The effect of deposition power on the electrical properties of Al-doped zinc oxide thin films

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We investigated the effect on the electronic properties of aluminum (Al)-zinc oxide (ZnO) films by modulating the radio frequency sputtering power. Our experimental results show that increasing the sputtering power increases the Al doping concentration, decreases the resistivity, and also shifts the Zn $2p$ and O $1s$ to higher binding energy states. Our local-density approximation (LDA) and LDA+U calculations show that the shift in higher binding energy and resistivity decrease are due to an enhancement of the O $2p$–Zn $3d$ coupling and the modification of the Zn $4s$–O $2p$ interaction in ZnO induced by Al doping. © *2010 American Institute of Physics*.
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The zinc oxide (ZnO) film has received considerable attention recently due to its potential application as a transparent and conductive coating material.[1,2] ZnO is an n-type wide band gap (3.3 eV at room temperature) semiconductor, and its electrical conductivity dominated by Zn interstitial atoms and oxygen vacancies. The large exciton binding energy (BE) (60 meV) and band gap energy of ZnO can be tuned by doping with appropriate elements to enhance its optical and electrical performance. To get a low resistivity as well as a high transmittance in the visible region, the ZnO is usually doped with group III elements such as aluminum (Al), indium (In), gallium (Ga), and boron (B).[3–5] Doped ZnO has similar electrical and optical properties to indium tin oxide but it is also much cheaper, more temperature stable, and moreover it is nontoxic.

In the group III element, Al is considered as the most promising dopant. The highest conductivity values have been found in films with an Al concentration of 2–3 at. %.[6,7] When the ZnO is heavily doped with Al, however, the resistivity increases because of the depletion in carrier concentration due to reduction in the number of oxygen vacancies in Al-ZnO and the neutral impurity scattering due to formation of a sodium (Na) zeolite structure.[5,7]

Many techniques have been employed to prepare Al-ZnO thin films, such as magnetron sputtering,[8] pulsed laser deposition,[9] and chemical deposition.[10] It was found that the properties of Al-ZnO films are strongly dependent upon the preparation conditions such as the deposition methods, chamber pressure, and substrate temperature.[8–10] Furthermore, it was suggested by Cong *et al.*[11] recently that the Al doping can induce an enhancement of $p-d$ coupling in ZnO. However, no theoretical study has been presented and the origin of the effect of Al doping on electrical properties is still not clear.[12,13]

Here, in this letter, we systematically investigated the effect of radio frequency (rf) sputtering power on the electrical properties of Al-doped ZnO films. Our experiments show that by increasing the sputtering power, the Al doping concentration is increased, which decreases the resistivity and also moves the Zn $2p$ and O $1s$ to high BEs energy states. Our local-density approximation (LDA) and LDA+U calculations clearly show that the Al doping enhances the $p-d$ coupling and also modifies $s-p$ interaction in Al doped ZnO which shifts the BE and increases the conductivity, respectively.

The Al-ZnO thin film samples were prepared on (1 in. $\times$1 in.) glass substrates at room temperature using a rf magnetron sputtering system with a base pressure at about 3×10^{-7} Torr. An Al (2 at. %)-ZnO (98 at. %) alloy target (purity 99.95%, 2 in. in diameter, Super Conductor Materials Inc.) was used for the deposition. The sputtering was conducted in Ar atmosphere with a target-to-substrate distance of 7 cm. The working pressure was 2×10^{-3} Torr and the applied sputtering power was in the range of 60–180 W.

A Quantum Design Physical Property Measurement System (PPMS) was used to measure the electrical properties of the Al-ZnO film. The x-ray diffraction (XRD) of the films was carried out in a Rigaku x-ray diffractometer using a Cu $K\alpha$ radiation. The chemical state in the films was investigated by x-ray photoelectron spectrometer (XPS) using an Omicron Nanotechnology Spectroscopy system equipped with a monochromated Al $K\alpha$ x-ray source providing a high intensity 1486.7 eV line.

