Epitaxial Growth of Zinc Oxide for Ultraviolet Light-Emitting Devices

Akihiko Yoshikawa¹, Yoshikazu Kaifuchi², Koji Omichi², Syunichiro Hirafune², and Munehisa Fujimaki³

We achieved a high temperature growth of Zn-polar ZnO homoepitaxial film using a high power laser diode module and a novel structure zinc-ionizer. The film grown at 850 °C showed an island structure, which consisted of steps and terraces with a monolayer step-height of 0.26 nm. The full width at half maximum (FWHM) values of X-ray rocking curve (XRC) for ZnO (0002) and ZnO (1012) were 30.9 arcsec and 53.9 arcsec, respectively. The high temperature growth of ZnO homoepitaxial film is an excellent method to improve its surface morphology and its crystalline quality.

1. Introduction

Zinc oxide (ZnO) has attracted considerable attention as a material for light-emitting devices operating ultraviolet wavelength region because it has a wide direct bandgap of 3.37 eV. In addition, a large exciton binding energy of 60 meV at room temperature enables it to achieve high emission efficiency. Although many researchers have reported ZnO epitaxial growth, they have not fabricated light-emitting devices with high emission efficiency, yet. There are some key points for fabricating ZnO based light-emitting devices such as an atomically flat surface to fabricate steep hetero interface, a high crystalline structural quality with a superior optical property and a high hole density with p-type conductivity. It seems that homoepitaxial growth is one of the most favorable approaches to realize light-emitting devices. In addition, a high temperature growth has a potential to achieve a high crystalline quality with an atomically flat surface due to an effect of a surface migration enhancement of adsorbed zinc species. However, high temperature growth of ZnO film has not been realized because zinc species do not adsorb onto substrate due to very low zinc-sticking coefficient at high growth temperature.

In this paper, we proposed a high temperature growth of Zn-polar ZnO homoepitaxial film to improve its surface morphology. In addition, we characterized Zn-polar and O-polar ZnO homoepitaxial films to select more favorable polarity for realizing light-emitting devices.

2. Crystal growth of ZnO by molecular beam epitaxy

ZnO films were grown by molecular beam epitaxy (MBE). This epitaxial growth method has an advantage of obtaining a high purity compound semiconductor crystal because it is grown under an ultra high vacuum degree ¹. Figure 1 shows the schematic diagram of the MBE apparatus used in this study. This MBE apparatus has some unique components such as a hydrogen thermal cracking cell for a substrate cleaning, a high power laser diode module for substrate heating and a novel structure zinc ionizer. A hydrogen...
thermal cracking cell was used to obtain extremely clean surface before homoepitaxial growth. A high power laser diode module was employed to perform high temperature growth under an ultra high vacuum degree, which should be resulted in reduction of impurities incorporated in epitaxial film. A novel structure zinc-ionizer with an extraction grid and an energy-acceleration function was designed to realize effective zinc-ionization and higher zinc-sticking coefficient at high growth temperatures\(^{2,3}\).

Table 1 shows the growth condition of the ZnO homoepitaxial films. Zinc (6N grade) evaporated from Knudsen cell and oxygen radical (O\(_2\) gas with 6N grade) supplied from RF plasma cell were used for undoped ZnO homoepitaxial growth. In the case of nitrogen doped ZnO homoepitaxial growth, nitrogen radical (N\(_2\) gas with 6N grade) supplied from RF plasma cell was used as an acceptor dopant. We used ZnO(0001) or ZnO(000\bar{1}) substrate grown by a hydrothermal method (Tokyo Denpa co.,Ltd), which is probably the best crystalline quality on the basis of full width at half maximum (FWHM) value of X-ray rocking curve (XRC) at the present time\(^{4}\). Growth temperatures measured by a radiation thermometer were set to be 650 °C or 850 °C.

