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Highly transparent and conductive annealed ZnO nanoparticles thin film prepared by pulsed laser deposition

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ABSTRACT

A thin film can be applied to a wide variety of microelectronic devices, sensors, anti-reflective and protective coatings, transparent electrodes, etc. It increases the efficiency and versatility of the equipment. The nanostructured particles of zinc oxide (ZnO) were synthesized using a microwave method with an average grain size of 25.7 nm. High-quality ZnO thin films are being deposited using the Pulsed Laser Deposition (PLD) technique at room temperature, one of the most advanced Physical Vapor Deposition techniques. After one hour of air annealing at 400 °C, grazing incident X-ray diffractometer (GIXRD) confirms polycrystalline hexagonal wurtzite formation with an average grain size of 7.7 nm. The transmission spectrum indicates high transparency in the visible region, with an average value of 95%. The calculated activation energy and dc conductivity were 32 meV and 950 $\Omega^{-1}.m^{-1}$, respectively. The highly transparent-conductive ZnO thin film may present a new avenue for electrodes with transparent conductivity.

1. Introduction

Zinc oxide is a technologically significant material that displays multifunctional properties [1 – 4]. This material is effective in a wide variety of optoelectronic device applications, such as transparent electrodes, solar cells, gas sensors, flat panel displays, smart windows, and thin-film resistors [1, 4 – 6]. Recently, several studies have been conducted on transparent conducting electrodes [1 – 12]. According to B. Benhaoua *et al.* [7], Al-doped ZnO thin films were prepared using the ultrasonic spray technique. The influences of Al-doping on structural, optical, and electrical properties of the annealed ZnO thin films were measured. The average transmittance and electrical conductivity of the films were found to be 80% and 19 $\Omega^{-1}.m^{-1}$, respectively. A. Gahtar *et al.* [8] deposited ZnO and Al-doped ZnO films on substrates of glass using the ultrasonic spray technique. The effects of ethyl alcohol and methanol solutions on the structural, optical, and electrical properties of the thin films before and after doping were examined. All films show average optical transparency of about 90% in the visible spectrum. Using a sol-gel method, X. Liu *et al.* [9] have prepared transparent conducting Al-doped ZnO thin films on quartz substrates. The conductivity of the films increases from 31 $\Omega^{-1}.m^{-1}$ to 70.4 $\Omega^{-1}.m^{-1}$, while the average transmission in the visible region increases from 82.9% to 86.7%.

A. Al-Ghamdi *et al.* [10] have deposited thin films of Al-doped ZnO using spin coating technique onto glass substrates. The electrical conductivity was increased to 100 $\Omega^{-1}.m^{-1}$ by increasing the Al-doping concentration to 4 wt %. As a result, Al-doped ZnO thin films reveal high transparency in the visible region with an average value of 86%.

In our study, the annealed ZnO thin film fabricated by the PLD technique was characterized for its structural, optical, and electrical properties. The results showed that the annealed film at 400 °C for 1 hour exhibits a transparent–conductive behavior.

2. Experimental procedures

The thin films of ZnO were deposited using a PLD system on glass substrates. By using a microwave method [11], the nanoscale particles of ZnO with an ultra-high purity were produced. Nanoparticles of ZnO have an average grain size of 25.7 nm. The glass sheets used as substrates for thin films formation of ZnO were pre-cleaned in an ultrasonic bath for 5 minutes with ethyl alcohol before inserting them into the apparatus. Then, using a 3 cm distance between each substrate and the target surface, they were placed parallel to each other. In this experiment, a Q-switched Nd:YAG laser (l = 532 nm, pulse width 6 ns) was used at a repetition rate of 10 Hz. At a 45° angle of incidence, the laser beam was focused onto the ZnO nanoparticles by a 20 cm focal lens. The powder nanoparticles are rotated at a constant speed during deposition to prevent drilling and ensure a smooth film deposition. The laser beam energy was set around 18.2

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mJoules per pulse during the experiment, which produced nearly 137.6 J/cm^2 of energy density at the target surface. Turbo-molecular and rotary pumps evacuate the thin-film production chamber to 8 x 10^{-4} Pa. In the evacuation chamber, ZnO thin films were deposited for 5 minutes at room temperature. Based on absorption measurements, the film layer depth was about 105 nm. Thin films of ZnO were fabricated at room temperature; annealed in an open atmosphere for one hour at 400 ^{o}C.

The crystal structure and particle dimensions of the thin films were characterized by grazing incident X-ray diffractometer (GIXRD) pattern using Cu K_α radiation (Panalytical, X'Pert Pro, Netherlands). The GIXRD data were collected for 2θ at 20° to 80° with a resolution of 0.02°. The morphology of the annealed film was investigated by scanning electron microscope (SEM), Model Quanta 250 Field Emission Gun, Netherlands. An optical transmittance measurement was performed on ZnO film by UV/Visible spectrometer (Model T80+, PG Instruments Limited) in the wavelength range of 0.200–0.800 mm. A multimeter (ISO-TECHIDM 303) was used to collect the dc conductivity data, measured by the two-probe method with silver paste electrodes. The dc conductivity measurements were conducted over a temperature range of 300 to 450 K.

