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p-Type MgZnO thin films grown using N delta-doping by plasma-assisted molecular beam epitaxy

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ABSTRACT

Uniform N-doped MgZnO (MgZnO:N) films and the films with layer structure of MgZnO:N/Zn_3N_2/MgZnO:N (δ-doped MgZnO:N) were grown on c-plane sapphire by plasma-assisted molecular beam epitaxy in the temperature range of 350–650 °C, respectively. The δ-doped MgZnO:N shows n-type conductivity in the growth temperatures ranging from 650 to 450 °C, but p-type conductivity with hole concentration of 3.41×10^{17} cm^{-3}, mobility of 0.49 cm^2/V s and resistivity of 48.50 Ω cm at the growth temperature of 350 °C. However, all of the MgZnO:N films show n-type conductivity. The p-type δ-doped MgZnO:N is proven to be stable and reproducible, indicating that δ-doping technique combined with low growth temperature is an efficient way to fabricate p-type MgZnO:N films. The effects of the Zn_3N_2 δ layer on the formation and properties of the p-type δ-doped MgZnO:N is discussed.

1. Introduction

Attribute to its wide and direct band gap (3.37 eV), large exciton binding energy (60 meV) and high radiation hardness at room temperature, ZnO is regarded as a promising material for preparation of short wavelength light emitting diodes and laser diodes with low thresholds [1,2]. For fabricating a double heterostructure laser diode using a ZnO active layer, two critical challenges are p-type doping and band gap engineering in alloy semiconductors. Since band gap of MgZnO alloy is larger than that of ZnO and it also can be tuned by changing Mg content, it is considered as candidate barrier material of ZnO based heterostructure [3,4].

However, MgZnO material has largely failed to live up to its potential, because LED and LD require both high quality n-type and p-type MgZnO, and it has been proven to be very difficult to produce a stable and reproducible p-type MgZnO with high conductivity and mobility. Minegishi et al. obtained a p-type ZnO layer in 1997 through nitrogen doping [5]. After this development, p-type MgZnO films were prepared by N, P, Sb, Li, intrinsic doping (by tuning oxygen pressure or Mg concentration in the growth environment), and co-doping of N with group-III elements [6–12]. A method of growing stable and reproducible p-type ZnO with repeated temperature modulation technique has been reported by Tsukazaki et al. [13]. They have reported violet luminescence from a ZnO p-i-n homojunction diode. However, these developments do not be helpful in producing reliable optoelectronic devices due to poor optical and electrical properties of the p-type ZnO and MgZnO films.

Inferiority in optical and electrical properties of the p-type MgZnO films can be attributed to low solubility of acceptor dopant, strong self-compensating effect and high ionization energy of acceptor. In order to enhance the electrical properties of p-type MgZnO, p-type doping was performed at low temperature. Since the doping is far from thermodynamic equilibrium state, the solubility of the p-type dopant can be enhanced greatly at low growth temperature, resulting in improvement of the p-type conduction [14]. In order to improve the electrical properties of the p-type MgZnO or ZnO by increasing the solubility of acceptor dopant, acceptor and donor co-doping method was also suggested to fabricate p-type MgZnO and ZnO films [12,15]. However, the p-type ZnO or MgZnO thin films, as mentioned above, were obtained by means of post-annealing.

As a novel doping method, δ-doping was first used for fabricating highly conductive p-type ZnSe and ZnS by inserting heavily N-doped ZnTe single layers into undoped ZnSe layers in 1996 [16]. The N doping is performed simultaneously with the incorporation of Te, which is expected to enhance the N incorporation rate. Later, δ-doping was used for fabricating p-type GaN and HgTe thin films and obtained a good result [17,18]. Moreover, it has been reported that δ-doping can reduce the density of threading dislocations in the highly faulted nitride layers and, therefore, to improve the

