

MBE growth and properties of
ZnO and ZnCdO thin films

Keiichiro SAKURAI

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This thesis is based on the research work to which the
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from Apr.1996 through Jan.2001.

"Repair when broke. To pieces when beyond."

————— *author's motto*

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Chapter 1

Introduction

1.1 Backgrounds

Information technologies have been applied to various fields and have been wildly permeating into every aspect of our life. These new technologies support communications to be faster and easier, and to be useful than ever. Following this trend, the size and power consumption of information appliances are preferred to be smaller, while their functions and capacity dramatically increase. Consequently, there have been strong demands on optical semiconductor devices, for shorter wavelength, higher efficiency, and integration possibilities. These demands on semiconductor devices involved higher storage density which requires laser diodes (LDs) shorter in their wavelength, or full-color luminescence which requires light emitting diodes (LEDs) of all three primary colors; red, green and blue. Recently, wide-bandgap semiconductor compounds, including ZnSe and GaN, have been introduced to the world as short-wavelength optical device materials. ZnSe-based compounds have realized pure green LEDs and LDs [1], and GaN-based compounds have made LEDs and LDs operating at blue and shorter wavelengths [2, 3] possible. These new semiconductor compounds are being applied as full-color light sources and short-wavelength lasers for storage devices. But still, under the current fast development of information appliances, smaller size, higher

density of integration, lower power consumption and higher efficiency, are strongly demanded. In view of these persisting demands on optical devices, Zinc oxide (ZnO) is an attracting candidate material.

1.2 Zinc oxide

1.2.1 Properties of ZnO

ZnO is a material that bears closely to our daily lives. It is characteristic of many useful properties, such as piezoelectric behavior, transparency to visible light, conductivity, sensitivity to various gases. These properties make ZnO one of the most widely and commonly used material applied to the industry, widely applied for passive devices such as piezoelectric devices [4, 5, 6], gas sensors[7, 8], varistors, and transparent electrodes[9].

From a different point of view, as a semiconductor material, ZnO closely resembles the famous GaN. ZnO has a wide bandgap of 3.4eV which corresponds to ultraviolet (UV) light [10]. It also has a wurtzite (WZ) structure with lattice constants of $a = 3.24 \text{ \AA}$ and $c = 5.19 \text{ \AA}$ [11], which is quite similar to those of GaN[12]. In addition to these properties, ZnO is particular of two major attractive points.

Excitonic properties: The first point is that ZnO has a large exciton binding energy of $E_b = 60\text{meV}$ [10, 13], which is more than two times larger than that of GaN (28meV) [14] or ZnSe (21meV) [15]. An exciton is a pair of loosely bound electron and hole, described by a model close to that of a hydrogen atom [16]. And similar to a hydrogen molecule, two excitons can also form an excitonic molecule (biexciton) [17, 18]. By utilizing excitons and biexcitons, it is expected that high-efficiency lasing can be realized by contribution of exciton to the optical gain [19, 20, 21, 22]. Also, the nonlinear optical effects of excitons are pointed out to be applicable for future ultra-fast optical switching devices [23, 24].

However, excitons are known to dissociate at high temperatures, or change to electron hole plasma (EHP) at higher excitation density by

screening effect[22]. With larger E_b , excitons become more stable and thus become easier to be utilized at higher temperature or density. In the case of GaN- and ZnSe- related alloys, though excitons were clearly observed at low temperatures and their contribution to optical gain were pointed out [17, 25], excitons tended to dissociate by the thermal energy of room temperature (26meV). In the case of ZnO, with its large exciton binding energy, excitons can be observed even at room temperatures [26], and quite low lasing threshold was also reported at low temperatures [27]. Moreover, the binding energy of excitons can be strengthened by confining in low-dimensional structures; in the case of quantum wells, an ideal well can boost the binding energy up to a factor of four[28]. As ZnO naturally has a large binding energy, the increment of binding energy by confinement can be also large, which may exceed any other semiconductor device materials. Thus ZnO is a promising candidate material for future high-efficiency short-wavelength lasing devices, and nonlinear optical devices utilizing excitons.

Connection with present ZnO devices: The second point is that ZnO is already widely applied to the industry, as mentioned above. By adding functions as active elements to present ZnO devices, integration of existing passive elements with transistors, LEDs and nonlinear optical devices, all based on ZnO, can be realized. This would lead to higher density of integration and increase the functionality of present passive devices. In addition, as semiconductor devices require the highest qualities in both electrical and optical properties, the research for ZnO active devices would improve the quality of the present passive devices. Conventional ZnO passive devices would benefit from the improved quality of ZnO crystals, resulting in lower rates in optical, electrical and physical losses.

1.2.2 Research progress

Although ZnO has these attractive properties as semiconductor devices, as it had long been considered as a material for passive devices, two major developments have been needed to be made; optical and electrical quality, and band structure modulation.

Conventional growth techniques such as chemical vapor deposition (CVD) [29] or sputtering [30] had been successful on fabrication of passive ZnO devices. However, as a passive device material, the optical properties of ZnO had mainly been evaluated by its transparency, or efficiency as a phosphor. Suppression of deep-level luminescence and nonradiative recombination centers, bandgap modification for quantum confinement and tuning of the applicable wavelength, which are inevitable as an optical device material, had not been examined sufficiently. Under strong demands for further developments in optical quality and controllability of band structure, pulsed laser deposition (PLD)[31], molecular beam epitaxy (MBE)[32, 33], and vapor transport[27] was applied for ZnO epitaxy. Works on these new growth methods have significantly improved the optical quality of ZnO films, successfully obtaining ZnO films that are free of deep-level luminescence and capable of lasing at room temperature (RT) by optical excitation [26, 34]. Still, further enhancements in film quality, such as crystallinity or electrical properties, was required for fabrication of active semiconductor devices.

Another large hurdle is the band structure modulation, including conduction type control and bandgap modification. ZnO has n-type conduction nature. Conventional growth methods such as hydrothermal synthesis, MOCVD and sputtering, have been successful in obtaining ZnO films with desired high n type conductivity [35, 36], while no successful reports on p-type conduction had been made. The n-type inclination of ZnO is caused by defects originating from interstitial zinc or oxygen vacancy [37, 38, 39]. Fabrication of p-n ZnO heterojunction semiconductor devices requires suppression of the intrinsic donors and therefore avoid self compensation on p type doping. Thus, higher crystallinity and

suppression of defects have been required from the standpoint of conduction type controlling. Co-doping technique is said to ease this difficulty of p-type doping[40], and p-type conduction in ZnO films are being reported[41, 42, 43] by utilizing this theoretical prediction. However, to date, p-type doping of ZnO still has problems in hole concentration, or optical quality, or reproducibility; no group has reported successful fabrication of p-n heterojunctions by ZnO. On the other hand, for efficient utilization of the excitons, fabrication of deep and efficient confinement structures is required. Widening of the bandgap makes potential of barrier layers higher, while narrowing of the bandgap makes wells deeper. Moreover, by bandgap modification, the applicable wavelength range of ZnO would widen from the visible ($>400\text{nm}$) region to the far-UV ($<300\text{nm}$) region. Ohtomo et al. have reported that the bandgap of ZnO can be widened up to 4.0eV by alloying with MgO [44], which corresponds to a wavelength of 310nm. However, the bandgap of ZnO has not been narrowed much in the previous studies; narrowing to 3.0eV was reported by alloying with CdO[45], but no further reports have been made.

1.3 Objectives of this study

The study presented in this thesis was done based on the background mentioned above. The first objective of this study was to obtain information and knowledge on growth parameters that have influence on the quality of ZnO films, and thus improve the optical and electrical properties of ZnO films for optical semiconductor devices. The second objective of this study was to modify the bandgap and luminescence wavelength of ZnO down to the visible region, in order to enhance confinement potential and expand applicable wavelength range of the future ZnO-based optical semiconductor devices.

In this study, MBE method was chosen for growth of ZnO and its respective alloys. Among the growth methods being applied for optical device-quality ZnO epitaxy, MBE is a promising technique. MBE is

a method that is applied for mass production, while it is also suitable for fundamental research activities. Thus the techniques developed in the research stage can directly be applied for mass production. The residual pressure during growth is low enough (typically in the range of $10^{-5} \sim 10^{-9}$ Torr), which enables in-situ observation methods using electron beam, such as reflection high energy electron diffraction (RHEED). RHEED is a powerful analysis method of the growing crystal surface, which makes it possible to observe few monolayers of the surface from low-incident electron beam diffraction patterns, and provides useful information such as surface morphology, crystallographic orientation and growth speed [46, 47]. And compared to PLD, MBE can dynamically change the supply of each source material, without being restricted by compositions of the prepared ablation targets.

However, at the time this study had begun, reports on growth of ZnO by MBE method were quite few, and most of the growth parameters were still unclear of their effects on the quality of ZnO films. This study was done in parallel with the early development of research on growth of ZnO films by MBE method, investigating the effects of fundamental growth parameters and putting the obtained knowledge to practical use for higher quality of the ZnO films.

The latter part of this study is dedicated to alloying of ZnO with CdO, to search for possibilities of narrowing the bandgap for further fabrication of confinement structures and utilization of ZnO at longer wavelength range.

1.4 Outline of this thesis

This thesis is organized in five chapters.

Chapter 2 concerns gas source MBE (GSMBE) of ZnO films, using NO_2 as oxygen source material. NO_2 and N_2O , which were used for MBE of ZnO films for the first time in this work, are described in this chapter.

Chapter 3 concerns radical source MBE (RSMBE) growth of ZnO, using radical oxygen as oxygen source. Various growth parameters of

ZnO, including the growth temperature, Zn partial pressure, parameters concerning the radical source and substrate orientation, were examined in this chapter. The effects of each parameter on RSMBE growth of ZnO films are described.

Chapter 4 deals with alloying of ZnO with CdO, using the RSMBE method described in the previous chapter. The characteristics of ZnCdO films with varied Cd contents are described. Blue luminescence from ZnCdO films is observed for the first time, and its characteristics are also described.

Finally, the results obtained in this study are summarized in Chapter 5.

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Chapter 2

MBE growth of ZnO using nitrogen oxide

2.1 Introduction

At the time this study had begun, reports on MBE growth of ZnO were quite few. As oxygen source material, radical oxygen was used [1], but its advantages to other oxidizers were still unclear. Among the oxygen source candidates, NO_x gases were attractive candidates for MBE growth of ZnO. NO_x gases have been widely used in growth of ZnO by MOCVD method, but had not been used in the case of MBE of ZnO. In the case of MBE method using liquid nitrogen shrouds, NO_x gases, with their high condensation points (21.2 °C for NO₂ and -88.5 °C for N₂O), would easily be adsorbed to shrouds and thus the residual vacuum level during growth would be quite low, which makes in-situ measurements much easier than the case of radical oxygen.

In this chapter, two types of NO_x gas, N₂O and NO₂ ¹, were used for MBE of ZnO films for the first time, and their merits and demerits for MBE of ZnO were evaluated. Radical oxygen was also examined for comparison.

¹NO was not examined, as it has a lower condensation point (-151.8 °C) and did not adsorb well to the shroud as the other two.

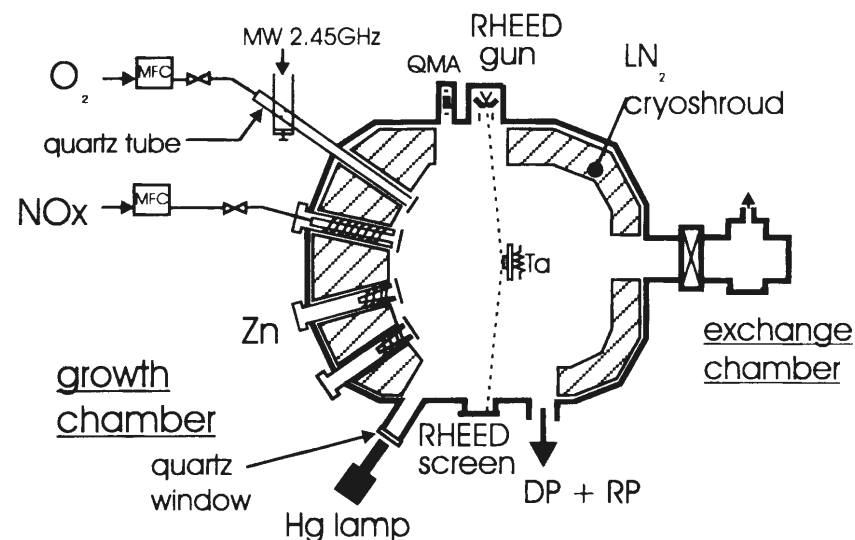


Figure 2.1: Schematic diagram of the gas-source MBE system.

2.2 GSMBE system

Overview: The epitaxial growth of films described in this chapter was carried out using a GSMBE system schematically described in Fig.2.1. The used system was a modified ANELVA KMV-101 GSMBE system, originally designed for MOMBE growth of ZnMgSSe alloys. The system consisted of one exchange chamber and one growth chamber, and sample exchange did not require repressurization of the growth chamber. The growth chamber was equipped with an effusion cell for zinc, a gas cracking cell for NO_x gases, and a radical cell for radical oxygen. All cells were equipped with individual shutters. The growth chamber was also equipped with a quadrupole mass spectrometer (QMS; ULVAC MSQ-101) for analysis of residual gas, and a reflection high energy electron diffraction (RHEED) system for in-situ real-time observation of surface

structures of the samples.

Pumping system: The growth chamber was pumped by an oil diffusion pump (Edwards EO6K), equipped with a liquid nitrogen trap (Vacuum Generator CCT-150) and supported by a rotary pump (ULVAC GCD-200XA). All pumps and oils were anti-corrosion type. The overall pumping speed of this pumping system was about $450\ell/\text{sec}$. The growth chamber was also equipped with a liquid nitrogen cryoshroud, and cooled to liquid nitrogen temperature (77K) during growth for adsorption of remaining gases. At the best condition, the pressure inside the chamber was maintained lower than 1×10^{-9} Torr. To avoid corrosion from remaining corrosive elements (Se, S) and oxidizers, aluminum gaskets were used for sealing. The baking temperature after maintenance was kept lower than 120°C in order to avoid softening of gaskets.

Substrate heating system: The substrate holder was made of molybdenum, and heated up to 800°C by a tantalum heater placed backside. Substrates were soldered to the holder by 6N indium. The substrate temperature (T_{sub}) was monitored by a thermocouple at the back side of the holder. The measured value of the thermocouple was corrected by referring the eutectic point of Al/Si (577°C) and Au/Si (363°C).

Zinc supply: Metallic zinc of 6N purity was evaporated from a low-temperature type Knudsen cell (K-cell; EPI EPI-40-LT; Fig.2.2). Zinc was held in a 40cc crucible made of pyrolytic boron nitride (PBN). The crucible was equipped with a $2\text{mm}\phi$ orifice in order to raise the cell temperature for equivalent zinc output, thus improving controllability of zinc supply. To prevent the orifice from choking up, the heater wire was placed denser at the exit edge of the crucible [2]. The temperature of the crucible was controlled by a temperature controller (Eurotherm model818). The temperature was stabilized within $\pm 0.3^\circ\text{C}$. The flux of Zn was measured as partial pressure by a nude ionization gauge (NIG).

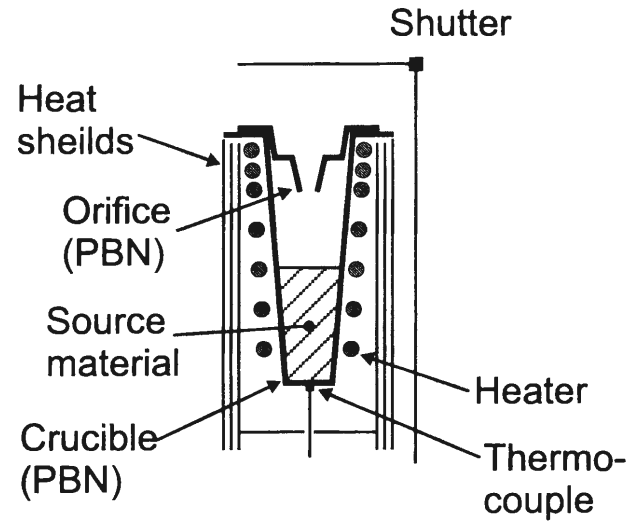


Figure 2.2: Schematic diagram of a K-cell. The zinc cell was equipped with an orifice for improved controllability of zinc flux.

NO_x supply: NO_x (N₂O or NO₂) gases were supplied from a gas cell. The gas cell was designed for thermal cracking of metalorganic gases, equipped with heaters and tantalum baffles (Fig.2.3). In this work, the temperature of the gas cell was kept at 40°C to avoid condensation of NO_x gases inside the cell. In the case of NO₂, all pipings and valves were also heated and kept above 30°C. The flow rate of the NO_x gases was controlled by a mass flow controller (MFC; STEC SEC-3400S).

Oxygen supply: For comparison with NO_x gases, radical oxygen was supplied from a radical cell. The radical cell was originally designed for nitrogen doping to ZnSe and its respective alloys. Microwave (2.45GHz) was applied for excitation of oxygen. The applied power of the microwave was 250W at maximum. Radical oxygen was injected through a 0.2mm ϕ crystal orifice. The distance between the orifice and the substrate location was approximately 850mm. The emission spectrum from the radical cell was dominated by atomic transitions at 777nm and 845nm [3] as

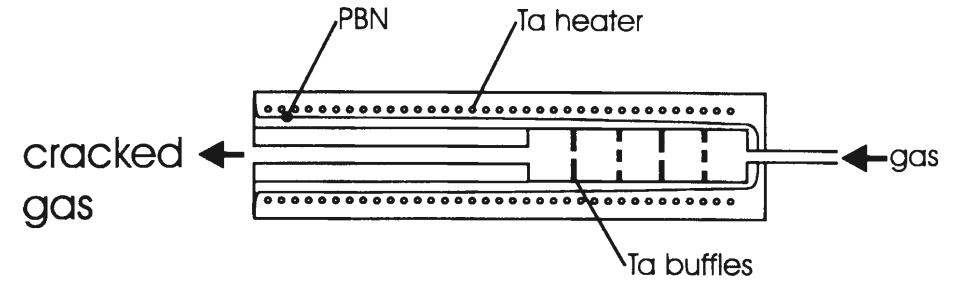


Figure 2.3: Schematic diagram of the gas cell used for injection of NO_x gases.

shown in Fig.2.4, and the color during operation was yellowish white.