3. Results and discussion

Figure 1 reveals a GIXRD pattern of the prepared thin film of ZnO on the glass substrate annealed at 400 °C for 1 h. The diffraction peaks indicate a nanocrystalline structure. In the GIXRD pattern, the annealed film shows (002) as its preferred orientation peak. Furthermore, more peaks are observed at (100), (101), (102), (110), (103), and (112). JCPDS card no. 04-015-0825, which is used to evaluate these results, agrees well. As a result, the annealed thin films of ZnO exhibited hexagonal crystallization in the preferred *c*-axis direction perpendicular to the surface of the substrate [11].

According to Debye–Sherrer's formula [12, 13], the average crystallite size of the ZnO annealed thin film was 7.7 nm:

$$D = k\lambda/(\beta \cos \Theta) \tag{1}$$

where (D) is the crystallite size, (k ~ 1) is the correction factor, (λ = 0.15406 nm) is the wavelength of Cu-K_α radiation, (Θ) is the angle of diffraction, and (β) is the full width half maximum (FWHM) of the most intense peak in units of radians.

Microscopy of thin films using SEM is a convenient way of studying their microstructure. The ZnO thin film annealed on a glass substrate is depicted in fig. 2, which shows an SEM surface micrograph. The annealed thin film fabricated using ZnO nanoparticle targets exhibits rough surface properties and compact crystalline grains of different sizes can be observed in a spherical shape.

Figure 3 shows the spectra of optical transmission of ZnO thin film annealed at 400 °C for an hour. In the spectral range 0.400–0.800 mm, the average transmittance of the films is about 95%. In the annealed film, the sharp fall in transmittance at the absorbance edge illustrates the direct bandgap and crystalline characteristics of the annealed film.

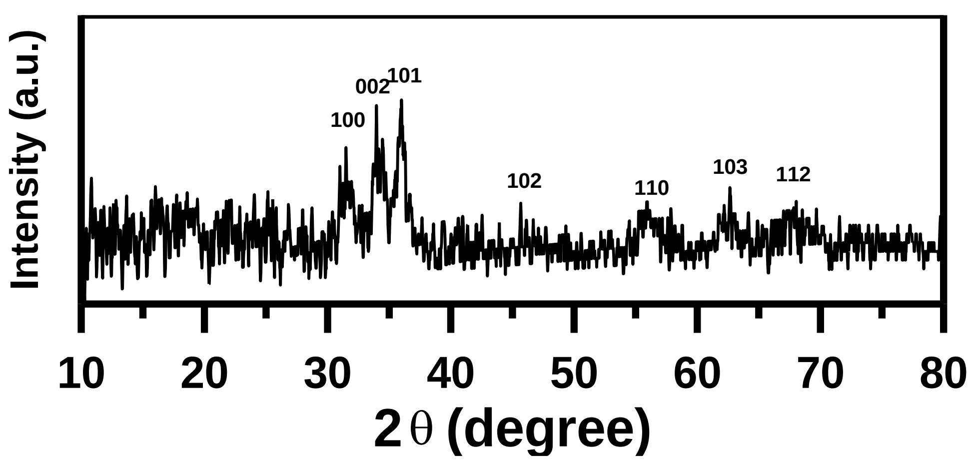

Fig. (1): GIXRD pattern of ZnO thin films annealed at 400 °C for 1h.

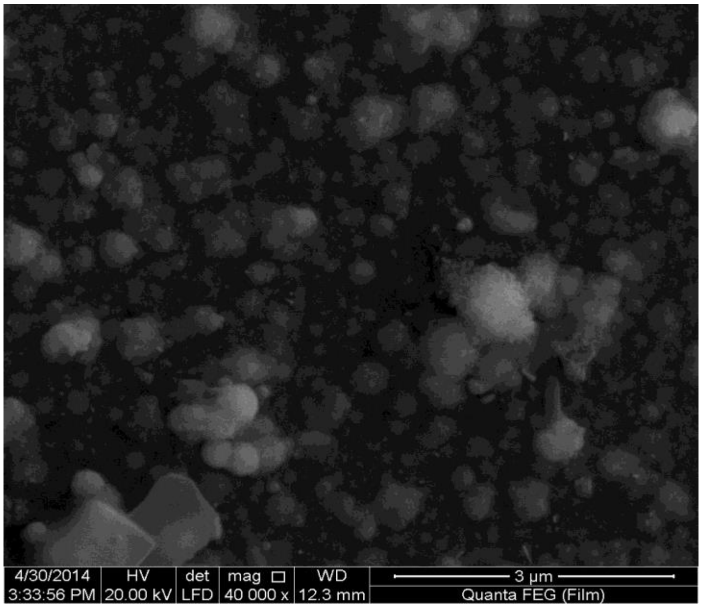

Fig. (2): SEM image of the annealed ZnO thin film.

