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Realization of *p*-type conduction in undoped $Mg_xZn_{1-x}O$ thin films by controlling Mg content

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Undoped $Mg_xZn_{1-x}O$ thin films with Mg content of $0 \leqslant x \leqslant 0.20$ were grown on *c*-sapphire substrate by plasma-assisted molecular beam epitaxy. The $Mg_xZn_{1-x}O$ shows *n*-type conduction in Mg content of $x \leqslant 0.05$, and the carrier concentration decreases slowly from 10^{18} to 10^{17} cm^{-3} with increasing Mg content. However, as $x \geqslant 0.10$, the $Mg_xZn_{1-x}O$ begins to show *p*-type conduction, and the carrier concentration goes down sharply to 10^{15} cm^{-3} firstly and then increases slowly with increasing Mg content from 10^{15} to 10^{16} cm^{-3}. The mechanism of transformation from *n* to *p* type and change of the carrier concentrations with Mg content were investigated by photoluminescence and absorption measurements as well as first-principle calculation. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2816914]

Zinc oxide (ZnO) has attracted much attention in recent years because of its potential application in blue and ultraviolet (UV) light-emitting devices (LEDs) and laser diodes (LDs).[1] Up to now, although electroluminescence (EL) of *p-n* homojunction ZnO has been reported by many groups,[2–5] the EL emissions are in visible but not UV region. In order to obtain UV electroluminescence, it is necessary to fabricate ZnO-based LED with quantum well or superlattice as active layer, which needs a suitable potential barrier material. Recently, the UV LED and LD with an active layer of quantum well were fabricated using BeZnO as barrier layers and ZnO as well layers.[6,7] However, it may be very difficult to fabricate the BeZnO alloy safely due to the toxicity of Be metal. Another potential barrier material, MgZnO alloy was proposed and has been investigated widely in the recent years. The *n*-type MgZnO with high crystal quality has been prepared successfully now. However, fabrication of *p*-type MgZnO with high optical quality and stable conductivity is still very difficult. Many efforts have been done to prepare *p*-type MgZnO, but research progress is limited. Heo *et al.* prepared phosphor doping *p*-type MgZnO,[8] and Zhang *et al.* fabricated *p*-type MgZnO by N-Al codoping.[9] Last year, our research group prepared N-doped *p*-type MgZnO.[10,11] However, no UV LED is prepared using the *p*-type MgZnO as barrier material up to now, indicating that the properties and optical quality of *p*-type MgZnO still need to improve. It is known that doping can make crystal quality bad, resulting in a decrease of optical and electrical properties. If *p*-type conductivity is realized in undoped MgZnO, the *p*-type MgZnO may have good crystal quality.

In the present work, we prepared an undoped *p*-type MgZnO by controlling Mg content and investigated the optical and electrical properties as well as condition and mechanism of formation of the *p*-type MgZnO.

The MgZnO alloy thin films were deposited on *c*-sapphire substrate by plasma-assisted molecular beam epitaxy (*p*-MBE). O_2 gas was used as O source and the flux was fixed at 0.8 SCCM (SCCM denotes cubic centimeter per minute at standard temperature and pressure). The zinc source and substrate temperatures were fixed at 235 and 425 °C, respectively. The Mg source temperature (T_{Mg}) was 240, 255, 265, and 270 °C. The thickness of the as-deposited MgZnO film is 1200 nm. The MgZnO film grown at $T_{Mg}=270$ °C was annealed for 15 min at 600 °C under O_2 ambient. The room temperature absorbance measurement was performed using an UV-visible-near infrared spectrophotometer (Shimadzu) and the temperature-dependent photoluminescence (PL) was measured using He–Cd laser line of 325 nm as an excitation source. Electrical properties were measured in the van der Pauw configuration by a Hall effect measurement system at room temperature.