2.3 Experimental procedures

2.3.1 Selection of substrate

In the case of MBE growth of ZnO, preferably, the substrate should be stable under irradiation of oxidizers, and match the hexagonal structure of ZnO crystal, which is wurtzite (WZ) with lattice parameters of $a = 3.243\text{\AA}$, $c = 5.195\text{\AA}$ (Fig.2.5). One attractive candidate was *c*-plane sapphire. Sapphire (α -Al₂O₃) is a transparent oxide substrate which has a hexagonal corundum structure with lattice parameters of $a = 4.754\text{\AA}$ and $c = 12.99\text{\AA}$, and quite stable under oxidizing environments or high temperature. As it was commonly used as substrates for GaN (which has a lattice constant quite similar to that of ZnO) and its respective alloys, it was commercially available at an affordable cost; while other candidates, such as SiC [3] or ScAlMgO₄[4], was quite expensive. In addition, sapphire substrates are transparent in the whole visible region and up to UV region of $\lambda \sim 250\text{nm}$ ², which make input / output of light through the substrates possible. In turn, sapphire is highly insulative ($\sim 10^{14}\Omega \cdot \text{cm}$) which disallows contacts to be molded to the substrate, and requires

²from vendor catalogues

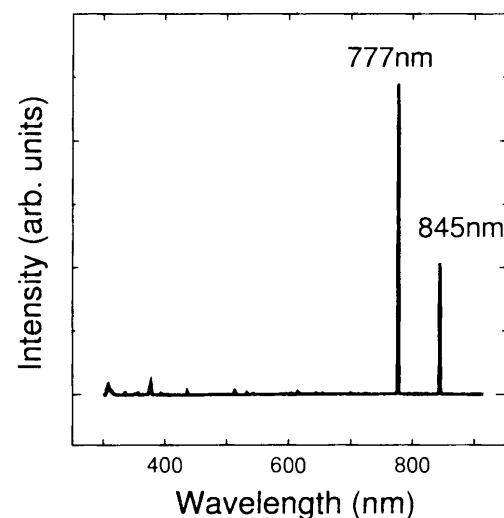


Figure 2.4: Typical spectrum of emission from oxygen plasma operating at oxygen flow rate = 0.474ccm and MW power = 250W. The spectrum was dominated by atomic transitions at 777nm and 845nm.

additional etching processes in device fabrication. And though it has a hexagonal structure, there is a large lattice mismatch between ZnO and sapphire in their *c*-planes, of about 18% (see Fig.2.9). However, taking future mass production in consideration, the low cost, high quality and availability of sapphire substrates were attractive enough to hold out the few disadvantages. Considering the factors mentioned above, *c*-plane sapphire was used as the substrate for works done in this chapter.

2.3.2 Substrate preparation

c-plane double side polished sapphire manufactured at Union Carbide (presently Bicon) by Czochralski (CZ) method was used as substrates. The thickness of the substrate was 0.33mm, and the error range of surface orientation was 0.3 degree from *c*-plane. The substrate was degreased in organic solvents, and etched in a mixed solvent of $\text{H}_2\text{SO}_3\cdot\text{H}_3\text{PO}_4$

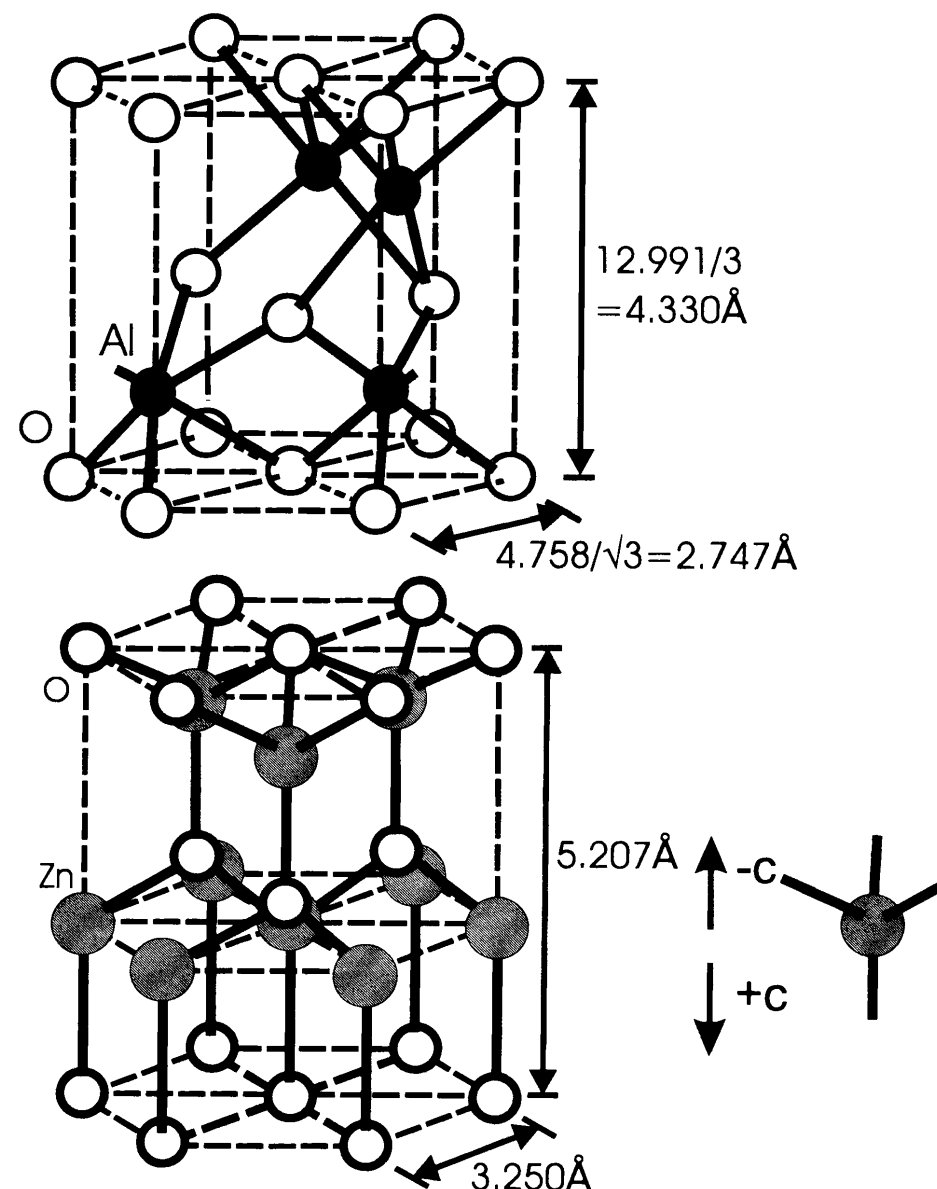


Figure 2.5: Schematic diagrams of sapphire (corundum structure) and ZnO (wurtzite structure). Figures are not drawn to scale. (Note that the diagram of sapphire does not describe a whole unit cell; see Fig.2.9).

1:3 at 100°C for 10 – 20 min. Glass dippers were used for holding the substrate³. The substrates were then rinsed with deionized water and blown with dry nitrogen. Extending the formula reported by Reisman et al.[5] to 373K, the etch rate of sapphire at this condition was estimated to be in the rage of 0.3 ~ 5nm/h⁴. This low etching rate is apparently insufficient for complete removal of the damaged layer possibly remaining at the substrate surface. However, it was estimated to be effective for removal of small bumps with heights of few monolayers, which were often seen on the substrate surface (Fig.2.6(a)). After etching, the sapphire substrate showed steps with 1/6 height [6] of one unit cell (12.99Å / 6), as seen in Fig.2.6(b). After introducing into the chamber, the substrates were thermally cleaned by heating up to 800 °C for 2min. After thermal cleaning, the substrates were cooled to 350 °C and put under irradiation of radical oxygen for 10–30 min[7]. After the pre-growth treatments, the substrate showed streaky RHEED patterns, which indicate smooth surface.

2.3.3 Growth procedures

After the preparation of the substrate, the substrate was heated to growth temperature (T_{gr}). Oxidizing gas (radical oxygen or NO_x gas) was injected into the chamber with the shutter closed, after a few minutes interval for stabilizing the gas flow, Zn and oxygen source (radical oxygen or NO_x gas) were irradiated simultaneously to the substrate. In the case of two step growth described in section 2.6, low-temperature (LT) buffer layer was grown and annealed prior to the growth at higher temperature. After growth, the shutters of cells were closed and the substrate was cooled to room temperature.

³Any kind of plastics examined could not stand this etching process, resulting in contamination of the substrate surface.

⁴0.3 is for pure H₃PO₄ and 5 is for H₂SO₃: H₃PO₄= 9:1 solution.

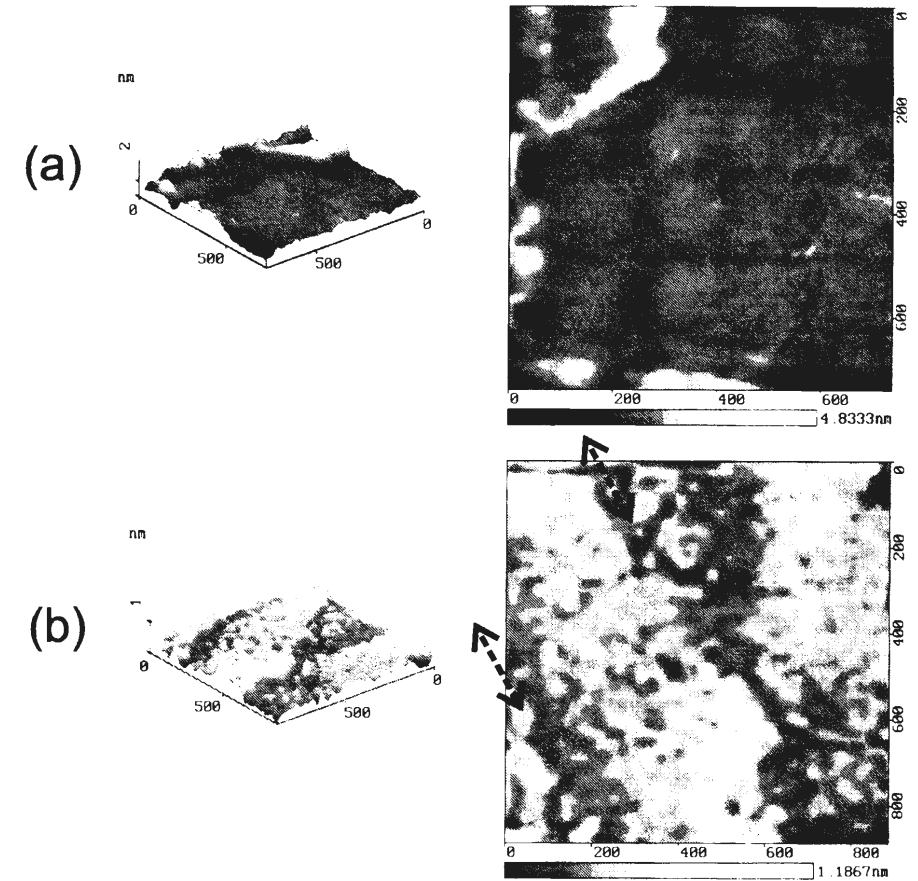


Figure 2.6: AFM images of c-plane sapphire substrates (manufactured by Union Carbide). (a):as degreased, (b):after etching in H₂SO₃:H₃PO₄= 1:3 at 100°C for 10 min. 1/6 height steps[6] are visible. Small bumps are observed for (a).

2.3.4 Characterization

The grown films were characterized by RHEED, X-ray diffraction (XRD) by $\theta - 2\theta$ and rocking curve (XRC) method, photoluminescence (PL) using a He-Cd laser irradiation at 325nm as excitation source, absorption measurement using a Xenon lamp for excitation. Atomic Force Microscopy (AFM; SII SPI3700), and scanning electron microscopy (SEM; Hitachi S-4500 SEM). Growth rates were measured from cross-sectional SEM images of the cleaved samples. Carrier concentration and resistivity were measured by a Hall measurement system (Resistest8300). Contacts for Hall measurement were made by gold wires soldered to the film surface by pure indium.

2.4 Growth of ZnO using NO₂

Growth of ZnO films using NO₂ by MBE method was examined. Beam pressure of zinc was varied between 2.5×10^{-7} Torr, flow rate of NO₂ was varied between 1.12–3.75 ccm. Growth temperature was varied between $T_{gr} = 200$ –600 °C. Growth duration time was 3–5 hours.

2.4.1 Adsorption of NO₂ gas to LN₂ shroud

It is worth noting that the background pressure was kept below 1×10^{-7} Torr during growth, low enough for use of RHEED and other means of in-situ monitoring equipments that require high vacuum level. This low background pressure was made possible by the existence of liquid nitrogen shroud. Residual NO₂ gas was adsorbed to the shroud during growth, and desorbed when the shroud was gradually heated to room temperature after growth. Fig.2.7 shows the change of background pressure of the chamber after growth with the pumping system working; the NO₂ gas desorbs abruptly at a specific temperature.

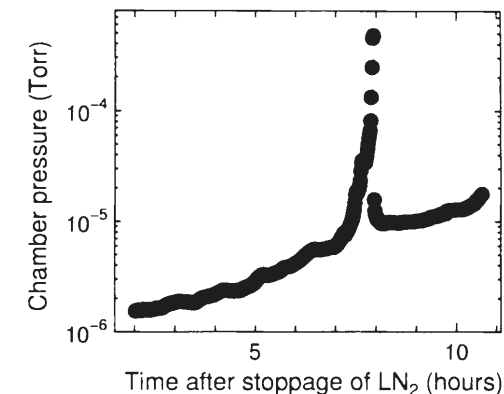


Figure 2.7: Typical record of chamber pressure after growth run, as adsorbed N₂O detaches from LN₂ shroud with rising temperature. The gas detaches abruptly at a certain temperature. NO₂ shows the same trend.

2.4.2 At optimum temperatures

For growth at $350 \leq T_{gr} \leq 500$ °C, *c*-axis oriented growth of ZnO was observed by XRD measurements. No other growth directions were observed in XRD measurements, and the narrowest value of full width at half maximum (FWHM) of XRC was 0.848 degree. The RHEED patterns of the grown ZnO films showed six-fold *c*-axis oriented growth (Fig.2.8). However, the RHEED patterns were spotty, which indicated rough surfaces⁵. 30 degrees rotation in the basal plane with respect to the sapphire substrate was observed. This is because the oxygen atom dominates the surface structure of sapphire, as schematically drawn in Fig.2.9 [8, 9]. This is analogous to the case of GaN (WZ; $a = 3.180$, $c = 5.178$) epitaxy on *c*-plane sapphire [10, 11, 12]. Typical PL spectra measured at 20K and RT are shown in Fig.2.10. The spectra showed almost no deep-level luminescence (DL) up to RT, indicating high optical quality

⁵The RHEED patterns should be “streaky” when the surface is smoother than the incident angle (typically lower than 10°) of the electron beam: see Page 20 of Ref.[46] of Chapter 1.

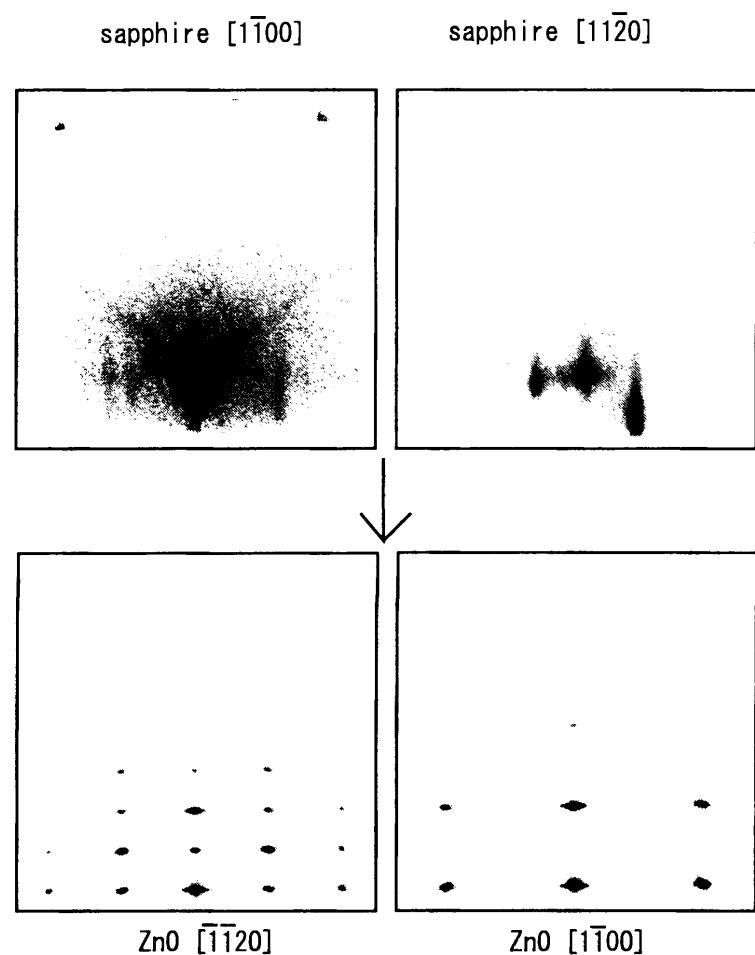


Figure 2.8: Typical RHEED patterns of a c-plane sapphire substrate and a ZnO film grown by using N_2O gas as oxidizer. The ZnO crystals were 30 degrees rotated in the basal plane with respect to the substrate (c.f. Fig.2.9).

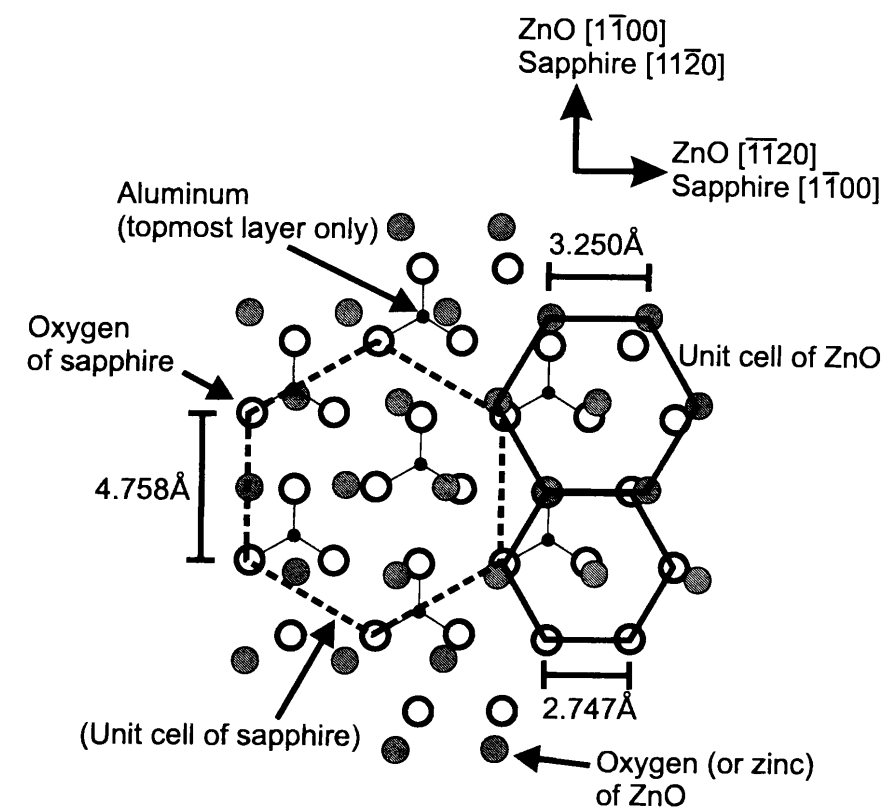


Figure 2.9: Schematic drawings of atomic arrangement of ZnO on c-plane (0001) sapphire. For Al, only the topmost layer is shown (the second layer of Al is slightly below the first layer of Al[9] and not shown).

