The Influence of Hydrogen Gas Treatment on the Characteristics of ZnO Films

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Abstract: This study presents a zinc oxide (ZnO) film deposited on a glass substrate by ultrasonic spraying pyrolysis. The ZnO nanostructure was formed by treating the as-deposited ZnO films with hydrogen. The root-mean-square (RMS) roughness increases from 5.83 nm to 12.53 nm during the treatment for 20 min, but slightly decreases to 11.87 nm at a treatment time of 30 min. In the range 400-500 nm, the transparency of all the films with hydrogen treatment is slightly lower than that of the untreated films. The slight drop in the transparency of the films with hydrogen treatment is caused by scattering from pin-holes or nanostructures on the surface.

Key Words: Zinc oxide, hydrogen gas treatment, ultrasonic spraying pyrolysis.

1. INTRODUCTION

Because of having a wide direct band gap energy of 3.37 eV and a large exciton binding energy of 60 meV, zinc oxide (ZnO) is regarded as a promising material for use in optical devices [1-3]. Therefore, ZnO film has been extensively used in light-emitting diodes (LEDs), laser diodes (LDs), ultraviolet (UV) detection devices, and other optoelectronic devices [3-9]. Moreover ZnO and related materials, which are doped with transition metal (TM) ions, have high-Curie-temperature ferromagnetism such that it is expected to have applications in spintronics, information storage and data processing devices [10].

On the other hand, ZnO films with one-dimensional structures have attracted increasing interests because of their potential for use in nanometer-scale optoelectronic devices. The manufacture of the ZnO nanostructures by treating with hydrogen gas or hydrogen-containing gas has been reported [11-14]. However, the characteristics of the ZnO films with hydrogen treatment are still unclear. This work will investigate the characteristics of hydrogen-treated p-ZnO nanostructures. An N-In codoped p-type dopant was deposited on a glass substrate by ultrasonic spraying pyrolysis. The morphology and crystallinity of the ZnO films are studied. Finally, the optoelectronic properties of the p-ZnO nanostructure formed by hydrogen treatment are elucidated.

2. EXPERIMENTAL

N-In codoped ZnO films were deposited by ultrasonic spray pyrolysis at atmospheric pressure on glass substrates. Three aqueous solutions, $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.5 mol/l), CH_3COONH_4 (2.5 mol/l) and $In(NO_3)_3$ (0.5 mol/l), were used as sources of zinc, nitrogen, and indium, respectively. The atomic ratio of Zn/N was 1:2 in the N-doped film, and that of Zn/N/In was 1:2:0.15 in the N-In codoped film [15]. Glass was used as the substrate, which was etched with HCl for 5 min before deposition. An aerosol of the precursor solution was generated by using a commercial ultrasonic nebulizer. P-type N-In codoped ZnO films were obtained by heating the substrate to 650 °C, and then ZnO films were carried out with a post-deposition annealing at 500 °C for 10 min in oxygen ambient to improve the film quality. Finally, the ZnO films were studied by Hall measurements. The ohmic contacts for electrical measurements were made by evaporating Ni/Au alloy at the four corners of the samples using electron-beam evaporation technique at a base pressure of 1×10^{-6} Torr. The hole concentration and mobility of p-ZnO were about 1×10^{17} cm^{-3} and about 46 $cm^2/V\text{-}s$, respectively. These results are consistent with those of Ref. [16]. The crystalline structure were studied by X-ray diffraction (XRD) using a rotating anode Rigaku x-ray powder diffractometer (Mac Science Corp. M03XHF, Japan) with Cu-$K\alpha_1$ radiation of 1.54056 Å, radiation generated at 40 kV and 50 mA, and the films had a polycrystalline structure.

P-ZnO etching process was performed in hydrogen atmosphere and the morphology was studied by atomic force microscopy (AFM). A JEOL JSM-5600 scanning electron microscope (SEM) was used to study the surface morphology of the P-ZnO films. A 30-W deuterium lamp and a 35-W halogen lamp were used as light sources in the transmittance spectra studies at wavelengths from 300 to 800 nm and the optical band gap energy was calculated. All measurements were made at room temperature.

