



Synthesis, diffused reflectance and electrical properties of nanocrystalline Fe-doped ZnO via sol–gel calcination technique

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ABSTRACT

The nanocrystalline ZnO:Fe semiconductor oxides were successfully synthesized via the sol–gel calcination method. Structural, optical and electrical properties of the investigated samples were characterized by various techniques such as atomic force microscopy (AFM), UV–vis absorption and electrical transport measurements. The optical band gap for undoped ZnO (3.19 eV) decreases (2.75 eV) with increasing Fe-doped ZnO (20%). The temperature dependences of the electrical conductivities of undoped ZnO and Fe-doped ZnO were measured and analyzed by Arrhenius equation. The electrical conductivity of the samples decreases with the increase of Fe doping ratio; hence, the electrical conductivity mechanism is controlled by thermally activated processes. To support the nanostructure of Fe-doped ZnO, AFM micrographs were performed.

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1. Introduction

Semiconductor ZnO has become one of the most popular materials for electrical and optical applications over the time. It is promising material for many optoelectronic applications such as ultraviolet lasers, light-emitting diodes, p–n junction devices, thin-film transistor, solar cells, acoustic devices, chemical and biological sensors. For applications of transparent and conducting electrode in solar cells and thin-film transistor, the development of low-resistive ZnO films with high transparency is crucial [1]. Due to its large binding energy (60 meV), wide band gap (3.37 eV) and easy facilitate synthesis and assembly methods, the utilization of ZnO has covered various fields such as electric transistors [2], photovoltaic devices [3] and chemical sensors [4]. Nowadays, the nanostructure ZnO materials such as ZnO nanowires [5], nanoparticles [6], and nanotetrapods [7] have attracted the wide attention since their large surface area and enhanced quantum confinement that lead to novel electrical and optical properties for device application. Studies have showed that the surface of ZnO nanocrystals can play an important role in carrier transport. The unbounded oxygen chemisorbed on nanocrystal

surface serves as traps for charge carriers, thus, increasing the interfacial potential and lowering carrier mobility [1].

However, in order to enhance the versatility of ZnO to meet the different requirements of application, structural modifications have usually been utilized, among which metal ion doping is the most well known and effective approach. The nanomaterials described by the formula MFe_2O_4 can be prepared using various metals ions (like $M=Fe(II)$, $Mn(II)$, $Co(II)$, $Ni(II)$ and $Zn(II)$) [8–14]. Such doping was proved to control the electrical conductive type, modify the carrier concentration and adjust the energy band structure. Fe^{3+} doping metal oxide is expected to enhance the potential ferromagnetic properties [15].

Spintronics (spin-based electronics) based on diluted magnetic semiconductor oxides, is currently an active area of research because spin-based multifunctional electronic devices have several advantages over the conventional charge based devices regarding data-processing speed, nonvolatility, and higher integration densities [16]. Diluted magnetic semiconductors (DMSs), i.e., semiconductors with dilute concentration of magnetic dopants are expected to be promising materials for spin-based multifunctional devices. An ideal DMS must satisfy certain conditions, such as high Curie temperature (T_C) and the easy incorporation of p- and n-type carriers. Besides the need for materials with high Curie temperature along with high magnetic moments, the critical point is to assure that dopant atoms are uniformly dissolved into the host lattice and that the resulting

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ferromagnetism (FM) indeed originates from the doped matrices [16,17].

The sol–gel method has advantages such as low cost, easy to handle, safe, and the non-vacuum method, to prepare ZnO materials over conventional synthesis methods such as magnetic sputtering, chemical vapor deposition, and hydrothermal reaction [18]. Moreover, it is easy to realize the dopants incorporation using a one-route process simply by modulating the ingredient of the precursors.

In this communication, synthesis of nanopowders based on Fe-doped ZnO via the sol–gel calcination method is introduced. Up to our knowledge, there are a few works on the characterization of sol–gel synthesized Fe-doped ZnO nanopowders especially optical band gap calculations based on the measured diffused reflectance. The structure and morphology of the Fe-doped ZnO have then been characterized by AFM micrographs. In addition, the diffused reflectance was used to determine the optical constants of Fe-doped ZnO nanopowders. Also, the electrical conductivity of Fe-doped ZnO nanopowders was determined.