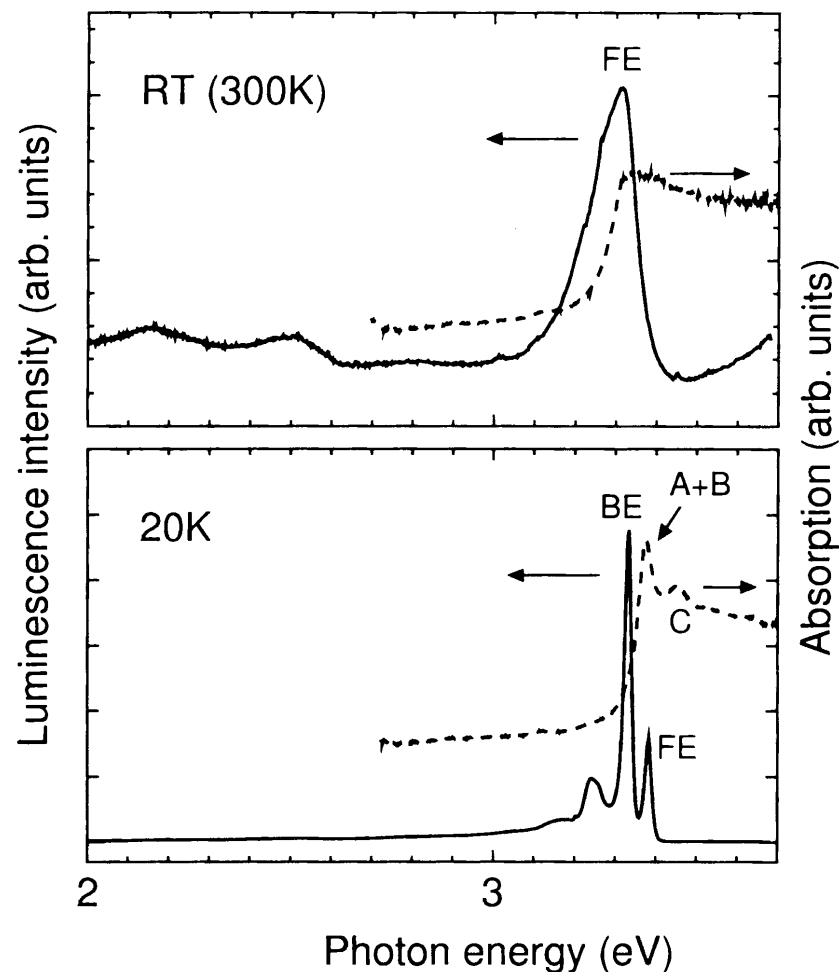


Figure 2.10: Photoluminescence and absorption spectra of a typical ZnO film with columnar structures. Excitonic peaks were clearly observed.

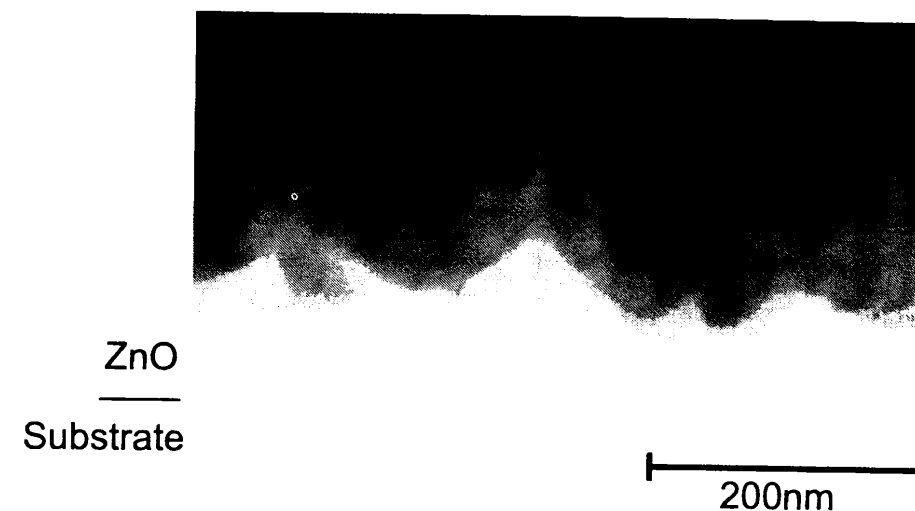


Figure 2.11: SEM image of a typical ZnO film grown directly on sapphire using NO_2 gas. Rough structures were observed.

of the grown layers as being dominated by near-bandedge luminescence. At low temperatures, the absorption spectra clearly exhibited two absorption peaks, each corresponding to A&B excitons (3.378, 3.393 eV) and C excitons (3.433 eV). Referring to the well-known band structure [13], the absorption peak at lower energy was assigned to the mixture of absorption by A (3.378 eV) and B (3.393 eV) excitons, and that at the higher energy by C (3.433 eV) excitons. Here, A and B excitons cannot be distinguished because of the low resolution (~ 15 meV). These excitonic absorption peaks were observed until near RT. Observing the PL spectra again, the peak at 20 K was found to be at 3.379 eV. As this energy value agreed well with the absorption peak of A & B excitons, it was assumed that the PL at 20K was due to radiative recombination of free A excitons. The PL peak at RT was also close to the A & B excitonic absorption peak, suggesting free exciton emission.

The surface morphology was observed by SEM. Typical SEM images are shown in Fig.2.11. The structure was disordered, i.e. the ZnO crystal consisted of sparse islands and thin columns with irregular heights and

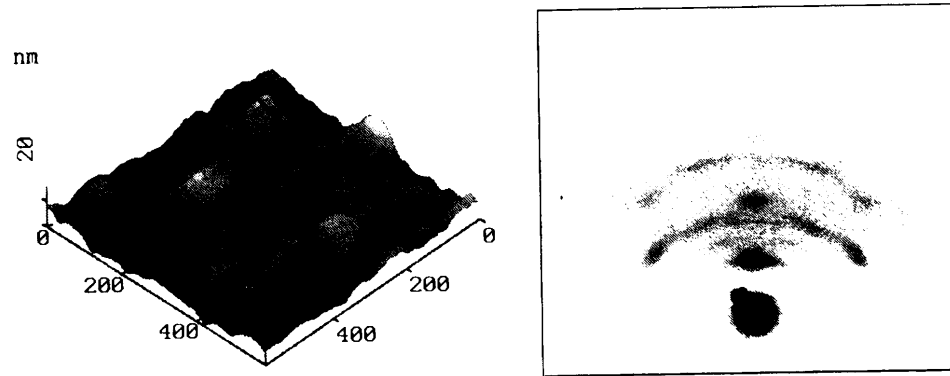


Figure 2.12: AFM image and RHEED pattern of ZnO film grown at 300°C. Dense nucleation was observed, although RHEED indicated polycrystal growth.

sizes. Further, the reproducibility was quite low, with the structure differing largely between the samples, including those grown at the same condition. Observed by the cross-sectional SEM images of the cleaved samples, the structure of the initial growth layer extremely differed from sample to sample. From these results, it was estimated that control of the initial nucleation was required for higher reproducibility, and possibly for better morphology of the film, which would be further examined in section 2.6.

2.4.3 At non-optimum temperatures

For films grown at $T_{gr} \leq 300$ °C, relatively uniform and dense initial nucleation on sapphire was observed (Fig.2.12). These films showed ring-shapes in RHEED patterns, which meant that the film was polycrystal and not perfectly *c*-axis oriented. No luminescence peak could be observed by PL measurements. Nevertheless, the reproducibility at $T_{gr} \leq 300$ °C was much better than the case of films grown at higher T_{gr} . These results suggested that growth at $T_{gr} \leq 300$ °C can be used as

low-temperature buffer layers for uniform nucleation and improved morphology. Considering these results, use of low-temperature buffer layers was examined in section 2.6.

For $T_{gr} \geq 600$ °C, no growth was observed. This can be attributed to higher desorption rate of ZnO or source materials from the surface of the sample by higher T_{gr} . Though it was not examined in this work, it is possible that growth could occur at higher temperatures with increased zinc and NO₂ supply.

2.5 Comparison with other oxygen sources

2.5.1 Comparison with N₂O

Use of N₂O as oxidizer was also examined. N₂O is commercially available with high purity, and also adsorbs well to LN₂ cryoshrouds. Several experiments were conducted at N₂O flow rate = 0.5 – 10.0 ccm, Zn pressure = $2 - 8 \times 10^{-7}$ Torr, T_{gr} = 250 – 300 °C. However, as far as we tried, no epitaxy was observed for most conditions, with few exceptions that formed small grains (Fig.2.13), showing only initial nucleation on the substrate.

From these results, it was shown that additional excitation (such as activation by plasma) was required for use of N₂O gas as oxidizer in the case of ZnO epitaxy by MBE method.

2.5.2 Comparison with radical oxygen

For comparison, use of radical oxygen as oxygen source was also examined on the same MBE system, using a plasma cell with its orifice placed about 85cm far from the growth position. The Zn flux was varied between $6 \times 10^{-8} - 6 \times 10^{-7}$ Torr. The growth temperature was varied between 200 – 500 °C. The flow rate of oxygen was limited to 1.0ccm, as the pressure inside the chamber went over 1×10^{-4} Torr at that flow rate. Growth was conducted for 5 hours.

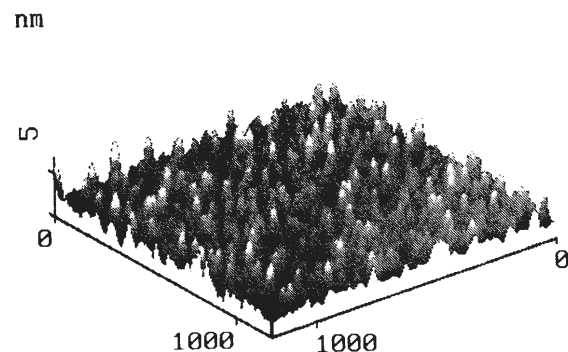


Figure 2.13: AFM image of ZnO on sapphire, grown by using N_2O gas as oxidizer. Only initial nucleation was observed.

The RHEED patterns indicated polycrystal growth (Fig.2.14). The morphology of the films was rough, though no columnar structures were observed. PL spectra showed strong deep level peaks (Fig.2.15). The intensity ratio of near-bandedge luminescence to deep level luminescence was larger with higher growth temperature. Thus higher growth temperature was preferred for better optical quality. However, the growth rate was extremely lower than the case of NO_2 , and no growth was observed for $T_{gr} > 400^\circ\text{C}$ (Fig.2.16). This low growth rate could be ascribed to insufficient oxygen supply, as the growth speed was clearly limited by the oxygen flow rate. The growth rate rapidly decreased with smaller flow rates, and could not be measured for samples grown at flow rates lower than 0.95ccm , as the films were too thin. At flow rates smaller than 0.8ccm , no growth was observed. The film thickness did not increase with varied Zn pressures.

From the above results, it was shown that larger oxygen flux and more efficient pumping system is required for use of radical oxygen as oxidizer. However, it was also shown that radical oxygen has advantage in dense and relatively uniform growth compared to the case of NO_2 gas.

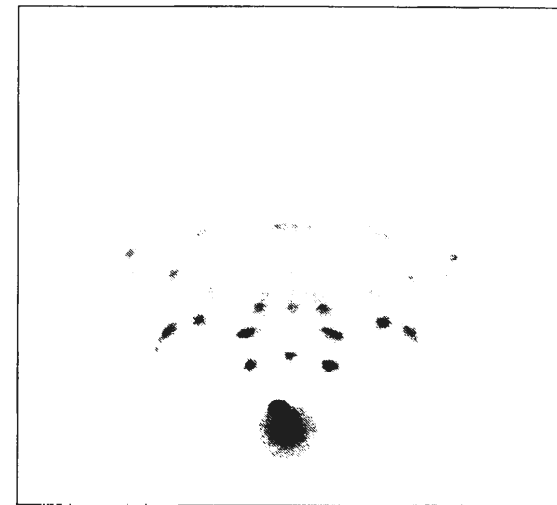


Figure 2.14: Typical RHEED pattern of ZnO film grown under insufficient supply of radical oxygen, indicating polycrystal growth. Radical oxygen was irradiated from a distance of 850mm .

2.6 Two-step growth

As described in section 2.4.2, ZnO epitaxy was shown to be possible by using NO_2 as oxidizer. However, at higher growth temperatures where the optical properties of the films were better, the surface structure was quite rough and reproducibility was poor. This could be ascribed to sparse and irregular initial nucleation of ZnO crystals at the substrate surface. On the other hand, at lower growth temperatures of $T_{gr} \leq 300^\circ\text{C}$, dense initial growth and high reproducibility was observed, as described in section 2.4.3. In expectation that use of low temperature (LT) buffer layer may contribute for dense initial nucleation and improved morphology, two-step growth using LT buffer layer was examined.

LT buffer layer was grown at 250°C for a thickness of $\sim 100\text{nm}$, and then annealed at 450°C for 20 min under NO_2 irradiation. By this annealing process, the ring pattern in RHEED was eliminated and

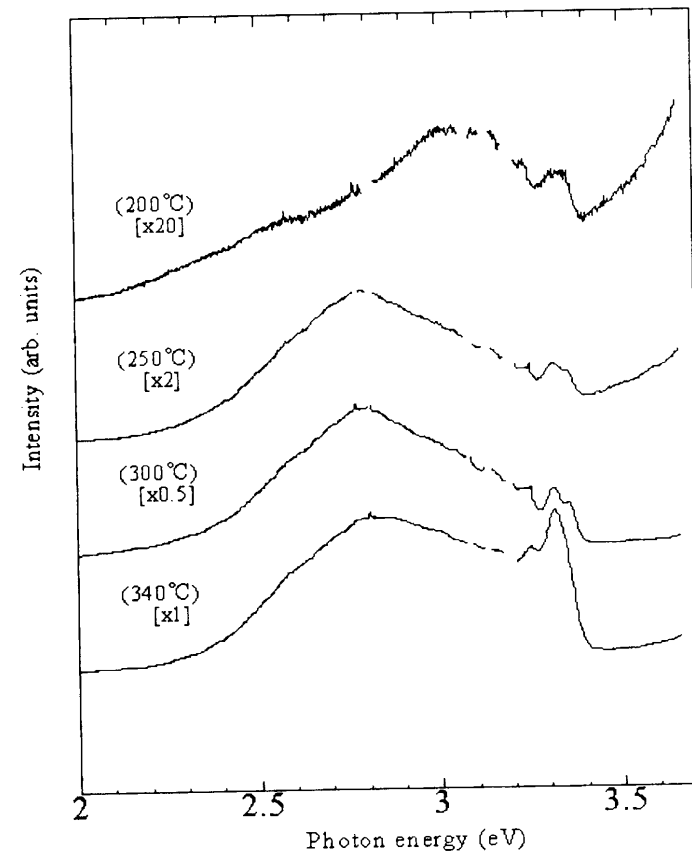


Figure 2.15: PL spectra of ZnO grown with insufficient supply of radical oxygen at various growth temperatures.

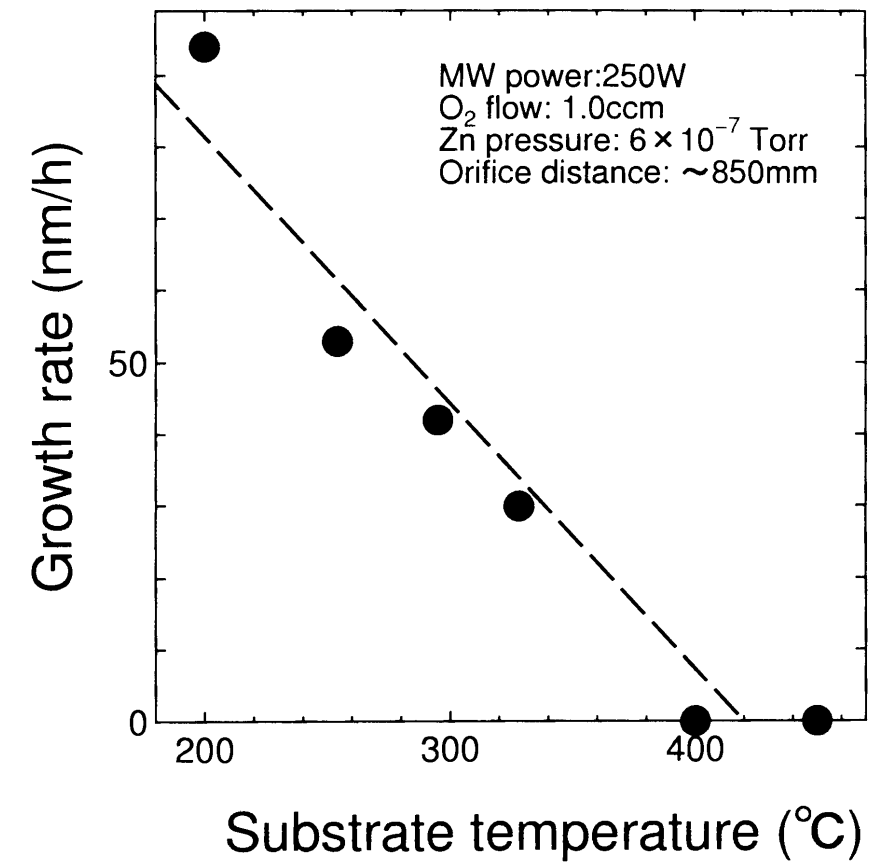


Figure 2.16: Typical growth rate of ZnO using radical oxygen irradiated from a distance of 850mm. No epitaxy was observed for $T_{gr} > 400$ °C .

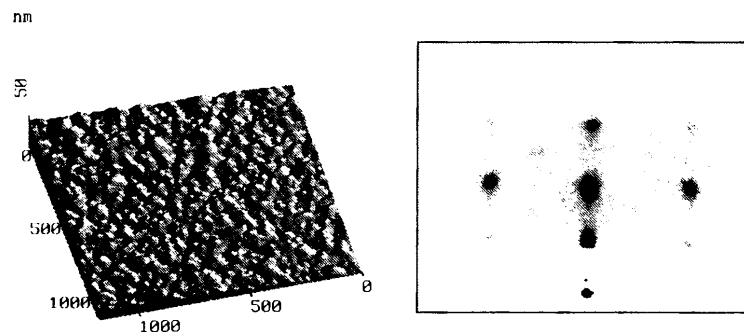


Figure 2.17: AFM image and RHEED pattern of the LT buffer layer after annealing. The ring pattern in RHEED is eliminated, while the dense nucleation is preserved.

the pattern was aligned in six-fold c -oriented pattern (Fig.2.17). The surface of the buffer layer was covered with small and dense hillocks. After annealing of LT buffer, growth of the main layer was conducted at 400 °C .

