

## Effect of oxygen partial pressure on the Fermi level of ZnO<sub>1-x</sub> films fabricated by pulsed laser deposition

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We investigated the influence of oxygen deficiency on the Fermi level ( $E_F$ ) of ZnO thin film prepared by pulsed laser deposition (PLD). For this purpose, we adopted *in situ* x-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy. The oxygen deficiency was effectively controlled by varying the oxygen partial pressure [ $P(O_2)$ ] during the PLD. The  $E_F$  shifted by +0.6 eV as the  $P(O_2)$  decreased from 10 to 3.3 Pa. This shift indicates a significant change in the energy balance in the oxygen-deficient ZnO films. This fact suggests that the very large change in the resistivity of ZnO thin films resulting from the oxygen deficiency could be attributed to the  $E_F$  shift rather than grain boundary formation in the ZnO film. © 2010 American Institute of Physics. [doi:10.1063/1.3432398]

Zinc oxide (ZnO) has gained attention as one of the most useful materials for developing transparent conductive oxides.<sup>1,2</sup> For several decades, the resistivity of ZnO films has been continuously decreased by doping with suitable impurities.<sup>3</sup> In this regard, the report, stating that the resistivity of polycrystalline undoped ZnO films can be changed by more than ten orders of magnitude by controlling the oxygen partial pressure [ $P(O_2)$ ] during rf magnetron sputtering,<sup>4</sup> attracted a lot of attention. The sudden increase in the resistivity of polycrystalline ZnO with increasing  $P(O_2)$  was explained by adopting the grain boundary trapping model, in which mobile carriers are trapped among the boundaries of identical one-dimensional crystallites by interstitial oxygen atoms and the trapped carriers become energy barriers among the grains.<sup>4-6</sup>

However, this explanation appears to have some inconsistencies. First, the grain boundaries of the polycrystalline ZnO films are at least of two dimensional nature. The films are usually grown with (002) c-axis texture and have columnar grains, and their resistivities are generally measured perpendicular to the c-axis, so that the current flows through the grain boundaries on the a-b plane. Therefore, the grain boundary trapping model in which the grains are assumed to be one-dimensional does not take into account the multidimensional scattering process for the polycrystalline ZnO films.<sup>7</sup> Further, the oxygen vacancy, which increases the mobile carrier density,<sup>8</sup> possibly influences the electronic structure throughout the entire volume rather than a specific location such as the grain boundary. Therefore, the presence of the oxygen vacancy is expected to change the global energy balance in the thin film, and the Fermi level ( $E_F$ ), which is defined as the chemical potential in equilibrium between the

formations of holes and electrons, can be easily changed depending on the oxygen vacancy. In this study, we carried out *in situ* photoelectron spectroscopic measurement to show that  $E_F$  is indeed influenced by the oxygen vacancy in ZnO film. This suggests that the reason for the oxygen vacancy causing an abrupt change in the resistivity of ZnO films might be the change in  $E_F$  rather than the formation of the grain boundary, as previously believed.

The density of the oxygen vacancy was easily controlled by varying the  $P(O_2)$  during ZnO film deposition. The ZnO films in our experiment were prepared at room temperature by pulsed laser deposition (PLD) using a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser at a wavelength of 266 nm, an average energy density of 1.1 J/cm<sup>2</sup> per pulse, and a repetition rate of 10 Hz. We used amorphous SiO<sub>2</sub> substrates cleaned with acetone in an ultrasonic bath.  $P(O_2)$  was varied from 0 to 10 Pa during the PLD growth. The thickness of the films as estimated by the ellipsometry was  $100 \pm 20$  nm. For *in situ* photoelectron spectroscopy (PES) measurement, after PLD growth, the films were transferred from the growth chamber to a PES chamber without breaking the vacuum; the PES chamber was equipped with a CLAM4 spectrometer. An Al  $K\alpha$  x-ray ( $h\nu=1486.6$  eV) and a He I source ( $h\nu=21.2$  eV) were used for soft x-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS), respectively. The energy resolutions in XPS and UPS were 1.0 eV and 0.04 eV, respectively. The energy calibration for UPS was performed by using the Fermi edge of a clean Au foil and that for XPS was performed by setting the binding energy (BE) of the Au 4f<sub>7/2</sub> core-level as 84.0 eV. In order to prevent the space-charging effect, the films were bridged to the sample holder (and to ground) using silver paint. The base pressure in the PLD chamber was below  $4.0 \times 10^{-7}$  Pa and that in the PES chamber was below  $1.3 \times 10^{-8}$  Pa. By x-ray diffraction, we con-