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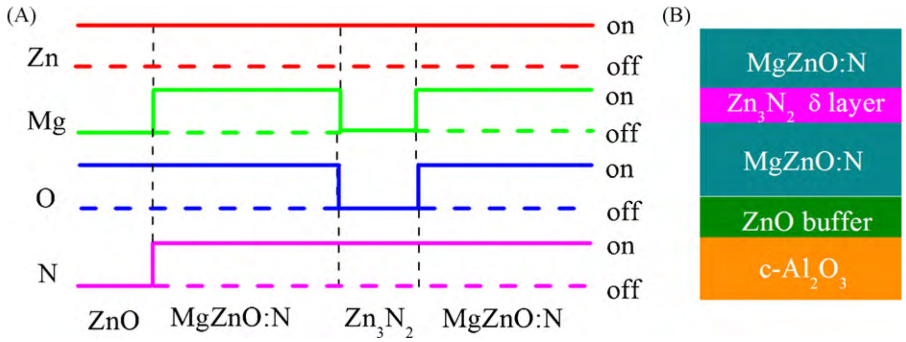

Fig. 1. (a) shutter control sequence and (b) the layer structure of the δ-doped MgZnO:N films.

crystalline structure of the host semiconductor [19]. The detailed information about δ-doping can be seen in literature [20].

In the present work, *p*-type MgZnO:N was produced by plasma-assisted molecular beam epitaxy using δ-doping method of growing a layer of Zn_3N_2 between two uniform N-doped MgZnO layers, and the effects of the Zn_3N_2 layer on the formation and properties of the *p*-type δ-doped MgZnO:N were discussed.

2. Experimental procedures

The nitrogen δ-doped MgZnO samples were grown by a V80H molecular beam epitaxy (MBE) system. The *c*-plane sapphire was used as substrate. 6*N*-pure Zn and Mg metal were used as the Zn and Mg source, respectively. RF plasma activated O_2 (5*N* in purity) and N_2 (5*N* in purity) were introduced into growth chamber as the oxygen and the *p*-type dopant sources, respectively. The growth temperature was controlled from 350 to 650 °C by adjusting heating power. The flow rates of the O_2 and N_2 were maintained at constants of 0.6 and 0.8 sccm during the growth process, respectively. The detail growth process can be seen elsewhere [21]. For fabricating N δ-doped MgZnO film, a sample with a layer structure, as shown in Fig. 1(b), was grown by controlling shutter on or off order as shown in Fig. 1(a). In the δ-doping process, 100 nm ZnO buffer layer was first deposited on Al_2O_3 (0 0 0 1) at 600 °C, followed by the growth of the 300 nm thick uniform N-doped MgZnO layer and then the growth was interrupted for the N δ-doping. Before growth of δ layer, all of the shutters were closed for 30 s to exclude the disturbance of the Mg and O. The N δ-doping was carried out by directing both N and Zn beams onto the MgZnO surface for 30 s, where the Zn flux was maintained during the N δ doping in order to enhance the N sticking coefficient. Finally, a uniform N-doped MgZnO cap layer with a thickness of 150 nm was deposited. In order to comparison, a uniform N-doped MgZnO films were also fabricated under identical conditions to the δ-doped MgZnO:N films, except that without the Zn_3N_2 δ-doped layer.

Structures of the films were characterized by a D/max-RA X-ray diffractometer (XRD) (Rigaku International Corp., Japan) with CuKα radiation of 0.1506 nm, and all the diffraction peaks were calibrated by the (0 0 6) diffraction peak of the Al_2O_3 at 41.68°. A hatachi S4800 energy dispersive spectroscopy (EDS) was used for determining the Mg content in the MgZnO films, and the acceleration voltage and the magnification of EDS were 15 kV and 5000, respectively. Photoluminescence (PL) measurement was performed by the excitation from a 325 nm He–Cd laser with 50 mW power. Electrical properties of the samples were measured in Van der Pauw configuration by a Hall analyzer (Lakeshore7707) at room temperature.

