Conversion of p-type to n-type conductivity in ZnO thin films by increasing temperature

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ABSTRACT: ZnO thin films with the thickness of about 15nm on (0001) substrates were prepared by pulsed laser deposition. X-ray photoelectron spectroscopy indicated that both as grown and then annealed ZnO thin films were oxygen rich. Hydrogen (H_2) sensing measurements of the films indicated that the conductivity type of both the unannealed and annealed ZnO films converted from p-type to n-type in process of increasing the operating temperature. However, the two films showed different conversion temperatures. The origin of the p-type conductivity in the unannealed and annealed ZnO films should be attributed to oxygen related defects and Zinc vacancies related defects, respectively. The conversion of the conductivity type was due to the annealing out of the correlated defects. Moreover, p-type ZnO films can work at lower temperature than n-type ZnO films without obvious sensitivity loss.

Keywords: ZnO thin films, Conductivity conversion, Defects, H_2 sensitivity.

1. Introduction

ZnO is one of the most promising candidates for light-emitting diodes, laser diodes and UV photo detectors [1]. The growth of high-quality p-type ZnO is essential for the application of ZnO devices. It is very difficult to growth of p-type ZnO material. For the widely investigated doped p-type ZnO, low solubility of the acceptor dopants, deep acceptor level, and the compensation effect between the acceptor dopants and the native donors are still obstacles for high quality doped p-type ZnO [2]. Besides, p-type conductivity was also found in undoped ZnO [3, 4]. Look et al. [5, 6] have proved the existence of native acceptors in undoped ZnO theoretically and

experimentally. P-type behavior in undoped ZnO is based on native acceptor defects indicated to zinc vacancies absorbed oxygen in the grain boundary [4]. However, the mechanism of p-type conductivity in undoped ZnO is still not fully understood. On the other hand, the conversion of conductivity type, which could help to understand the mechanism of p-type conductivity, has been observed in diamond and GaN [7,8]. However, the conversion of conductivity type of ZnO has been seldom reported. In this paper, the conversion of ZnO from p-type to n-type was presented by means of increasing the operating temperature, indicated from H_2 sensing measurements results, and the mechanism of the conversion was discussed. This work provides experimental evidence of the intrinsic defects existing in undoped p-type ZnO and show the way to make the high quality p-type ZnO material.

2. Experimental Details

ZnO films were deposited on substrates by pulsed laser (248nm KrF excimer) ablation of ZnO target (purity – 99.999%). The films were grown at 600°C in oxygen ambient of 2.6×10^{-4} mTorr for 8min. The grown ZnO films were annealed at 700°C in air ambient for 1 h. The thicknesses of these films were about 15 nm, determined by the transmittance spectra. Structure and surface morphology of the ZnO films were investigated by X-ray diffraction (XRD) and atomic force microscope (AFM). X-ray photoelectron spectroscopy (XPS) of the samples was performed on a system described previously [9] to identify the composition of the films. The conductivity type of the films was determined by Hall measurements at room temperature together with H_2 sensing measurements at higher temperatures. The sensing properties were evaluated at various operating temperatures by measuring the resistances of the films in air and H_2, respectively. The hydrogen concentration in N_2 gas could be operated from 5 to 5000ppm.

3. Result and discussion

Fig. 1 (i) shows XRD pattern of the unannealed ZnO film. Only diffraction from hexagonal ZnO (0002) was observed, indicating good crystalline quality and c-axis preferential growth. AFM image of the sample is shown in the inset of Fig. 1. The surface of the film is uniform and smooth. The root mean square value of it was only 0.899 nm. Hall measurement of the unannealed ZnO film was carried out at room temperature. Positive Hall coefficient revealed p-type conductivity of the film. Hole concentration and hole mobility of the film were 1.5×10^{18} cm^{-3} and 15 cm^2/Vs, respectively. It can be seen that the film was of high hole concentration. The film annealed at 700°C was too resistive to be taken Hall measurement.

Fig. 2 presents XPS of the unannealed and 700°C annealed ZnO films. The binding energies were calibrated by taking carbon peak (284.6 eV) as reference. The O1s observed at 531 eV, and $Zn2p_{3/2}$, $Zn2p_{1/2}$ locating at 1022 and 1045 eV, correspond to O and Zn on normal wurtzite structure of ZnO single crystal, respectively [10]. The quantitative analysis of XPS was carried out by using the software "XPS peak". A Shirley-type back-ground subtraction was applied to the photoemission spectra.

