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Effect of $^4\text{He}^{2+}$ ion irradiation on the optical, electrical, morphological, and structural properties of ZnO thin films

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Abstract

A study of the effect of 2.5 MeV $^4\text{He}^{2+}$ ion irradiation on the optical, electrical, morphological and structural properties of ZnO thin films is presented. Polycrystalline zinc oxide thin films were deposited on soda lime glass substrates using the spray pyrolysis technique. During the process, the substrates' surfaces were kept at 400, 450 and 500 °C. The samples were analyzed by different techniques and the optical results showed a red shift in the energy band gap after irradiation. It was also confirmed that the wurtzite-type hexagonal structure of the ZnO films remained after irradiation, the crystallite size increased and the lattice parameters decreased due to He$^{2+}$ irradiation. SEM micrographs revealed that ion irradiation favors the nucleation and the formation of grains in the films. Micrographs showed nanometric particles with spherical and flake-like forms, which depend on the deposition temperature. A decrement in the average particle size of the samples deposited at 400 and 450 °C was observed after irradiation; meanwhile, an increase in the particle size was detected in the film deposited at 500 °C. The resistivity values increased with He$^{2+}$ ion irradiation.

1. Introduction

Zinc oxide (ZnO) is an II-VI semiconductor with a band gap of 3.3 eV and excitonic energy of 60 meV, abundant in nature, low cost, and low toxicity. These properties have made it a highly appreciated material for research and applications, especially in optoelectronics and photocatalysis.

ZnO can absorb UV light; however, if the goal is to increase the photocatalytic activity, it is required to enhance the ability of the semiconductor to absorb light between 400 and 700 nm. To achieve this, the decrement of its band gap is mandatory. Some research [1, 2] have carried out to reduce the band gap by doping ZnO with transition metals since this procedure does not modify the crystalline structure of the semiconductor; however, some other physical properties are changed. In this sense, alternatives have been sought to modify the band gap without substantially changing the material’s properties.

Ion implantation is a technique capable of tailoring the physical properties of materials since there is sufficient control over the experimental conditions, such as the type of ion, its energy, the fluence, and the implantation angle of the projectile; which can modify the defects produced in the structure of the material, the depth of the doping region, the number of defects produced in the material and the possibility of implanting at the surface when a low energy accelerator is not available, respectively. Changing these setup conditions makes it possible to modify well-defined areas of the material, as small or large as required. It is also feasible to alter the material’s surface or an internal region by changing the ion energy, its angle of implantation, or both. This is the main reason why ion irradiation has become an important technique to modify the physical properties of materials and several groups have studied the irradiation of different semiconductors, such as silicon, silicon carbide, germanium, gallium arsenide and in particular ZnO [3, 4], by using different ions at different energies and fluences. For instance, Tomic, et al [5] worked with silicon and showed evidence that a 23 MeV I beam can anneal the pre-existing damage of the material’s structure. Levalois and Marie [6] studied the electrical behavior...
of germanium irradiated with an 880 MeV Pb beam at different fluences. They showed that resistivity increased at low fluences, reached a maximum value and decreased when fluence is increased. They also reported that the energy gap of silicon carbide decreased with fluence when the material was irradiated with 5.5 GeV Xe ions. On the other hand, Andrey Kamarou [7] reported that the irradiation of gallium arsenide with 390 MeV Xe ions reduced the number of structural defects and recrystallized the previously damaged material with 600 keV Se ions.

ZnO is obtained in a wide variety of forms from bulk to nanoparticles samples, and it is well known that the quality of the material is strongly affected by the growth conditions. ZnO films have been deposited by diverse techniques, such as sputtering evaporation, pulsed laser deposition, chemical vapor deposition, sol/gel, electrodeposition and spray pyrolysis. In this work, the spray pyrolysis technique was used to deposit ZnO thin films because it is a better option than similar techniques. The main advantages can be summarized as follows [8–12]. Spray pyrolysis is a simple and low-cost technique that can produce reproducible and high-quality films with uniform thickness. Almost any substrate material with complex geometry can be coated. No high temperatures are required during the synthesis of the samples. It has a straightforward way to dope films with almost any element in any proportion by only adding it to the spray solution. Unlike vapor deposition methods, spray pyrolysis does not require high-quality targets or a vacuum system. The film’s deposition rate and thickness can be controlled by changing the spray parameters. Layered films can be produced by changing the composition of the spray solution during the spray process.

