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Effect of the Deposition Times on the Properties of ZnO Thin Films Deposited by Ultrasonic Spray Pyrolysis for Optoelectronic Applications

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In the present work, undoped ZnO thin films have been deposited on glass substrates at 300 °C by ultrasonic spray pyrolysis technique. Zinc acetate, acetic acid and methanol have been used as precursors and solvents. The prepared thin films have a thickness ranging from 216 to 680 nm. Structural transformation has been observed as a function of deposition time. Thin films obtained at low deposition time are polycrystalline in nature, they crystallized under hexagonal wurtzite structure and presented a preferential orientation along the c-axis perpendicular to the substrate, where the maximum crystallite size was found to be 14.4 nm for a smallest deposition time of 5 min. However, those obtained at deposition time higher than 15 min exhibit amorphous nature and we observed a disappearance of diffraction peaks. Scanning electron microscopy has been applied for a morphology characterization of the films. A growth of nanowires in a length scale of few microns can be seen clearly for a deposition time of 5 min and enhanced at 10 min. An amorphous nature of ZnO thin films was obtained at deposition time of 15 and 20 min. The average transmittance of all films is over 80 % in the visible region and the band gap energy for crystalline phase increases from 3.17 to 3.45 eV with the increase of the deposition time. Low resistivities in the range of 6.91×10^{-3} and 6.60 $(\Omega.\mathrm{cm})^{-1}$ were produced when the deposition time increases from 5 to 10 min, and more than 1.90×10^{5} $(\Omega.\mathrm{cm})^{-1}$ for deposition time greater than 10 min. The Urbach energy decreases from 324 to 314 meV with increasing deposition time from 1 to 4 min due to the strain and disorder in the thin films. The optical and electrical properties of deposited thin films revealed that these thin films have potential applications in optoelectronic devices especially in solar cells.

Keywords: Undoped ZnO, Thin films, Ultrasonic spray pyrolysis, Transparent conducting materials.

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1. INTRODUCTION

In the past few decades, the fabrication and development of transparent conductive oxide (TCO) materials have gained an enormous research interest owing to their enhanced and tunable optical and electrical properties. These materials including indium tin oxide (ITO) have potential applications as window materials in solar cell structures, transparent electrodes, flat panel displays, light emitting diodes and sensors [1]. However, the cost of ITO has motivated the researchers to develop new materials as its substitutes. Zinc oxide has being low cost and wide band gap material attracts a lot of research interest. ZnO exhibits novel electrical and optical properties when synthesized as nanocrystals and thin films. ZnO has become an excellent and efficient candidate for viability of advanced electro- and optoelectronic devices like solar cells, sensors, light emitting diodes and surface acoustic wave devices. Several methods have been reported for deposition of ZnO thin films with adequate properties (low resistivity, high crystallinity and high transmittance), such as chemical vapor deposition (CVD) [2], magnetron sputtering [3], laser molecular beam epitaxy [4] and sol-gel [1]. Among this, ultrasonic spray pyrolysis technique is a unique method to deposit ZnO thin films on a variety of substrates [5]. This methodology is simple, cost effective and capable to produce uniform and homogeneous thin films of ZnO. It has also been successfully used to prepare binary, ternary and quaternary materials such as ZnS, MgO, $CuInS_2$ (CIS) and Cu_2ZnSnS_4 (CZTS).

The present work describes the investigations on the dependence of structural, morphological, optical and electrical properties of ZnO thin films deposited on glass substrates by ultrasonic spray pyrolysis technique as a function of deposition time. The obtained results are compared and discussed with the specified results carried out by several researchers to validate the possible applications of these thin films.

2. EXPERIMENTAL DETAILS

ZnO thin films were prepared on glass substrates using ultrasonic spray pyrolysis technique. The spray solution was prepared by dissolving zinc acetate in methanol followed by addition of few drops of acetic acid solution as a stabilizing agent. The concentration of final solution was kept 0.1 M. The mixture was then stirred vigorously at 30 °C for one hour to yield a clear, homogeneous and transparent solution. The solution and compressed air (carrier gas) were fed into a spray nozzle at a pre-adjusted constant atomization pressure. The flow rate of the solution was kept at 8 ml/min and fixed substrate temperature of 300 °C. The distance between the nozzle (0.1 mm) and the substrate was kept 17 cm. The time of

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deposition varied from 5 to 20 min.