XRD patterns of the 200 nm thick Al-ZnO films are shown in Fig. 1(a) for films grown on glass substrate at different sputtering powers. The Al-ZnO films deposited under different power conditions showed strong ZnO (002) diffraction peaks. To examine the quality of the Al-doped ZnO films, the ZnO (002) diffraction peaks were investigated. The positions of ZnO (002) diffraction peaks were 34.3°, 34.2°, and 34° for films grown at 60 W, 120 W, and 180 W, respec-

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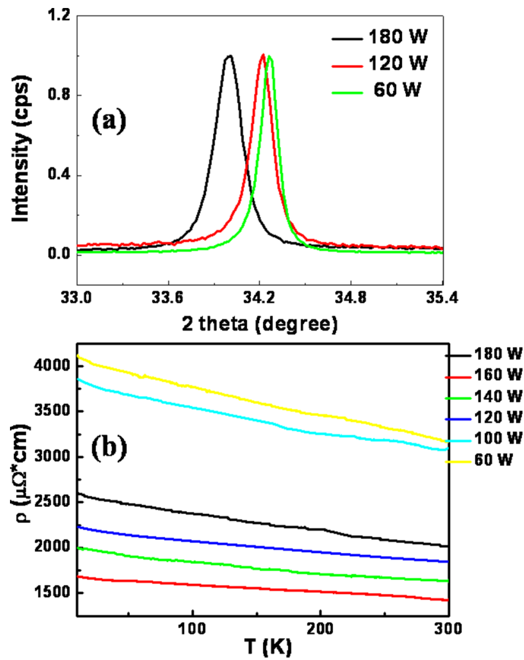

FIG. 1. (Color online) (a) XRD spectra and (b) electrical resistivity of Al-ZnO films as a function of sputtering power. A shift in diffraction peaks toward lower angles indicates a higher Al doping concentration with sputtering power results in lower resistivity up to 160 W of sputtering power.

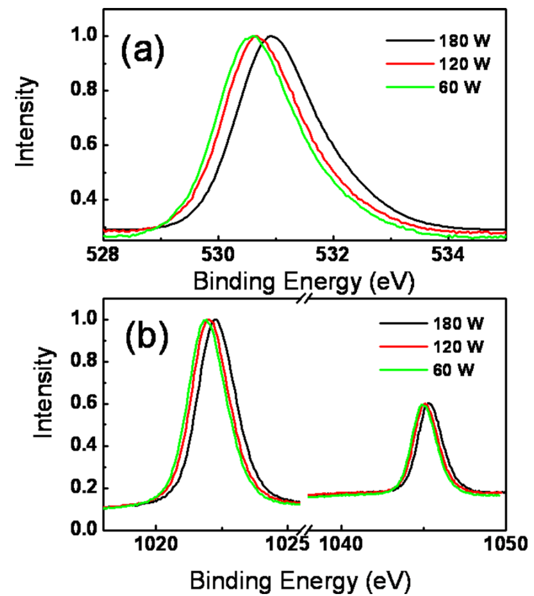

FIG. 2. (Color online) (a) O 1*s* and (b) Zn 2*p* peaks in the XPS spectrum of the Al-ZnO films as a function of sputtering power. Both O 1*s* and Zn 2*p* shift to higher BEs with increased the sputtering power during growth.

tively. The presence of a strong (002) diffraction peak indicates a strong *c*-axis orientation to surface of the substrates since the (002) plane is the most closely-packed plane of the ZnO. The (002) diffraction peak obtained in all XRD patterns is very close to that of the pure ZnO film (34.45°). There is a small difference in the diffraction angles from the standard angle (diffraction peak of pure ZnO film; 34.45°) which appears to be due to the addition of Al to ZnO and the ZnO (002) diffraction peaks shift toward lower angles indicates a higher Al doping concentration with sputtering power.[14]

Figure 1(b) shows the temperature dependent resistivity curves for the films with different sputtering powers. In the Al-ZnO films, the electrical conductivity depends on the contribution from Zn, Al interstitial atoms, and oxygen vacancies. Up to 160 W of sputtering power, the overall resistivity observed in Al-ZnO films is that the resistivity decreases when the films are grown at higher sputtering power. All the films show nonmetallic dependence of resistivity versus temperature. Above 160 W of sputtering power, however, the resistivity increases with increasing power.