In order to achieve the goal of modifying the physical properties of ZnO, in this work, we have irradiated ZnO thin films using a 2.5 MeV $^4\text{He}^{2+}$ beam, with an average fluence of $3.1 \times 10^{10}$ He cm$^{-2}$, and the results have been compared with other studies that use different ions and energies as a tool to produce physical changes in ZnO films. In this sense, Shasha et al [13] studied the enhancement of ZnO’s photocatalytic properties after N implantation. Iqbal et al [14], Kondkar et al [3] and Vijayakumar et al [15] improved ZnO film resistivity by irradiating the material with C, Au and O ions, respectively. On the other hand, the studies made by Chattopadhyay et al [16], Khawal et al [17] and Abdel-Galil et al [18] showed changes in the band gap and the resistivity of ZnO when it was irradiated with Ar, Li and O ions, respectively. These works show that even light ions can produce essential changes in the optical and electrical properties of the semiconductor; however, limited reports have been found regarding the irradiation of $^4\text{He}^{2+}$ ions in ZnO.

The main reason for studying the $^4\text{He}^{2+}$ irradiation of ZnO thin films is that very little research has been done on the effects of chemically inert He ions on ZnO thin films; besides, the use of He ions as projectiles avoids any chemical interaction that other active elements could produce in the material. The use of He ions as projectiles is beneficial for controlling the number of defects without inducing amorphization because the energy deposition process is dominated by inelastic interactions (electronic stopping) between He and target electrons, which produces a hot electron gas that surrounds the ion trajectory (thermal spikes), decreasing the number of defects due to a similar process that is produced during a thermal process.

2. Methods

ZnO thin films were prepared on a substrate of soda lime glass using the spray pyrolysis technique [19, 20] at 400, 450 and 500 ºC. In the following, the samples will be labeled as T-400, T-450 and T-500, indicating the substrate deposition temperature. In order to prepare the spraying solution, 10.97 g of zinc acetate 2-hydrated was dissolved in 250 ml of deionized water. Afterward, 50 ml of acetic acid was added under agitation, ending with deposition temperature. In order to achieve the goal of modifying the physical properties of ZnO, in this work, we have irradiated ZnO thin films using a 2.5 MeV $^4\text{He}^{2+}$ beam, with an average fluence of $3.1 \times 10^{10}$ He cm$^{-2}$, and the results have been compared with other studies that use different ions and energies as a tool to produce physical changes in ZnO films. In this sense, Shasha et al [13] studied the enhancement of ZnO’s photocatalytic properties after N implantation. Iqbal et al [14], Kondkar et al [3] and Vijayakumar et al [15] improved ZnO film resistivity by irradiating the material with C, Au and O ions, respectively. On the other hand, the studies made by Chattopadhyay et al [16], Khawal et al [17] and Abdel-Galil et al [18] showed changes in the band gap and the resistivity of ZnO when it was irradiated with Ar, Li and O ions, respectively. These works show that even light ions can produce essential changes in the optical and electrical properties of the semiconductor; however, limited reports have been found regarding the irradiation of $^4\text{He}^{2+}$ ions in ZnO.

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In order to study the effect of the irradiation of He$^{2+}$ ions on the optical, electrical, morphological and structural properties of ZnO thin films, the samples were irradiated using a 2.5 MeV $^4\text{He}^{2+}$ beam, with an average fluence of $3.1 \times 10^{10}$ He cm$^{-2}$. Before (as-grown samples) and after He$^{2+}$ irradiations (irradiated samples), ZnO samples were studied by the following techniques to measure the changes in their physical properties. The elemental analysis and the thickness of the films were carried out at the 3 MV Pelletron accelerator with Rutherford Backscattering Spectrometry (RBS). The RBS analysis was performed with a 2.5 MeV alpha beam of 1 mm in diameter. The incident and the scattering angles were 0° and 167°, respectively. The scattered ions coming from the elastic reaction between the alpha particles and the elements that form the sample were acquired by a silicon surface barrier detector. RBS spectrum is obtained by the analog signals that leave the detector and is processed by a multichannel analyzer. The SIMNRA code [21] was used to fit the RBS spectra. Transmittance studies were performed at room temperature, in the 300–1000 nm range, with an Agilent HP 8453 UV–vis spectrophotometer. The microstructure of the ZnO thin films was conducted by x-ray Diffraction Analysis
(XRD) analysis, using a Bruker D8 Advanced Diffractometer, with Cu kα radiation. The morphology of the samples, as well as their particle size, were analyzed with the Scanning Electron Microscope (SEM) FEG JEOL JSM-7800. Resistivity measurements were carried out with a Jandel Multi Height Micro position probe equipment, using the four-point probe method.

