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Electrical conduction effects at low temperatures in undoped ZnO thin films grown by Pulsed Laser Deposition on Si substrates

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Abstract

The electrical properties of undoped ZnO films grown by Pulsed Laser Deposition on Si substrates at growth temperatures between 150 and 250 °C and low O_2 partial pressures, were studied by resistivity and Hall coefficient measurements in the temperature range of 80 to 350 K. We report acceptor band and hopping conduction effects in these ZnO films, for the first time. P-type conduction is found to be dominant in these films for temperatures higher than approximately 235 K, while at temperatures lower than 235 K the films exhibit a conversion from p- to n-type conductivity. The electrical conductivity studies revealed a conduction mechanism by hopping in the acceptor band in the temperature range between 80 and 270 K. For temperatures higher than 270 K a thermally activated behavior, between the native acceptor band (Zn vacancies) and the valence band is dominant. The acceptor activation energy values extracted from the ln$p$ versus T^{-1} curves were found to be of 0.1 eV. The electrical mobility values fall-off rapidly from 90 to 8 cm^2/V s for temperatures below 270 K, providing evidence that a mobility edge exists between transport in the valence band and transport in the acceptor band.

Keywords: Zinc-oxide; Acceptor band; Laser ablation; Hopping conductivity; Si

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1. Introduction

ZnO is a very promising material for electronic and optoelectronic devices [1–3], having also a good potential for applications in spintronic devices [4]. It is a wide band-gap semiconductor material having a large exciton binding energy (60 meV), which is important for applications in highly efficient room temperature UV Lasers and Light Emitting Diodes [4–6], as well as transparent electronic devices [7].

Undoped ZnO usually exhibits n-type conduction with high electron concentrations, which is attributed to a stoichiometric deviation from the native defects, such as oxygen vacancies (deep donors), Zn interstitials [8–10], and/or shallow hydrogenic donor defects that have been reported in the past few years [11–13]. The growth of stable p-type ZnO films doped with deep acceptors [7,13] demonstrating reproducible properties is a very difficult task mainly due to the self-compensation effects caused by the native shallow donor states [8,9]. The p-type conductivity of ZnO is necessary for applications in p–n junction devices, such as UV diode lasers and other optoelectronic devices [5]. Such applications also require the use of p-type ZnO films having hole concentrations higher than 10^{18} cm^{-3}. Undoped p-type ZnO films grown by Pulsed Laser Deposition (PLD), Chemical Vapor Deposition and Metalorganic Vapor Phase Epitaxy techniques in O_2 rich conditions have been reported [14,15]. Our recent report indicates that PLD growth at low O_2 overpressures and low temperatures produces stable undoped p-type ZnO [16]. The p-character of these ZnO films is believed to be associated with the high competition effects occurring between the native shallow or deep donor and acceptor defects [8,10]. The compensation effects are revealed by the temperature dependence of the apparent carrier concentration deduced by Hall effect measurements. High compensation

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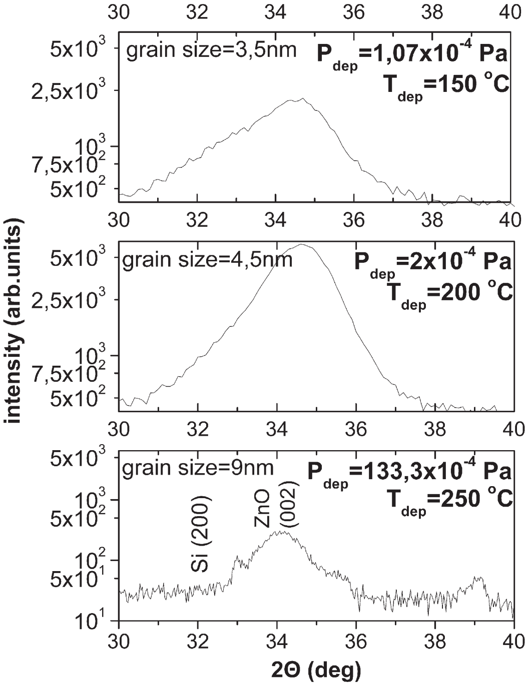

Fig. 1. X-ray diffraction patterns of ZnO films grown on Si at different O_2 partial pressures of 1.07×10^{-4}, 2.00×10^{-4} and 133.30×10^{-4} Pa, and growth temperatures of 150, 200 and 250 °C, respectively. The measurements were performed with a Rigaku 18 kW rotating anode source X-ray diffractometer using the Cu Kα line.

effects, disorder effects and/or high doping levels are often responsible for the low temperature impurity band conduction effects observed in semiconductors [17–20].