The chemical states of the films were investigated by XPS. Figures 2(a) and 2(b) show the O 1*s* and Zn 2*p* regions, respectively, obtained for the Al-ZnO samples grown at different sputtering powers. All regions of each sample have been consistently energy shifted in order to position the peak in the C 1*s* region at a BE of 284.7 eV. These shifts are less than 0.3 eV. One can clearly see from Figs. 2(a) and 2(b) that both O 1*s* and Zn 2*p* shift to higher BEs with increased the sputtering power during growth. For the films at 60 W, 120 W, and 180 W, the BE for O 1*s* are 530.6 eV, 530.7 eV, and 530.9 eV, respectively. Our XPS measurements further show that the Al doping concentration increased by increasing the sputtering power during growth.[11]

In order to understand the effect of Al doping on the electronic structure of ZnO, we present in Figs. 3 and 4 the calculated electronic structures for an undoped ZnO and for a 3% Al doped ZnO, respectively. The ZnO has a wurtzite crystal structure with four atoms in the primitive cell. In our calculations, we consider 64 $(2\times4\times2)$ atoms. The electronic structure calculation was performed using the Vienna *ab initio* simulation package.[15] We employed the projected augmented plane wave[16,17] and the valence configures of $3d^{10}4s^2$ for Zn, $2s^22p^4$ for O, and $3s^23p^1$ for Al were used.

Figures 3(a) and 3(b) show the partial density of states (DOS) for undoped ZnO from the LDA and LDA+U calculations, respectively. For the LDA+U simulations in this work, we use U=6.0 eV and J=0 eV.[18] One can see from Fig. 3 that the band gap is defined by the O 2*p*–Zn 4*s* in-

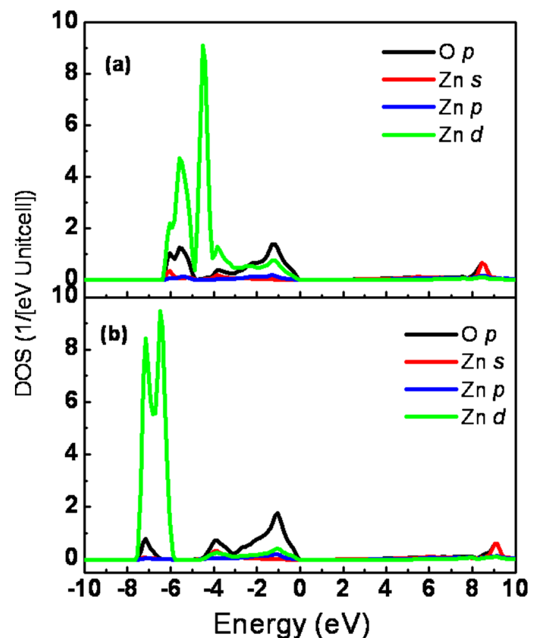

FIG. 3. (Color online) Partial DOS for undoped ZnO (a) LDA and (b) LDA+U calculations where the O 2*p*, Zn 4*p*, 4*s*, and 3*d* bands are shown.