3. Results and discussion

XRD patterns of the δ-doped MgZnO:N films grown at different temperatures were shown in Fig. 2. The strongest (0 0 2) diffraction peak is observed around 34.45°, indicating that all the δ-doped MgZnO:N films were of single wurtzite structure with (0 0 2) pref-

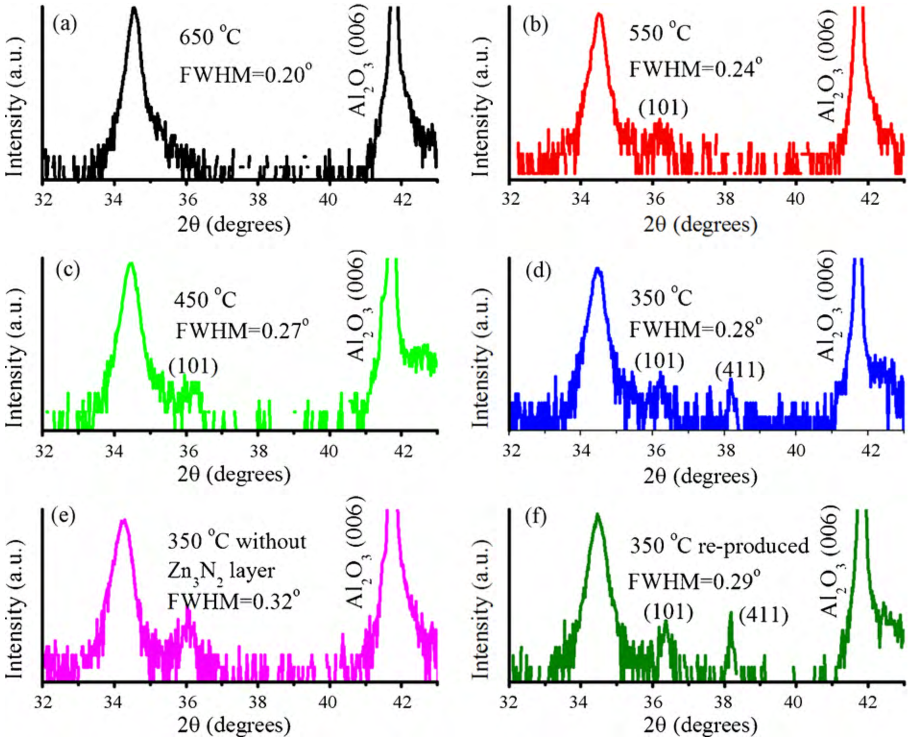

Fig. 2. X-ray diffraction spectrum of the δ-doped MgZnO:N films at different temperatures (film grown at 350 °C without Zn_3N_2 δ layer and re-produced film at 350 °C with Zn_3N_2 δ layer are also shown, respectively).

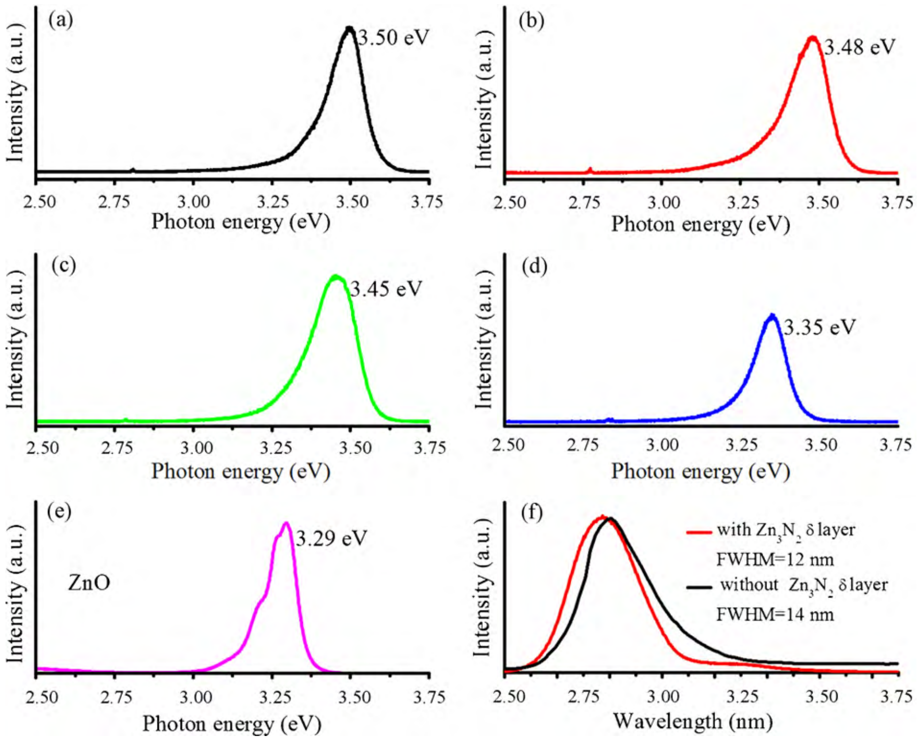

Fig. 3. PL spectrum of the δ-doped MgZnO:N films grown at different temperatures: (a) 650 °C, (b) 550 °C, (c) 450 °C, (d) 350 °C, (e) PL spectra of ZnO, (f) 350 °C with and without Zn_3N_2 δ layer.