2. Experimental details

2.1. Samples preparation and characterization

The nanocrystalline ZnO and Fe-doped ZnO samples were synthesized by sol–gel calcination route similar to the other metal oxide [19]. The appropriate amounts of 0.2 M zinc acetate dehydrate ($(\text{ZnCH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and 0.2 M iron chloride 6-hydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were dissolved in 2-methoxyethanol (0.2 M) at a constant magnetic stirring for 10 min then, mono-ethanolamine (0.2 M) as stabilizer was added to the solution during the stirring and the solution was stirred constantly for 2 h at 60 °C. The ZnO precursor containing Fe-dopants were prepared with different percents (5, 10, 15 and 20%) of iron chloride 6-hydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$). The gels of undoped and ZnO doped with 5, 10, 15 and 20% Fe contents were calcinated at 600 °C for 5 h in a tube furnace to evaporate the solvents, the nanopowders ZnO with the dopants is formed accordingly. The obtained nanopowders were reground and pelletized under hydraulic pressure of 5 ton and were sintered at 1100 °C in air for 30 min.

The electrical conductivity of the samples was measured as a function of temperature using a KEITHLEY 6517A electrometer. The structural properties of the nanopowders were investigated by Park System XE-100E atomic force microscopy (AFM). The diffuse reflectance spectra of the investigated samples were performed using a Shimadzu UV–vis–NIR 3600 spectrophotometer using integrating sphere attachments.

3. Results and discussion

3.1. Optical properties of undoped and Fe-doped ZnO nanopowders

3.1.1. Diffused reflectance: Theoretical background

When electromagnetic radiation in the UV/vis/NIR wavelength range interacts with a sample, four results are possible: the radiation is absorbed, transmitted, reflected or scattered. Typically UV/vis/NIR spectrometers are equipped to measure the transmittance or absorbance of a transparent solid or homogeneous solution. Reflectance spectroscopy is used for samples that are difficult to analyze by transmission measurements. The samples can usually be analyzed without the need of preparation or any modifications. Reflectance measurements can be divided into two basic categories: internal and external reflectances. The technique of attenuated total reflection (ATR) is employed for

internal reflectance measurements as the beam of radiation passes through an ATR element (crystal) in good contact with the sample. For external reflectance measurements, the beam of radiation is reflected directly from the sample surface [20–22].

However, when spectrometer equipped with the proper accessories, it is possible to measure the reflected and scattered energy from a sample and the reflected radiation can be either specular or diffuse. An integrating sphere, when integrating sphere used in combination with the spectrometer, is a valuable tool for collecting and measuring specular and/or diffuse reflectance. In addition, an integrating sphere can be used to capture the scattered light from a sample.

The integrating sphere is placed in the sample beam of the spectrometer and is used in the place of the sample beam detector. The instrument detector, external to the sphere, detects the reference beam as shown in Fig. 1(a–d). The sphere can be used over the wavelengths range for either diffuse reflectance or diffuse transmittance. The external reflectance measurements can divide into two types as follows.

3.1.1.1. Diffuse reflectance (DR). Diffuse reflectance is an excellent diagnostic tool for powdered, crystalline and nanostructure materials in different spectral ranges. In external reflectance, incident radiation is focused onto the sample and two forms of reflection can occur i.e. diffuse and specular. Energy from the incident beam that penetrates one or more particles is reflected in all directions and this component of light is called diffuse reflectance. On a rough or irregular surface material, such as a powder, specularly reflected light is a minor contributor to the overall signal. Therefore, reflectance accessories are optimized to increase collection of the diffuse reflectance component and decrease the specular component. Collection of the diffusely scattered light can be made directly from a sample or by using an abrasive sampling pad for intractable samples. Many samples will give diffusely reflected spectra including powders, fibers or matt surfaced samples such as textiles [20–22].