The surface morphology of homoepitaxial ZnO film was examined by atomic force microscopy (AFM, SII SPA300 system). We evaluated the surface smoothness by root mean square (RMS) roughness. The nitrogen atomic concentration of nitrogen doped ZnO homoepitaxial film was measured by secondary ion mass spectroscopy (SIMS, Physical Electronics PHI 6650 system). The crystalline quality of ZnO homoepitaxial film was evaluated by XRC measurement of X-ray diffraction (XRD, PANalytical X’Pert MRD system). The FWHM values of XRC for ZnO(0002) and ZnO(10\bar{1}2) were equivalent for a density of screw dislocation, edge dislocation and their mixed dislocation. The optical property of ZnO homoepitaxial film was measured by photoluminescence (PL) measurement. In this PL measurement, the 325 nm line from a He-Cd laser with output power of 8 mW was used for excitation source and a luminescence from ZnO homoepitaxial film was detected by a spectroscope (Jobin Yvon, HR-640 system).

### Table 1. Growth condition of the ZnO homoepitaxial films.

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>–</td>
<td>hydrothermally grown ZnO(0001)</td>
</tr>
<tr>
<td>Growth temperature</td>
<td>°C</td>
<td>650, 850</td>
</tr>
<tr>
<td>Zinc condition</td>
<td>Zinc vapor pressure</td>
<td>Torr</td>
</tr>
<tr>
<td>Oxygen condition</td>
<td>O(_2) flow rate</td>
<td>sccm</td>
</tr>
<tr>
<td>Nitrogen condition</td>
<td>N(_2) flow rate</td>
<td>sccm</td>
</tr>
<tr>
<td>Film thickness</td>
<td>nm</td>
<td>400 - 750</td>
</tr>
</tbody>
</table>

3. Difference of characteristic for Zn-polar and O-polar ZnO homoepitaxial films

Wurzite structure ZnO has two different polarities along the c-axis: [0001] Zn-polar and [000\bar{1}] O-polar. It is known that a difference between these polarities affects growth mode, impurity incorporation and formation mechanism of dislocation. However, this difference has not been clarified in the case of homoepitaxial growth. In this chapter, we report difference of surface morphology and nitrogen acceptor incorporation efficiency for Zn-polar and O-polar ZnO homoepitaxial films.

Figure 2 shows the AFM images of Zn-polar and O-polar ZnO homoepitaxial films grown at 650 °C. Surface morphology of Zn-polar ZnO homoepitaxial film

![AFM images of Zn-polar and O-polar ZnO homoepitaxial films](image_url)

(a) Zn-polar ZnO homoepitaxial film

(b) O-polar ZnO homoepitaxial film

Fig.2. AFM images of the (a) Zn-polar ZnO homoepitaxial film and (b) O-polar ZnO homoepitaxial film grown at 650 °C.
showed island structure with large RMS roughness of 21 nm. On the contrary, less than 1 nm of the RMS roughness was obtained at O-polar ZnO homoepitaxial film. This difference of surface morphology between the two polarities might be caused by the differences of surface smoothness of ZnO substrate and surface migration length of adsorbed zinc species 5).

Figure 3 shows the depth profiles of nitrogen concentration in the nitrogen doped Zn-polar ZnO homoeitaxial films grown at 650 °C. The nitrogen concentration was about $5 \times 10^{19}$ /cm$^3$ in the Zn-polar homoepitaxial film. On the contrary, the O-polar ZnO homoeitaxial film was lower than the detection limit ($3 \times 10^{17}$ /cm$^3$). It was confirmed that the result corresponds to the ZnO heteroepitaxial film grown on a GaN template substrate 6).

In this chapter, we demonstrated the difference of the surface morphology and the nitrogen acceptor incorporation efficiency of the Zn-polar and O-polar ZnO homoeitaxial films. Neither Zn-polar nor O-polar ZnO homoeitaxial film had both an atomically flat surface and a high nitrogen acceptor incorporation efficiency. Therefore, it is necessary to develop the growth process, which realized either an atomically flat Zn-polar ZnO homoeitaxial film or a high nitrogen acceptor incorporated O-polar ZnO homoeitaxial film.