3. RESULTS AND DISCUSSION

The AFM was used to measure the surface roughness of the films over an area of 5 cm × 5 cm. Fig. (**1**) presents an AFM image of the p-type ZnO film, which was deposited on a glass substrate with hydrogen gas treatment at 450 °C. The ZnO film with a thickness of about 1.0 μm was formed on the glass substrate. As compared with the as-deposited

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films, the films with hydrogen treatment would increase the surface roughness. Fig. (**2a**) plots the root-mean-square (RMS) surface roughness of films. Fig. (**2b**) shows the carrier concentration of films for different treatment time. The RMS roughness increases from 5.83 to 12.53 nm during the treatment for 20 min, but then it slightly decreases to 11.87 nm as the treatment continues for 30 min. However, the carrier concentration increases with the increase in treatment time owing to the vacancy raise of oxygen. The ZnO film in an environment of hydrogen would be etched, according to the following reaction.

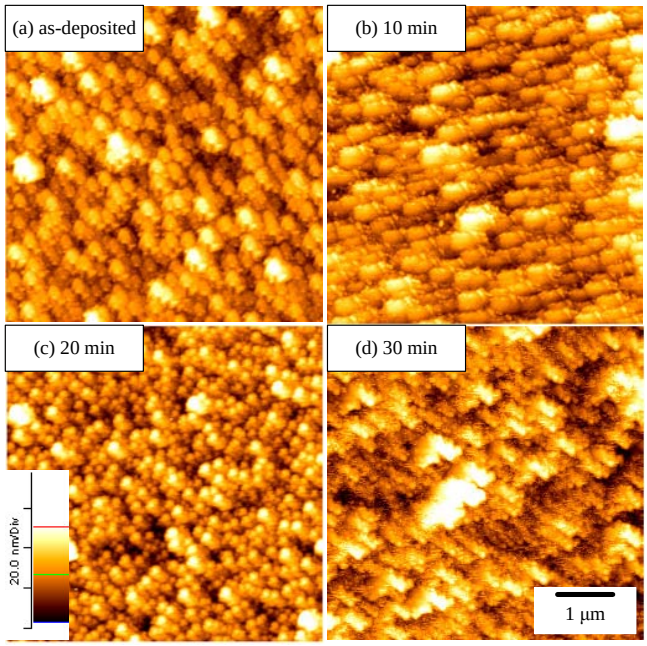
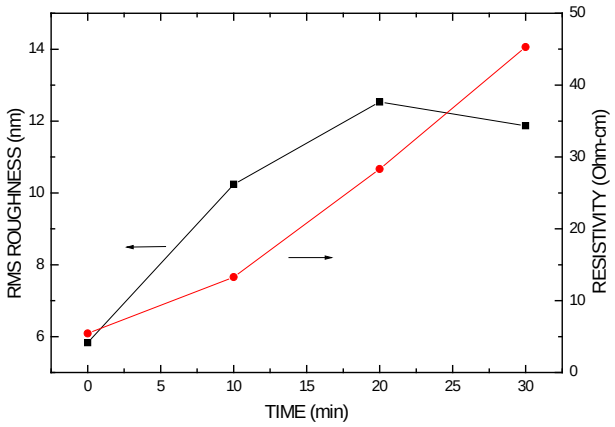


Fig. (1). The AFM image of the p-type ZnO film deposited on a glass substrate with hydrogen-gas treatment at 450 °C.

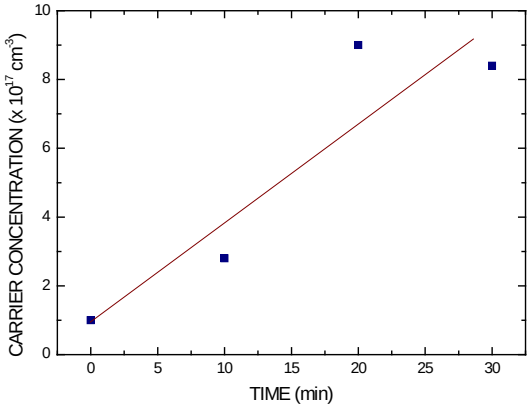
$$ZnO + H_2 \rightarrow Zn + H_2O \quad (1)$$

Therefore, the ZnO film is roughened, as presented in Fig. (**1**). Fig. (**3**) shows the SEM micrographs of the ZnO films with nitrogen-gas treatment for different time. The micrographs indicate that the surface of the film consisted of small particles. The average particle sizes were approximately 0.1, 0.12, and 0.24 μm, respectively. The films with hydrogen treatment would increase the particle sizes. This result matched with that of AFM image.