Diffuse reflectance relies upon the focused projection of the spectrometer beam into the sample where it is reflected, scattered and transmitted through the sample material (shown on the right). The back reflected and diffusely scattered light (some of which is absorbed by the sample) are then collected by the accessory and directed to the detector optics. Only the part of the beam that is scattered within a sample and returned to the surface is considered to be diffuse reflection. Some powders may be analyzed by diffuse reflectance as neat samples (coal samples, soil samples, diffuse coatings on a reflective base) [23].

3.1.1.2. Specular reflectance. Specular reflectance is a non-destructive method for surface measurements using a mirror-like reflection from the shiny (or matt) surface of a sample. Specular reflectance occurs when the reflected angle of radiation equals the angle of incidence. The amount of light reflected depends on the angle of incidence, the refractive index, surface roughness and absorption properties of the sample. A particularly useful application of specular reflectance is the study of surface coatings, such as surface treated metals, paints and polymers. Increased path lengths through thin coatings can be achieved using grazing angles of incidence (typically 85° angle) and this gives increased sensitivity. Thicker coatings in the micrometer thickness range can be studied using angles typically at 30° incidence. The band intensities depend on the type and degree of polarization of light [20–24].

The Kubelka–Munk theory is generally used for analyzing the diffuse reflectance spectra obtained from weakly absorbing samples. In this case; the Kubelka–Munk equation at any

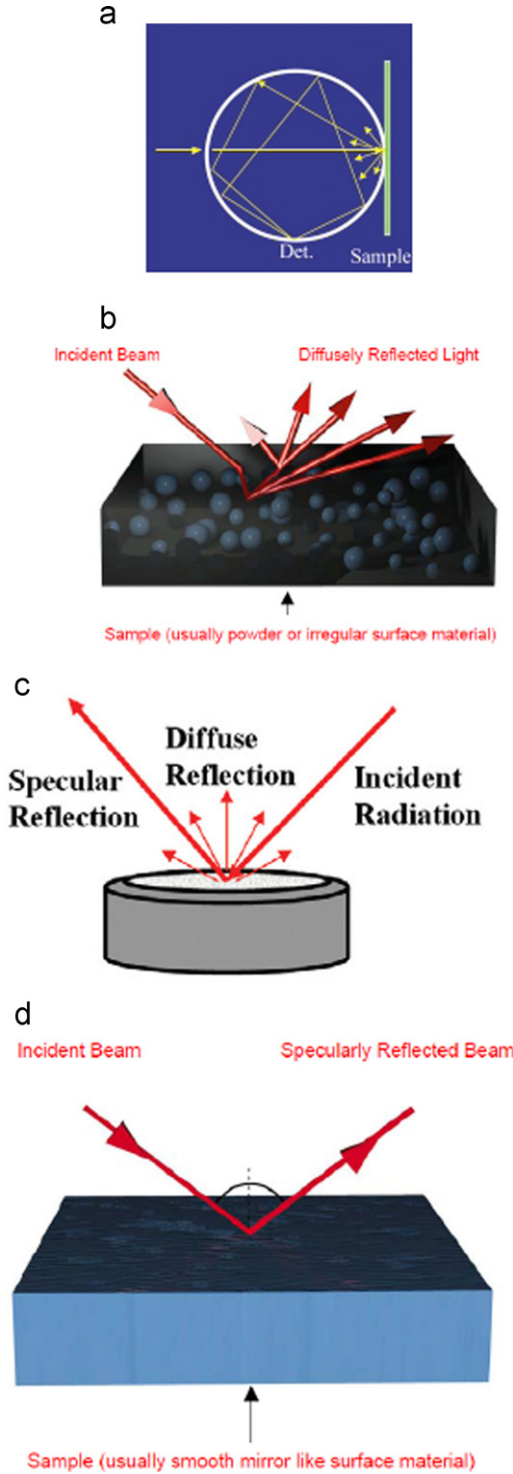


Fig. 1. (a) Shows diagrammatically how the light enters the sphere, bounces around and ultimately ends up at the detector. (b) Shows schematically the diffused reflected light. (c) Shows diagrammatically the incident radiation, diffuse reflection and specular reflection. (d) Shows diagrammatically the incident beam and the specular reflection according to the mirror.

wavelength becomes [23–30]

$$F(R) = \frac{(1-R)^2}{2R}, \quad (1)$$

where R is the absolute reflectance of the sampled and $F(R)$ is the so-called Kubelka–Munk function. Fig. 2 presents the plots of the