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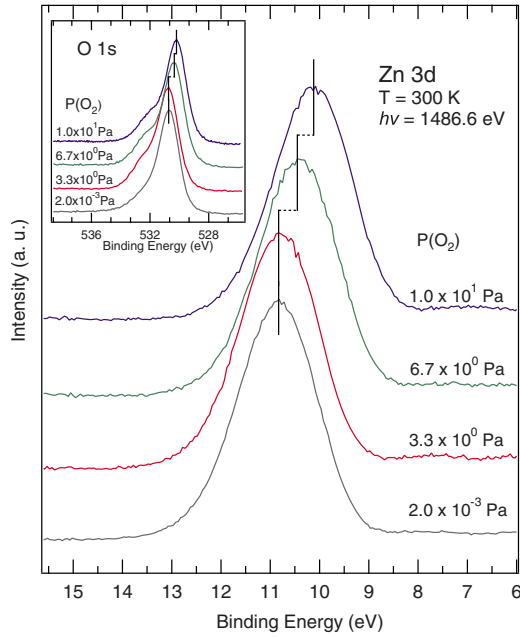


FIG. 1. (Color online) The XPS spectra of Zn 3d and O 1s (inset) core levels. The BEs of the Zn 3d and O 1s core-levels shifted to higher values as  $P(O_2)$  decreased.

firmed that the films fabricated under various  $P(O_2)$  were randomly oriented, although a few favorable orientations did exist.

Figure 1 shows the XPS spectra of the Zn 3d and O 1s (inset) core-levels of the oxygen-deficient ZnO films for various  $P(O_2)$  from 10 to  $2 \times 10^{-3}$  Pa (from the top curve to the bottom). As shown in this figure and Table I, as  $P(O_2)$  decreased from 10 to 3.3 Pa, BE shifts of +0.7 eV and +0.5 eV appeared in the Zn 3d and O 1s XPS spectra, respectively, whereas almost no further BE shifts were observed for  $P(O_2) < 3.3$  Pa. In general, the XPS BE shift can be represented as the sum of contributions from the changes in a partial atomic charge and those in  $E_F$  (neglecting the difference in relaxation energy), which are called a chemical shift and a  $E_F$  shift, respectively. We can differentiate between the two contributions on the basis of their directions of BE shifts, which are assigned to a leading plus or minus sign on the BE shift. The chemical shift is related to the charge transfer between the zinc and oxygen ions, and hence, its contribution at the zinc and oxygen ions should have the opposite direction. In contrast, the  $E_F$  shift causes apparent rigid BE shift in the same direction irrespective of the atomic species involved, since the BE, by definition, is given as the energy difference from the  $E_F$ . Thus, BE shifts of +0.7 and +0.5 eV for the zinc and oxygen ions, are a result of the  $E_F$  shift of 0.6 eV toward the conduction band minimum of ZnO (+0.6  $E_F$  shift) and a chemical shift of  $\pm 0.1$  eV. The  $E_F$  shift is significant compared to the band gap ( $\sim 3.4$  eV). The  $E_F$  shift of +0.6 eV in the oxygen-deficient ZnO films suggests

TABLE I. BE of Zn 3d and O 1s for different  $P(O_2)$ .

$P(O_2)$ (Pa)	BE <sub>Zn 3d</sub> (eV)	BE <sub>O 1s</sub> (eV)
10	10.1	530.2
$2.0 \times 10^{-3}$	10.8	530.7

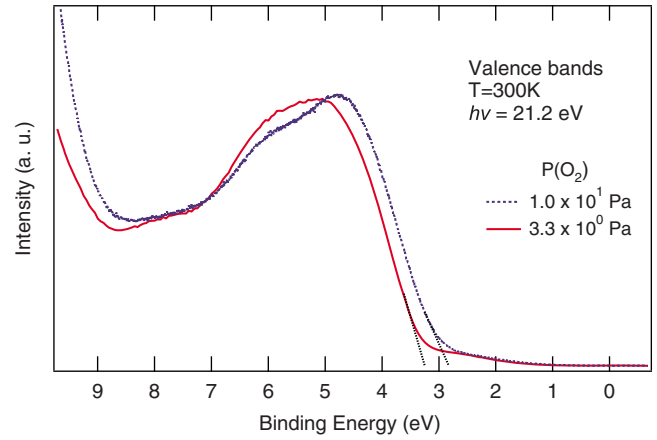


FIG. 2. (Color online) The valence spectra of ZnO for different  $P(O_2)$ . Changes in  $P(O_2)$  cause a 0.4 eV of difference in the VB edge.

that the overall change in the electron-hole balance occurs throughout the films and is not confined to a specific region such as the grain boundary. For  $P(O_2) < 3.3$  Pa, the maximum possible defect formation occurs and thus  $E_F$  does not change further.