All of the ZnO films grown on LT buffer layers showed sparse columnar growth as shown in Fig.2.18. The facets of the columns were aligned in hexagonal shapes, and the height of the columns was regular for each sample. Compared to the films grown without LT buffers, the morphology of these films were fairly ordered, and reproducibility was greatly improved by use of LT buffers. However, no remarkable improvement by use of LT buffer was seen in the results of RHEED, XRD, and PL measurements. Growth rates were zinc-determined at this growth condition, with a maximum value of $\sim 70\text{nm/h}$ (Fig.2.19).

2.7 Indium contamination

The grown films showed n type conduction and were highly conductive. Resistivity of the films were lower than $3 \times 10^{-2} \Omega \cdot \text{cm}$, and the carrier concentration was higher than $1 \times 10^{19} \text{cm}^{-3}$, though most part of each

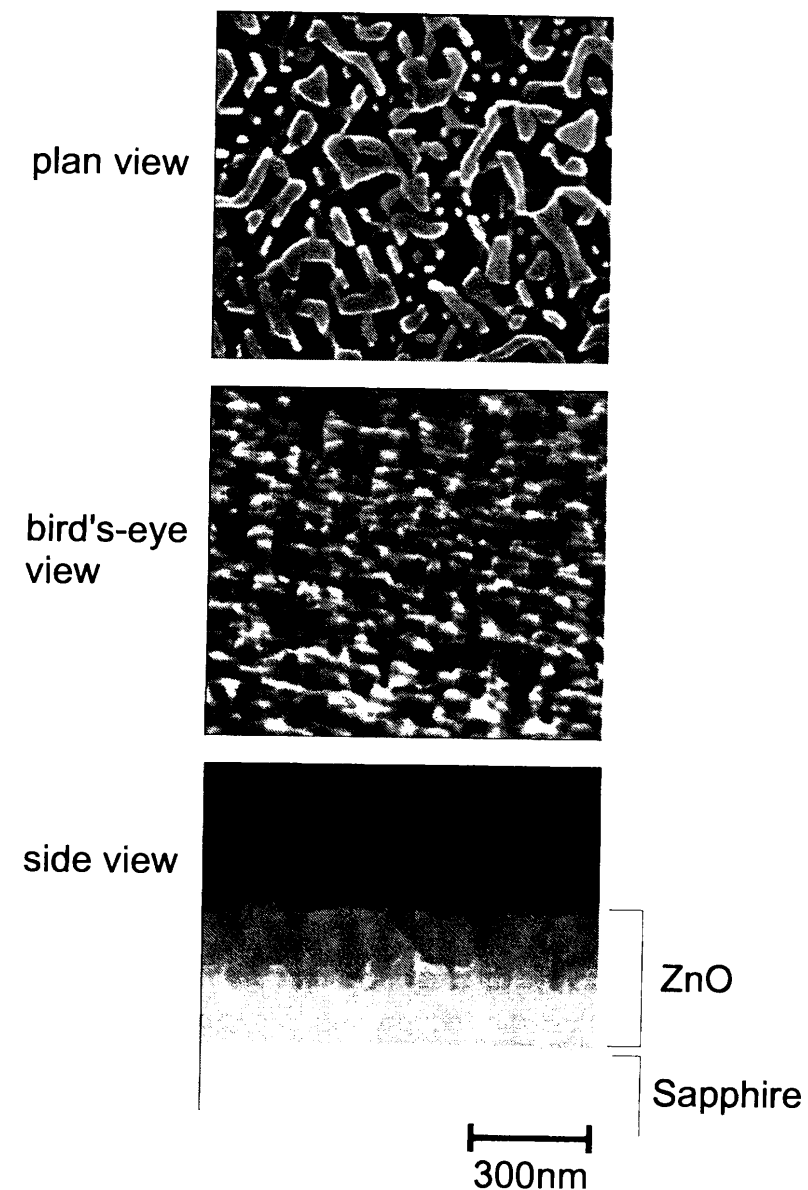


Figure 2.18: SEM image of a typical ZnO film grown with use of LT-buffer layer. Columnar growth with hexagonally aligned facets was observed.

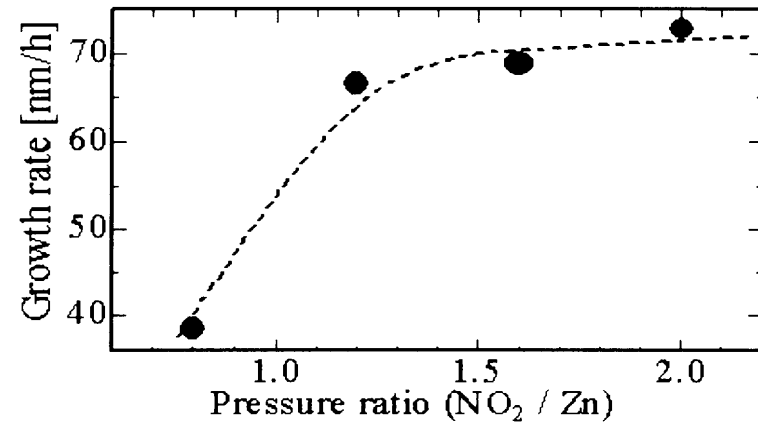


Figure 2.19: Growth rate of ZnO by using NO_2 gas as oxidizer. Growth rate is controlled by flow rate of NO_2 at this growth condition ($T_{gr}=400^\circ\text{C}$, Zn pressure $\sim 2 \times 10^{-7}$ Torr).

film consisted of columnar structures. These electrical properties are quite unsuitable for use of ZnO as semiconductors, as it would obstruct p-type conduction control.

To investigate the cause of this extraordinary high donor concentration, impurity incorporation was measured by secondary ion mass spectrometry (SIMS). From the measurement result of SIMS shown in Fig.2.20, it was found that the indium used for substrate soldering was highly incorporated into the film. As indium works as donors in ZnO [14], one cause of high donor concentration was ascribed to indium contamination. By problems peculiar to the equipments used in this work, indium contamination was quite difficult to be avoided. Even with use of indium-free substrate holder, indium contamination could not be completely avoided, as the whole system was considered to be contaminated with indium and difficult to remove the contamination.⁶

⁶Indium was contained in the thick layer of various materials deposited inside the

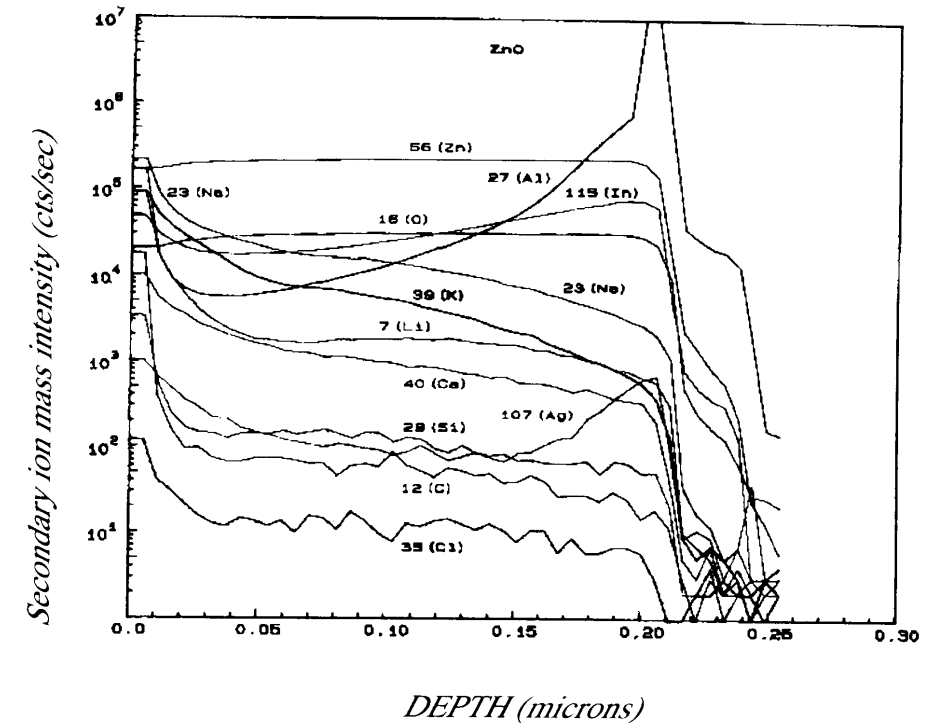


Figure 2.20: SIMS depth profile of a typical ZnO film grown in a indium contaminated MBE system.

Considering the cost of cleaning the whole system and the advantages of designing a new system exclusively for ZnO epitaxy, further works on ZnO epitaxy was done on a new radical source MBE system, which is described in the following chapters.

2.8 Summary

In this chapter, gas-source MBE (GSMBE) growth of ZnO using NO₂ as oxygen source material was demonstrated for the first time.

Major achievements and problems described in this chapter are:

1. It was shown that ZnO can be grown by simply irradiating Zn and NO₂ on the substrate, without using thermal cracking or activation by plasma.
2. Using NO₂ as oxidizer, the reproducibility of ZnO films were low and their morphology differed largely between samples. The reproducibility was improved by use of low-temperature buffer layer.
3. It was shown that NO₂ and N₂O gases adsorb well to liquid nitrogen shrouds and thus lower the residual pressure during growth. In the case of a MBE system with liquid nitrogen shroud and small pumping speed, like the MBE system used in this chapter, use of NO₂ gas may greatly increase the upper limit of effective oxygen supply and growth rate.
4. For improved growth rate and film quality, larger supply of zinc and higher growth temperature were preferred.
5. Indium used for substrate soldering was found to be a major source of contamination.

chamber in nearly 10 years of operation. The cells were contaminated with indium when the system was baked after maintenance.

6. For use of radical oxygen as oxidizer, improvements in equipments for further efficient supply of oxygen were found to be inevitable. However, without the buffer layer, the morphology and reproducibility of the epilayers were better than the case of NO_x gases.

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Chapter 3

MBE growth of ZnO using radical oxygen

3.1 Introduction

In the previous chapter, NO_x gases and radical oxygen were used as oxygen sources, and each examined oxidizer (NO_x , radical oxygen) was shown to have its own advantages. Taking the results of the previous chapter in account, a new MBE system was designed exclusively for epitaxy of ZnO. The important point to consider was the oxygen source. NO_x gases did have advantages in systems with liquid nitrogen shrouds, but anti-corrosive equipments significantly raises the cost of the system. In addition, in the case of NO_2 gas, commercially available gases were low in their purity (3N), and on-site purification was required for further investigations. On the other hand, radical oxygen did not require anti-corrosive pumping systems, and highly pure oxygen (5N) gases were commercially available. However, in contrast to the case of NO_x gases, activation of oxygen with high efficiency was essential for use of oxygen gas, as found in the previous chapter. Considering the advantages and disadvantages of each gas, radical oxygen was chosen as oxidizer in the new MBE (radical-source MBE; RSMBE) system.

At the time this work had begun, MBE was a still premature tech-

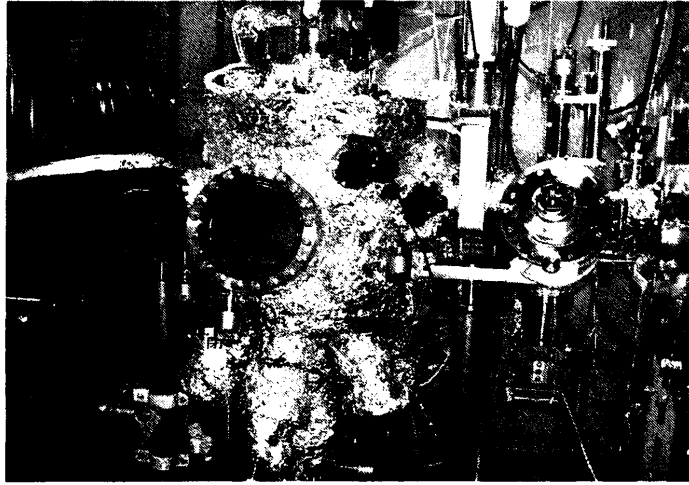


Figure 3.1: The RSMBE system used in chapter 3 and 4.

nique for MBE of ZnO, and effects of many fundamental growth parameters, from the growth temperature to the preferable substrate configuration, were unclear. In this chapter, the effects of the following fundamental growth parameters on RSMBE of ZnO films were evaluated and roughly optimized. Examined parameters are: growth temperature, oxygen flow rate, radio frequency (RF) power, distance of the radical cell, orifice size of the radical cell, substrate preparation (involving surface smoothness), substrate orientation, and miscut angles. Related with optimization of these parameters, typical type of surface facetting and in plane rotational twinning of ZnO were investigated. Their elimination, also involving control of $+c$ / $-c$ polarity of ZnO, is described.

3.2 RSMBE system

Overview: The epitaxial growth of films described in this chapter was carried out using a RSMBE system based on an Eiko EW-100 water-cooled MBE system (Fig.3.2, Fig.3.1). The system consisted of one

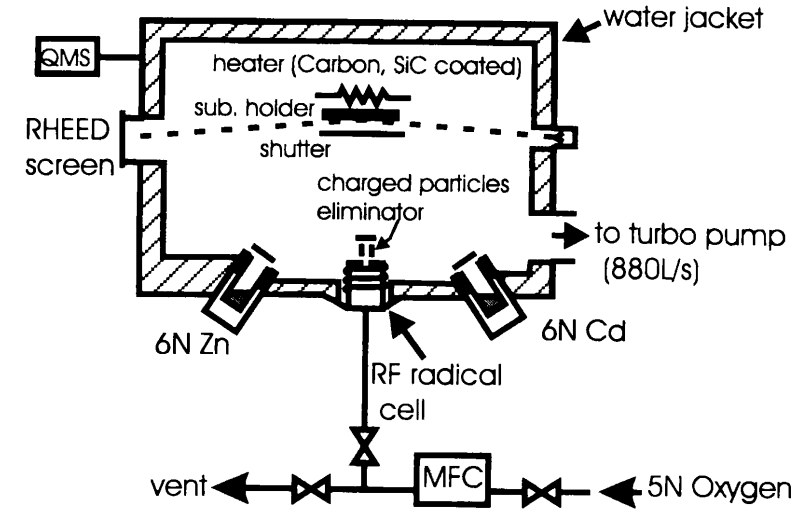


Figure 3.2: Schematic diagram of the RSMBE system.

exchange chamber and one growth chamber. The growth chamber was equipped with effusion cells and a radical cell, with individual shutters. The growth chamber was also equipped with a quadrupole mass spectrometer (QMS; ULVAC MSQ-101) and a reflection high energy electron diffraction (RHEED; Vieetech VE-026+VP-026) system. As the flux of radical oxygen was found to be essential in chapter 2, the distance between the radical cell and growth position was designed to be smaller and variable. Also, to avoid contamination of the epilayers by indium solder, the system was built to be solder-free.

Pumping and cooling system: The growth chamber was pumped by a turbo molecular pump (TMP; Pfeiffer Vacuum TMU 1000) supported by a rotary pump (RP; Alcatel model 2021 or 2033). The pumping speed of the TMP was 880ℓ/sec. For sealing, conventional Cu gaskets were used. As far as we have investigated, contamination of grown films by copper was not observed in secondary ion mass spectrometry (SIMS) measurements. The samples were transferred via an exchange chamber,

which was pumped separately by a TMP (Shimazu TMP-50) and RP (ULVAC GLD-50). This RSMBE system had no liquid nitrogen (LN₂) shroud. Instead, it was equipped with a water jacket, which was cooled with chilled (16 °C) water. The jacket kept the chamber walls around the cells from excess heating, which causes evaporation of various materials deposited on the wall. The advantage of this water-cooling system is ease of baking and maintenance, and low running cost. The system could be quickly baked or repressurized after growth runs, as there was no need to wait LN₂ shrouds to heat up to room temperature (RT). This was a great advantage for a system that required frequent refilling of zinc, a material that exhausted very quickly. Though this water-cooling system was expected not to provide extensive cryopumping as LN₂ shrouds do, the lowest pressure inside the growth chamber was below 1×10^{-9} Torr at the best condition.

Radical oxygen supply: Radical oxygen was supplied from an RF (13.56MHz) radical cell (Eiko ER-1000; Fig.3.3). The maximum RF power applied to the cell was 450W¹. The walls of the excitation room were made of high-purity synthetic quartz (NSG ES-grade; Al < 0.1ppm, Cu < 0.01ppm, Li < 0.05ppm) to suppress contamination by impurities contained in quartz. The erosion of walls by oxygen plasma was strong at the corners of the excitation room, and sharp trenches were formed. Though there was apparent erosion of the quartz parts, no sign of contamination by silicon was observed by SIMS measurements of the grown films (see Fig.3.31). The distance between the radical cell and the substrate was variable between 100–200mm by changing a spacer flange. However, at a distance of 125mm or smaller, though the radical cell did not directly obstruct the molecular beam from other cells, the re-evaporation from the surface of the radical cell badly interfered with the uniformity of the epilayers. Thus most of the experiments were done at a distance of 150–200mm. The radical cell was equipped with a charged

¹The rated RF power of the cell was 300W.

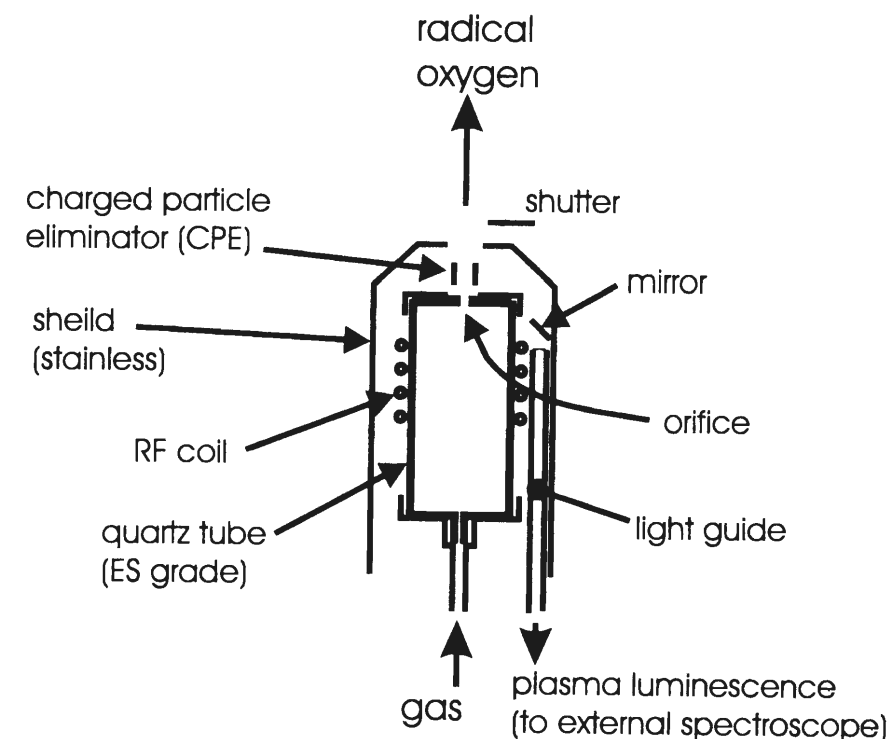


Figure 3.3: Schematic diagram of the radical oxygen cell. High voltage (DC600V) was applied to the CPE during operation.

particle eliminator (CPE), which consisted of a pair of stainless (SUS-304)² electrodes. The voltage applied to the CPE was DC 600 V. 6N pure oxygen gas was supplied to the radical cell. The flow rate of oxygen was controlled by a mass flow controller (MFC; STEC SEC-7320). The error range of the MFC was $\pm 1\%$. To avoid excessive gas injection to the growth chamber, the gas was first vent to the exchange chamber until the flow rate is stabilized, and then the flow was switched to the radical cell pipings. After stoppage of growth and shutdown of the radical cell, the gas flow was immediately vent to the exchange chamber. The emitted light from oxygen plasma was observed from outside the chamber through quartz piping. The color of oxygen plasma was reddish to eyes, and the spectra were dominated by emission peaks from atomic oxygen at 777nm and 845nm [1](Fig.3.4). Monitored at the 777nm line, the emission intensity from radical oxygen varied with oxygen flow rate, RF power, and the orifice size of the radical cell. The emission intensity showed peak intensities at specific flow rates, depending on the orifice size and applied RF power (Fig.3.5). The relationship between the emission intensity and the properties of the grown films was also investigated.