Fig. (**4a**) plots typical results of the absorption experiment in the wavelength range 300-800 nm. All of the films are highly transparent in the visible region. The optical transmittance in the visible range is 80-99%, but is slightly lower film in the range 400-500 nm after hydrogen treatment. In the range 500-800 nm, the light energy was well below the band gap of the films and the wavelength of the radiation markedly exceeds the grain size, the pin-hole size, and the surface roughness of the films. Therefore, in this range, no scattering occurs in the films and the loss of transparency is mainly due to the reflection of the light. However, in the range 400-500 nm, the transparency of all the treated films is slightly lower, because of the electron transitions between the valence and conduction bands. Additionally, radiation in the range 400 500 nm can be scattered by smaller defects than by radiation with longer wavelengths. The slight drop in the transparency of the films with hydrogen treatment must be caused by the scattering from pin-holes or nanostructures on the surface. Fig. (**4b**) plots the absorption squared as a function of photon energy. The absorption coefficient α is expected to vary as $\alpha \propto (\hbar\nu - E_g)^{1/2}$, where E_g is the direct optical band gap. An extrapolation of the linear part of the curve to the horizontal axis in this figure yields the band-gap energy of ZnO. All of the films have an absorption edge of 3.3 eV.



(a)



(b)

Fig. (2). (**a**) The RMS surface roughness and resistivity of films. (**b**) The carrier concentration of films.

Fig. (**5**) presents a typical XRD pattern of a ZnO film, which was deposited on a glass substrate prepared by ultrasonic spraying pyrolysis. Two dominant diffraction peaks, ZnO(002) ($2\theta = 34.48°$) and ZnO(101) ($2\theta = 36.34°$), are observed. The film had a polycrystalline (multiple phases) structure, which is barely changed by treatment with hydrogen.

4. CONCLUSION

ZnO films were deposited on glass substrates by ultrasonic spraying pyrolysis. The ZnO nanostructure

was formed by treating the as-deposited ZnO films with hydrogen. The RMS roughness increases from 5.83 to 12.53 nm during 20-min treatment, but decreases slightly to 11.87 nm as the treatment continues for 30 min. All of films had an absorption edge of 3.3 eV. However, in the range 400-500 nm, the transparency of all hydrogen-treated films is slightly lower than that of the untreated films. Scattering from pin-holes or nanostructures on the surface is responsible for the slight drop in the transparency of the films with hydrogen treatment.