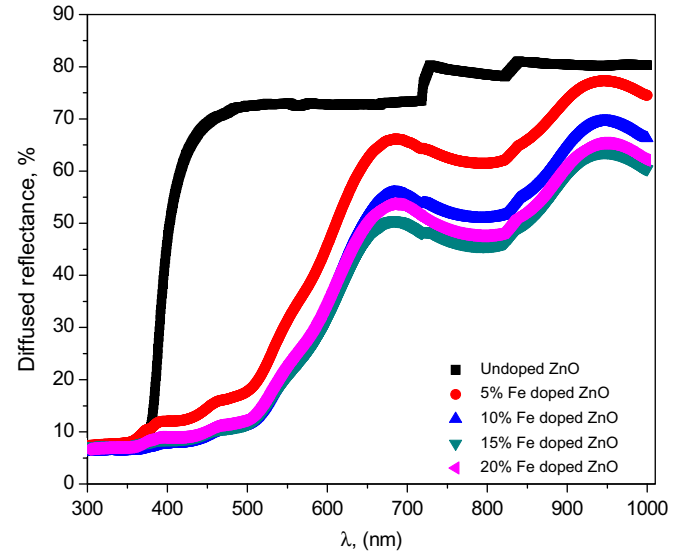


Fig. 2. Plotting of the diffused reflectance versus wavelengths for undoped ZnO and 5%, 10%, 15%, 20% Fe-doped ZnO nanopowders.

diffused reflectance for undoped and Fe-doped ZnO nanopowders. It is clear that the diffused reflectance for undoped and doped samples increased with increasing wavelengths. Also, the incorporation of Fe dopants into the host ZnO leads to the decrease of the diffused reflectance. These data are in good agreement with the data reported before by Saleh et al. [31] for Fe-doped ZnO with concentrations 5–31%. As seen in Fig. 2, the absorption edge changes strongly with increasing Fe dopants, this indicates that a strong interaction between Zn and Fe molecules. $F(R)$ values were converted to the linear absorption coefficient by the following relation [30,32]:

$$\alpha = \frac{F(R)}{t} = \frac{\text{absorbance}}{t} \quad (2)$$

where t is the thickness of pure and Fe-doped ZnO pellets which approximately equals 0.5 mm. It is well known that the optical transitions in semiconductor materials are taken place by direct and indirect transitions. The value of the optical band gap E_g can be calculated using the fundamental absorption, which corresponds to electron excitation from the valance band to the conduction band. The optical band gap of samples can be then determined by the following relation [33]:

$$\alpha h\nu = A(h\nu - E_g)^n. \quad (3)$$

This equation can be rewritten as for the diffused reflectance calculations

$$(\alpha h\nu) = \left(\frac{F(R)h\nu}{t} \right) = A(h\nu - E_g)^n, \quad (4)$$

where A is an energy-independent constant and E_g is the optical band gap, n is a constant which determines the type of optical transitions and for indirect allowed transition, $n=2$; and indirect forbidden transition, $n=3$, for direct allowed transition, $n=1/2$; for direct forbidden transition, $n=3/2$. The optical band gap of the samples was determined from the plots of $(F(R)h\nu/t)^2$ as a function of photo energy $h\nu$ (see Fig. 3). Extrapolating the linear portions of these plots to the x -axis (photon energy) i.e. $h\nu=0$, values of the optical band gap for pure and Fe-doped ZnO were obtained as shown in Table 1. In details, the optical band gap of undoped ZnO sample is 3.19 eV, which is smaller than the band gap of bulk ZnO materials (3.37 eV) but E_g value is in good agreement with the determined band gap from diffused reflectance calculated by