Figure 1 shows plots of $(\alpha h\nu)^2$ as a function of $h\nu$ for the as-grown ZnO and MgZnO films grown at various Mg source temperatures and the film annealed at 600 °C, where α is the absorption coefficient of the MgZnO and $h\nu$ is the photon energy. By using the relation between α and band gap: $\alpha(h\nu)=A(h\nu-E_g)^{1/2}$, the band gap was evaluated to be 3.254, 3.279, 3.354, 3.445, 3.584, and 3.659 eV, respectively, for the as-grown ZnO and MgZnO grown at $T_{Mg}=240$, 255, 265, 270 °C as well as the MgZnO annealed at 600 °C, indicating that the Mg content increases with increasing Mg source temperature. The Mg content can be evaluated to be $x=0.01$, 0.05, 0.10, 0.17, and 0.20, respec-

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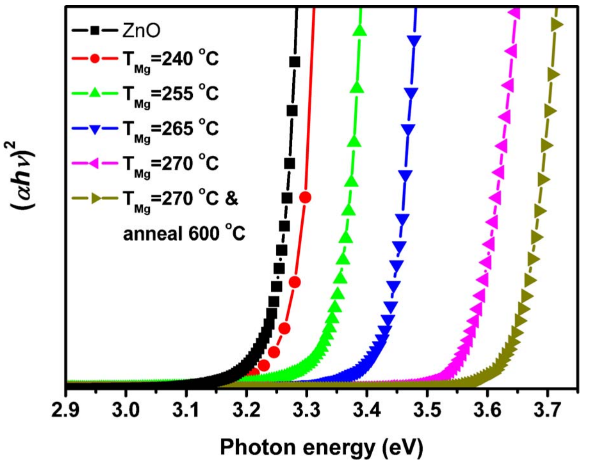

FIG. 1. (Color online) Optical absorption spectra of as-grown ZnO and MgZnO thin films grown at different Mg source temperatures as well as annealed MgZnO at 600 °C.

tively, for the $Mg_xZn_{1-x}O$ film grown at $T_{Mg}=240$, 255, 265, 270 °C, and the annealed $Mg_xZn_{1-x}O$ films, by using the relation between band gap and Mg content.[12] The band gap of the annealed MgZnO film has a blueshift. The band gap shift is due to the increase of Mg content. Because the bond of Mg–O is stronger than that of Zn–O, after high temperature annealing, the decrease of Zn results in the increase of Mg content.

Hall resistivity of the MgZnO thin films as a function of Mg content is shown in Fig. 2. The resistivity of *n*-type MgZnO is 1.7, 3.0, and 7.5 Ω cm for Mg content of $x=0$, 1, and 5 at. %, respectively, and increases with the increase of Mg content. However, the resistivity rapidly increases to 4.6×10^2 Ω cm when *n*-type transforms into *p*-type conduction at Mg content of 10 at. %. For *n*-type MgZnO, the increase of resistivity is due to the decrease of carrier density with increasing Mg content (shown in Fig. 2). For *p*-type MgZnO, the hole carrier density slightly increases with increasing Mg content. The resistivity of $Mg_{0.17}Zn_{0.83}O$ is higher than one of $Mg_{0.1}Zn_{0.9}O$. That is because more Mg doping leads to decrease of mobility. After annealing, the crystalline quality of MgZnO film is improved and its mobility increases. Thus, the $Mg_{0.2}Zn_{0.8}O$ film has a lower resistivity than $Mg_{0.17}Zn_{0.83}O$. The relationship between electron density and donor ionization energy is expressed as