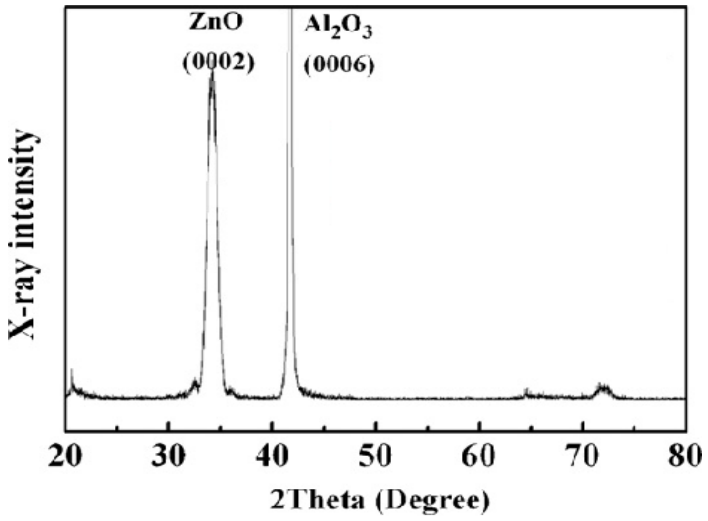

Fig. 1 (i)

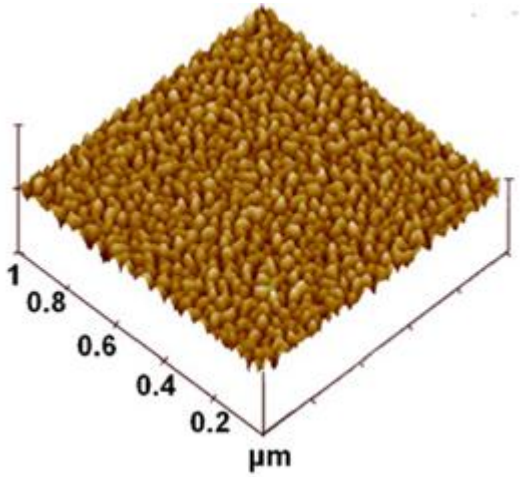

Fig. 1 (ii)

Fig. 1. (i) XRD pattern of unannealed ZnO film on (0001) Al_2O_3 substrate.
(ii) AFM image of ZnO film on Al_2O_3 substrate.

The relatively quantitative results were obtained according to the following equation:

$$\frac{N_O}{N_{Zn}} = \frac{\frac{A_O}{S_o}}{\frac{A_{Zn}}{S_{Zn}}}$$

where N, A, and S refer to the relative content of atomics, the XPS peak area of the element, and the elemental sensitivity factor, respectively. S_o and S_{Zn} were 0.711 and 3.726 for O1s and Zn_2p_2/3peaks, respectively. The calculated relative contents of O of the two samples were nearly the same, while the relative content of Zn decreased dramatically after annealing. The ratios of O and Zn atoms of the unannealed and 700 $^{\circ}$C annealed ZnO films were 1.1 and 2.1, respectively. In other words, both films were oxygen-rich, and the annealed sample showed a ratio much larger than stoichiometry

ratio of ZnO. It was found that both Zn and O atoms lost during the vacuum annealing process [11].

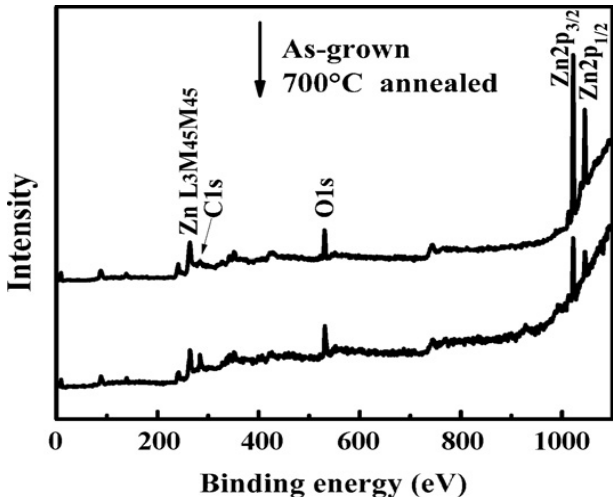

Fig. 2. XPS full spectra of unannealed and 700 ◦C annealed ZnO films.