We also measured the resistivity of the oxygen-deficient samples using a four-probe apparatus. While the resistivities of the samples under  $P(O_2)$  less than 3.3 Pa were approximately  $10^{-2}$   $\Omega$  cm, those of the samples under  $P(O_2)$  greater than 6.7 Pa exceeded the upper limit of our measurement instrument ( $10^4$   $\Omega$  cm). This abrupt change in the resistivity coincided with that in  $E_F$ . This strongly suggests that the electrical properties were correlated with  $E_F$ . The range of  $P(O_2)$  that induces the abrupt change in resistivity is different from that in the case of the rf sputtered-deposited ZnO films previously reported by Carcia *et al.*<sup>4</sup> [ $10^{-4} < P(O_2) < 10^{-3}$  Pa]. This difference is probably because of the differences in the environments in which PLD and rf sputtering deposition were carried out.

The chemical shift of  $\pm 0.1$  eV indicates a slight change in the partial atomic charge with decreasing  $P(O_2)$ . We roughly estimated the stoichiometry of our films from the intensity ratios of O 1s and Zn 3d core-levels. The stoichiometry for  $P(O_2) = 10$  Pa is set to be perfect and the contributions of the higher BE shoulders (BE  $\sim 532.5$  eV) in the O 1s spectra (inset of Fig. 1) were neglected because they might originate from the hydrogenation caused by the remanent vapors in the vacuum chamber.<sup>9</sup> The deduced empirical formulae were ZnO<sub>0.83</sub>, ZnO<sub>0.87</sub>, ZnO<sub>0.95</sub>, and ZnO for the samples of  $P(O_2) = 0.002, 3.3, 6.7,$  and 10 Pa, respectively. This fact indicates that the population of oxygen defects or the interstitial oxygen in the film is controlled by  $P(O_2)$ , and this causes a change in the partial atomic charge and  $E_F$ .

Figure 2 shows the valence band (VB) spectra of the films prepared under  $P(O_2) = 3.3$  and 10 Pa by using the He I source. The features near BE  $\sim 5$  eV are attributed to the nonbonding O 2p states, whereas those near BE  $\sim 8$  eV are attributed to the bonding O 2p states.<sup>10</sup> The VB edge was determined by extrapolating the lowest-BE features of the nonbonding O 2p states. The BE of the VB edge for  $P(O_2) = 3.3$  Pa was +0.4 eV higher than that for  $P(O_2) = 10$  Pa. This increase also reflects the  $E_F$  shift but its magnitude is smaller than that determined from the core-level spectra. This apparent decrease in the amount of the  $E_F$  shift

might be caused either by the changes in line shape of the VB spectra or by surface band bending. As  $P(\text{O}_2)$  decreased to 3.3 Pa, the feature of lowest BE ( $BE \sim 4$  eV) slightly increased compensating the  $E_F$  shift in part. Also, the oxygen ionic diffusion at the surface can cause the surface band bending due to different chemical environment, so that the surface sensitive UPS primarily observes the density of states with respect to the surface  $E_F$  rather than the bulk  $E_F$ .<sup>11,12</sup> However, the both contributions did not change the  $P(\text{O}_2)$  dependence of the bulk  $E_F$ .

The  $E_F$  shift of +0.6 eV induces significant changes in the electrical properties of the oxygen-deficient ZnO films. This value is not negligible compared to the band gap of the ZnO ( $\sim 3.4$  eV). The  $E_F$  shift toward the conduction band minimum generally generates more conduction electrons because of thermal excitations to the conduction band edge. If we assume that the band gap is unchanged, the carrier concentration can be roughly estimated using the expression for semiconductors as follows:

$$n_c(T) \propto \exp[-(E_c - E_F)/k_B T], \quad (1)$$

where  $E_c$  is the conduction band minimum energy,  $k_B$  is Boltzmann's constant, and  $T$  is the temperature in Kelvin.<sup>13</sup> Thus, the ratio of the  $n_c$  values for the samples under  $P(\text{O}_2) = 3.3$  and 10 Pa at room temperature ( $k_B T \sim 25$  meV), is estimated to be  $\exp(0.6/0.025) \sim 10^{10}$ . Although this is a rough estimate in which the possibility of any polaron-induced band bending is neglected, it shows that the carrier number in the oxygen-deficient ZnO films itself can significantly increase. This strongly suggests that we should not consider the effect of the oxygen vacancy in our oxide films to be restricted to grain boundaries, as previously assumed, since in PES, the average electronic properties are determined over the entire film rather than in a small volume fraction such as grain boundaries. The resistivity of the ZnO film should exhibit the inverse trends as the carrier number. Further investigation of

the electron mobility of the system is required to fully understand the influence of the oxygen vacancy on the resistivity of the ZnO thin films.

In conclusion, the  $E_F$  of ZnO thin films prepared under different oxygen partial pressure  $P(\text{O}_2)$  during PLD growth was found to shift by +0.6 eV as the  $P(\text{O}_2)$  decreased from 10 to 3.3 Pa. This indicates a significant change in the energy balance and electronic structures in oxygen-deficient ZnO films. We suggest that the effect of oxygen deficiency in the ZnO film should be characterized by the  $E_F$  change rather than by grain boundary formation and that this  $E_F$  change is the main cause of the abrupt change in resistivity.

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