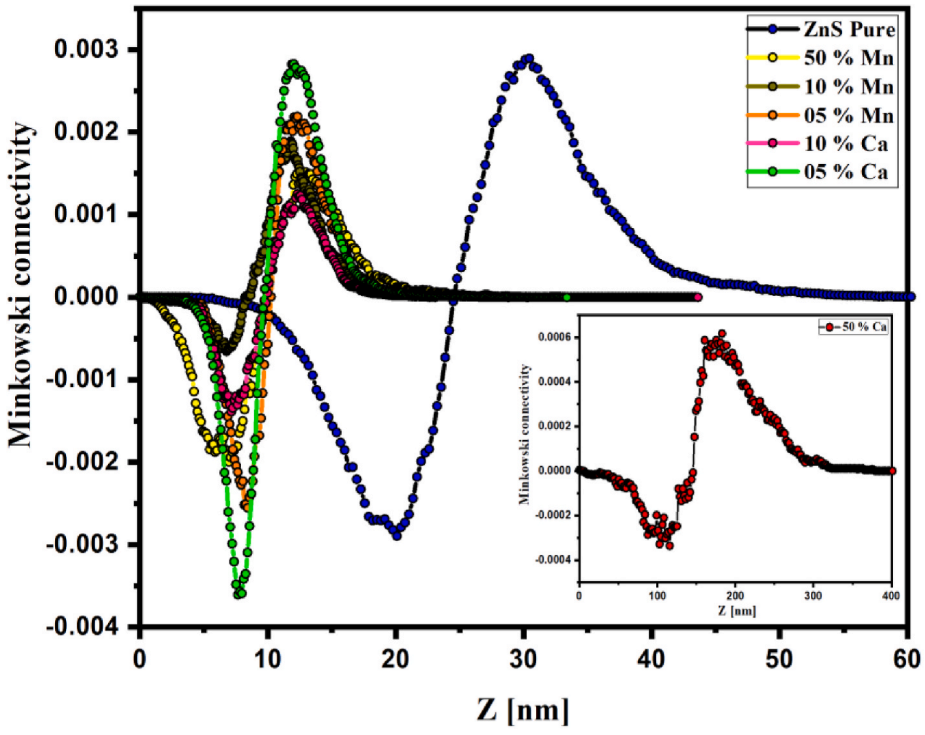


Fig. 10. The Minkowski connectivity χ(z) [no unit] for the scanning areas of 15 μm × 15 μm for 50% ZnS_ 50%Ca and 5 μm × 5 μm for all the samples.

have been determined.

Figs. 2–8 represent 2D pictures, 3D pictures, and profiles of the elaborated thin films.

As the 3d and 2D pictures show the doping of ZnS thin films influences the morphological properties of the film. The doping with Mn leads to the formation of smaller, sharper, and more uniform nanograins, which exhibit different morphological properties compared to undoped ZnS. The addition of Mn to ZnS influenced the grain size of the thin film, and similar results were found [47]. In general, doping Mn leads to the formation of smaller grains and influences the surface roughness of ZnS thin films, as illustrated in Table 2, the value of roughness is twice as smaller as that of undoped ZnS. The addition of Mn leads to a smoother surface, which can improve the optical and electronic properties of the material. Wille doping of ZnS thin films with Ca

