GROWTH AND PROPERTIES OF ZnO FILMS GROWN USING PA-MOVPE WITH DMZn AND N_2O

Takayuki Nakano, Kazuki Nishimoto, Masatomo Sumiya, Shunro Fuke

Abstract:

ZnO films were grown by plasma-assisted metal organic vapor phase epitaxy (PA-MOVPE) using dimethylzinc (DMZn) and N_2O gases. The crystallinity and surface morphology of ZnO films were investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The crystallinity of ZnO improved (a) when the N_2O flow rate was increased, because vapor phase reaction was suppressed while surface migration was enhanced, and (b) when the growth temperature was increased, because surface diffusion was enhanced. In the PA-MOVPE method with N_2O gases and DMZn, both the N_2O flow rate and crystal growth temperature strongly affected the crystallinity of ZnO films.

Keywords: *ZnO, PA-MOVPE, epitaxial growth, DMZn, N_2O, temperature modulation growth.*

1. Introduction

Recently, wide band-gap semiconductors have attracted much attention due to the ever-increasing commercial demand for short wavelength light emitting devices (LED) [1]. ZnO is a good candidate for these devices due to its wide band gap of 3.37 eV and to its extremely high exton binding energy of 60 meV at room temperature (RT), which in principle should allow efficient excitonic lasing mechanism at RT [2]. ZnO thin films have been prepared by numerous methods, such as sputtering [3], ion beam-assisted reactive deposition [4], metal organic vapor phase Epitaxy (MOVPE) [5], plasma-assisted MOVE (PA-MOVPE) [6], molecular beam epitaxy (MBE) [7] and pulsed laser deposition (PLD) [8]. Much progress has been achieved in experimental and theoretical investigations of ZnO, and origins of luminescence have been proposed. Among film-preparation methods, PA-MOVPE has an advantage in growing high quality films due to its versatility in controlling various thermodynamic interactions. A disadvantage, however, is that adduct formed by vapor phase reaction is deposited on the substrate surface and obstructs the crystal growth. To obtain high-quality ZnO films, different precursors have therefore been adopted in the growth methods of ZnO films. Here, we report the characteristics of ZnO grown on a-plane sapphire with DMZn and N_2O as precursors.

2. Experimental

ZnO films were deposited on a-plane sapphire substrates at 800 °C for 90 minutes by PA-MOVPE with dimethylzinc (DMZn) and N_2O as Zn and O precursors, respectively. The carrier gas for DMZn was N_2, and the chamber pressure was about 9×10^{-2} Torr. N_2O flow rates were used 20 ccm. The properties of the ZnO film were evaluated using interference microscopy, X-ray diffractometer (XRD), photoluminescence (PL) and field emission scanning electron microscopy (FE-SEM).

3. Results and discussion

3.1. High quality ZnO epitaxial growth

ZnO films were grown at various N_2O flow rates (5 to 20 ccm). Figure 1 shows SEM images of ZnO surface, and Fig. 2 shows the X-ray rocking curve (XRC) measurement results. At N2O flow rates of 5 and 10 ccm (Figs. 1a and b, respectively); the ZnO film was formed by aggregation of granular crystals, indicating that the ZnO growth model for these two flow rates is the Volmer-Weber type. At the lower flow rate (5 ccm), the crystal grain had irregular shape (Fig. 1a), whereas at the higher flow rate (10 ccm), the crystal grain on the surface had hexagonal facet (Fig. 1b). This result indicates that adhesive growth occurred when the N_2O flow rate was 5 ccm. When the N_2O flow rate was increased to 15 and 20 ccm (Figs. 1c and 1d, respectively), the surface became flat, indicating that increasing the N_2O flow rate promoted surface migration.

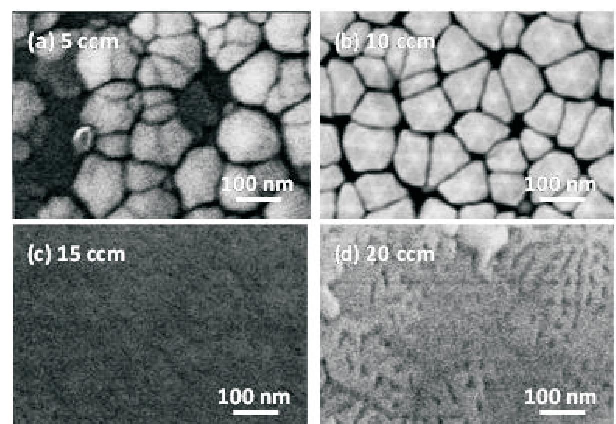

Fig. 1. SEM images of ZnO films at different N_2O flow rates: (a) 5, (b) 10, (c) 15, and (d) 20 ccm.