3. Results and discussion

3.1. RBS analysis

The SRIM 2013 simulation code [22] was used to calculate the ion beam energy loss and the projected range when the projectiles collide with the target atoms. According to this code, the projected range of the He²⁺ ions in the sample (ZnO + soda lime) is 8.67 μm. This distance is greater than the ZnO films’ thickness (100 nm on average), which ensures that the He ions cross the film and stop in the substrate; inducing ionization and excitation effects when the projectiles interact with the electrons of the target and defects in the material when they collide with their nucleus.

During an RBS experiment, the projectile loses energy as it impinges on the nucleus of an element that composes the material. This lost energy is directly related to the stopping power of the projectile. If the stopping power data of the He²⁺ ions is known [22] and the energy loss of the projectiles is directly measured from the RBS spectrum, then the thickness of the films (X) can be calculated from the following equation [23]:

\[ X = \frac{\Delta E}{\varepsilon} \]  

where \( \Delta E \) and \( \varepsilon \) are the energy loss and the stopping power of the He ions, respectively, as they interact with each element that composes the sample.

The thickness of the samples was calculated with equation (1) and the results are summarized in Table 1.

The results in Table 1 show a small increment in film thickness as deposition temperature is increased, and it is the result of the improvement in film adhesion as substrate temperature rises, as a consequence of the enhancement of the nucleation centers, which can enlarge film thickness.

Zn traces in the substrate were found during the SIMNRA analysis, indicating the film element diffusion through the substrate. The depth where Zn traces were detected increases slightly (817, 838, and 842 nm) as the deposition temperature rises from 400 to 500 °C. The diffusion is due to the energy transfer from the deposition plate to the substrate produced during the synthesis of the films.

The quantitative elemental composition of the samples was obtained through the RBS analysis using a 2.5 MeV alpha particles beam. Zn and O signals from the film, and Si and O, as a part of the substrate, were identified by the SIMNRA code [21], which allows for obtaining the elemental composition of the materials. Figure 1 shows the elemental percentage concentration of Zn and O in the ZnO thin films for each deposition temperature. Inset, the atomic ratio of Zn/O in the film is displayed.

The results in Figure 1 reveal that as temperature increases, the Zn/O ratio approaches one; until at 500 °C, the desirable stoichiometric film is finally obtained. The excess of O at lower temperatures could be explained as follows. As the film is being deposited, oxygen atoms move into the ZnO structure as interstitial atoms, but as temperature rises, interstitial oxygen atoms bond with hydrogen atoms and form an H₂O molecule, which can evaporate and leave the material.

3.2. Optical results

The optical properties of the ZnO thin films were studied by employing the optical transmittance curves in the range of 300–1000 nm. From these data, the value of the band gap of the semiconductor was calculated.

The results of the transmittance spectra are presented in Figure 2, which shows curves with a flat appearance. The transmittance spectra of the as-grown samples indicate the presence of very transparent films, revealing values over 80% transmittance in the visible region of the spectrum. The curves show low transmittance values in the region below 400 nm; which are associated with the ZnO nanoparticles’ fundamental absorption bands.
the case of the as-grown film T-400, an increment in the transmittance value around 360 nm was detected. This enhancement can be related to the reduction of the density of the film grain boundaries. Above this point, transmittance values tend to increase in all cases, indicating a low amount of impurities in the films [24].

Optical transmittance spectra of the irradiated ZnO films show similar curves to the as-grown films for T-450 and T-500; meanwhile, the irradiated sample T-400 shows a significant enhancement in the transmittance value around 360 nm, which doubles the value of the as-grown film T-400 in this region. This fact assumes the reduction of defects in the lattice material. It is supported by figure 6 (b), where the nucleation and crystal growth of the ZnO nanometric particles are favored by He$^{2+}$ irradiation. This behavior is also observed in materials subjected to thermal treatments, and it is due to a rapid and local temperature increase which improves film crystallinity.