Zinc supply: Metal zinc was evaporated from a Knudsen cell (K-cell; Eiko MB-3000C, or EPI EPI-40-LT with an 2ϕ PBN orifice). The temperature of the crucible was controlled by a temperature controller (RKC REX-P300 or Eurotherm model818). The source metal inside the crucible was gradually oxidized during growth. To stabilize the temperature of the source metal and output flux, source metal was once heated up to melting point after refilling, to perfectly fit the crucible and avoid isolation by oxidized layers. The flux of Zn was measured as partial pressure by a nude ionization gauge (NIG).

²For the material of the electrodes of CPE, Inconel was also examined, but a highly insulative layer have formed at the surface of the electrodes, thus killing the efficacy of the CPE.

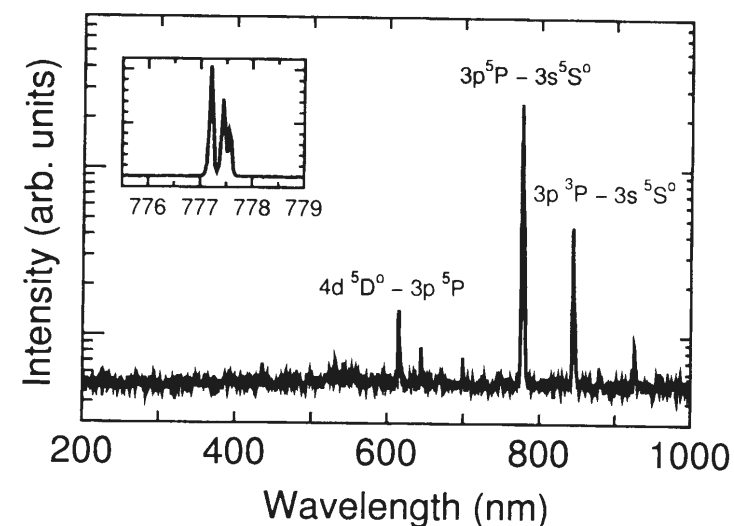


Figure 3.4: Typical emission spectra of oxygen plasma from the radical cell. The spectra were dominated by atomic transition peaks. Inset shows the triplet at 777.2, 777.4, 777.5 nm.

Substrate heating system: The substrate holder was made of Inconel³ and was indium-free (Fig.3.6). Most of the substrates used in this chapter were cut in a fixed size and then polished by the vendor. The substrate holder was designed to exactly match the size of substrate and avoid nonuniform heating caused by previously deposited materials on the holder surface. The substrates were pressed to the holder by Inconel retainers, which were pinned to the holder by Inconel screws. The holder was heated by radiant heat of a SiC-coated carbon heater placed at the back side. The substrate temperature (T_{sub}) was monitored by a thermocouple placed closely at the back side of the holder. The measured value of the thermocouple was corrected by referring the eutectic point of Al/Si(577°C) and Au/Si(363°C). The substrate was rotated at a constant speed during growth for uniformity.

³Inconel-600: Ni > 52%, Cr 14 ~ 17 %, Fe 6 ~ 10 %, Mn < 1 %, C < 0.15%

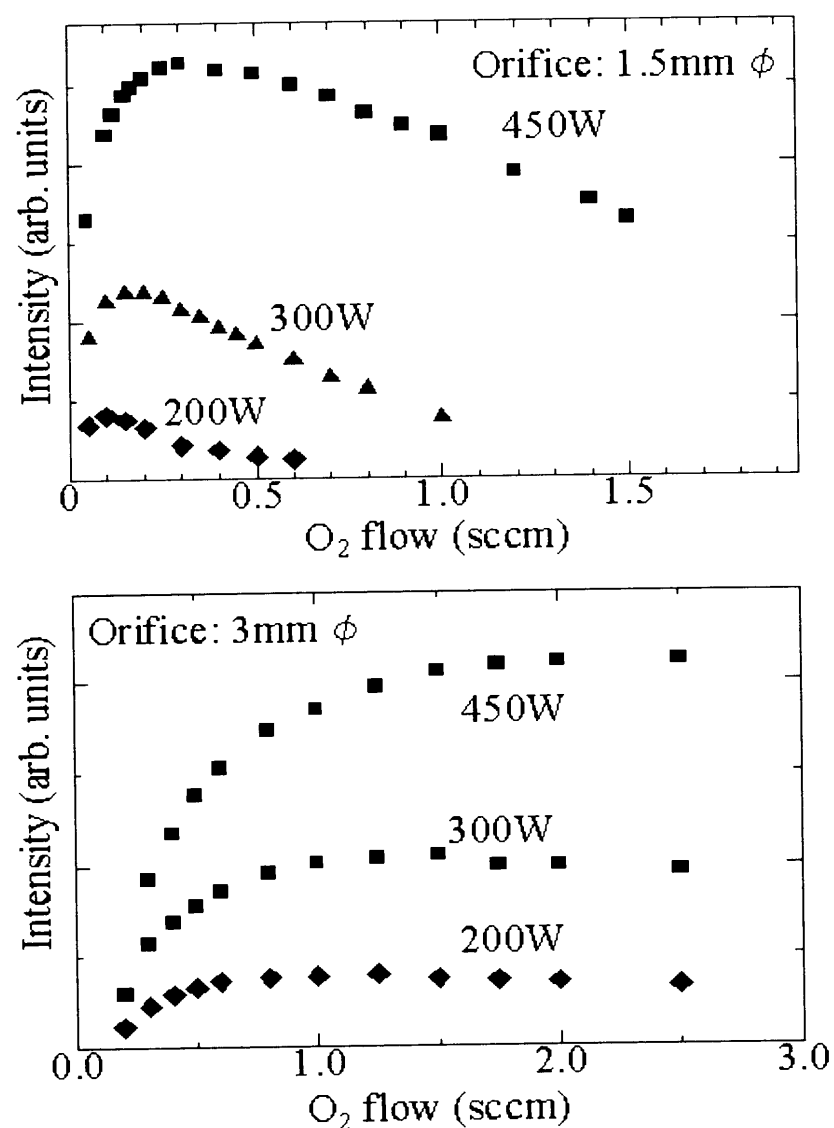


Figure 3.5: Emission intensity from radical oxygen monitored at 777nm. The peak position (R_{opt}) varied with orifice size and RF power.

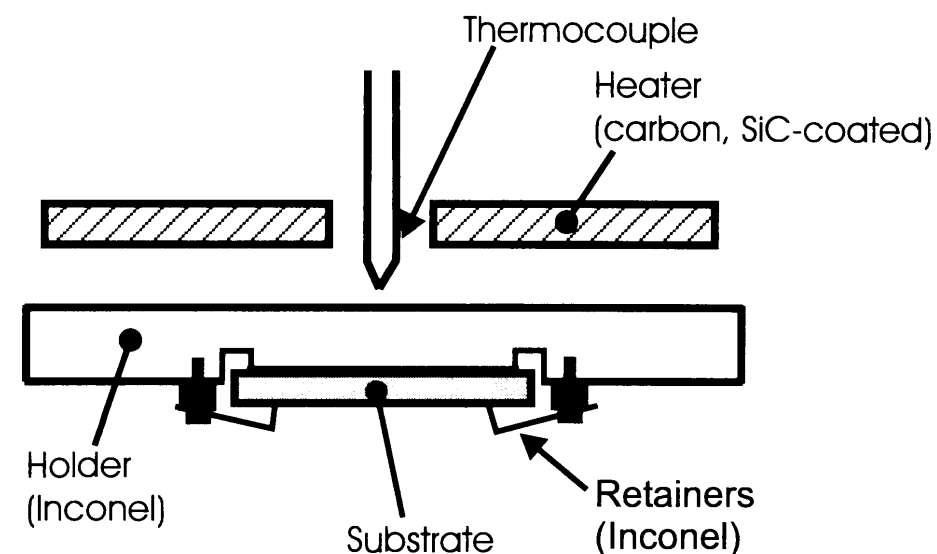


Figure 3.6: Schematics of the substrate heating system. The holder can be rotated during growth at a constant speed. The holder was designed especially for substrates cut in a regular size by the vendor. The trenches around the contact area was designed to avoid deposition on the contact area, which spoils uniform and steady heating.

3.3 Experimental procedures

Sapphire substrates were degreased in organic solvents, followed by rinsing with deionized water and blowing with dry nitrogen. After introducing into the chamber, the substrates were thermally cleaned by heating up to 700 °C for 10–15 min. The substrates were not etched (the reason is discussed in section 3.7.2). Irradiation of radical oxygen during thermal cleaning was not conducted neither ⁴. After the preparation of the substrate, the substrate temperature (T_{sub}) was changed to growth temperature (T_{gr}). After stabilizing operation of the radical cell, Zn and radical oxygen was irradiated simultaneously to the substrate by opening the substrate shutter. After growth, substrates were cooled down to RT in 10–30 min. The grown films were characterized by RHEED, XRD, SEM, PL, Hall, and AFM. Also, coaxial impact collision ion scattering spectroscopy (CAICISS) was used for determination of polarity of ZnO in section 3.6.

3.4 Optimization of radical cell configuration

Considering future fabrication of device structures, one important point is the growth rate. If the growth rate is too slow, the thickness of each layer would be made etching and fabrication of contacts too difficult, or it would significantly increase the operation cost. In this section, the orifice size and distance of the radical cell were examined, in order to gain higher growth rate while ensuring crystallinity of the grown ZnO films.

⁴This was because slight growth of ZnO during thermal cleaning was observed by RHEED, even when the shutter of the zinc cell was closed.

3.4.1 Orifice size

The growth rates as functions of oxygen flow rate with different radical configurations are shown in Fig.3.7. Maximum growth rates could be obtained around an optimum flow rate (R_{opt}) determined by the orifice size and applied RF power, where the emission from radical oxygen was strongest. Supply of oxygen exceeding R_{opt} led to decrease in growth rates and degradation in film crystallinity, as confirmed by polycrystal RHEED patterns (Fig.3.8). This was possibly caused by insufficient activation of oxygen molecules. In addition, flux of zinc would have decreased by oxidizing of the zinc source in the crucible ⁵, thus reducing the growth rate under oxygen-rich conditions. With smaller orifice size, stable operation of radical cell was able to be maintained at smaller oxygen flow rates. However, with other growth conditions fixed, no significant improvement in film quality or growth rate was observed by reducing the orifice size.

From these results, it was made clear that not only the oxygen flow rate should be optimized but also the orifice size should match the desired oxygen flow rate to give stable and maximum activation of radical oxygen.

3.4.2 Distance from the radical cell

The cell distance was varied by changing the spacer flange attached to the radical cell in the range of 120 – 200mm. The maximum growth rate significantly increased with smaller distance, as shown in Fig.3.9. However, with other growth conditions fixed, the surface morphology roughened with smaller distance.

⁵The metallic zinc in the K-cell was gradually oxidized, and a fragile ZnO layer was formed at the surface. Therefore, the actual zinc flux was supposed to be somewhat dependent on the oxygen flow rate.

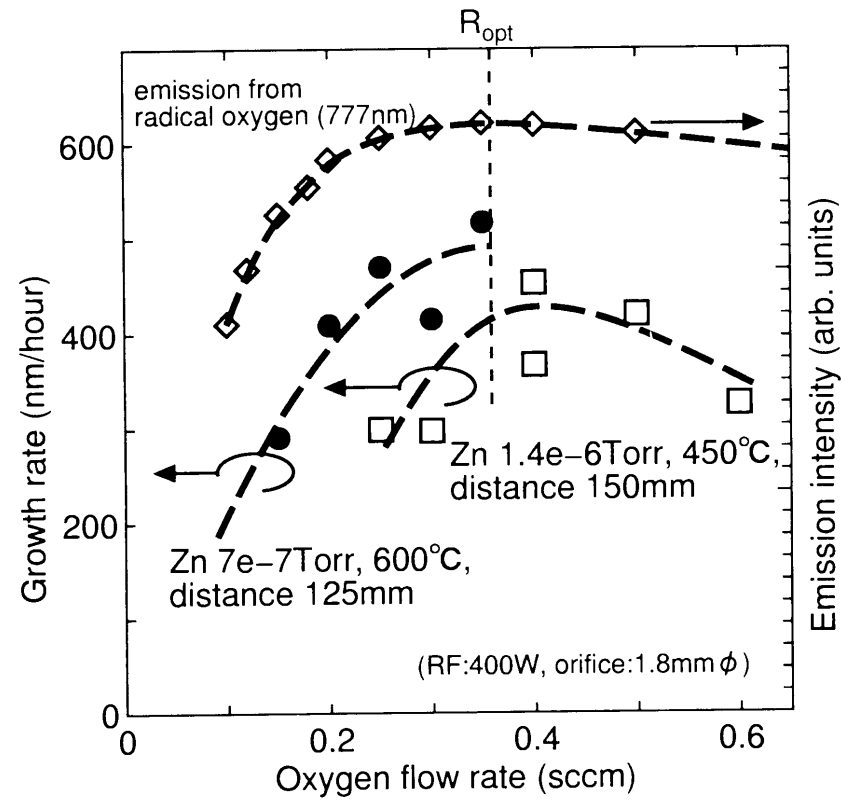
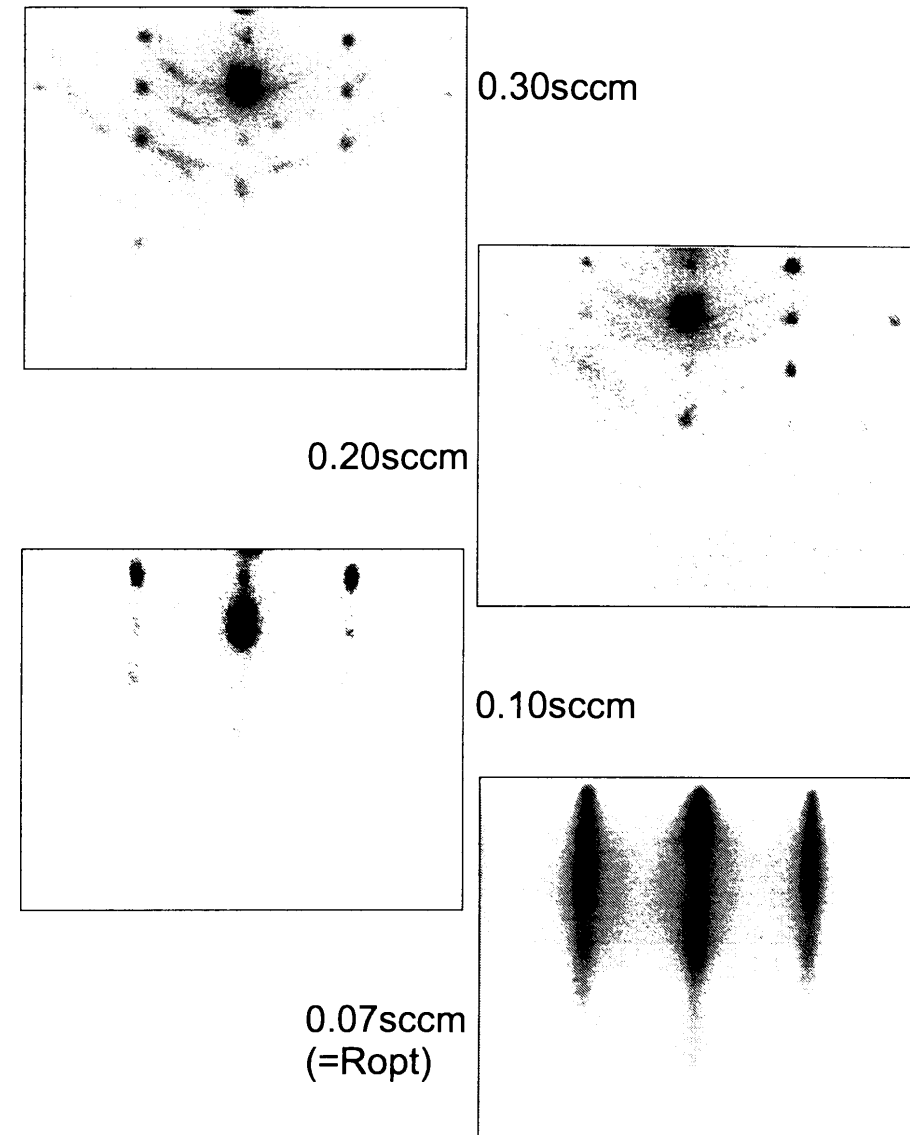


Figure 3.7: Growth rates as functions of oxygen flow. The maximum growth rate was obtained around the flow rate where the emission intensity from radical oxygen was the strongest. Excessive supply of either zinc or oxygen led to decreased growth rates.



($T_g = 600^\circ\text{C}$, RF power = 300W, Zn pressure = $5e-7$ Torr, orifice:1mm, cell distance = 200mm; Beam along: ZnO[11 $\bar{2}$ 0] azimuth)

Figure 3.8: RHEED patterns of ZnO films grown with excess oxygen flow rate ($> R_{opt}$). Ring patterns from polycrystal structures were observed.