First the sample was annealed in air, so O_2 should compensate the loss of O atoms, leading to a decrease of Zn content and subsequently the larger non-stoichiometry of the annealed films, compared with the unannealed ZnO film. Besides, the oxygen adsorbed on the surface of the annealed ZnO during the annealing process in air would contribute to the high O ratio of it. The conductivity type of the ZnO films can be confirmed by the hydrogen sensing properties of them. For n-type ZnO films, the oxygen molecules chemisorbing on the surface of the films will extract electrons from the conduction band of ZnO, leading to the increase of the resistance. When the films are exposed to H_2, H_2 molecules react with chemisorbed O_2, giving rise to a decreased resistance due to the release of electrons to the conduction band [12]. For p-type ZnO, the resistance shows reverse changes to n-type ZnO in the same gas ambient. The transient response–recovery curves of the unannealed ZnO film to H_2 with different concentration recorded at 150 and 200 ˚C are presented in Fig. 3(a). The two curves

showed totally opposite response trends to air and H_2 with the H_2 concentrations changing from 5 to 5000 ppm.

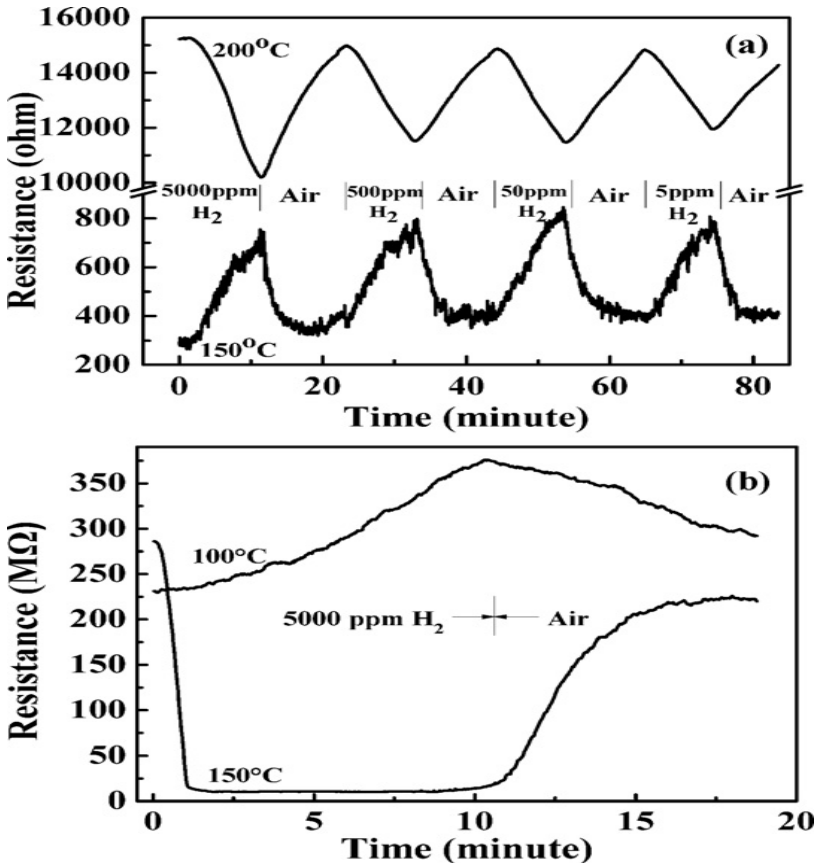

Fig. 3. The transient response–recovery curves of (a) unannealed ZnO film to different H_2 concentration recorded at 150 and 200 ˚C, (b) 700 ˚C annealed ZnO films to 5000ppm H_2 recorded at 100 and 150 ˚C, respectively.

The conversion of conductivity type could be clearly observed. The increase and decrease of resistance in different gas ambient showed good repeatability, indicating that the conductivity is stable. Furthermore, the response in H_2 ambient at 150 ˚C