In Fig. 2, XRC measurement results confirmed that the crystallinity improved when the N_2O flow rate was increased. Table 1 shows the partial pressure of N_2O, DMZn, N_2 at various N_2O flow rates studied here. At low N_2O flow rate (5 to 10 ccm), the partial pressure of DMZn increased and the reaction rate in the vapor phase increased. Therefore, adduct that was generated by vapor phase reaction and adhered to the surface, inhibited the crystal growth. When the N_2O flow rate was increased, the partial pres-

sure of DMZn decreased, thus suppressing the vapor-phase reaction, resulting in a flat ZnO surface. These results suggest that the advantage of PA-MOVPE with N_2O is the suppression of the vapor phase reaction by lowering the DMZn partial pressure.

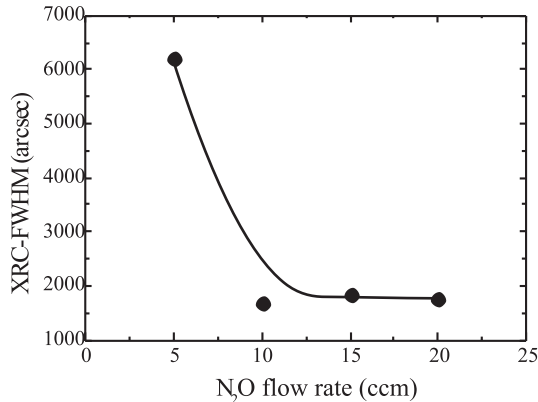

Fig. 2. Dependence of ZnO film crystallinity on N_2O flow rate evaluated using XRC-FWHM.

Table 1. Partial pressure of N_2O, DMZn, and N_2 at various N_2O flow rates studied here.

N_2O flow rate (ccm)	P_{N_2O} ($\times10^{-2}$ Torr)	P_{DMZn} ($\times10^{-2}$ Torr)	P_{N_2} ($\times10^{-2}$ Torr)
5.0	1.450	0.114	7.436
10	4.840	0.078	5.082
15	5.150	0.058	3.792
20	6.300	0.041	2.659

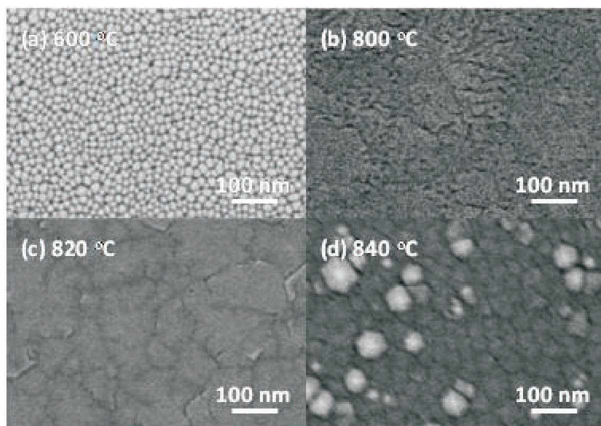

Fig. 3. SEM images of ZnO films at different growth temperature: (a) 600 °C, (b) 800 °C, (c) 820 °C, and (d) 840 °C.

Next, the dependence of the ZnO film on growth temperature was evaluated at an N_2O flow rate of 20 ccm. Figure 3 and 4 show SEM images and XRC measurement results, respectively. At a growth temperature of 600 °C, the ZnO film was actually crystal grains. At 800 °C, the ZnO film became continuous and flat. At 820 °C, the film was the flattest because surface migration was promoted by the increase in growth temperature. In the high-temperature growth region (800-840 °C), Zn atoms can reach stable sites due to the increased surface migration, thus improving the surface flatness. Moreover, a high density of hexagonal grains appeared on the ZnO film at the high growth temperature of 840 °C. Above 840 °C, the ZnO thin film starts to evaporate, and the facet in which the evaporation is difficult to be generated has appeared on the surface.