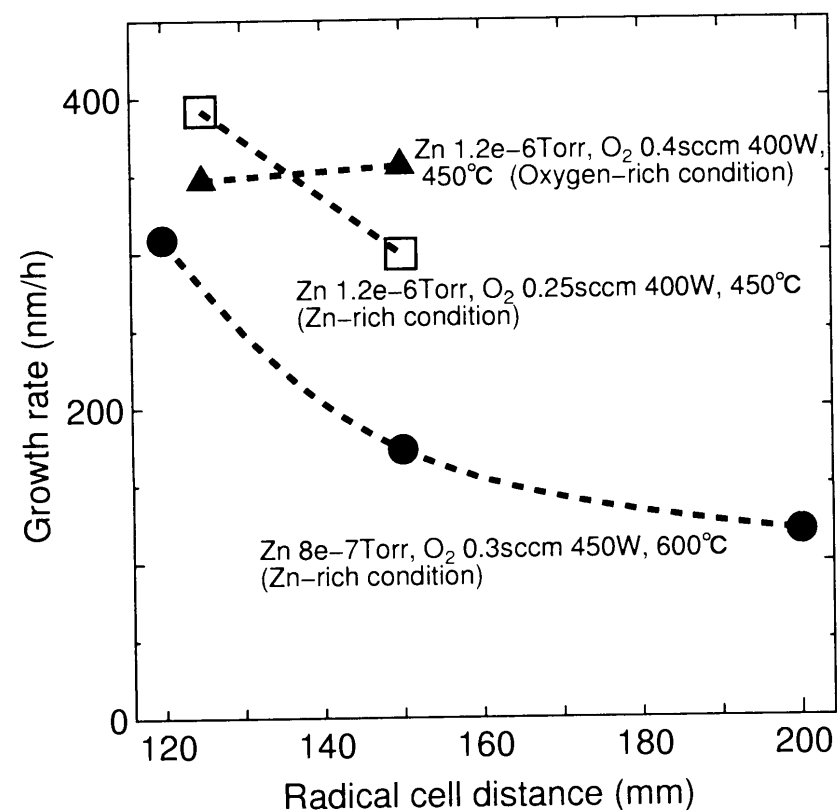


Figure 3.9: Growth rates as functions of distance between the radical cell and substrate.

3.5 Optimization of the fundamental growth parameters

For gaining optimal results in ZnO epitaxy, fundamental growth parameters were examined. The following growth parameters were examined and roughly optimized: growth temperature, oxygen flow rate, and RF power applied to the radical cell.

c-plane just-oriented sapphire (manufactured by Bicon) was used as substrates. Radical oxygen was irradiated to the substrate during thermal cleaning at 700 °C for 10 min. ZnO was grown directly on the substrate for 2 hours at $T_{gr} = 350 - 650$ °C. The flow rate of oxygen was varied between 0.2 – 1.0 sccm. The RF power applied to the radical cell was varied between 90 – 450 W. The pressure of Zn was $6 \times 10^{-7} - 1 \times 10^{-6}$ Torr. The distance between the orifice of the radical cell and the substrate holder was approximately 200 mm. The results were evaluated by FWHM of XRC, PL characteristics, growth rate and surface morphology.

3.5.1 Problems to be solved

On the process of this work, two typical problems have arisen, and were examined to be solved. One problem was a typical style of surface facetting that spoiled the morphology of the film, and the other was a twinned growth in two directions rotated in the *c*-plane. The problems are described below. Related factors and countermeasures are examined and discussed throughout this chapter.

Surface facetting: Many samples showed partly faceted surfaces that consisted of hexagonal hillocks and flat regions, as shown in the SEM images of Fig.3.10. Typical hexagonal hillocks consisted of facets with similar values of tilt angles (Fig.3.11). Deep cracks were often observed around these hexagonal hillocks, and some cracks at cleaved surfaces were found to be emerging from the very initial growth stage, near the

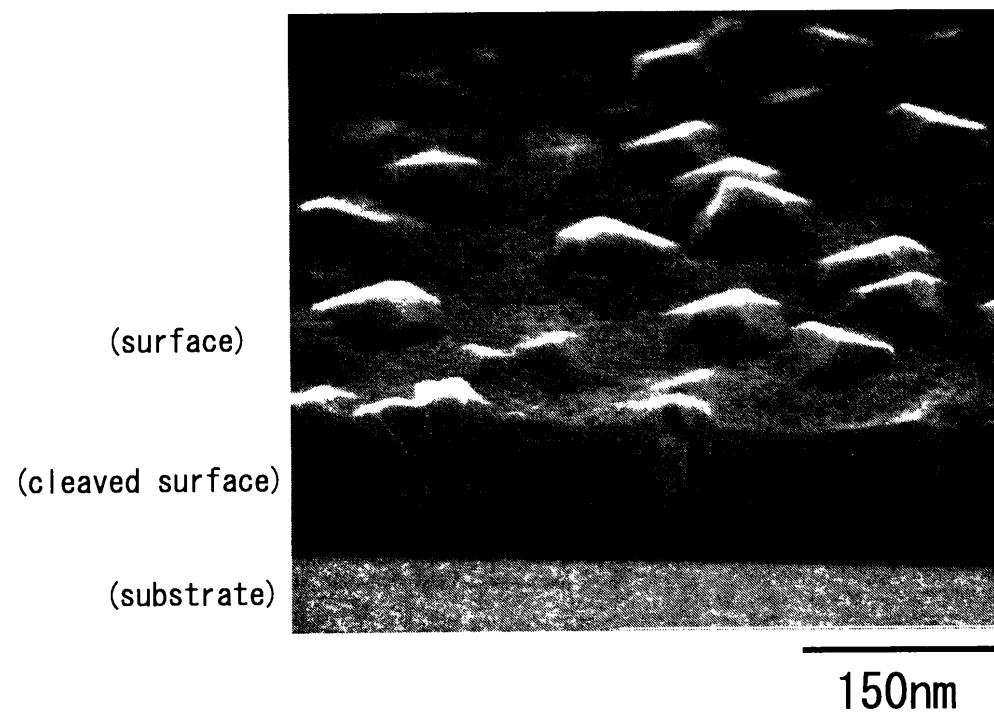


Figure 3.10: A bird's-eye view of a typical ZnO surface consisting of both hillocks and flat regions.

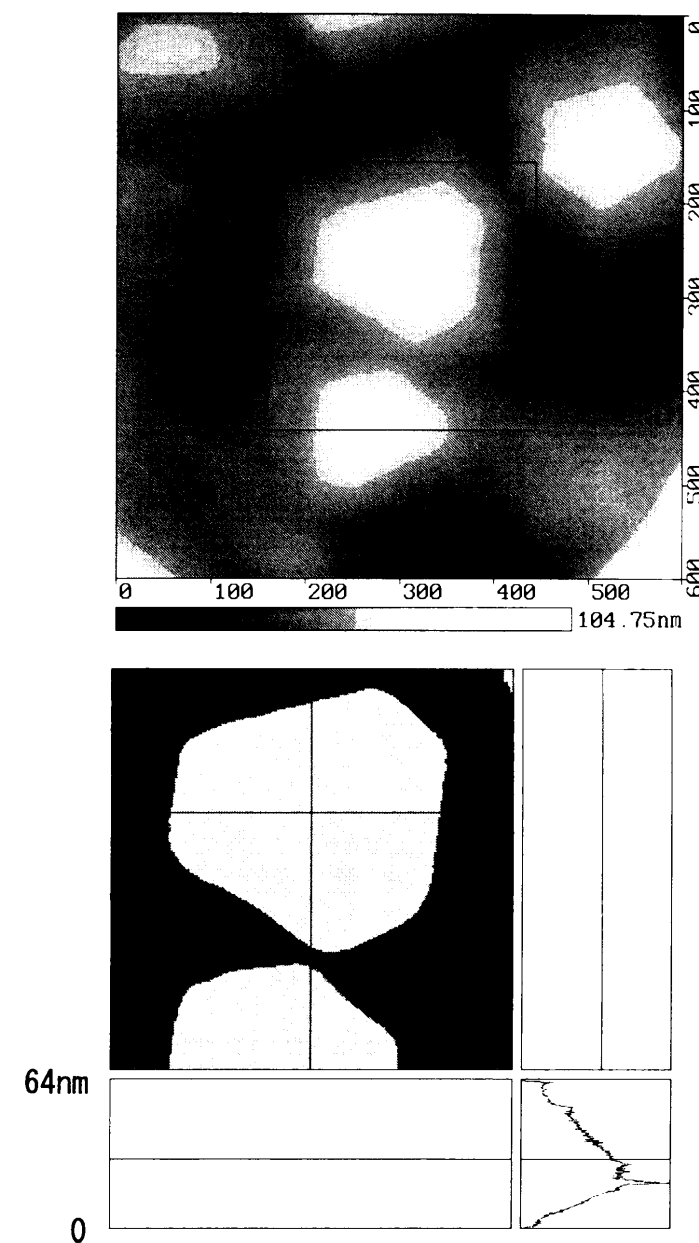


Figure 3.11: AFM image of a typical hexagonal hillock.

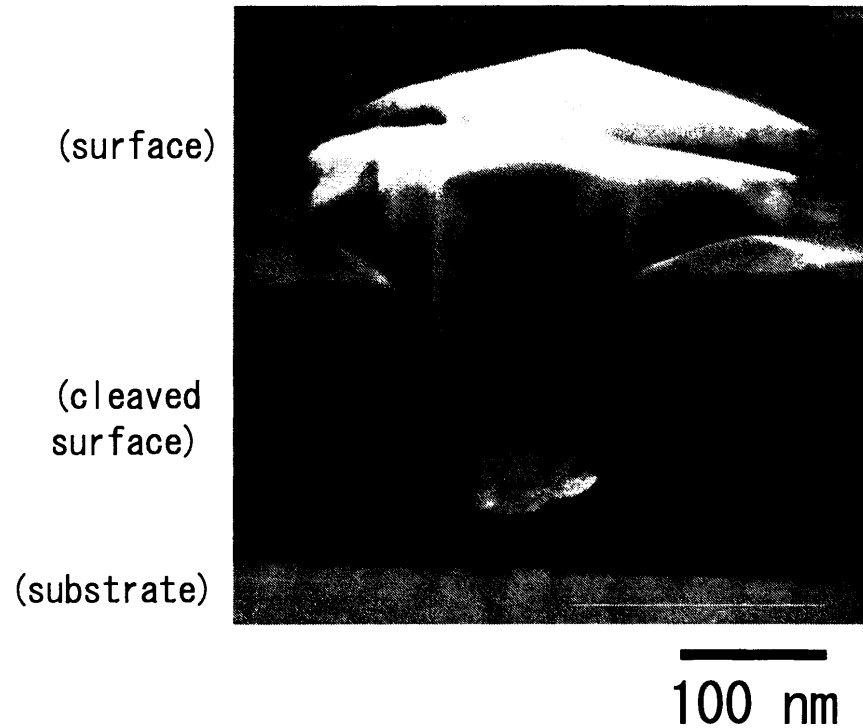


Figure 3.12: SEM image of a typical crack appeared at a cleaved surface.

heterointerface with the substrate (Fig.3.12).

Rotationally twinned growth: From the results of RHEED and XRD measurements, the ZnO films obtained in this section were found to be c axis oriented, with 30 deg rotation in the basal plane with respect to the substrate (see Fig.2.9). However, in this work, a number of ZnO films grown on c -plane sapphire showed twinned growth, which was a mixture of “30-degrees rotated” and “unrotated” domains in the c -plane, as schematically shown in Fig.3.13. This rotation was confirmed by XRD pole figure measurements as shown in Fig.3.14(a). The occur-

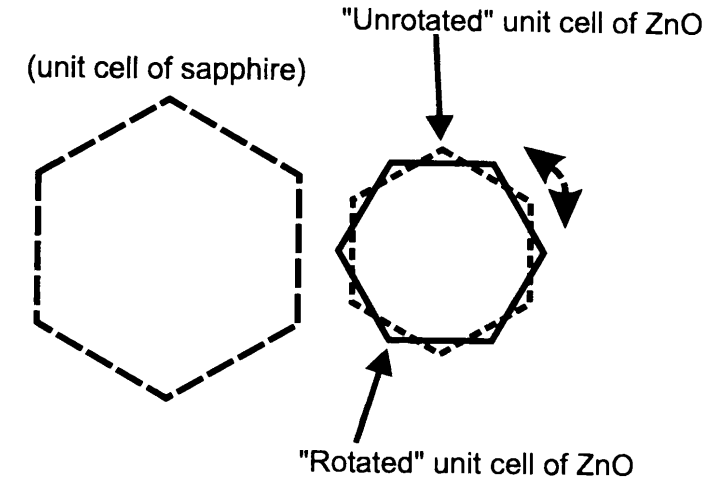


Figure 3.13: Schematics of rotationally twinned growth in the ZnO c -plane. (See also: Fig.2.9)

rence of the rotationally twinned growth was easily detected by RHEED observation, as “mixed” patterns as Fig.3.14(b). This was probably due to the large ($\sim 18\%$) mismatch between the six-fold oxygen lattice of c -plane sapphire and unit cell of ZnO (cf. Fig.2.9), which would make either “rotated” or “unrotated” growth unstable and mix with each other.

3.5.2 Growth temperature

Fig.3.15(b) shows effects of growth temperature on FWHM of ZnO(0002) peak of XRC. The RF power and oxygen flow rate were fixed at 300W and 0.5sccm for these samples. The best (= narrowest) value of FWHM of XRC was obtained at $T_{gr} = 550 \sim 600$ °C, and apparently degraded at $T_{gr} < 400$ °C. The PL characteristics (Fig.3.15(a)) showed the same tendency. From these results, $T_{gr} \geq 550$ °C was preferred for optimal crystallinity and optical quality of the films in the following experiments.

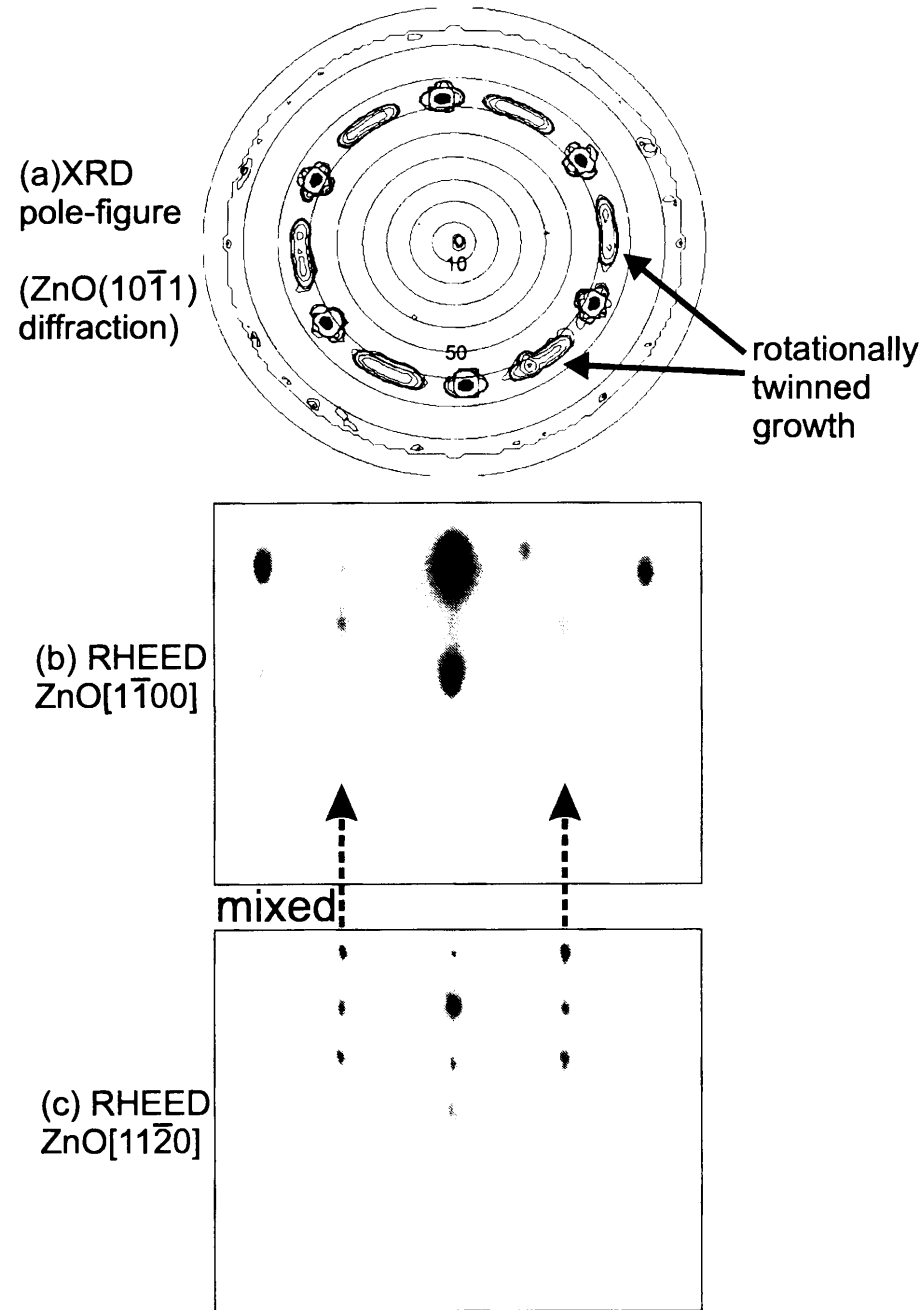


Figure 3.14: Rotationally twinned growth observed by (a): XRD pole figure and (b,c): RHEED patterns. Growth in two different directions is observed simultaneously (see Fig.3.13).

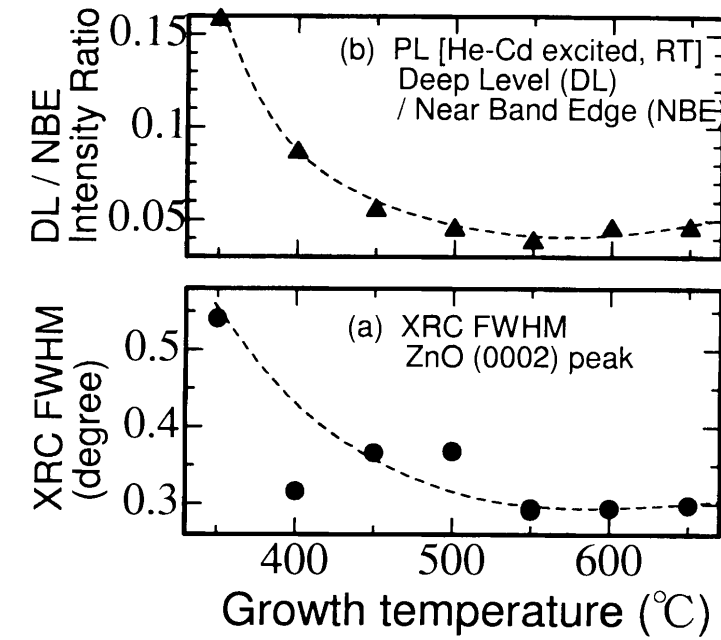


Figure 3.15: Typical trends of PL and XRD characteristics of ZnO films with varied growth temperatures. O_2 flow rate was 0.5sccm, and RF power was 300W for these samples.