The structural analysis was carried out by X-ray diffraction method using Philips X' Pert system with CuKα radiation (λCuKα = 1.5418 Å). The surface morphology and microstructure was investigated by scanning electron microscope embedded with EDX system. The optical properties were obtained using Shimadzu UV-3101 PC spectrophotometer in the wavelength range from 300 to 800 nm. The electrical conductivity was calculated in the dark at room temperature and in a coplanar structure with two evaporated gold stripes attached to the films surface.

3. RESULTS AND DISCUSSION

XRD patterns of ZnO thin films obtained at various deposition times are shown in Fig. 1. Thin films deposited after 5 and 10 min exhibit polycrystalline nature with occurrence of diffraction peaks at 2θ values of 32, 34 and 36 degree corresponding to (100), (002) and (101) planes of hexagonal structure ZnO; this result is in coherence with previously reported data [6]. The broad diffraction peaks depict that ZnO nanocrystals are deposited. For deposition time higher than 10 min, disappearance of diffraction peaks leads to an amorphous structure as shown in Fig. 1b. These observations demonstrated the dependence of structural properties of thin films on deposition time specifically when they are obtained via ultrasonic spray pyrolysis technique.

The crystallites sizes (D) corresponding to (002) orientation were estimated by Scherrer formula [7]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where λ is the wavelength of X-ray radiation, β represents the full width at half maximum (FWHM) and θ is the angle of diffraction. Table 1 shows the evolution of crystallite size at short deposition times. The crystallite size decreases as a function of increasing deposition time. The crystallites are observed to shrink slightly from 14.4 to 12 nm for deposition time of 5 and 10 min, respectively. The observed values of crystallite sizes are in well agreement with the reported data. However, for deposition time of 15 and 20 min, it is difficult to estimate crystallite size due to amorphous nature of the thin films.

Table 1 – Evolution of the crystallite size in short deposition times

Deposition time	Crystallite size, nm	FWHM, °2θ
5 min	14.4	0.4903
10 min	12	0.501

The morphology of ZnO thin films was analyzed by scanning electron microscopy (SEM) and the micrographs obtained at various deposition intervals are shown in Fig. 2. For deposition time of 5 min, growth of nanowires in a length scale of few microns can be seen clearly (Fig. 2a). The growth of ZnO nanowires enhances with uniform distribution throughout the substrate surface for deposition time of 10 minutes (Fig. 2b). The amorphous nature of ZnO thin films obtained at deposition time of 15 and 20 min is shown in Fig. 2c, d. These micrographs corroborate the observations of structural analysis of ZnO thin films.

The compositional analysis of ZnO thin films deposited on glass substrates was carried out by energy dispersive X-ray spectroscopy (EDX). This analysis revealed that deposited thin films are quasi-stoichiometric and the supposed composition has been substantially achieved.

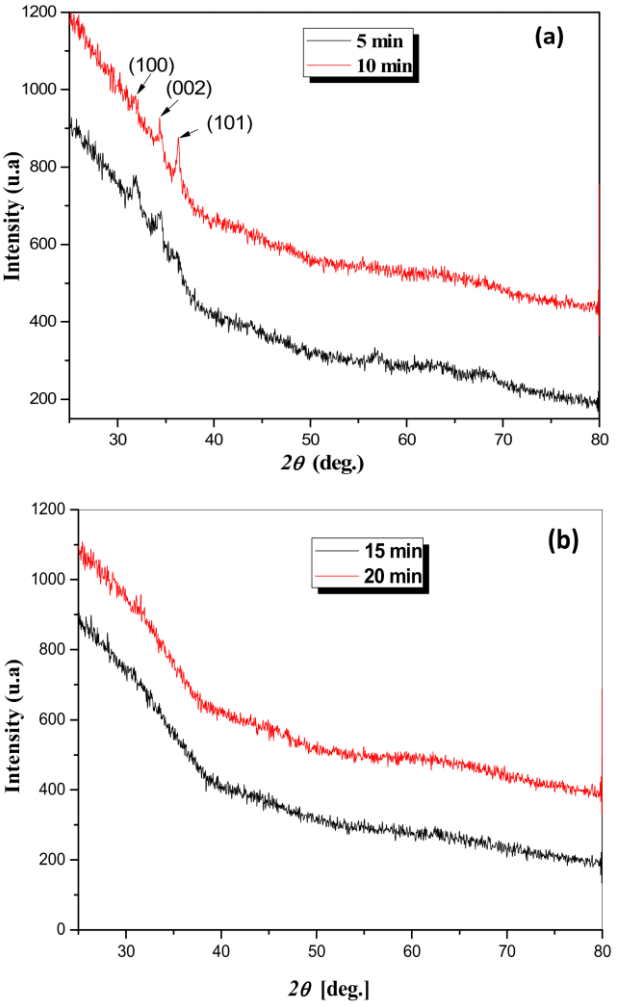
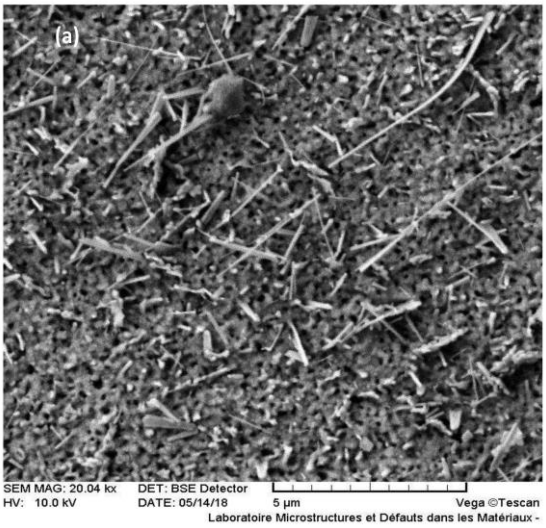