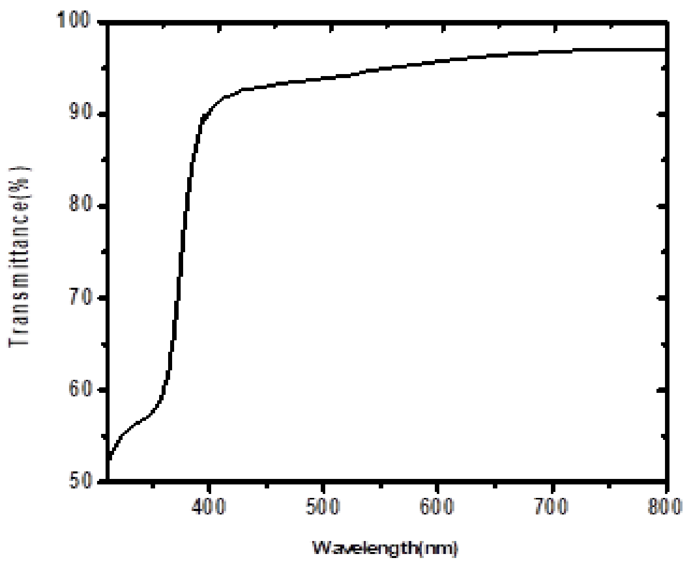

Fig. (3): The transmission spectra of the annealed ZnO thin film.

Figure 4 shows an Arrhenius relation [11] accordance with a semiconducting temperature variation of the dc conductivity (σ) of ZnO thin film annealed at 400 °C for 1 hour:

$$\sigma = \sigma_0 e^{-E_a/k_B T} \quad (2)$$

Where σ_0, E_a, K_B and T are the pre-exponential factor, activation energy, Boltzmann's constant, and absolute temperature, respectively. The activation energy was calculated from the slope of the curve for the film and the pre-exponential factor was obtained from the interception of the least square straight-line fits of the data.

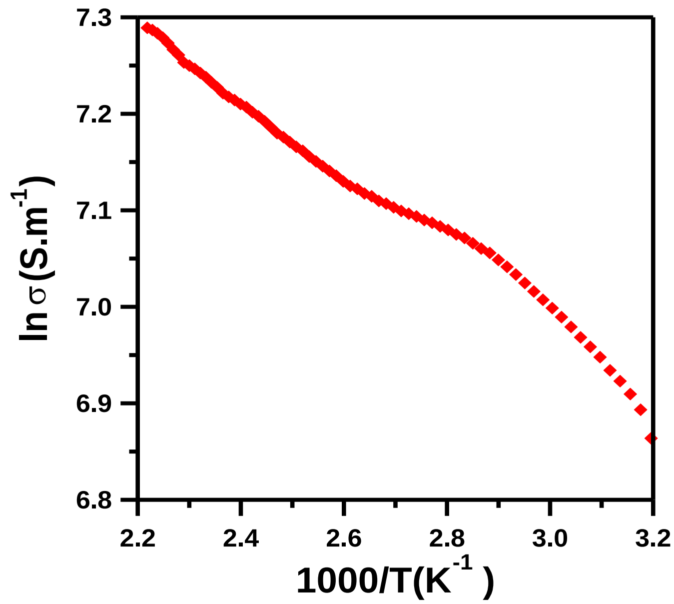

Fig (4): Variation of dc conductivity (ln σ) as a function of the inverse of temperature (T^{-1}) for ZnO thin films annealed at 400 °C for 1 h.

As in semiconductors, the straight line form of the Arrhenius relation indicates that conduction is thermally activated.

The calculated σ_0 and E_a for the annealed thin film were 8.109 $\Omega^{-1}.m^{-1}$ and 0.032 eV, respectively [11]. Furthermore, σ was found to be 950 $\Omega^{-1}.m^{-1}$ at room temperature. According to Arrhenius equation (2), the large difference between the two conductivities arises from the dc conductivity at 300 K, which is exponentially related to the pre-exponential factor that is the theoretical dc conductivity at 0 K. Finally, the high transmittance and high conductivity of annealed ZnO thin films annealed for 1 hour at 400 °C may open a new avenue for transparent-conductive electrode application in the near future.

Conclusion

A thin ZnO film is deposited on a glass substrate at 300 K using the PLD technique. The fabricated film is then annealed for 1 hour at 400 °C in the air. We investigated the effects of annealing temperature on the structure, surface morphology, optical, and electrical properties of annealed ZnO thin films with GIXRD, SEM, UV/Vis spectrophotometer, and dc conductivity. GIXRD revealed that the nanocrystals had a size of 7.7 nm. The SEM image shows rough surface and crystalline grains in spherical shapes. There is a high level of transparency in the visible region, with an average value of 95%. The dc conductivity and the activation energy at room temperature are 950 $\Omega^{-1}m^{-1}$ and 0.032 eV, respectively. Thin films of annealed ZnO, which are highly transparent and conductive, can be used as transparent conductive electrodes in solar cells.

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