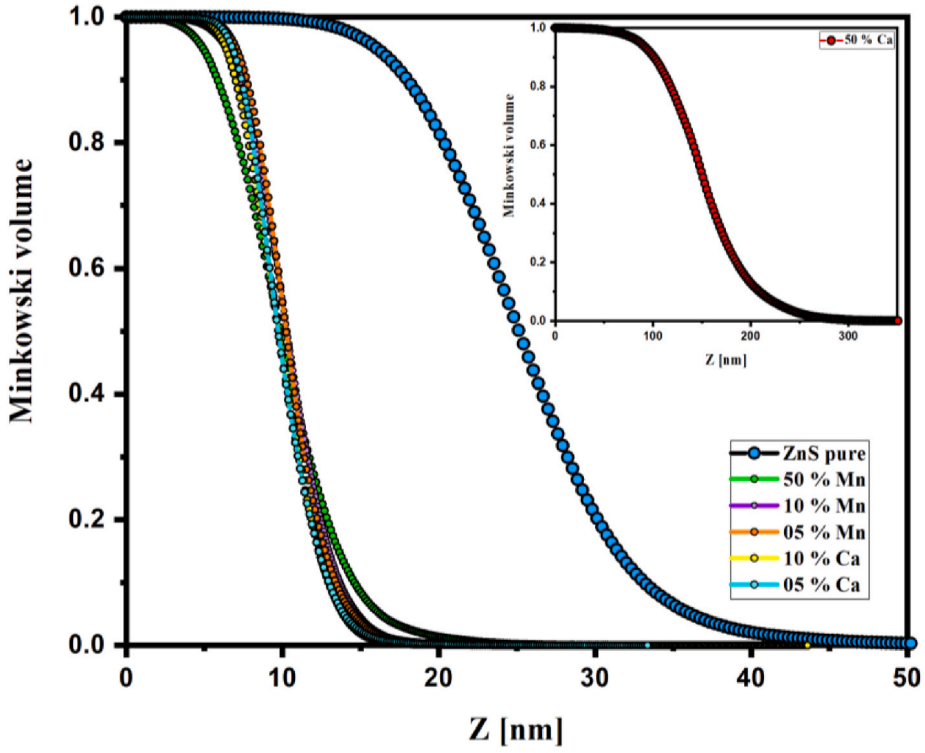


Fig. 11. The Minkowski volume V(z) [no unit] for the scanning areas of 15 μm × 15 μm for 50% ZnS_ 50%Ca and 5 μm × 5 μm for all the samples.

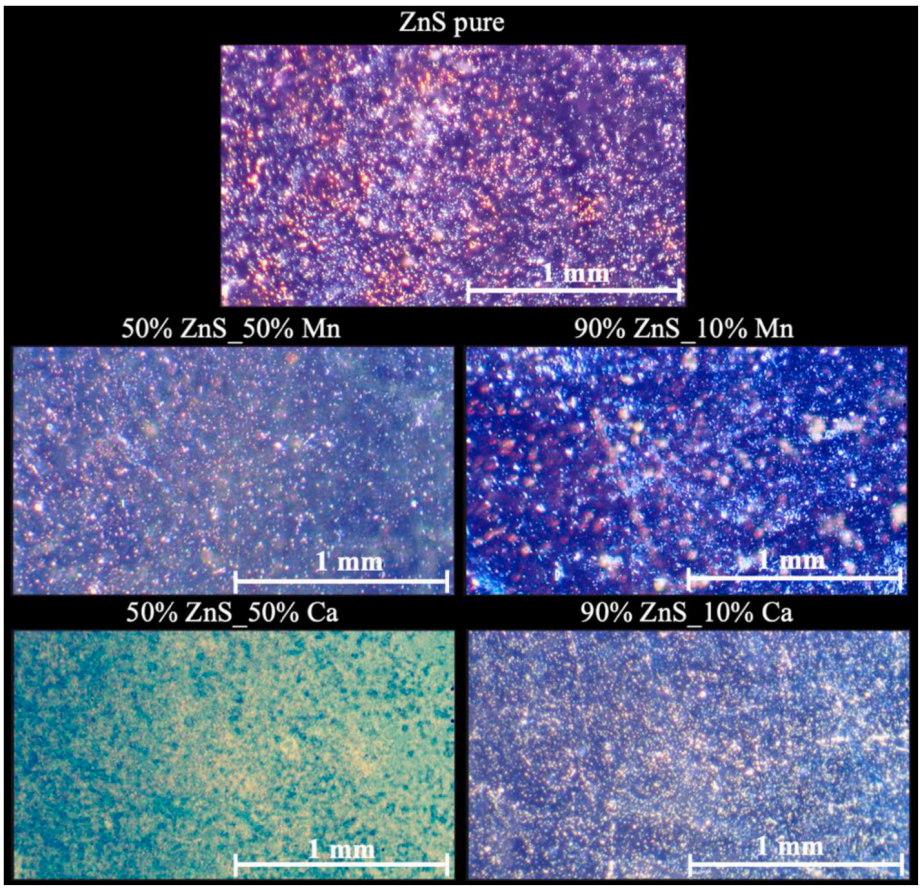


Fig. 12. Optical images of ZnS Pure and Mn/Ca Doped Thin Films at Different Concentrations.