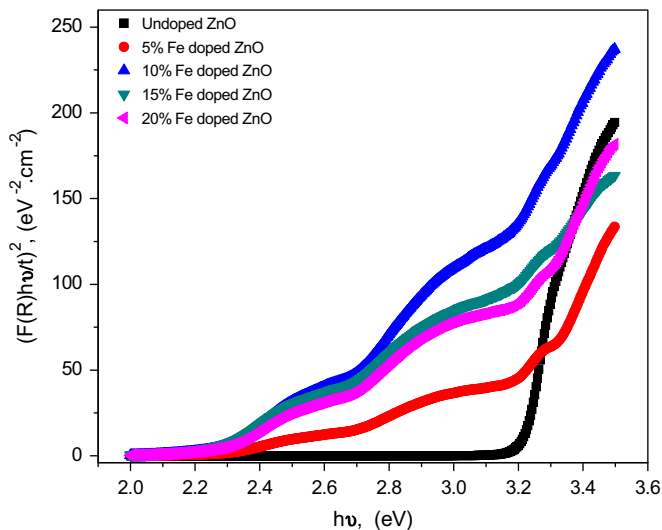


Fig. 3. Plotting of $(F(R)hv/t)^2$ versus the photon energy for undoped ZnO, and 5%, 10%, 15%, 20% Fe-doped ZnO nanopowders.

Table 1

Optical band gap E_g and the electrical activation energy ΔE_A of undoped and Fe-doped ZnO nanopowders.

Samples	Optical band gap	Activation energy (ΔE_A) (meV)	
	E_g (eV)	(ΔE_{A1}) (eV) for region (I)	(ΔE_{A2}) (eV) for region (II)
Undoped ZnO	3.19	0.187	0.358
5% Fe doped ZnO	3.08	0.424	0.855
10% Fe doped ZnO	2.83	0.458	0.886
15% Fe doped ZnO	2.79	0.361	0.646
20% Fe doped ZnO	2.75	0.354	0.986

other authors i.e. equals 3.22 eV [27]. With the increase of Fe doping, the optical band gap decreases from 3.19 eV of undoped sample to 2.75 eV of 20% doped sample (Table 1). Table 1 shows that the absorption edge shifts to the higher wavelengths with increase of Fe dopant and leads to the decrease of the band gap of the Fe-doped ZnO. This indicates that the optical band gap of ZnO changes strongly with Fe-dopants. It is expected that the changes of the band gap of ZnO doped with Fe are due to the increase of carrier concentrations which lead to the Burstein–Moss effect [34]. The shift in the optical band gap of semiconductor due to doping effect is known as Burstein–Moss shift. In order to further support our results based on the calculations of the optical constants of undoped and Fe-doped ZnO, we calculated the absorption index k based on the diffused reflectance data from the following equation: $k = \alpha\lambda/4\pi$. Plotting of the absorption index as a function of wavelengths is shown in Fig. 4. It is clear that the absorption index undoped ZnO nanopowders is very small (10^{-4}) compared with Fe-doped ZnO nanopowders. These lower values of the absorption index comply with the calculations of the optical constants based on the diffused reflectance. In general, The Kubelka–Munk theory is used for analyzing the diffuse reflectance spectra obtained for weakly absorbing samples. The dependence of E_g on Fe dopants in general is less than the undoped ZnO. Diouri et al. [35] and Bylsma et al. [36] have attributed the band-gap decrease of transition-metal doped II–VI semiconductors to the sp – d spin-exchange interactions between the band electrons and the localized d electrons of the transition-metal ion substituting the cation, which has been experimentally confirmed by Ando et al. [37] in $Zn_{1-x}Co_xO$. Thus, in films, the s – d

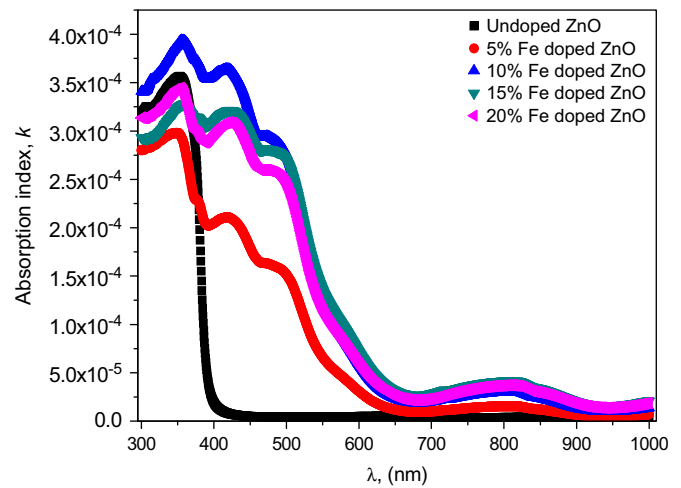


Fig. 4. Plotting of the absorption index versus the photon energy for undoped and 5%, 10%, 15%, 20% Fe-doped ZnO nanopowders.