4. High temperature growth of Zn-polar ZnO homoeitaxial film

We proposed a high temperature growth of Zn-polar ZnO homoeitaxial film to improve its surface morphology. It was demonstrated that our MBE apparatus can keep zinc-sticking coefficient higher using a high power laser diode module and the zinc-ionizer. We set the growth temperature to be 850 °C during a growth of Zn-polar ZnO homoeitaxial film.

Figure 4 shows the AFM image of the Zn-polar ZnO homoeitaxial film grown at 850 °C. The RMS roughness of about 4 nm is much smaller than that of Zn-polar ZnO homoeitaxial film grown at 650 °C. Furthermore, it should be noted that the surface morphology of the film shows island structure, which consists of steps and terraces with a monolayer step-height of 0.26 nm. This result indicates that the surface migration of adsorbed zinc species is enhanced by a high growth temperature.

![AFM image of the Zn-polar ZnO homoeitaxial film grown at 850 °C.](image)

**Table 2. FWHM values of XRC for the Zn-polar ZnO homoeitaxial film grown at 850 °C, ZnO heteroepitaxial film and device grade GaN film.**

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Zn-polar ZnO homoeitaxial film grown at 850 °C</td>
<td>ZnO(0002) arccsec</td>
<td>30.9</td>
</tr>
<tr>
<td></td>
<td>ZnO(1012)</td>
<td>53.9</td>
</tr>
<tr>
<td>ZnO heteroepitaxial film</td>
<td>ZnO(0002) arccsec</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>ZnO(1012)</td>
<td>378</td>
</tr>
<tr>
<td>Device grade GaN</td>
<td>GaN(0002) arccsec</td>
<td>420</td>
</tr>
<tr>
<td></td>
<td>GaN(1012)</td>
<td>556</td>
</tr>
</tbody>
</table>

![Room temperature PL spectrum of the Zn-polar ZnO homoeitaxial film grown at 850 °C.](image)
We investigated the crystalline quality and the optical property of the Zn-polar ZnO homoepitaxial film. The FWHM values of ZnO(0002) and ZnO(10\bar{1}2) for the Zn-polar ZnO homoepitaxial film were 30.9 arcsec and 53.9 arcsec, respectively. It should be noted that these values are very close to those of Zn-polar ZnO substrate (43.9 arcsec and 30.0 arcsec). These values are narrower than those of the ZnO heteroepitaxial film (41 arcsec and 378 arcsec) and also the device grade GaN (420 arcsec and 556 arcsec) as shown in Table 2. This result indicates that the Zn-polar ZnO homoepitaxial film grown at 850 °C has high crystalline quality with low dislocation density.

Figure 5 shows the room temperature PL spectrum of the Zn-polar ZnO homoepitaxial film grown at 850 °C. Only the strong near band-edge emission at about 380 nm due to the recombination of free excitons was observed, while the deep level emission at about 500 nm originated from defects and/or impurities was not observed. The narrow FWHM value of about 10 nm for the near band-edge emission indicates that the Zn-polar ZnO homoepitaxial film grown at 850 °C has a high crystalline quality. Furthermore, no deep level emission indicates that defects and/or impurities in the film were extremely suppressed.

From these results, the high temperature growth of ZnO homoepitaxial film is an excellent method to improve not only its surface morphology but also its crystalline quality.

5. Conclusion

We achieved a high temperature growth of Zn-polar ZnO homoepitaxial film using a high power laser diode module and a novel structure zinc-ionizer to achieve a smooth surface. The Zn-polar ZnO homoepitaxial film showed island structure, which consists of steps and terraces with a monolayer step-height of 0.26 nm. Surface morphology of ZnO film was much smoother with increasing growth temperature. The FWHM values of XRC for ZnO(0002) and ZnO(10\bar{1}2) were 30.9 arcsec and 53.9 arcsec, respectively. In PL measurement, only the near band-edge emission at about 380 nm due to the recombination of free excitons was observed. It was confirmed that the high temperature growth of ZnO homoepitaxial film is an excellent method to improve not only its surface morphology but also its crystalline quality.

References