In material science, the removal of lattice defects from crystals is usually done by thermal annealing. The electronic stopping generated during ion irradiation when the projectile interacts with the electron’s target and loses part of its energy produces a hot electron gas that surrounds the ion trajectory, known as a thermal spike. Thermal spikes increase temperature throughout the path of the projectile in a very short time, causing passivation of defects, particle nucleation and improving the crystallinity, as is supported by figures 6 (a) and (b). In this sense, thermal spikes could be similar to annealing.

The thermal spike model [25] describes the damage induced by swift heavy ions and applies to any metal, semiconductor or insulator material. When a high-energy ion penetrates a material, it first interacts with the target electrons, causing their excitation and ionization and lowering their energy due to an electronic energy...
loss. When the ion has lost part of its energy interacting with the material’s electrons, it collides with the target nuclei and nuclear energy loss occurs, producing defects in the crystal lattice. The thermal spike model is based on the electronic excitation of the material and induces a spike along the path of the ion.

The thermal spike process involved during ionic irradiation can be explained in 4 steps [26, 27]. In the first step, the incident ions transfer their energy to the target electrons through ion-electron collisions. Secondly, electron-electron collisions take place and share their energy with cold electrons. During the third step, energy is transferred to the lattice via electron-phonon coupling. Finally, energy is dissipated among atoms.

The transmittance data allow us to calculate the energy band gap of the films using the Tauc [17] relation.

\[
(\alpha h\nu) = A(h\nu - E)^{1/2}
\]

(2)

In equation (2), \(\alpha\) is the absorption coefficient of the material, \(h\nu\) is the photon energy, \(A\) is a constant related to the refractive index of the semiconductor and \(E\) is the band gap. The absorption coefficient is defined as:

\[
\frac{I_1}{I_2} = e^{-\alpha x}
\]

(3)

where \(I_1\) is the intensity of light as it reaches the material’s surface, \(I_2\) is the intensity of light penetrating the material and \(x\) is the thickness of the film. The ratio \(I_1/I_2\) in equation (3) is defined as the transmittance \(T\), so getting the absorption coefficient from the transmittance values is natural.

Once the absorption coefficient is calculated, the value \((\alpha h\nu)^{1/2}\) is plotted as a function of the photon energy, as is depicted in figure 3. The band gap of the material is achieved from the extrapolated linear part of the curve when it intercepts the photon energy axis, as can be noticed in figure 3.

The band gap values of the as-grown and irradiated ZnO films are depicted in figure 4. Firstly, the results reveal a decrease in the optical band gap with temperature. This behavior has been observed by several groups and depends on different factors, such as crystallite dimension, quantum size effects, changes in the density of impurities, variations in crystallinity, defects, film thickness, residual stresses and strains. In particular, the band gap decrement is related to an improvement in crystallinity [28], a reduction in the lattice strain [29, 30], an increase in crystallite size [31] and an increase in film thickness [32]. In our work, these variables are related to substrate temperature, so the reduction in band gap with substrate temperature is related to film thickness, as is shown in table 1; to the increase in crystallite size and to the reduction in the microstrain of the film, as is observed in table 2, and to the improvement in crystallinity as is verified in the SEM micrographs.

Figure 4 also revealed a decrement in the energy band gap of the samples after irradiation. The optical band gap of the as-grown films varied from 3.11 to 3.21 eV; meanwhile, this value changed from 3.09 to 3.18 eV in the case of the irradiated samples. The reduction in the optical band gap with He\(^{2+}\) irradiation has been observed by Shasha et al [13], Khawal et al [17] and Abdel-Galil et al [18] and is related to oxygen vacancies and zinc interstitials that produce changes in the crystalline matrix, which narrow the optical band gap.