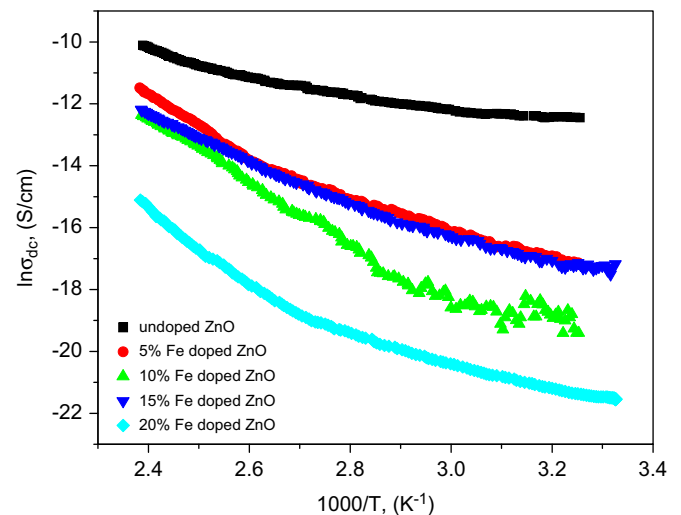


Fig. 5. Temperature dependent of the electrical conductivity of undoped and Fe-doped ZnO nanopowders.

and p – d exchange interactions give rise to a negative and a positive correction to the conduction- and the valence-band edges, respectively, reducing the band-gap. Other groups reported that the red-shift in the band gap energy of transition-metal doped II–VI semiconductors is attributed to the sp – d spin exchange interaction between the band electrons and the localized d electrons of the transition metal ion substituting the cation [38,39,31].

3.2. Electrical conductivity of undoped and Fe-doped ZnO nanopowders

The electrical transport mechanisms of Fe-doped ZnO samples were studied by the temperature dependent conductivity as seen in Fig. 5. The electrical conductivity increases with increasing temperature of all samples. All the curves can be separated into two linear regions (I and II). In each region, the electrical conductivity can be all analyzed by Arrhenius's equation [40]:

$$\sigma_{dc} = \sigma_0 \exp \left(\frac{\Delta E_A}{kT} \right) \quad (5)$$

where σ_0 is the pre-exponential factor, k is the Boltzmann's constant and ΔE_A is the activation energy for the conductivity.

Table 1 demonstrates the ΔE_A values in various regions calculated from the linear portions of curves in Fig. 5. The electrical conductivity results indicate that the electrical conduction mechanism is thermally activated process and dc conductivity increases exponentially over the studied range of temperatures. The electrical conductivity of the ZnO decreases with increasing Fe dopants. The variation of activation energy indicates different conduction mechanisms in different temperature regions. The electrons are excited thermally from donor levels to the conduction band, as the temperature is increased. The obtained activation energy values correspond to the defect energy levels in optical band gap of the samples. The defect levels are intrinsically formed and their positions in the band gap vary with Fe dopants. These levels affect negatively the electrical conductivity of the samples. With increasing temperature, more charge carriers overcome the activation energy barrier and these carriers participate in the electrical conduction.

3.3. Atomic Force Microscopy (AFM) analysis

Atomic Force Microscopy (AFM) has been implemented as a structural characterization technique for the examination of nanopowders materials in contact mode. AFM offers the significant advantage of probing in high details; the surface topography qualitatively (by surface images) and quantitatively (by mathematical quantities like surface roughness) due to its nanometer-scale spatial resolution, both lateral and vertical. AFM has proved to be very helpful for the determination and verification of various morphological features and parameters. The AFM images of Fe-doped ZnO nanopowder samples are shown in Fig. 6. The undoped ZnO and Fe-doped ZnO samples show a spherical grain of varying sizes with Fe dopants. The samples are formed from cluster spheres with varying sizes. The mean values of the grain size of clusters are determined for undoped and Fe-doped ZnO which changed with Fe-dopants. The calculated crystallite size of

the undoped and Fe-doped ZnO samples is given in Table 2. It is clear from this table that the size of the crystallite changes from 17 nm to its maximum 24 nm of 15% Fe dopant and after that it decreases to 19 nm for 20% Fe dopant.