Fig. 1 – XRD patterns of ZnO thin films deposited at 5 min and 10 min (a), 15 min and 20 min (b)



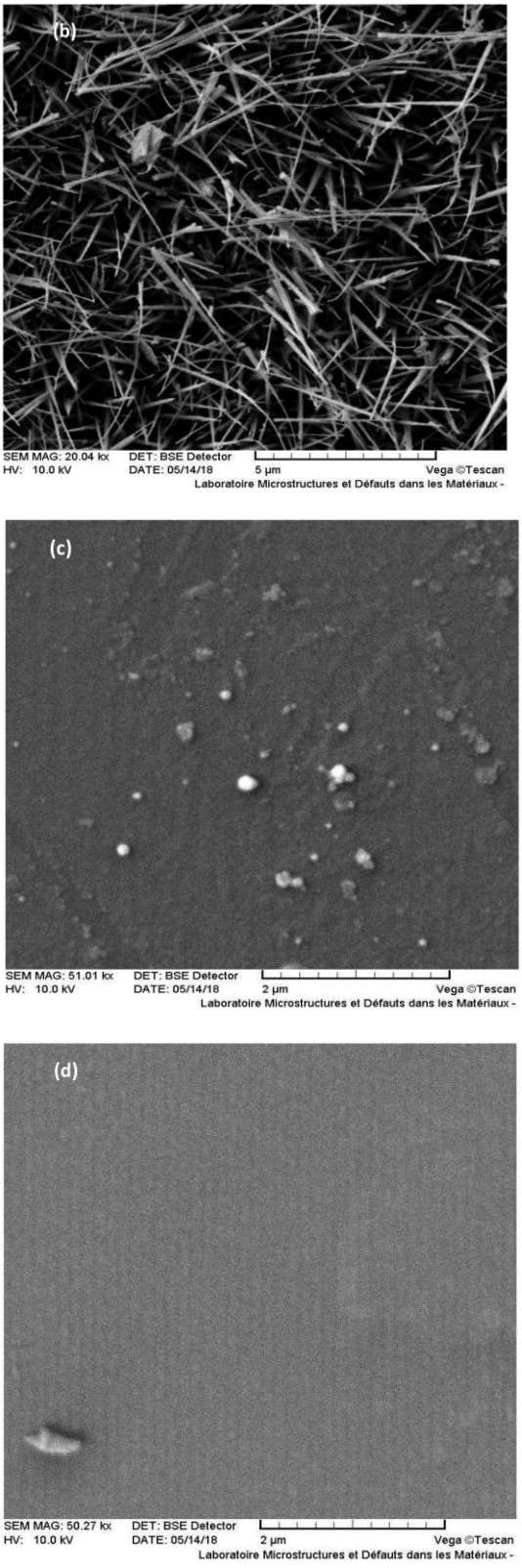


Fig. 2 – Scanning electron micrographs of ZnO thin films with different deposition times: 5 min (a), 10 min (b), 15 min (c) and 20 min (d)

Fig. 3 shows EDX pattern of compositional analysis of thin films obtained after 5 min of deposition. The real composition of ZnO material is evident from the presence of Zn and O elements in the thin films.