erential orientation. For δ-doped MgZnO:N films, the full width at half maximums (FWHM) of the (0 0 2) diffraction peak increases from 0.20° to 0.28° with decreasing growth temperature from 650 to 350 °C, indicating that the crystal quality of the δ-doped MgZnO:N films were degraded for low growth temperature. With decreasing growth temperature, two additional weak diffraction peaks around 36.07° and 38.16° were observed in the δ-doped MgZnO films. According to the JCPDS files, Cards No. 80-0075 and 88-0618, the peak at 36.07° was attributed to the (1 0 1) diffraction peak of the MgZnO films and the peak at 38.16° was attributed to the (4 1 1) diffraction peak of the Zn_3N_2 for its only close to the (4 1 1) diffraction peak of Zn_3N_2, indicating that the preferred orientation of the films were slightly degraded for low growth temperature and the layer structure shown in Fig. 1(b) was successfully obtained. The FWHM for the re-produced δ-doped MgZnO:N films, as shown in Fig. 2(f), was nearly equal to that of the films grown before, means that the crystal quality of the δ-doped films can be reproducible. From Fig. 2(d) and (e), it can be found that the FWHM (0.28°) of the δ-doped MgZnO:N film grown at 350 °C is smaller than that (0.32°) of the film grown at 350 °C without Zn_3N_2 layer, indicating that the crystal quality can be improved by using δ-doping method. It has been reported that δ-doping with silicon is an effective way to reduce threading screw dislocation density in GaN epitaxy [19]. This reduction was associated with bending of screw dislocations and "pairing" with equivalent neighboring dislocations with opposite Burgers vectors. Therefore, the good crystal quality of the films grown at low temperature in this investigation can be attributed to the Zn_3N_2 δ layer. The diffraction angle of the (0 0 2) diffraction peak increases from 34.45° to 34.54° with increasing growth temperature, which is tentatively ascribed to the substitution of Mg ions with a small ionic radius of 0.057 nm for Zn (0.060 nm) sites. It is well known that vapor pressure of the Zn atom is higher than that of the Mg atom and the vapor pressure increases with increasing temperature. Therefore, the Mg content relative to Zn will be increased with increasing growth temperature. EDS measurement indicates that the Mg content in the δ-doped MgZnO:N films was increased from 5.46% to 12.54% with increasing growth temperature, which was consistent with the changes of the diffraction angle of the (0 0 2) peak as shown in Fig. 2.

Room temperature PL spectrum of the δ-doped MgZnO:N films grown at different temperatures were shown in Fig. 3(a)–(d). For comparing, the PL spectrum of ZnO was also shown in Fig. 3(e). In the PL spectrum, all the films exhibit one peak located in the ultraviolet (UV) region, which originates from the excitonic near-band-gap emission. Furthermore, no deep level emission peaks were observed, indicating that all the films have high crystal quality. Decreasing growth temperature, the UV emission peak shows red-shift from 3.50 to 3.35 eV and the intensity of the emission peak shows decreases. The optical degradation of the δ-doped MgZnO:N film is attributed to the increase of non-radiative recombination

Table 1
Electrical properties of the δ-doped MgZnO:N films with Zn_3N_2 layer grown at different temperatures and the films grown at 350 °C without Zn_3N_2 δ layer also shown.