3.3. Structural results

In order to study the crystalline structure of the ZnO thin films, XRD analysis was acquired. The main diffraction peaks (100), (002), (101), (102), (110) and (103) of a wurtzite-type hexagonal structure were identified in the diffractograms of figure 5 [33]. The spectra show that the films are polycrystalline and have a preferred growth orientation along the c-axis.
The width of the strongest peak in an XRD diffractogram and Scherrer’s formula [34] are used to calculate the average crystallite size ($D$).

$$D = \frac{k \lambda}{\beta \cos\theta}$$  \hspace{1cm} (4)

where $k$ is the shape factor (0.9), $\lambda$ is the wavelength of the Cu K$_{\alpha}$, $\theta$ is the Bragg angle, and $\beta$ is the FWHM of the strongest peak of the XRD spectrum.

Some lattice strains could be developed during film formation and are related to crystal imperfections. The microstrains ($\varepsilon$) were calculated with equation (5) [35]:

Table 2. The average crystallite size and micro strain values before and after irradiation.

| Sample | As-grown Average crystallite size (nm) | Irradiated Average crystallite size (nm) | As-grown Microstrain $\times 10^{-3}$ | Irradiated Microstrain $\times 10^{-3}$ |
|--------|---------------------------------------|----------------------------------------|--------------------------------------|----------------------------------------|
| T-400  | 21.43                                 | 41.67                                  | 2.85                                 | 1.47                                   |
| T-450  | 33.25                                 | 43.34                                  | 1.84                                 | 1.41                                   |
| T-500  | 35.74                                 | 47.10                                  | 1.71                                 | 1.30                                   |

Figure 4. Comparative optical band gap values of the as-grown and the irradiated ZnO thin films.

Figure 5. Diffraction pattern of ZnO (a) as-grown ZnO and (b) irradiated ZnO films.
The crystallinity of the ZnO concentration of Zn atoms in the ZnO increases, both in as-grown and irradiated samples. This fact can be attributed to the increase in the owing to the substitution of He²⁺ ions in the ZnO lattice. However, since He has a smaller atomic radius than Zn and O, the crystal structure tends to shrink, and a decrement in lattice parameters is observed. However, it is also noticed an increase in the size of the particles that compose the irradiated ZnO thin films. The only case where irradiation is not improving crystallinity is at sample T-400, where the diffractions lines (100) and (101) are barely visible. At 400 °C, the formation of the film begins, and its diffraction peaks are tiny, so any sputtering effect induced by the He²⁺ projectiles during irradiation may be responsible for the loss of crystallinity of the ZnO film.

Figure 5 also shows an increase in the intensity of the diffraction peaks as the growth temperature of the films increases, both in as-grown and irradiated samples. This fact can be attributed to the increase in the concentration of Zn atoms in the ZnO film as the temperature of the substrate increases. This is verified in figure 1, where the elemental concentrations of the films are displayed. This behavior has been observed by Durgajanani et al. [38], Benny et al. [39], and Zaier et al. [40].

The lattice parameters of the as-grown and irradiated ZnO films were calculated using equation (6), which relates the interplanar distance, the Miller index, and the lattice constants in a hexagonal structure. The results are presented in Table 3.

Table 3. Comparison of the lattice parameters of the as-grown and irradiated ZnO thin films.

| Sample | As-grown a (nm) | Irradiated a (nm) | As-grown c (nm) | Irradiated c (nm) |
|--------|----------------|------------------|----------------|------------------|
| T-400  | 0.3351         | No detected      | 0.5445         | 0.5438           |
| T-450  | 0.3378         | 0.3360           | 0.5457         | 0.5444           |
| T-500  | 0.3382         | 0.3367           | 0.5460         | 0.5449           |

Table 2 displays the average crystallite size and the microstrain for the as-grown and irradiated ZnO thin films. The results show that the average crystallite size increases with temperature. This fact is due to the rate of the deposition reaction that increases with temperature and consequently the crystallites grow faster, resulting in a larger size [36].

Table 2 also shows that crystallite size increases after irradiation in all the cases, especially in sample T-400, where the increment was almost 50%. It is noticeable that He²⁺ ion irradiation favors crystal growth and improves ZnO film’s crystallinity, as was verified by SEM studies. Khan et al. [37] observed the increment of crystallite size with ion irradiation when they irradiated ZnO thin films with Ni²⁺ ions. They concluded that the increment of crystallite size is related to the reduction in strain due to an annealing effect (thermal spikes) produced during irradiation.