3.5.3 RF power

Fig.3.16 shows effects of RF power on FWHM of ZnO(0002) peak of XRC at $T_{gr} = 600\text{ }^{\circ}\text{C}$ and oxygen flow rate of 0.5sccm. Higher RF power gave better results in crystallinity of the ZnO films. All samples showed facetting surface with the hexagonal hillocks. With larger RF power, the hillocks increased in their size and tended to coalesce with other hillocks. However, the hillocks did not disappear by simply raising the applied RF power. At RF power lower than 200 W, the growth rate rapidly decreased. Below 50 W, no epitaxy or quite sparse and small island growth on the substrate surface was observed.

Considering the above results, higher RF power was preferred for optimal quality of the films. In this work, the radical cell was operated at its maximum operational RF power of 400–450W.

3.5.4 Oxygen flow rate

With other growth parameters fixed, the surface morphology was largely dependent on flow rate of oxygen. With lower oxygen flow rate, the hillocks became sparse and finally disappeared (Fig.3.17). This difference was apparent in RHEED patterns from the very initial growth stage. Surfaces with hillocks showed “arrow-head” patterns, which are indicative of facetting surfaces, while the smooth surfaces showed “streaky” patterns. From experiments at different zinc pressures, it was found that the emergence of the hexagonal hillocks was caused by excess supply of oxygen gas relative to zinc pressure. In other words, growth at zinc-rich condition led to smoothing of the film surfaces. The zinc rich condition was able to obtain by supplying excessive zinc relative to oxygen supply, and also by growing at low temperatures, where the vapor pressure of zinc is lower and thus re evaporation of zinc atoms from the growing surface would decrease. Though the surface morphology was largely affected by the morphology of the initial growth stage, the morphology gradually smoothed or roughened by adjusting the growth conditions to zinc rich or oxygen rich, respectively.

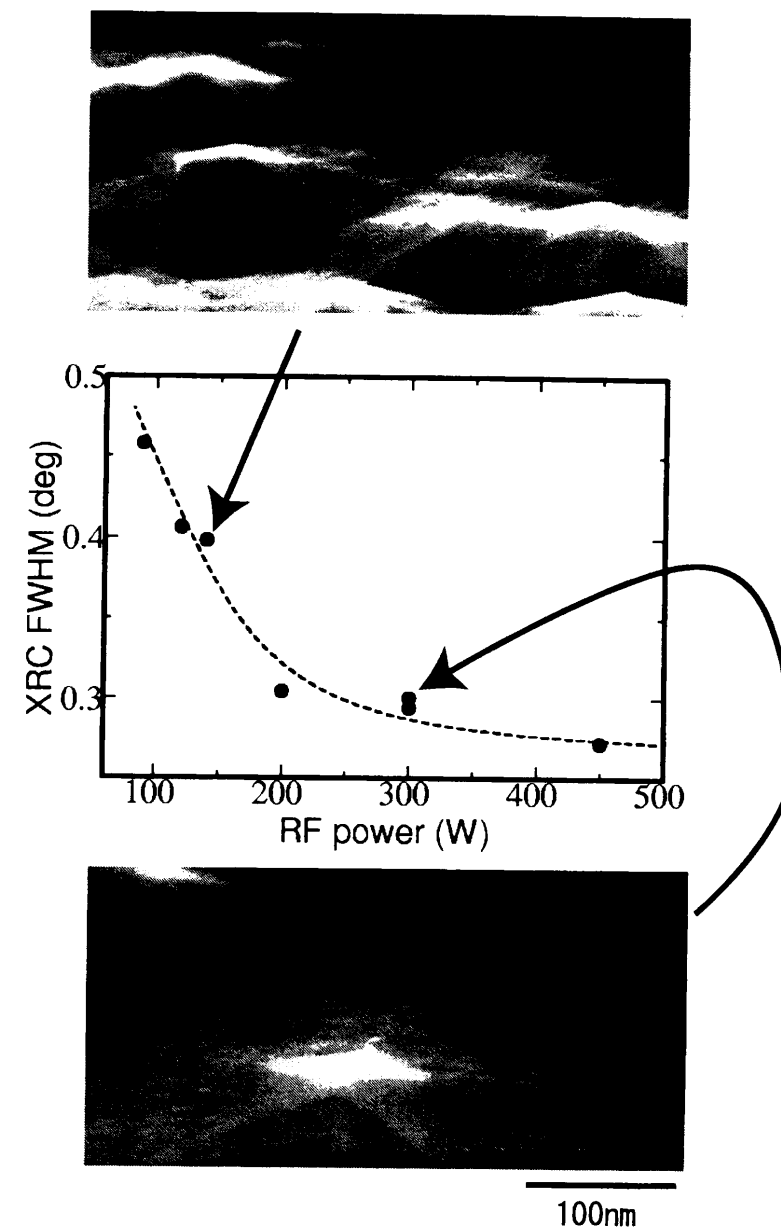


Figure 3.16: FWHM of ZnO(0002) peak in XRC as a function of RF power applied to the oxygen radical cell, shown together with typical surface morphology of the ZnO films.

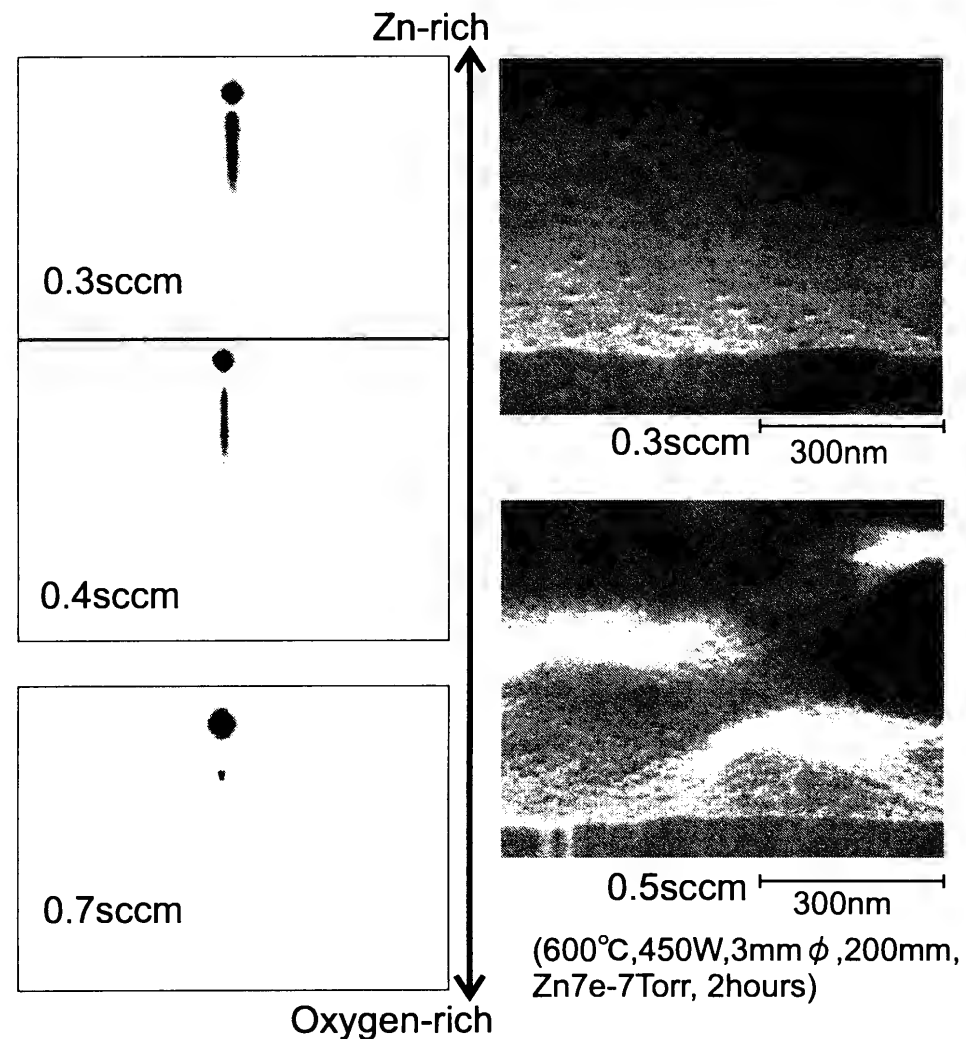


Figure 3.17: Surface morphology of ZnO films grown on *c* plane sapphire substrates with varied oxygen supply. Excess oxygen led to faceting surfaces, indicated by arrow head RHEED patterns and observed as hexagonal hillocks in SEM images.

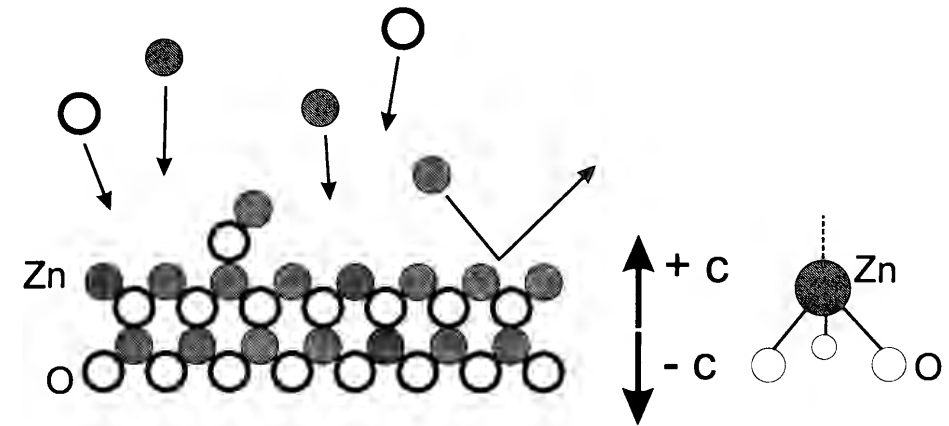


Figure 3.18: Schematic drawing of ZnO surface under Zn-rich growth condition, shown with the bonding arrangements of a zinc atom at surface possessing one dangling bond. The surface is stabilized with zinc, which would induce bonding from oxygen of the newly bonding ZnO molecule. (See also: Fig.2.5.)

As shown in Fig.2.5, *c*-plane ZnO has a polar surface of either zinc or oxygen, with layers of each species heaped up alternately. ZnO is also asymmetric along its *c*-axis, distinguished by the name *+c* or *-c*. *+c* and *-c* directions are known to be terminated by zinc and oxygen surfaces, respectively[2]. Under zinc-rich growth conditions, the surface of ZnO would be dominated by zinc, and it would induce bonding between the surface zinc atom and the oxygen atom of newly formed ZnO molecules, thus inducing growth in the *+c* direction (Fig.3.18). The same discussion can be applied for oxygen rich condition, which would have promoted growth in *-c* direction. This possible relationship between the growth direction of ZnO and its surface morphology was examined in section 3.6.

3.6 Effects of polarity of ZnO c -axis

From the results previously described, it was found that the relative flux of radical oxygen to Zn pressure largely effects the morphology of the ZnO films, and this difference was estimated to be largely dependent on the initial growth condition. Considering the discussions of section 3.5.4, the direction of c axis of ZnO at the initial growth stage was estimated to largely affect the morphology of the grown film. To confirm this hypothesis, growth on bulk ZnO substrates with different c -axis polarities was examined.

Procedures Homo-epitaxy of ZnO on bulk ZnO substrates with $+c$ / $-c$ orientations was examined. Bulk ZnO substrates with $+c$ / $-c$ polarities were used⁶. The substrates were degreased and thermally cleaned prior to growth. The growth parameters were: Zn pressure = 5×10^{-7} Torr, T_{gr} = 520 °C, oxygen flow rate = 1.0 sccm, RF power = 230W. For comparison, growth on c -plane sapphire substrates was conducted at the same growth condition. The film thickness was measured by step heights of masked edges using a Sloan Dektak profilometer.

Results On $-c$ oriented bulk ZnO substrates, the grown ZnO layers showed spotty RHEED patterns. In SEM images, the surface of the films was completely covered with the hexagonal hillocks, and no smooth region was observed (Fig. 3.19(a)). On $+c$ oriented bulk ZnO substrates, the grown ZnO layers showed smooth surfaces as shown in Fig. 3.19(b). On c -plane sapphire substrates at the same growth condition, the surface of the ZnO film showed an intermediate surface structure, which consisted of both the hexagonal hillocks and smooth regions (Fig. 3.19(c)). The thickness of the epilayers was approximately 250nm, and no significant difference in growth rate was observed between different growth

⁶Substrates were manufactured by two vendors; some were grown by hydrothermal technique, others were by vapor transport technique[3]. Results were basically the same between vendors.

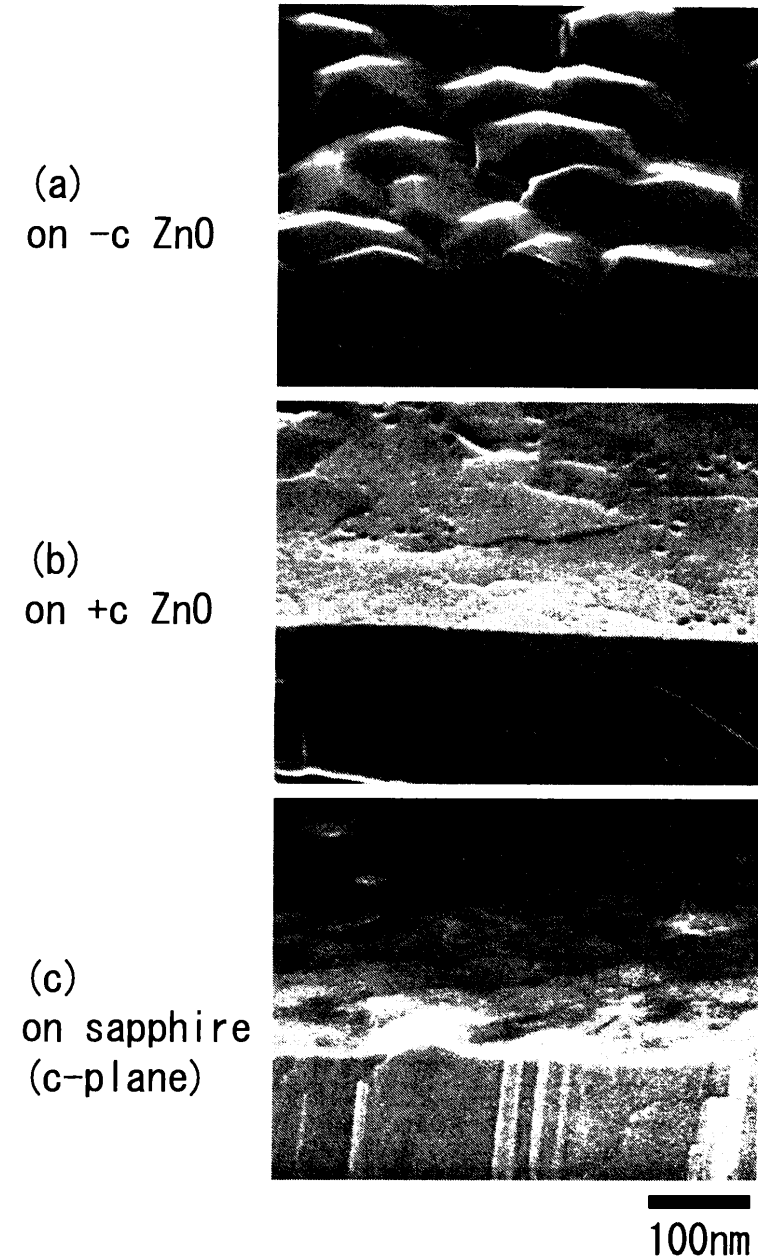


Figure 3.19: Surface morphology of ZnO films grown on bulk ZnO substrates. The morphology largely differs with the polarity of the substrate.

polarities.

The orientation of the c -axis of ZnO films was confirmed by CAICISS[4, 5]. The c -axis orientation and the species of the surface atoms were clearly distinguishable by the azimuth dependency of Zn signal intensity. The c -axis orientation of the films was consistent with those of the substrates for each sample. ZnO grown on $+c$ substrates had $+c$ orientation and zinc stabilized surfaces, while those grown on $-c$ substrates had $-c$ orientation and oxygen-stabilized surfaces.

From these results, it was shown that the hexagonal hillocks observed in this work were indicative of $-c$ oriented growth, while $+c$ oriented growth led to smooth surfaces. In addition, the emergence of the hexagonal hillocks (and thus, the surface morphology) of the epilayer was found to be heavily dependent on the growth direction at the initial growth stage. The mechanism how $-c$ orientation leads to emergence of hexagonal hillocks is still unclear. The preferable orientation of ZnO differs between reports; Ohnishi et al. reported that $-c$ oriented growth was preferable in the PLD method case[4], while Iwata et al. encourage growth under Zn-rich condition (that would lead to $+c$ oriented growth) for MBE method[6]. This difference between reports shows that the growth direction does not solely determine the surface morphology, and the preferable orientation of c -axis changes by other growth parameters. However, the orientation of ZnO c -axis was found to strongly affect the morphology of ZnO films, heavily dependent on the initial growth direction. This result encouraged research on effects of substrate configurations on morphology of films, which is described in section 3.7.

3.7 Dependence on orientation and morphology of substrates

From the results previously described in this chapter, the morphology of the ZnO films was found to be largely dependent on its initial growth stage, involving the direction of c axis of ZnO. On bulk ZnO substrates,

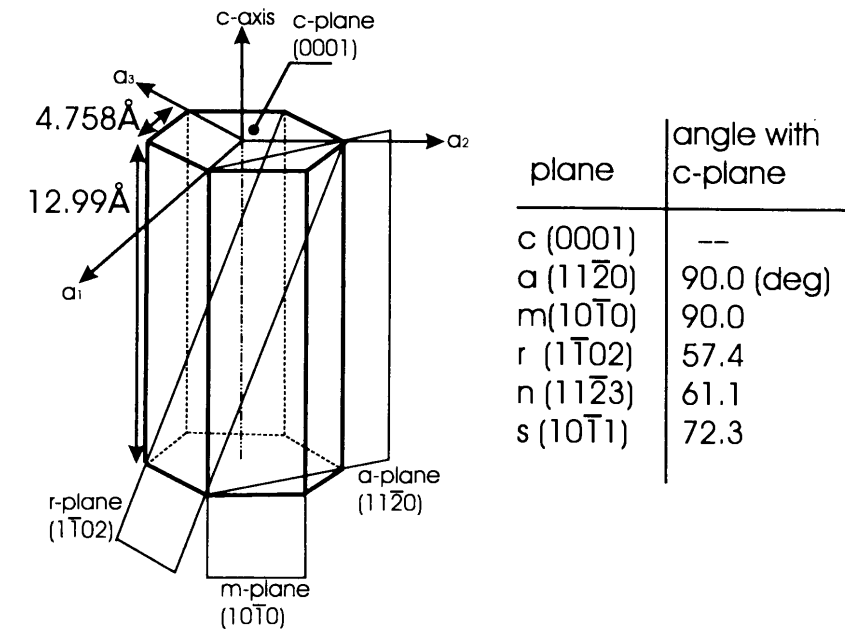


Figure 3.20: Common crystallographic planes of sapphire and their relative angles to c -plane.

the growth direction was strongly dependent on the substrate configuration. This can also be true in the case of growth on sapphire substrates. The morphology of ZnO films would be dependent on the substrate configuration. In this section, effects of the following parameters concerning the sapphire substrate was examined: crystallographical orientation, manufacturer, surface morphology, pre-growth preparation, and miscut angle.