$$n = Ne^{-(E_d+\Delta E)/KT} = n_0 e^{-\Delta E/KT}, \qquad (1)$$

where n, K, E_d, and ΔE are the electron density of MgZnO, Boltzmann constant, donor ionization energy of pure ZnO, and increment of donor ionization energy between MgZnO and ZnO. The quantity n_0 is electron density of pure ZnO and N is a constant related to effective mass of electron and temperature. It is well known that the band gap of MgZnO increases with increasing Mg content due to the increase in the energy of the conduction-band minimum (E_c) and decrease in the energy of valence-band maximum (E_v), namely, $\Delta E_g = \Delta E_c - \Delta E_v$, $\Delta E_c > 0$ and $\Delta E_v < 0$. Thus, the ionization energies of both donor and acceptor increase with the increase of the band gap of MgZnO. However, the increase of the ionization energy of donor is much larger than that of acceptor because the conduction-band offset is much larger than the valence-band offset ($\Delta E_c/\Delta E_v = 9/1$), and even valence-band offset can be neglected ($\Delta E_v \approx 0$).[23] Therefore, it is a reasonable assumption that ΔE is approximately equal to the band gap difference ΔE_g between MgZnO and ZnO. The calculated electron density using Eq. (1) sharply decreases with increasing Mg content (also shown in Fig. 2), in good agreement with experimental data for *n*-type samples. Because the valence-band offset is neglected, the calculated electron density is slightly lower than the measured one. The calculated electron density decreases to $\sim 10^{15}$ cm^{-3} at Mg content of 10 at. %, which is lower than the measured hole density of 5.8×10^{15} cm^{-3}. It was reported that the background hole density in undoped ZnO is in an order of magnitude of 10^{15} cm^{-3} (Ref. 13) so the transformation from *n*-type into *p*-type conduction is attributed to the electron density which is lower than the background hole density. However, the transformation mechanism of conduction type of MgZnO differs from that of ZnO. It is well known that *p*-type conduction can be obtained for ZnO under O-rich condition,[14] under which formation of oxygen vacancies (V_o) and interstitial Zn (Zn_i) donor defects are depressed but zinc vacancy (V_{Zn}) acceptor defects can be formed easily, leading to an amount of V_o and Zn_i decreases with increasing O content and an amount of V_{Zn} increases. Some groups have fabricated undoped *p*-type ZnO by increasing O_2 partial pressure.[15–18] However, in the present experiment, all MgZnO films with Mg content of 0 to 0.17 are prepared at the same O_2 flux, and the ZnO film is *n*-type conduction, implying that intrinsic acceptor defects cannot compensate for donor defects in the *n*-type ZnO. Thus, the transformation of conduction type of the MgZnO is related to Mg doping.

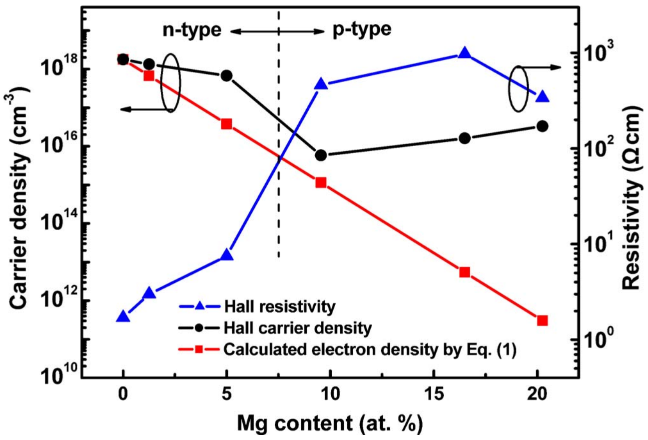

FIG. 2. (Color online) Hall resistivity and carrier density as well as calculated electron density by Eq. (1) as a function of Mg content.

In order to understand the origin of *p*-type behavior in undoped MgZnO films, the photoluminescence (PL) measurements were performed. Figures 3(a) and 3(b) illustrate the temperature-dependent PL spectra of *n*-type (Mg 1 at. %) and *p* type (Mg 17 at. %) MgZnO. From bottom to top, temperature increases from 85 to 300 K. For *n*-type sample, the 85 K PL spectrum shows three peaks at 3.377, 3.337, and 3.278 eV. The peak at 3.377 eV is free exciton emission owing to the redshift with increasing temperature. The peak at 3.278 eV can be due to recombination of the donor-acceptor pair (DAP). The peak at 3.337 eV can be due to the emission related to two-electron satellites of neutral-donor-bound excitons $(D^0X)_{2e}$.[19] However, for *p*-type sample, the special feature is that it has a strong peak and two weak packages in the UV region at low temperature. The peak at 3.538 eV is considered as a recombination of neutral acceptor-bound ex-