The change in XRC-FWHM of the ZnO films is evidence of the consideration for these SEM images. Surface migration is apparently promoted by the increase in growth temperature because the crystallinity also improved with increasing growth temperature. When the growth temperature was increased further (> 840 °C), the evaporation of ZnO increased and the crystallinity deteriorated. The sensitivity of the surface roughness to evaporation of the film explains why the surface roughness increases faster than the deterioration in crystallinity.

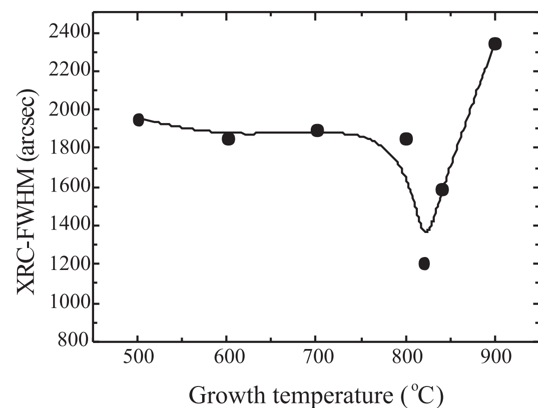

Fig. 4. Dependence of crystallinity of ZnO films on growth temperature evaluated using XRC-FWHM.

3.2. Temperature modulation ZnO epitaxial growth

To produce LED, p type ZnO films were fabricated in which N atoms of N_2O gas were incorporated into ZnO. In the low temperature growth region, incorporation efficiency of N atoms is high [9]. However, fabrication of high quality ZnO films at low temperature growth is difficult due to be not obtained sufficient surface migration. ZnO films with incorporated N atoms and with high quality crystallinity were therefore fabricated by temperature modulation growth involving low temperature (LT) growth (at 400 °C, 500 °C, 600 °C or 650 °C) and high temperature (HT) growth (820 °C, based on our results discussed in 3.1) at every 10 nm. Figure 5 shows SEM images of ZnO films grown using temperature modulation growth, and Fig. 6 shows and the XRC measurement results for these films. In Fig. 5a, the ZnO film grown at 400 °C in the LT growth region shows aggregation of granular crystals, indicating that this growth temperature did not sufficiently promote surface migration. When the growth temperature exceeded 500 °C in the LT growth region, the ZnO surface become flat and continuous. These results indicate that surface migration was sufficiently enhanced when the growth temperature was higher than 400 °C, thus improving the lattice for high-quality ZnO buffer layer. In addition, the ZnO surface grown at 600 °C and 650 °C in the LT growth region had good surface morphology which cannot observe the roughness of surface in SEM.

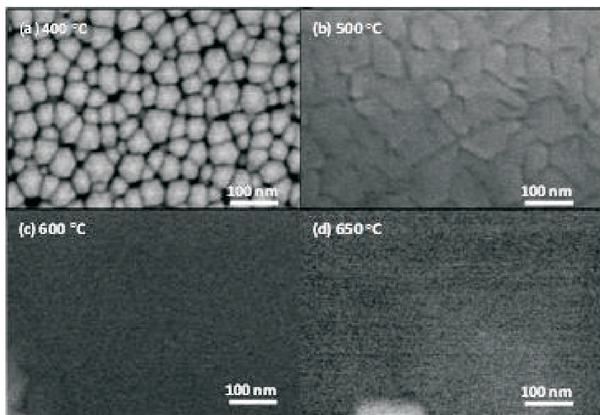

Fig. 5. SEM images of ZnO films grown using temperature modulation growth at different LT growth temperature: (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 650 °C.

The XRC measurement results (Fig. 6) confirm that the crystallinity of ZnO films grown by LT growth was the highest when the growth temperature was 600 °C. Moreover, the crystallinity was drastically improved by annealing the film in air at 900 °C for 30 min. Apparently this annealing causes the atoms in the interstice to move and thus reach stable sites.

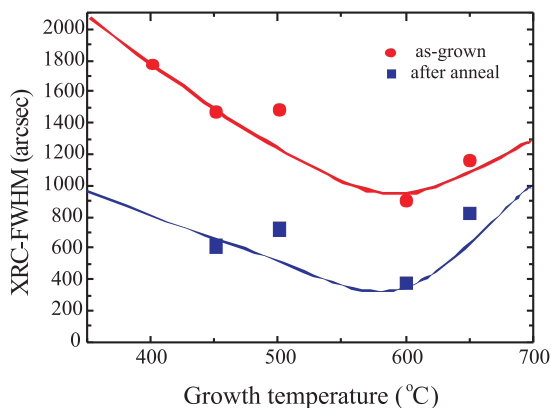

Fig. 6. Dependence of ZnO film crystallinity on LT growth temperature and on annealing, evaluated using XRC-FWHM.