The results indicate that irradiation shrinks the lattice parameters, which is related to compressive stresses owing to the substitution of He²⁺ ions in the lattice. This is a direct consequence of ionic irradiation since, during this process, the He²⁺ ions collide with the Zn and O atoms, losing energy due to collisions with the nuclei that form the material. These nuclear collisions can trigger the formation of point defects, such as vacancies, interstitials, and displacements of atoms in the lattice. In this way, He²⁺ ions can substitute Zn and O atoms in the crystal lattice. However, since He has a smaller atomic radius than Zn and O, the crystal structure tends to shrink, and a decrement in lattice parameters is observed [14, 37].

3.4. Morphological results
In order to analyze the surface morphology and to measure the grain size of the as-grown and irradiated ZnO films at different substrate temperatures (400, 450, and 500 °C) SEM analysis was performed. Comparative micrographs of the films are shown in figure 6, where a total coverage substrate with ZnO grains is observed in all the images. They reveal that the particles that compose the films are nanometric in size, show spherical and flake-like structures and are modified by irradiation. Micrographs also show that their density, size, and shape are strongly dependent on the deposition temperature.

When comparing the irradiated samples with the as-grown ones, it is observed that ionic irradiation favors the nucleation and the formation of grains, especially at low deposition temperatures. With the naked eye, a decrease in the size of the grains that make up the irradiated samples T-400 (figure 6(b)) and T-450 (figure 6(d)) is observed. However, it is also noticed an increase in the size of the particles that compose the irradiated film T-500 (figure 6(f)). Micrographs also exhibit a better filling of pores after irradiation, which is related to an increment of local annealing effect, just as was previously explained.
Micrographs related to as-grown samples T-400 (figure 6(a)) and T-450 (figure 6(c)) show diffuse particles with irregular forms. Nevertheless, the irradiation process tends to homogenize the size and shape of the particles. A bimodal particle size distribution is also appreciated, especially in the irradiated samples. In order to measure the average size of the particles before and after irradiation, the J-Image code was used. Results displayed in figure 7 support what is observed in the micrographs of figure 6 regarding the two different behaviors concerning the change in the particle size. The samples prepared at lower temperatures show a decrease in the average size of their particles after irradiation; meanwhile, in the sample synthesized at the higher temperature, the size of their particles increases with ionic irradiation. The explanation could be the following. During a pyrolysis process, deposition temperature is quite essential to form the particles that compose the film. When the temperature is low, the particles are not fully formed, so when He$^{+}$ ions collide with the material, a sputtering effect induced by the ion irradiation produces fractures in the grains, resulting in a decrease in the average particle size of the sample. In the case of the sample T-500, the grains are completely formed, and the irradiation produces particle nucleation due to the heat produced by the thermal spikes. As reported by Sharma et al[41], this coalescence effect increases the average particle size. We can also notice that the sample deposited...
at the lower temperature shows slight changes in particle size after irradiation. This effect has been observed by Kalita et al.\cite{42}. They explained that tiny particles are more tolerant to ionic irradiation because their large number of grain boundaries act as sinks for the defects induced during irradiation.

3.5. Electrical results

Figure 8 shows the variation of electrical resistivity of the as-grown and irradiated ZnO films. The curves show a decrement in resistivity at 450 °C and then an increase at 500 °C, indicating a variation related to the deposition temperature. The evolution of electrical resistivity with temperature can be explained by the combination of two properties of semiconductors: their behavior with temperature, which in the case of ZnO decreases with temperature, and their stoichiometry deviations. In our case, the decrement of resistivity in the range of 400 to 450 °C is explained based on the nature of ZnO, which predicts that this variable decreases with temperature. On the other hand, the enhancement of resistivity in the range of 450 to 500 °C is due to the atomic composition of the semiconductor, that at 500 °C fits the perfect ZnO stoichiometry, as can be verified in figure 1. There are several reports\cite{43–45} of temperature-dependent resistivity in ZnO thin films following the same resistivity evolution as ours.
The comparison of the resistivity of the as-grown and irradiated ZnO thin films results is also exhibited in figure 8. The results indicate that ZnO thin films become more resistive after ion irradiation, and that resistivity could be tailored in ZnO by changing the substrate temperature during the pyrolysis process. In the case of the as-grown samples, the resistivity of the films shows a value of $23.08 \times 10^{-2} \, \Omega \cdot \text{cm}$ at 400 °C, then the value drops to $2.18 \times 10^{-2} \, \Omega \cdot \text{cm}$ at 450 °C, and finally, the resistivity is increased, getting a value of $18.25 \times 10^{-2} \, \Omega \cdot \text{cm}$ at 500 °C. The irradiated films follow similar behavior as the pristine ones, where resistivity takes a very close value to the as-grown sample of $29.04 \times 10^{-2} \, \Omega \cdot \text{cm}$ at 400 °C. At 450 °C, resistivity has a value of $19.51 \times 10^{-2} \, \Omega \cdot \text{cm}$ and at 500 °C, the electrical resistivity value is $37.49 \times 10^{-2} \, \Omega \cdot \text{cm}$.