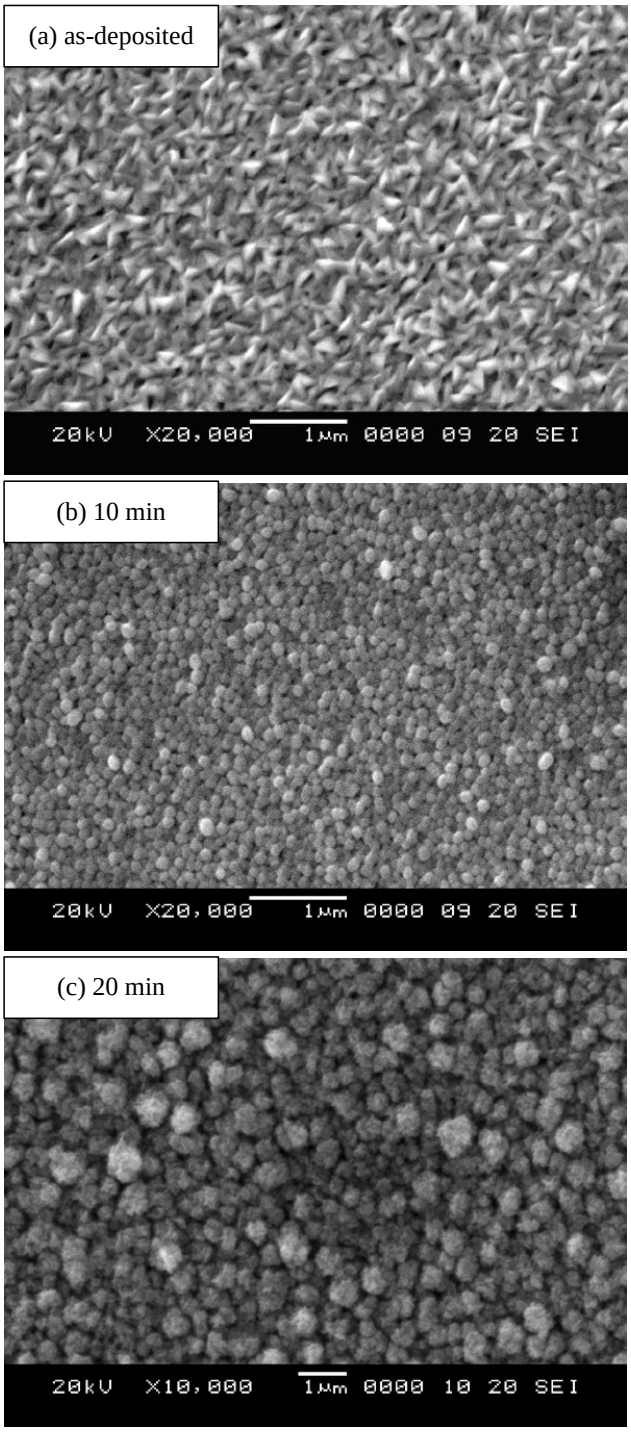
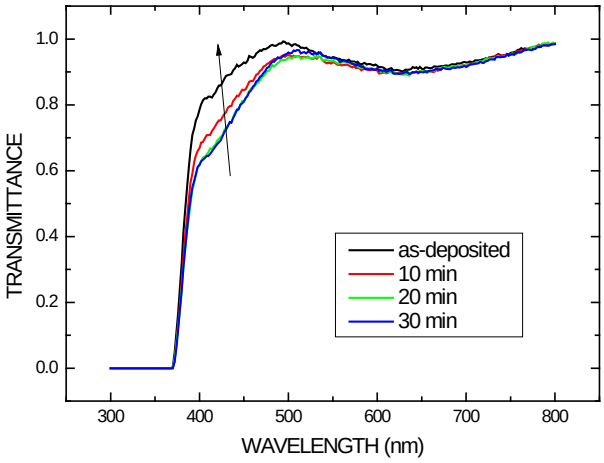
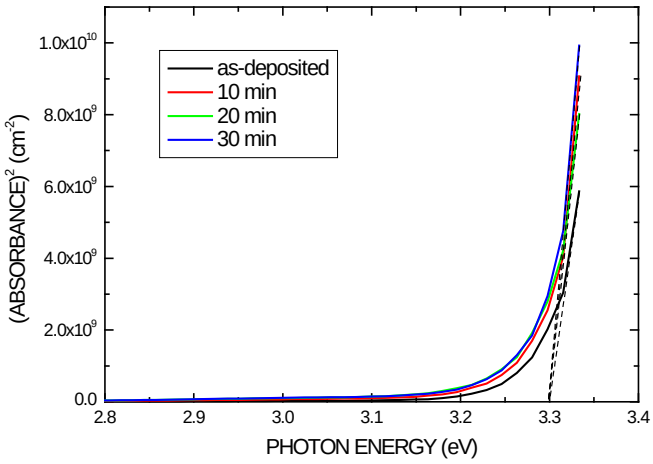


Fig. (3). SEM images of the ZnO films with hydrogen-gas treatment for: (**a**) 0, (**b**) 10, (**c**) 20 min.



(a)



(b)

Fig. (4). (**a**) Typical absorption spectra experiment in the wavelength range of 300-800 nm. (**b**) The relationship between absorption squared versus photon energy.

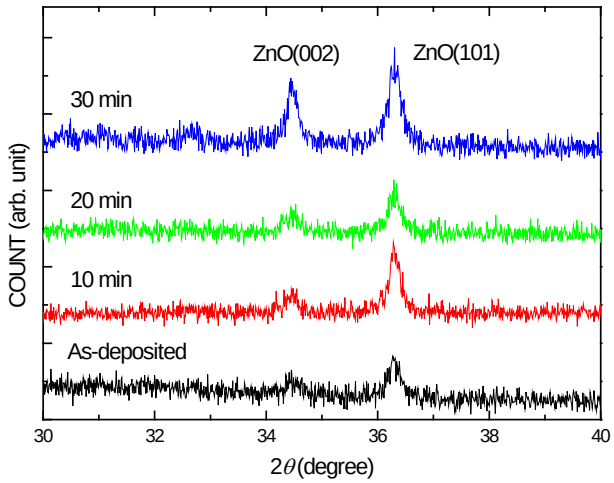


Fig. (5). Typical XRD pattern of ZnO film deposited on the glass substrate prepared.

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