Substrate temperature (°C)	Resistivity (Ω cm)	Carrier concentration (cm^{-3})	Hall mobility (cm^2/V s)	Carrier type
650	2.04	1.02E+18	3.06	*n*
550	10.2	4.45E+17	1.48	*n*
450	17.0	1.01E+18	0.35	*n*
350	51.6	2.06E+17	0.67	*p*
350 (re-measured)	135	6.82E+16	0.77	*p*
350 (re-produced)	48.5	3.41E+17	0.49	*p*
350 (without Zn_3N_2 layer)	226	5.28E+16	0.65	*n*

centers due to low growth temperature. Since the band gap of the MgZnO films can be tuned by adjusting Mg content [3], the red-shift of the UV emission peak was attributed to the decrement of Mg content in the δ-doped MgZnO:N films, which is consistent with the EDS measurement. From Fig. 3(f), it can be found that the FWHM value (12 nm) of the UV emission peak of the film grown with Zn_3N_2 δ layer is smaller than that (14 nm) of the film grown without Zn_3N_2, indicating that the δ-doped MgZnO:N film has a better crystal quality which is consistent with the results of XRD measurement.

In order to minimize inhomogeneity in the electrical properties, Hall measurements were performed under five different magnetic fields (3, 6, 9, 12, 15 kG). The Ohmic contact electrodes were placed at the sample corners for avoiding incorrect assignment of the carrier type [22]. The carrier concentration was found homogeneous during measuring process, therefore, it will not affect the measured carrier type. Room temperature electrical parameters of the δ-doped MgZnO:N films grown at different temperatures were listed in Table 1. It can be seen that the films grown in the temperature range of 650–450 °C show *n*-type conduction and electron concentration decreases with decreasing growth temperature. When the growth temperature decreases to 350 °C, the film converts to *p*-type conduction with hole concentration of 2.06×10^{17} cm^{-3}, mobility of 0.67 cm^2/V s and resistivity of 51.60 Ω cm. The *n*-type conduction of the films grown at high temperature is due to low solid solubility of N and many native donor defects (O vacancies and Zn interstitial) in the films, and the *p*-type conduction of the film grown at 350 °C can be attributed to enhancement of the solid solubility of N in the films. To verify the stability of the *p*-type δ-doped MgZnO:N film, Hall-effect measurements were carried out 40 days later and the result was also listed in Table 1, indicating that the film still shows *p*-type conduction, but the electrical properties degraded. The *p*-type δ-doped MgZnO:N film was re-produced under the same growth conditions in the present work, and has close electrical parameters each other. In order to understand the relationship between *p*-type conduction and Zn_3N_2 δ layer, a MgZnO:N film without Zn_3N_2 layer was prepared under the same growth conditions. The Hall measurements indicate that the film shows *n*-type conduction though the electron concentration was very low. Therefore, the *p*-type conduction of the δ-doped MgZnO:N film grown at 350 °C was attributed to the increment of the solid solubility of the N in the MgZnO:N film induced by Zn_3N_2 layer.

The undoped *p*-type MgZnO films were obtained by controlling Mg content [11]. It is found that the films show *n*-type conduction at low Mg content but *p*-type conduction at high Mg content. Form the measurements of EDS and PL spectrum, the Mg content decreases with decreasing growth temperature and the films grown at 350 °C have the lowest Mg content, indicating that the obtained *p*-type δ-doped MgZnO:N film was not attributed to the changes of Mg content in the films. As discussion mentioned above, it strongly suggest that the *p*-type conduction of the δ-doped MgZnO:N films grown at 350 °C was attributed to the enhancement of the solubility of the N in the MgZnO:N film by using low growth temperature and δ-doping technique. Therefore, it can be concluded that δ-doping technique combined with low growth temperature is an efficient way to fabricate *p*-type MgZnO:N film. Our future work will be concentrated on the correlations between thermodynamic mechanism and the excellent properties as well as the optimization of growth conditions for the *p*–*n* junction.

4. Conclusions

The *p*-type δ-doped MgZnO:N films with hole concentration of 3.41×10^{17} cm^{-3}, mobility of 0.49 cm^2/V s and resistivity of 48.50 Ω cm were grown on *c*-plane sapphire by MBE. Better crystal quality and enhancement of solid solubility of N was achieved by inserting Zn_3N_2 δ layer under low growth temperature, which suggest that δ-doping technique combined with low growth temperature is beneficial for obtaining highly conductive *p*-type MgZnO:N thin film.

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