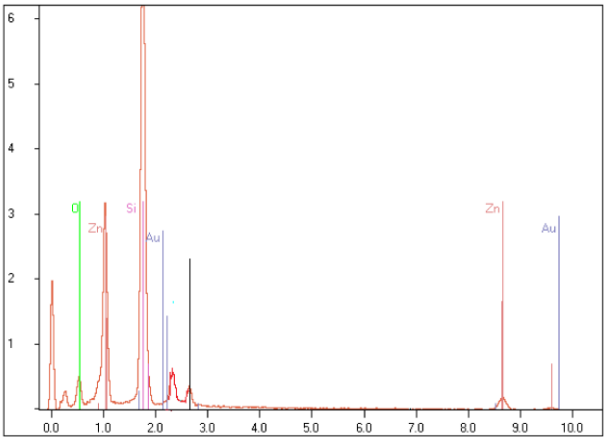


Fig. 3 – EDX spectrum for ZnO thin film deposited by spray pyrolysis at short deposition time (10 min)

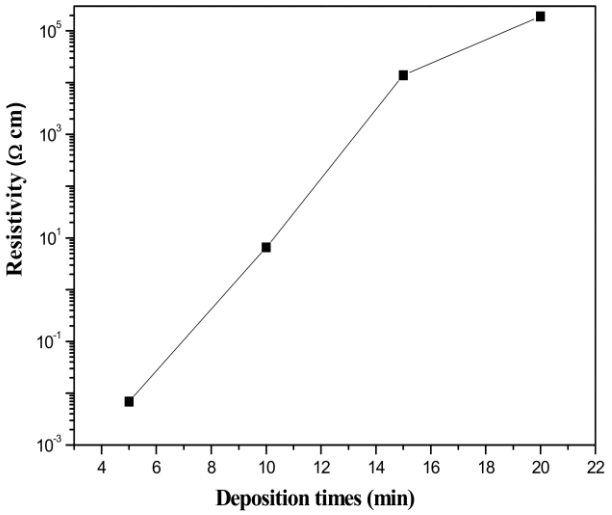


Fig. 4 – Resistivity measurements of the ZnO thin films as a function of deposition times

Electrical properties of deposited thin films were analyzed by calculating the resistivity of the samples as a function of deposition time as shown in Fig. 4. The resistivity is observed to increase when the deposition time increases from 5 to 20 min. For deposition time of 5 and 10 min, low value of resistivity is observed i.e. 6.91×10^{-3} and 6.60 $(\Omega.\text{cm})^{-1}$, respectively, which leads to a high conductivity. On the other hand, for deposition time greater than 10 min, high resistivity 1.90×10^{5} $(\Omega.\text{cm})^{-1}$ is observed, which leads to low conductivity of the samples. This electrical behavior of ZnO thin films is in good agreement with the reported values [8]. The elevation observed in the value of resistivity is probably due to the augmentation of the potential barriers [9] and increase of oxygen concentration when the deposition time is higher [10].

The optical properties of ZnO thin films deposited on glass substrates have been investigated by UV-Vis Spectrophotometer in the wavelength range of 280 to 800 nm. The transmittance spectra of ZnO films obtained at different deposition times are shown in Fig. 5. The average value of transmittance is observed to be more than 80 % for ZnO thin films deposited after 5, 10 and 15 min. A steep absorption edge of transmittance curve showed

that these thin films can have potential applications in solar cells as a transparent window material. However, the value of transmittance is observed to decrease as 62 % for ZnO thin films obtained after 20 min of deposition. This decrement is mainly due to film thickness and amorphous nature of thin films [11]. The same observations have already been reported in case of amorphous aluminum doped ZnO thin films [12] and un-doped ZnO thin films [13].

Tauc relation [14] was used to estimate the value of optical band gap energy for all samples by plotting $(ahv)^2$ as a function of photon energy hv. The extrapolation of this curve gives the value of band gap energy as shown in Fig. 6.