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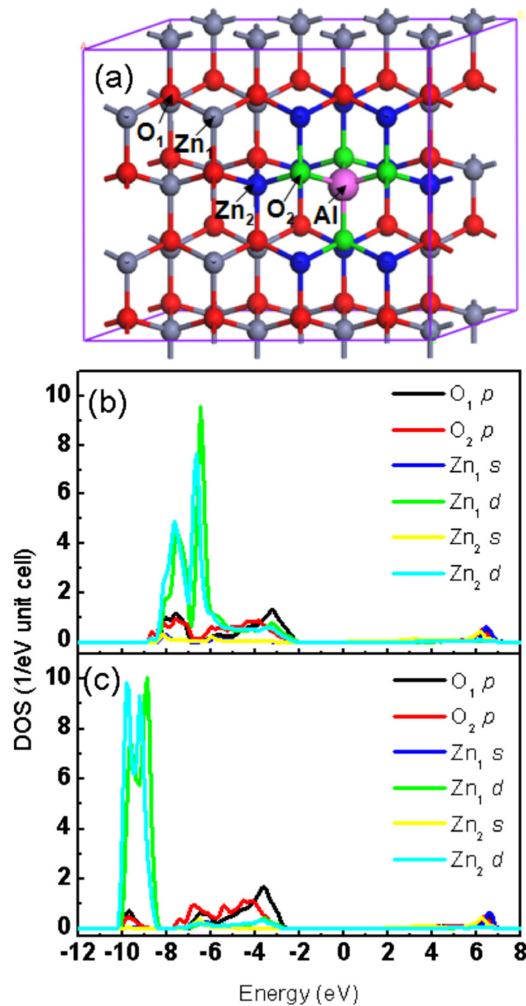

FIG. 4. (Color online) Partial DOS for Al 3% doped-ZnO (b) LDA and (c) LDA+U calculations, (a) where a Zn atom is substituted by Al atom.

teraction. A band gap of 0.8 eV is observed, which is consistent with other theoretical reports.[13,18] The LDA+U calculation shows a clear energy gap between −5 and −6 eV in the valence band. Both O 2*p* and Zn 3*d* wave functions are strongly localized and the O 2*p* states are very energetically close to the Zn 3*d* state, which implies a strong *p*–*d* hybridization.

Figures 4(b) and 4(c) show the partial DOS after geometry optimization for Al doped ZnO, where a Zn atom is substituted by an Al atom [marked as pink ball in Fig. 4(a)]. Due to strong *s*–*p* hybridizations between Al and O atoms, four inequivalent oxygen atoms (marked as green balls) come into existence. The bond length for Al–O is 1.82 Å which is much smaller than that of Zn–O of 1.97 Å, which increases the Zn–O bonds length formed between 9 s-next-to-Al-neighbor Zn atoms (marked as blue balls) and four inequivalent oxygen atoms from 1.97 to 2.06 Å. One can clearly see from Figs. 4(b) and 4(c) that the DOS for the equivalent Zn and O atoms are similar to the undoped ZnO. But for the inequivalent Zn and O atoms, the density of the *p*–*s*–*d* states is increased and O 2*p* states are shifted even closer to the Zn 3*d* levels.

Therefore, enhanced *p*–*d* hybridization is obviously observed from our calculations. The enhanced *p*–*d* coupling lowers the total energy and thus shifts the Zn 2*p* and O 1*s* to higher BE which is consistent with the XPS measurements. Moreover, one can see from Figs. 4(b) and 4(c) that the Zn 4*s* states of the inequivalent Zn atoms also shift to lower energy states of 250 meV. It was shown that for a 3% Al-doped ZnO film, the band gap is reduced by around 150 meV with respect to 1% doped film,[12] which is in the same energy range as the shift in Zn 4*s* states. Therefore, the shift in Zn 4*s* decreases the energy band gap and also increases the electrical current, which can explain decrease in the resistivity with increasing sputtering power up to 160 W.

For sputter powers above 160 W, the resistivity increases with increasing sputtering power. A possible reason is that the high doping level may lead to a decrease in the mobility of the Al-ZnO films and the depletion in carrier concentration due to reduction in the number of oxygen vacancies in Al-ZnO.[6,19]

In summary, we experimentally and theoretically investigate the effect of the rf sputtering power on the electrical properties of Al-ZnO films. Our experiments results show that by increasing the sputtering power, the Al doping concentration is increased which decreases the resistivity and shift the BE between Zn 2*p* and O 1*s* to high energy states. Our LDA and LDA+U calculations clearly show the enhancement of O 2*p*–Zn 3*d* coupling in Al-ZnO and the Zn 4*s*–O 2*p* interaction is responsible for the electrical properties.

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