4. Conclusion

ZnO:Fe semiconducting metal oxides were successfully synthesized by the sol-gel calcination method and investigated by different spectroscopic techniques that support the nanopowders structure of undoped and Fe-doped ZnO. In addition, AFM micrographs of Fe-doped ZnO samples show a spherical grain of varying sizes with Fe dopants. The surface morphology, optical and electrical properties of the undoped and Fe-doped ZnO nanopowders was investigated. The optical band gaps of undoped and Fe-doped ZnO samples were calculated which shows a significant change with Fe dopants percentage. The dependence of E_g on Fe doped ZnO compared with undoped ZnO interpreted by $sp-d$ spin-exchange interactions between the band electrons and the localized d electrons of the transition-metal ion substituting the cation. Moreover, the temperature dependence measurements show that the electrical conductivity is controlled by thermally activated processes.

Table 2
The calculated crystallite size of Fe-doped ZnO samples from AFM.

Samples	Crystallite size (nm)
Undoped ZnO	17.6
5% Fe doped ZnO	19.6
10% Fe doped ZnO	18.2
15% Fe doped ZnO	24.0
20% Fe doped ZnO	19.0

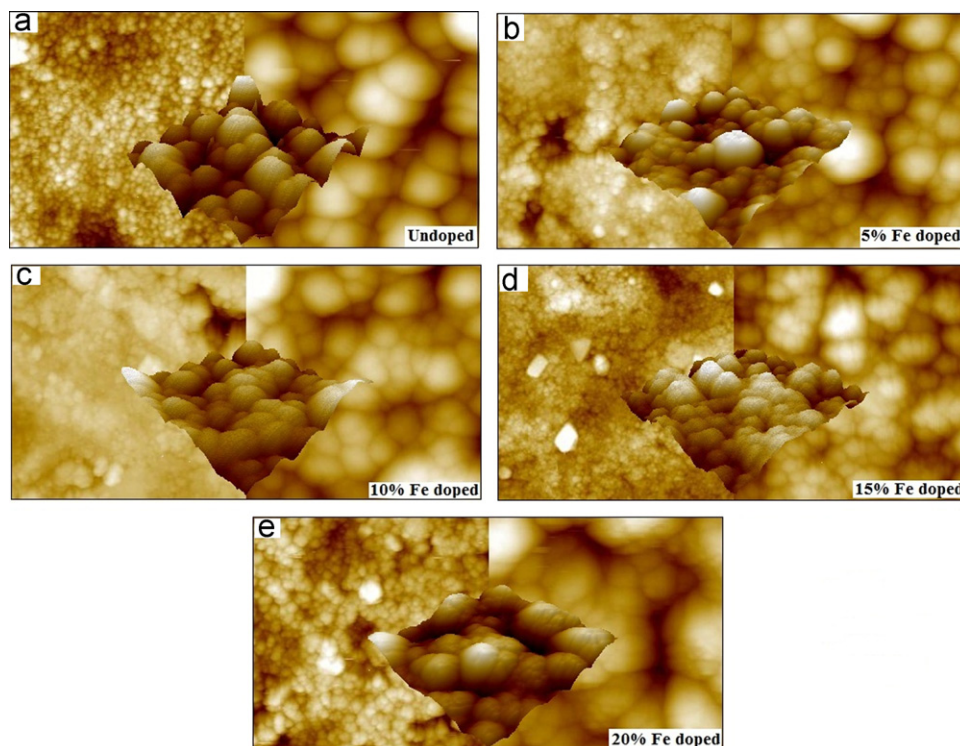


Fig. 6. AFM images of ZnO samples with different Fe doping ratios: (a) undoped, (b) 5%, (c) 10%, (d) 15% and (e) 20%.

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