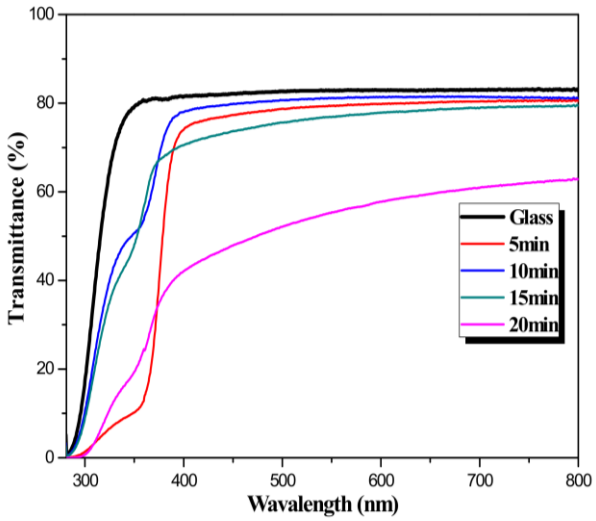


Fig. 5 – Transmission spectra of ZnO thin films deposited at different deposition times

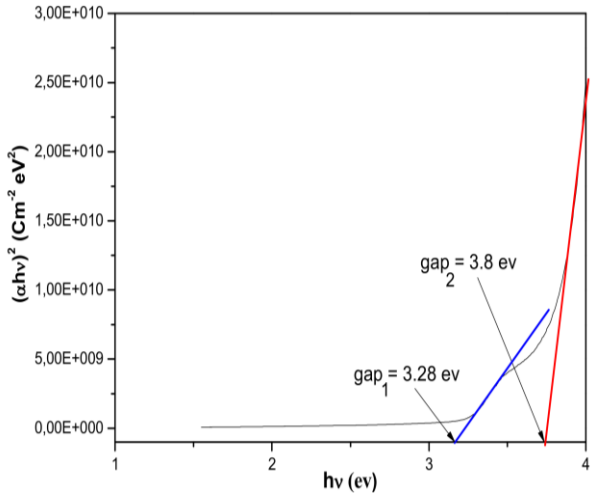


Fig. 6 – Variation of $(\alpha hv)^2$ versus hv with short deposition time (10 min) of ZnO thin film

$$(\alpha h\nu)^n = B(h\nu - E_g) \quad (2)$$

where E_g is the optical gap energy, α is the absorption coefficient, B is a constant and, hv is energy of incident photons.

The dependence of band gap energy on deposition time is represented in Fig. 7. Two different values of band gaps have been deduced for amorphous and crystalline thin films. It has also been observed that the value of band gap increases as the crystallinity of thin films improves as discussed earlier for gallium and indium doped zinc oxide thin films [12-14]. In the current study, the band gap value increases as a function of deposition time due to enhanced carrier density in thin films and Burstien-Moss effect [15]. The observed values of band gap are in the range from 3.17-3.45 eV and are in well agreement with reported data [16].

Urbach energy is used to estimate the disorder in the samples. This energy actually measures the width of localized energy states estimation and was obtained by Urbach energy which is a measure of the width of localized states appendage into the forbidden energy gap [17].

$$\alpha = \alpha_0 \exp \frac{h\nu}{E_u}, \quad (3)$$

where E_u represents the Urbach energy. Fig. 8 shows the dependence of optical band gap and Urbach energy on the deposition time. The variation in Urbach energy can be demonstrated by the strain and disorder in the thin films, as the quality of thin films improves the Urbach energy [18, 19]. The decrease in Urbach energy is attributed to the decrease of the defects as observed for Co doped ZnO thin films [20] which ultimately affect the optical properties of materials.