suggested p-type behavior, revealing that the origin of p-type conductivity was not from the oxygen absorbed on the film surface but from the intrinsic defects. The sensing properties of this film were also measured at 50, 100, 250 and 300 ˚C (data not shown). The film was p-type at 50–150 ˚C and n-type at 200–300 ˚C, indicating that the conductivity conversion temperature of the unannealed ZnO film was between 150 and 200 ˚C. Similar curves were also observed in the 700 ˚C annealed ZnO film. The transient response–recovery characteristics of the annealed ZnO film to 5000 ppm H2 recorded at 100 and 150 ˚C were presented in Fig. 3(b). The film showed p-type behavior at 100 ◦C and n-type behavior at 150 ◦C, indicating that the conductivity conversion temperature was between 100 and 150 ˚C. Thus both the unannealed and 700 ˚C annealed ZnO films showed conversion of conductivity type. However, the two films showed different conversion temperatures. Besides, the conversions of the conductivity type of both films were repeatable with the conversion temperatures unchangeable. And the conductivity type at the given temperatures was stable for each of the sample. To find the mechanism of the conversion, the origin of p-type conductivity should be considered firstly. Since both of the unannealed and annealed ZnO films were oxygen-rich, oxygen interstitial (Oi), oxygen antisites (OZn) might exist in the films. And because the thicknesses of both samples were very thin (only 15 nm), more native defects were contained in the films, compared with that of the bulk material or thick films. Two different VZn-related defects were confirmed in ZnO films. One of them was annealed out at 400 K. Meanwhile, Oi and OZn were annealed out at the temperature between 400 and 500K. According to the sensing properties of the ZnO films in this study, the conversion temperature for the annealed samples was between 100 and 150 ˚C, so the dominant defects in the annealed ZnO film were related to VZn defects. And the conversion temperature of conductivity type for the unannealed ZnO film was between 150 and 200 ˚C. Thus O_i and O_{Zn} might be dominant in the unannealed ZnO film. The annealing out of the defects with increasing the temperature could well explain the conversion of conductivity P-type of the ZnO films. The experimental results correspond well with previous researches. Moreover, further investigations on the defects of undoped ZnO are expected and the work is on the way.

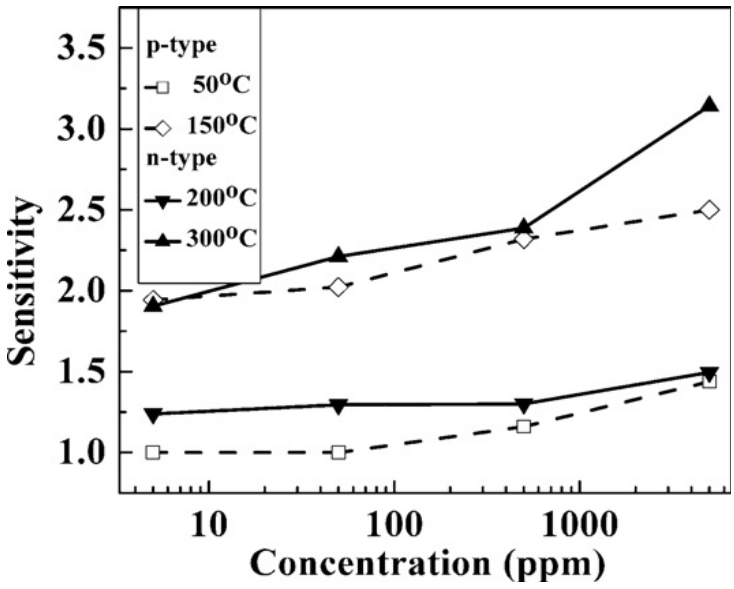

Fig. 4. Sensitivity to H_2 of the unannealed ZnO film vs. H_2 concentration at different Temperatures. The sensitivity was given by Ra/Rg for n-type ZnO and Rg/Ra for p-type ZnO film.

The sensitivity of the unannealed ZnO film to H_2 with different concentration recorded at 50–300°C is displayed in Fig. 4. The gas sensitivity is given by Ra/Rg for n-type ZnO and Rg/Ra for p-type ZnO, where Ra and Rg express the resistance of the sensor in air and after exposure to hydrogen for 10 min, respectively. The film showed p-type conductivity at the operating temperature of 50–150°C and n-type conductivity at 200–300°C. The gas sensitivity of the unannealed ZnO film increased with increasing the operating temperature, except where the conductivity of the film converted from p-type to n-type (150–200°C). It could be observe from Fig. 4 that p-type ZnO film showed as high sensitivity as n-type ZnO film at lower operating temperature. In other words, the p-type ZnO films can work at lower temperature than n-type ZnO films without obvious sensitivity loss.

4. Conclusion

ZnO films were fabricated by pulsed laser deposition. H_2 sensing measurements exhibited the conversion of p-type to n-type in both the unannealed and 700 °C annealed ZnO films with increasing the operating temperature. The origin of p-type conductivity is mostly attributed to the O_i and O_{Zn} for the unannealed ZnO film and V_{Zn} related defects for the annealed ZnO film. The conversion of conductivity type of the ZnO films is due to the annealing out of the correlated defects. Besides, it is found that p-type ZnO films can work at lower temperature than n-type ZnO films, without obvious sensitivity loss.

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