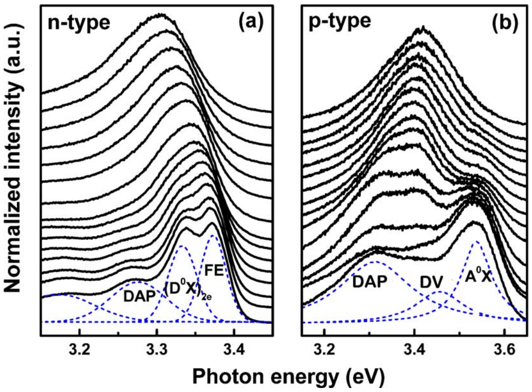

FIG. 3. (Color online) Temperature-dependent photoluminescence spectra of (a) *n*-type and (b) *p*-type MgZnO thin films. From bottom to top, temperature increases from 85 to 300 K.

citon (A^0X). Its intensity becomes weaker and weaker with the increase of temperature because A^0X is ionized and transforms into free exciton at high temperature. By fitting the intensity of A^0X, (Ref. 20) the binding energy is estimated to be 51 meV. The acceptor level is evaluated to 212 meV by the Haynes rule.[21] The acceptor level is 32 meV deeper than the calculated ionization energy of V_{Zn}, $\varepsilon(0/-1)=180$ meV, by Li *et al.*[22] Because the band gap of $Mg_{0.17}Zn_{0.83}O$ is 330 meV larger the one of ZnO, the valence band maximum slightly offsets to lower energy about 1/10 of the increment of the band gap. That agrees with the calculated offset by Ohtomo *et al.*[23] Thus, the A^0X emission is the recombination of exciton bound to V_{Zn}. The dash line in Fig. 3(b) shows Gaussian fitting to the two packages and the fitting peaks are at 3.456 and 3.313 eV. We assign them to the recombination of DAP and the recombination between donor level and valence band (labeled as DV). The blueshift of DAP with increasing temperature can be due to the ionization of acceptor but not due to the ionization of donor because the donor level is deeper than the acceptor level. As a result, the origin of *p*-type conduction comes from the contribution of V_{Zn} in MgZnO.

As discussed above, since the increment of band gap with increasing Mg concentration results in a slight increase of acceptor ionization energy for *p*-type MgZnO, the hole density should decrease with increasing Mg content. However, the measured hole density increases from 5.8×10^{15} to 3.3×10^{16} cm^{-3} with the increase of Mg content from 10 to 20 at. %. To better understand this problem, the formation energy of V_{Zn} in $Mg_xZn_{1-x}O$ with different Mg content was calculated by using the first principle calculation based on generally gradual approximation. The calculation method of defects formation energy can be found elsewhere.[24] Based on calculated results, it is concluded that: (i) the formation energy of V_{Zn} in $Mg_xZn_{1-x}O$ decreases with the increase of the chemical potential of Mg, indicating that V_{Zn} is easier to form at higher Mg source temperature; (ii) the formation energy of V_{Zn} is much lower under O-rich limit than under Zn-rich limit. Above conclusions imply that the amount of V_{Zn} in MgZnO increases with increasing Mg concentration, leading to an increment of hole concentration with increasing Mg concentration.

In summary, we have fabricated undoped *p*-type MgZnO thin films by controlling Mg content. The $Mg_xZn_{1-x}O$ shows *n*-type conduction in Mg content of $x\leqslant0.05$, and as $x\geqslant0.10$, the $Mg_xZn_{1-x}O$ begins to show *p*-type conduction. The PL measurement shows that the hole in the undoped MgZnO comes from the contribution of V_{Zn}. The first-principle calculation indicates that the amount of V_{Zn} in MgZnO increases with increasing Mg content, leading to the increase of hole density. The transformation from *n* to *p*-type conduction is attributed to the increment of band gap and amount of zinc vacancies with increasing Mg concentration.

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