Several groups have studied the behavior of electrical resistivity as ZnO is irradiated with different types of ions and energies. However, their results show either enhancement or decrement of this value, so no conclusions can be drawn. In this sense, some groups have found an increase in electrical resistivity after ion irradiation. For instance, Iqbal et al [14] worked with 800 keV C ions, concluding that the increment of resistivity with irradiation is due to the creation of defects in ZnO induced by the ion beam. They also mention that the ZnO structure was disordered due to the irradiation, which increases resistivity. Kondkar et al [3] used 75 MeV Au ions in their work. They attribute the resistivity enhancement to the increase in grain boundary scattering, which occurs as a consequence of nano-hillock formation in the irradiated films. They also assume that the increase in grain boundary scattering reduces the electronic mobility, increasing the material’s resistivity. Vijayakumar et al [15] argued that the rise in electrical resistivity with 100 keV O irradiation is due to oxygen interstitials and Zn vacancies produced during implantation that act as acceptors.

On the other hand, other reports show a decrease in electrical resistivity after ion irradiation. For instance, MatSunami et al [46] conducted their research using 100 keV Ne ions and concluded that the decrement of resistivity is due to an increase in carrier density. Lyadov et al [47] reported that the low resistivity found in their implanted ZnO films with 30 keV Ag ions is due to a high value of free electron concentration. Zhen et al [48] studied the resistivity of ZnO after 5 keV H ions irradiation and concluded that its decrement should be a consequence of the hydrogen that forms a shallow donor in the ZnO.

We consider that the enhancement of electrical resistivity values after ion irradiation (See figure 8) is related to the irradiation process. During ion irradiation, the projectiles can deflect the electrons of the atoms that form the material. Consequently, the mean free path for electron movement gets shorter and its drift velocity is reduced. This reduction causes a decrement in charge carrier mobility, increasing resistivity. On the other hand, He$^{2+}$ ions produced thermal spikes during irradiation, which improved the films’ crystallinity, enhancing the electrical resistivity of ZnO thin films.

4. Conclusions

The present work studied the effect of $^4$He$^{2+}$ ion irradiation on the optical, structural, morphological and electrical properties of ZnO thin films. The UV–vis results revealed a decrement in the energy band gap of the films after irradiation. This reduction is related to structural defects, especially oxygen vacancies and zinc interstitials that produce changes in the crystalline matrix, narrowing the optical band gap. The wurtzite-type hexagonal structure of the ZnO is maintained after irradiation. It is noticeable that He$^{2+}$ ion irradiation favors crystal growth, improves the crystallinity of ZnO films and increases crystallite size as a consequence of the reduction in strain due to thermal spikes. The results indicate that irradiation shrinks the lattice parameters, which is related to compressive stresses due to the substitution of He$^{2+}$ ions in the lattice. The SEM images reveal that the particles that compose the films are nanometric in size, show spherical and flake-like structures, and are modified by irradiation. Micrographs also show that their density, size, and shape strongly depend on the deposition temperature. The samples also follow different patterns concerning their average particle size after irradiation. While the average particle size of the samples prepared at lower temperatures decreased after irradiation, the opposite occurred with the sample synthesized at the higher temperature. The electrical results indicate that ZnO thin films become more resistive with ion irradiation and that resistivity values could be tailored by changing the substrate temperature during the pyrolysis process.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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Conflict of interest declaration

The authors declare that they have NO affiliations with or involvement in any organization or entity with any financial interest, or non-financial interest in the subject matter or materials discussed in this manuscript.

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