

MBE Growth of ZnO Using NO₂ as Oxygen Source

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1. Introduction

As a base material of short-wavelength light-emitting / receiving semiconductor devices, increasing attention is paid toward zinc oxide (ZnO). ZnO has a bandgap of 3.37eV at room temperature (RT) and a high exciton binding energy of 60meV [1], making it particularly attractive as novel devices utilizing excitons [2, 3]. To ensure controllability and avoid contamination from various gases, molecular beam epitaxy (MBE) method has been applied by several groups, with sources of laser ablated ZnO [4], or metallic zinc and oxygen plasma [1]. Oxygen plasma is a conventional oxygen source, but when applied for MBE, it tends to make pressure inside the growth chamber too high for use of sensitive filaments and heaters. Moreover, charged particles may damage the surface of substrates and films.

Compared to oxygen plasma, nitrogen dioxide (NO₂) is an attractive oxidizer. It has a relatively low vapor pressure and easily adsorbs to liquid nitrogen cryoshrouds, which makes it much easier to maintain high vacuum level during the growth. This enables use of convenient *in-situ* measurement methods, such as reflection high energy electron diffraction (RHEED). In this paper, we report use of NO₂ for MBE growth of ZnO.

2. Experiments

Schematic of our MBE system is shown as Fig.1. Sapphire c-plane substrates were degreased with organic solvents, and etched in H₂SO₄ : H₃PO₄ = 3 : 1 hot solution before being introduced. In vacuum, substrates were thermally cleaned at 800°C for 2 min, followed by oxygen plasma irradiation at 250°C for 10min. Then, ZnO epitaxy was held at 450°C for 5 hours. NO₂ gas was ejected from a conventional gas-cell. Cell temperature was kept at a mild 50°C to avoid both condensation or thermal cracking (which causes the chamber pressure to rise) of NO₂. Metallic zinc from a conventional Knudthen cell was used as zinc source. The growth chamber was extensively cryoshrouded by liquid nitrogen. Beam flux of zinc and NO₂ measured by an ionization gauge was 5×10^{-7} Torr and $3 \sim 7 \times 10^{-7}$ Torr,

respectively. During growth, pressure inside the chamber was kept lower than 1×10^{-7} Torr, much lower than the case of pure oxygen gas or plasma (over 1×10^{-4} Torr), and low enough for use of RHEED and other *in-situ* measurement equipments.

3. Results

RHEED patterns showed spotty single-crystal patterns (Fig.2) from the initial growth stage. 30 degrees of rotation in the basal plane was observed [5]. PL spectra at 20K were dominated by exciton luminescence (Fig.3) and no deep level peaks were observed up to RT. X-ray diffraction patterns showed (0002) and parallel peaks only. FWHM of (0002) peaks were 5.0~9.0 min.

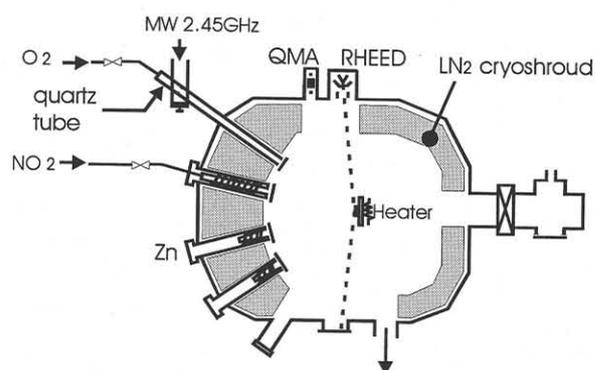


Fig.1 Schematic diagram of our MBE system.

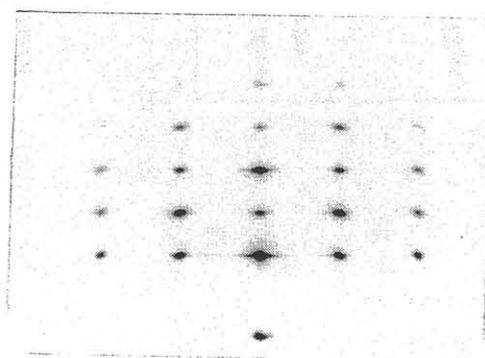


Fig.2 RHEED pattern of ZnO grown at 450°C (beam along [1120] direction)

SEM images differed largely between samples, though growth conditions were the same. Some samples showed island growth combined with columnar structures (Fig.4), while others showed scattered island growth and slower growth rate. Including the columns, growth rate varied between 20 - 130nm/h. PL spectra of the samples with fewer columns showed weaker shallow level peaks as Fig.3, while those of the samples with many columns were dominated by shallow level peaks.

When growth temperature was lowered to 250°C, or when oxygen plasma was used instead of NO₂ gas, growth occurred with better uniformity. However, RHEED patterns indicated polycrystal growth from the initial growth stage, and PL spectra were dominated by deep-level peaks.

From the present results, it is expected that the initial buffer layers on sapphire substrates, if grown at optimum conditions, can control the island growth characteristics of

the main ZnO layers, which potentially possess well-defined exciton properties. Therefore, control of initial growth stage using low-temperature grown buffer layer for better uniformity and reproducibility is currently under investigation.

4. Summary

We have reported the use of NO₂ gas as oxygen source for MBE growth of ZnO. Pressure of the growth chamber was lower by 3 orders than the case of oxygen, enabling *in-situ* measurements. *c*-axis oriented ZnO single crystals were obtained. PL spectra clearly showed exciton luminescence, with no deep level peaks up to RT.

References

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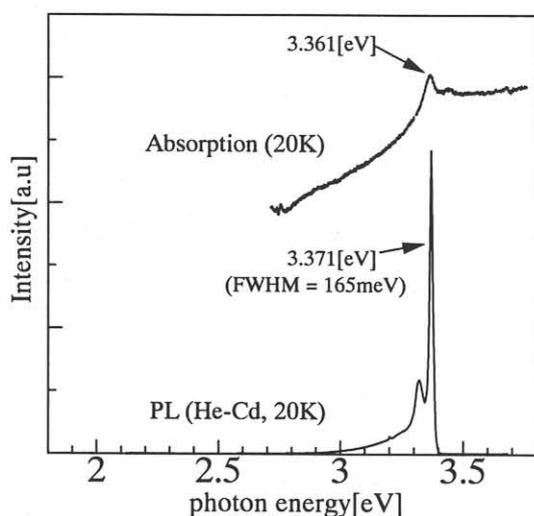


Fig.3 PL and absorption spectra of ZnO (without columnar structures).

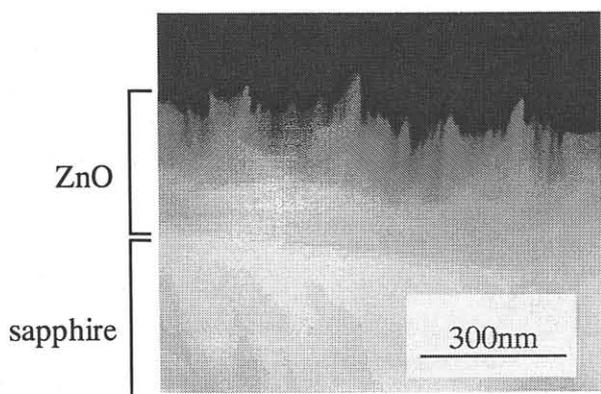


Fig.4 Typical cross-sectional SEM image of ZnO with columnar structures.