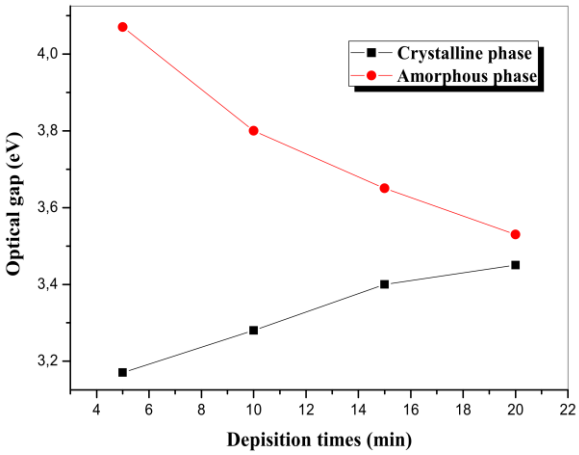


Fig. 7 – Optical gap variation as a function of deposition times

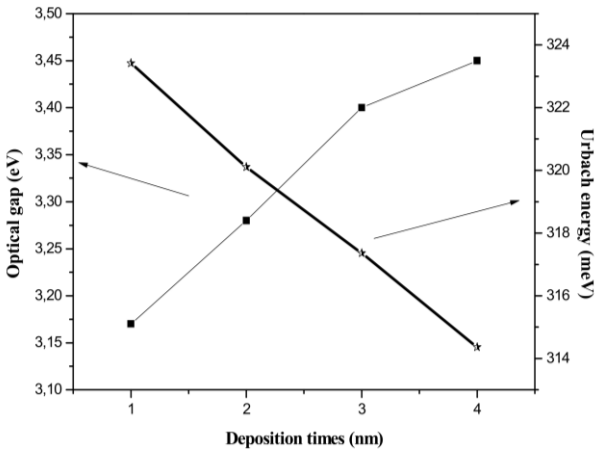


Fig. 8 – Band gap and Urbach energy variation of ZnO thin films as a function of different deposition times

4. CONCLUSIONS

In summary, ultrasonic spray pyrolysis technique has been employed to deposit ZnO thin films on glass substrates. The structural, morphological, electrical and optical properties of deposited thin films have been investigated as a function of deposition time (5-20 min.). The crystallinity of the thin films decreases as the time of deposition increases from 5 to 20 min. XRD patterns revealed that thin films lose their crystallinity and exhibit amorphous behavior when the time of deposition is between 15 and 20 min. The transformation from crystalline to amorphous phase is also evident from transmittance spectra. A maximum transparency i.e. greater than 80 % in the visible range has been observed. The thin films exhibiting crystalline nature deposited at 5 and 10 min have an optical gap of 3.17 and 3.28 eV, respectively, close to the ideal values. An increase of electrical resistivity with deposition time may result from enhanced oxygen concentration in the thin films. ZnO thin films obtained at a deposition time of 5 and 10 min seem to have suitable structural, optical and electrical properties and might have potential applications as a window for efficient thin film solar cell fabrication.

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Вплив часу осадження на властивості тонких плівок ZnO, осаджених ультразвуковим спрей-піролізом, для оптоелектронних застосувань

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Нелеговані тонкі плівки ZnO наносяться на скляні підкладки при 300 °C за допомогою ультразвукового спрей-піролізу. Ацетат цинку, оцтова кислота та метанол використовуються як прекурсори та розчинники. Підготовлені тонкі плівки мають товщину від 216 до 680 нм. Структурна трансформація спостерігається як функція часу осадження. Тонкі плівки, отримані за низького часу осадження, мають полікристалічну природу; вони кристалізуються у гексагональну структуру вюрциту і мають переважну орієнтацію вздовж осі *c* перпендикулярно підкладці, де максимальний розмір кристалітів становить 14,4 нм за найменшого часу осадження 5 хв. Однак ті плівки, які були отримані за час осадження вище 15 хв, демонструють аморфну природу, і ми спостерігаємо зникнення дифракційних піків. Для дослідження морфології плівок застосовувалася скануюча електронна мікроскопія. Зростання нанодротів у масштабі довжини у кілька мікрон добре видно для часу осадження 5 хв, а розширення – для часу 10 хв. Аморфна фаза тонких плівок ZnO була отримана при часі осадження 15 і 20 хв. Середній коефіцієнт пропускання усіх плівок перевищує 80 % у видимій області, а енергія забороненої зони для кристалічної фази збільшується з 3,17 до 3,45 еВ із збільшенням часу осадження. Низька питома провідність у діапазоні з $6{,}91 \times 10^{-3}$ до 6,60 $(\Omega.\text{см})^{-1}$ була отримана при збільшенні часу осадження з 5 до 10 хв, а провідність більше $1{,}90 \times 10^{5}$ $(\Omega.\text{см})^{-1}$ – для часу осадження більше ніж 10 хв. Енергія Урбаха зменшується з 324 до 314 меВ із збільшенням часу осадження з 1 до 4 хв через деформацію та руйнування порядку у тонких плівках. Оптичні та електричні властивості осаджених тонких плівок виявили, що ці тонкі плівки мають потенційне застосування в оптоелектронних пристроях, особливо в сонячних батареях.

Ключові слова: Нелегований ZnO, Тонкі плівки, Ультразвуковий розпилювальний піроліз, Прозорі електропровідні матеріали.