This work presents a study of the electrical conduction behavior of undoped ZnO films grown by PLD at low oxygen pressures and growth temperatures. Acceptor band and hopping conduction effects are observed in these undoped ZnO films, and reported here for the first time.

2. Experimental details

Undoped ZnO thin (300 nm) films were grown on (100) Si substrates by PLD using a KrF excimer laser at 239 nm to ablate a rotating stoichiometric ZnO target with a fluence of 0.8 J/cm^2. The films were grown under O_2 partial pressures of 1.07×10^{-4}, 2.00×10^{-4} and 133.30×10^{-4} Pa, at growth temperatures of 150, 200 and 250 °C, respectively. Based on our previous work [16], the growth temperature in the range of 150 to 250 °C had minimal effect on parameters such as specific resistivity, Hall voltage, and grain size, while the O_2 partial pressure was the main growth parameter that influenced the electrical and structural properties in this growth temperature range.

The electrical conduction parameters as a function of temperature were obtained by resistivity and Hall measurements utilizing the Van der Pauw technique. The measurements were made in the temperature range of 80 to 340 K using a liquid nitrogen cryostat system. An Oxford ITC-502 controller was used for temperature control. The structural properties of the films were studied by X-ray diffraction (XRD) measurements. The grain size in the grown films was obtained using the Scherrer formula [21] in conjunction with the *full-width at half maximum* of the XRD rocking curves. The X-ray diffraction measurements were performed at room temperature with a Rigaku 18 kW rotating anode source X-ray diffractometer using the Cu $K_{\alpha 1}$ line ($\lambda = 1.54$ Å, energy = 8.8 keV) and operating at 50 kV, 100 mA with slits set at 10×2 mm^2.

3. Results and discussion

Fig. 1 presents the XRD results of three ZnO films grown at O_2 partial pressures of 1.07×10^{-4}, 2.00×10^{-4} and 133.30×10^{-4} Pa. All grown films showed the ZnO wurtzite structure with a main peak positioned at 34.4° that corresponds to the (002) crystallographic direction. The intensity of the peak increases as the oxygen pressure increases from 1.07×10^{-4} to 2.00×10^{-4} Pa, while further increase in oxygen pressure to 133.30×10^{-4} Pa resulted in a decrease in the intensity of the (002) direction. The grain size values were found to be 3.5, 4.5 and 9 nm for oxygen pressures of 1.07×10^{-4}, 2.00×10^{-4} and 133.30×10^{-4} Pa, respectively.

The electrical resistivity (ρ) and Hall coefficient (R_H) results in the temperature range of 80 to 350 K are shown in Figs. 2 and 3, respectively. The electrical resistivity at temperatures between 80 and 225 K (Fig. 2) is almost constant or increases slowly with temperature exhibiting values of 1.5, 1.8 and 3.3×10^{-3} Ω cm for the films grown at 1.07×10^{-4}, 133.30×10^{-4} and 2.00×10^{-4} Pa, respectively. At temperatures between 225 and 250 K a fast reduction of about 30% is observed while for temperatures higher than 250 K the resistivity increases again indicating a change in the conduction mechanisms.

As shown in Fig. 3, the Hall coefficient R_H exhibits negative values at temperatures between 80 and 225 K in all three films, indicating n-type conduction. However, the R_H values tend to change from negative to positive at temperatures above 232, 231 and 242 K in films grown in O_2 pressure of 1.07×10^{-4}, 2.00×10^{-4} and 133.30×10^{-4} Pa, respectively, thereby signifying conversion of the conduction character of the films from n- to p-type. The p-type character of the films continues up to room temperature,

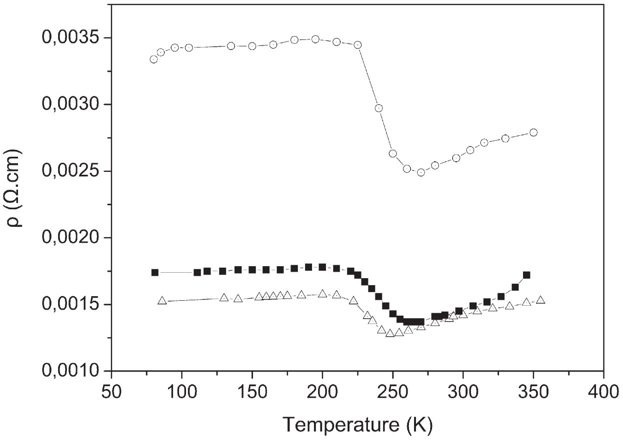

Fig. 2. Electrical resistivity results versus temperature for three ZnO films grown at O_2 partial pressures of 1.07×10^{-4} Pa (○), 2.00×10^{-4} Pa (Δ) and 133.30×10^{-4} Pa (■), and growth temperatures of 150, 200 and 250 °C, respectively.