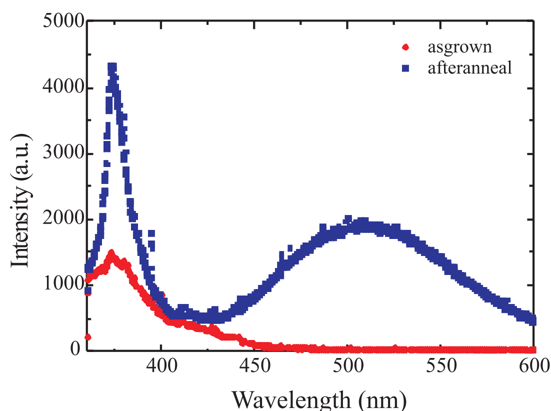

Fig. 7. Measured PL of ZnO films as-grown at 600 °C LT growth temperature and after annealing.

Figure 7 shows the measured PL of ZnO films grown at 600 °C by LT growth. The PL intensity in the near-band edge was increased by the annealing. The annealing apparently stabilized both atomic position and configuration, and enhanced the near-band edge luminescence. These results indicate that the temperature modulation growth was able to realize high-quality crystal growth in the low temperature region where incorporation of N atoms into the film was possible.

4. Conclusion

Results reported here show that gas flow rate and growth temperature significantly affect the surface diffusion in epitaxial growth by PA-MOVPE using N_2O and DMZn. High-quality ZnO films can therefore be fabricated by controlling the gas flow rate and growth temperature. Temperature modulation growth can be used to fabricate high-quality crystal growth in the region where incorporation of N atoms into the film is possible. Fabrication of p-ZnO by using PA-MOVPE seems to be possible by the examination of further process.

AUTHORS
Takayuki Nakano* - Department of Electrical and Electronic Engineering, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku Naka-ku Hamamatsu, 432-8561, Japan. E-mail: ttnakan@ipc.shizuoka.ac.jp
Kazuki Nishimoto - Department of Electrical and Electronic Engineering, Faculty of Engineering, Shizuoka University.
Masatomo Sumiya - National Institute for Materials Science, Tsukuba 305-0044, Japan.
Shunro Fuke - Department of Electrical and Electronic Engineering, Faculty of Engineering, Shizuoka University.
* Corresponding author

References

[1] Nakamura S., Mukai T., Senoh M. Iwasa N., *Journal of Applied Physics*, no. 76, 1994, 8189.
[2] Tang Z.K., Wang G.K.L., Yu P., *Appl. Phys. Lett.*, no. 72, 1998, 3270.
[3] Krupanidhi S.B., Sayer M., *J. Appl. Phys.*, no. 56, 1984, 3308.
[4] Zhamg D.H., Brodie D.E., *Thin Solid Films*, no. 238, 1994, 95.
[5] Fujimoto E., Sumiya M., Ohnishi T., Watanabe K., Lippmaa M., Matsumoto Y., Koinuma H., *Appl. Phys. Express*, no. 2, 2009, 045502.
[6] Minegishi K., Koiwai Y., Kikuchi Y., Yano K., Kasuga M., Shimizu A., *Jpn. J. Appl. Phys.*, no. 36, 1997, p. 1453 f.
[7] Segawa Y., Ohtomo A., M. Koinuma M., Z.K. Tang, P. Yu, and GK.L. Wong, *Phys. Stat. Sol. B*, no. 202, (1997) 669.
[8] Ryu Y.R., Zhu S., Budai J.D., Chandrasekhar H.R., Miceli P.F., White H.W., *Appl. Phys. Lett.*, no. 88, 2000, p. 20 f.
[9] Tsukazaki A., Onuma T., Ohtani M., Makino S., Sumiya M., Ohtani K., Chichibu S.F., Fuke S., Segawa Y., Ohno H., Koinuma H., Kawasaki M., *Nature Material*, no. 4, 2004, 42.