3.7.1 Substrate orientation

Sapphire substrates are available in many crystallographical orientations (Fig.3.20). r -plane has been widely used for fabrication of commercial ZnO devices. However, among the recent research works on optical-device-quality ZnO growth, only c plane was chosen as orientation of

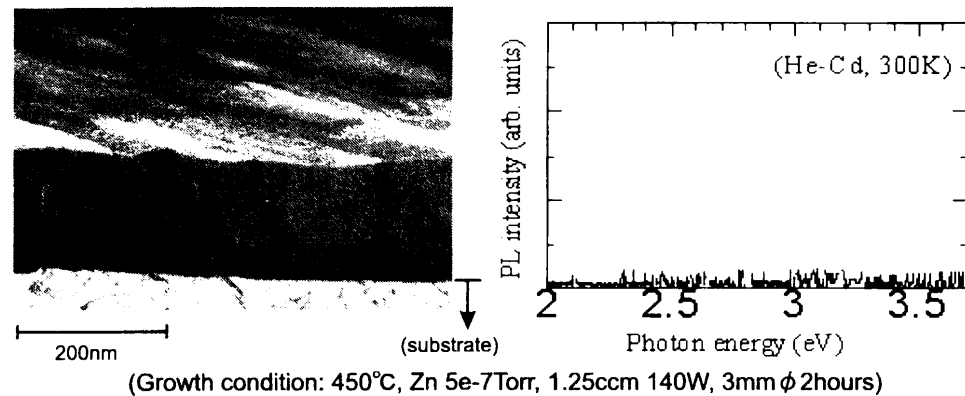


Figure 3.21: SEM image and PL spectrum of ZnO film grown on r -plane sapphire substrate. Though the surface morphology was smooth, the optical quality was inferior to those grown on c -plane.

sapphire substrates, although there is large mismatch between ZnO and sapphire. As previously described in this paper, the large mismatch between ZnO and sapphire in their c -planes would be one major factor of deteriorating the crystallinity of ZnO epilayer. Expecting that the other orientations would decrease the mismatch, growth on r -plane and a -plane sapphire substrates were examined.

on r -plane sapphire: On r -plane sapphire substrates, the c -axis of ZnO epilayers was parallel to the substrate surface. The morphology of the films was relatively smooth with columnar structures parallel to the surface (Fig.3.21). Determined by XRD $\theta - 2\theta$ measurements, the films were grown with their a -axis perpendicular to the substrate surface. However, as far as we have examined, these ZnO films showed no luminescence peaks in PL measurements. The cause of degradation in optical quality was unclear, but investigation on this orientation was discontinued.

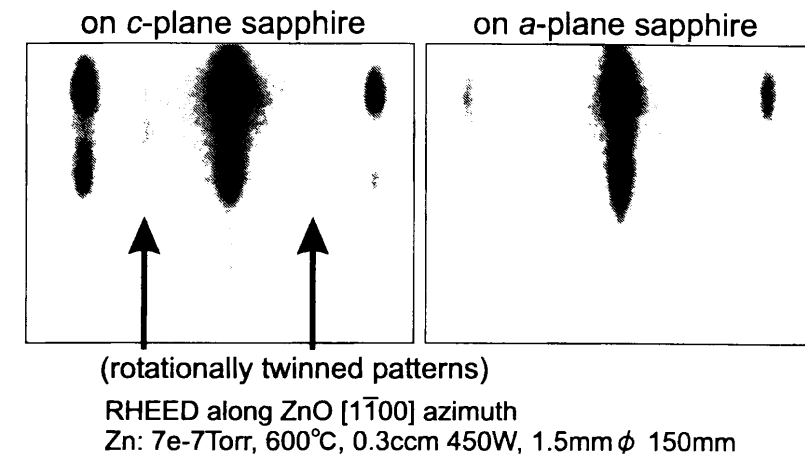


Figure 3.22: RHEED patterns of ZnO films grown on different orientations of sapphire. Rotationally twinned patterns are eliminated for films grown on a -plane sapphire.

on a -plane sapphire: On a -plane sapphire substrates, the properties of the grown ZnO films measured by XRC, PL, and AFM were basically the same to those grown on c -plane sapphire. However, the rotational twinned pattern in the RHEED patterns has significantly decreased, as seen in Fig.3.22. Fons et al. reported that use of a -plane improves the crystallinity of ZnO, significantly reducing the rotation in c -plane[7]. The reason of this improvement in crystallinity can be ascribed to the small mismatch between a -plane sapphire and ZnO, as schematically described in Fig.3.23. The c -axis of sapphire ($c = 12.99 \text{ \AA}$) and the a -axis of ZnO ($a = 3.250 \text{ \AA}$) are related almost exactly by a factor of 4, with a mismatch of 0.08%. Also, the m -axis of ZnO matches the m -axis of sapphire with a mismatch of 2.48%. This small mismatch would have strictly determined the in-plane orientation of ZnO relative to the sapphire to $\text{ZnO}\langle 11\bar{2}0 \rangle \parallel \text{sapphire}[0001]$, thus eliminating mixing of two different growth directions in ZnO c -plane[8].

Considering the results described above, a -plane sapphire was preferred as substrates for ZnO epitaxy.

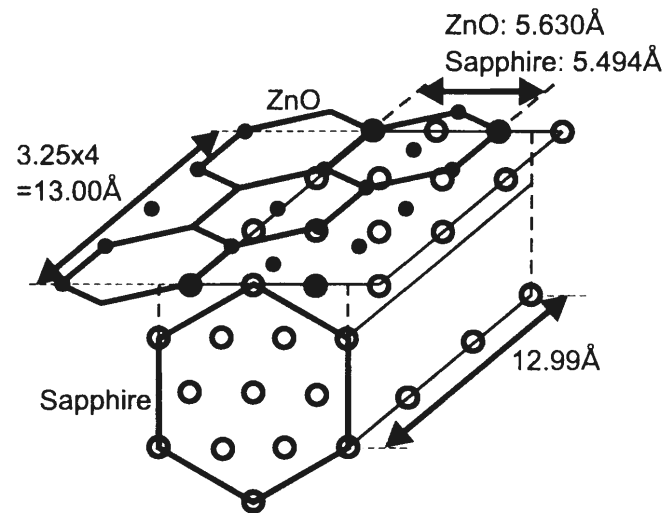
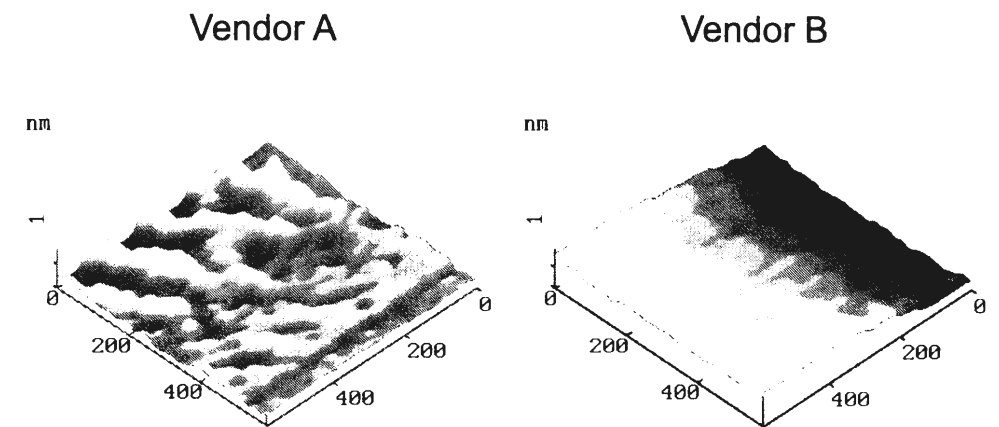


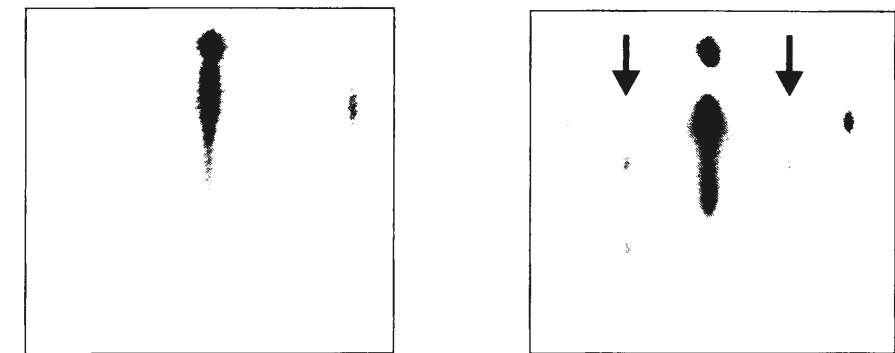
Figure 3.23: Schematic drawing of the crystallographical relationship between *a*-plane sapphire and *c* oriented ZnO. The lattices coincidentally match with a very small mismatch.

3.7.2 Surface morphology of the substrates

The effects of difference between substrate manufacturers and pre-growth treatments were examined. For *c*-plane sapphire substrates, three vendors using CZ or edge-defined film-fed (EFG) methods (A(CZ), B(EFG), C(CZ)) were compared. Observed by AFM, the *c*-plane substrates supplied by vendor B had the most smooth surfaces, while bumps and fluctuation of unit steps were observed in the other two (Fig.3.24(a)). The surface morphology of the grown ZnO films showed the opposite tendency. As far as examined in this work, in the case of *c*-plane substrates, the morphology of the grown films was rougher for smoother substrates, and signal from rotational twinned crystals was stronger in RHEED patterns, as seen in Fig.3.24(b). This undesirable influence of the substrate smoothness was confirmed by comparing the growth on as provided and pre annealed substrates of vendor B. *c* plane sapphire substrates provided from vendor B were pre annealed in 1atm pure oxy-



(a) : sapphire *c*-plane substrates



(b) : ZnO $[1\bar{1}00]$ RHEED patterns

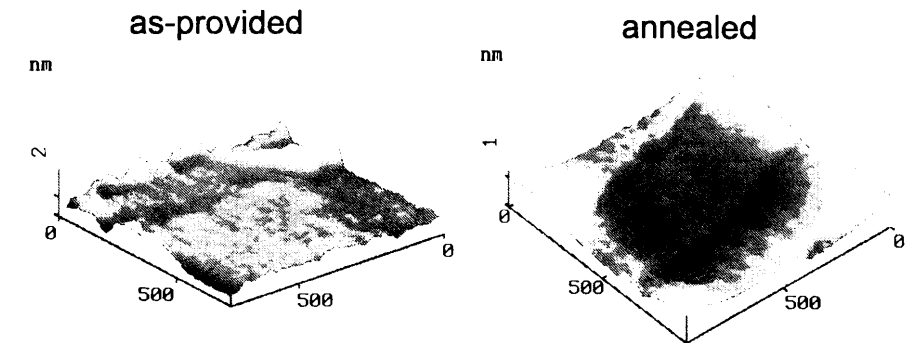
Figure 3.24: (a):AFM images of *c*-plane sapphire substrates from different vendors. (b):RHEED patterns of ZnO films grown on *c*-plane sapphire provided from different vendors at the same growth condition. Signal from rotational twinned crystals (indicated by arrows) was observed for *c* plane substrates with smoother surfaces. Growth conditions for these samples were: $T_{gr} = 600^\circ\text{C}$, Zn pressure = 1×10^{-6} Torr, oxygen flow rate = 0.3sccm, RF power = 450W.

gen at $\sim 1200^\circ\text{C}$ for 1 hour to have ultra smooth surfaces[9]. The films grown on pre-annealed substrates had distinctively rough surfaces, compared to those grown on as-provided substrates (Fig.3.25). Etching of the c -plane substrates, which smoothes the substrate surface as described in section 2.3.2, gave similar results to the ultra-smooth substrate case; the ZnO films showed rough surfaces from the initial stage of growth. Considering these results, the sapphire substrates were neither etched nor pre-annealed in the following works. By contrast, in the case of a -plane sapphire substrates, no significant difference was observed between ZnO films grown on substrates of different vendors. These results show that in the case of c -plane sapphire, moderate fluctuation on the surface of substrates is required for growth of ZnO with smooth surfaces, while the a -plane case is not.

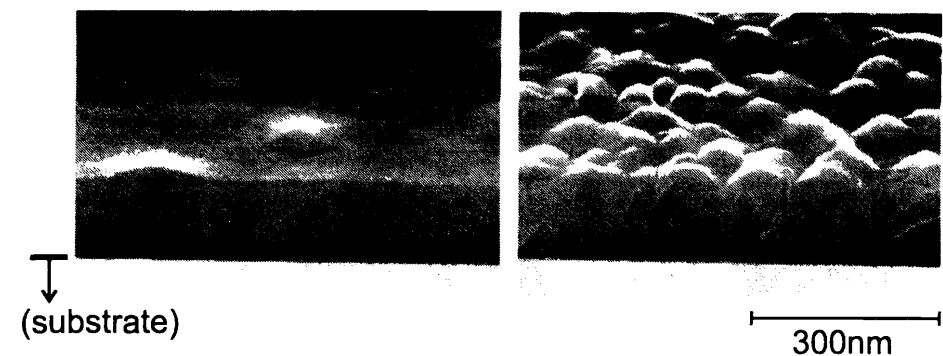
The difference between c - and a -plane sapphire may be due to the large lattice mismatch between ZnO and c -plane sapphire. Due to the mismatch, the ZnO atoms bonded to sapphire would feel a great strain, making initial nuclei unstable and sparse. Growth of the nuclei would be strictly restricted to a specific fashion, which may be relatively insensitive to other growth parameters and lead to surface roughening. In addition to the observed twinned growth, this surface roughening may have involved $-c$ -oriented growth (described in section 3.6), or transition from 2D-mode to S-K mode growth[10], or both of them. Presence of microscopic steps and kinks would have increased the chances of initial nucleation of ZnO in a fashion that led to smoother surfaces. On the other hand, as the mismatch between the lattices of a -plane sapphire and ZnO is quite smaller, initial nucleation would not be strictly restricted to a specific style, making it easier to obtain desired style of growth by controlling other growth parameters.

3.8 Growth on miscut sapphire substrates

As previously described in this chapter, in the case of growth on c -plane sapphire substrates, the morphology of the ZnO epilayers was heavily



(a) c -plane sapphire substrates



(b) grown ZnO films

Figure 3.25: (a): AFM images of c -plane sapphire substrate provided from the same vendor (Bicron), as-provided (left) and smoothed by annealing in 1atm oxygen at $\sim 1200^\circ\text{C}$ for 1 hour. (b): SEM images of ZnO grown on c -plane sapphire, on as-provided substrate (left) and annealed smooth substrate (right). The morphology of ZnO roughened by use of ultra-smooth substrates.

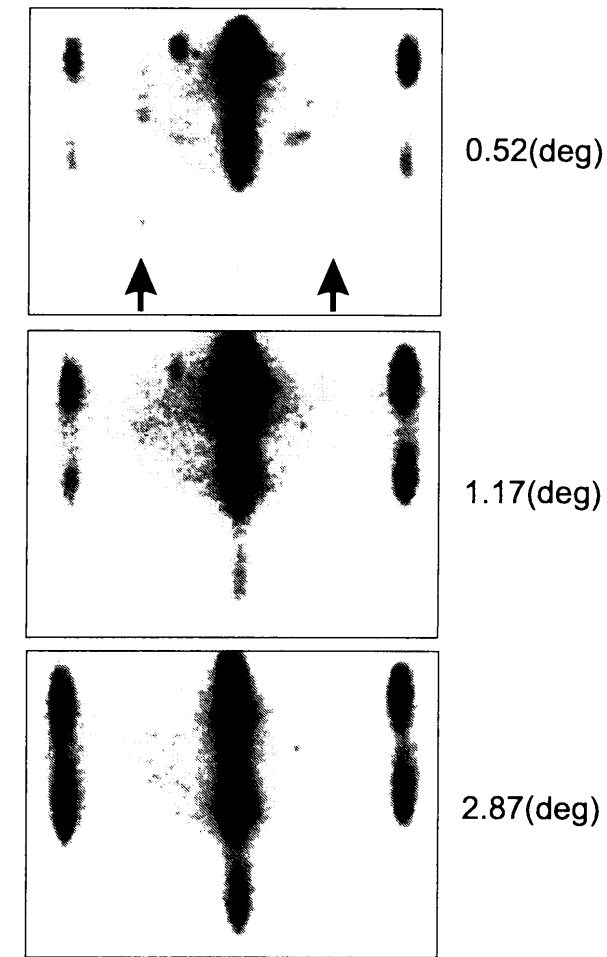
dependent on microscopic fluctuations of substrate surface. Thus it is natural to think that the small miscut angles of the substrates can take effect on the initial growth stage and change the morphology of the ZnO epilayers. Commercially available substrates usually have a small but a certain error margin in the surface direction, and there is a possibility that small miscut angles have recognizable effects on the crystallinity of ZnO epilayers. On the other hand, it may be possible to improve the morphology of the epilayers by controlling the initial growth conditions with use of intentionally miscut substrates.

Considering these possibilities, RSMBE growth and characteristics of ZnO on miscut sapphire substrates, on both c - and a -planes, were examined. Intentionally miscut sapphire manufactured by Kyocera using EFG method were used as substrates. These substrates had very smooth surfaces, which led to surface roughening and twinned growth in the case of growth of ZnO on c -plane sapphire, as described in section 3.7.2.

3.8.1 On c -plane

The substrates were miscut from c -plane to a - or m -axis direction, with a maximum miscut angle of 2.87 degrees. The growth temperature was $T_{gr} = 600^\circ\text{C}$, and the pressure of Zn was 8×10^{-7} Torr. The flow rate of oxygen was 0.3sccm, and the RF power was 450W. The growth time was 2 h.

The film thickness was approximately 300nm. PL spectra at RT were dominated by NBE peak, and deep level emissions were more than 30 times weaker than the NBE peak emission in their intensity. c -axis oriented ZnO films were obtained, with their c -axis tilted to align with the c -axis of the substrates. For samples with smaller substrate offset angles, the hexagonal hillocks, indicative of c -oriented growth, were observed at higher density on their surface. RHEED patterns were spotty and included twinned crystal patterns from the initial growth stage, as shown in Fig.3.26. With larger offset angles, twinned RHEED patterns weakened gradually, and no twinned patterns were observed for samples with offset



RHEED along ZnO $[1\bar{1}00]$ azimuth
Zn: $8\text{e-}7\text{Torr}$, 600°C , 0.3ccm 450W, 1.5mm ϕ 150mm

Figure 3.26: RHEED patterns of ZnO grown on miscut c -plane sapphire substrates. Rotationally twinned patterns decreased and was finally eliminated with larger miscut angles.

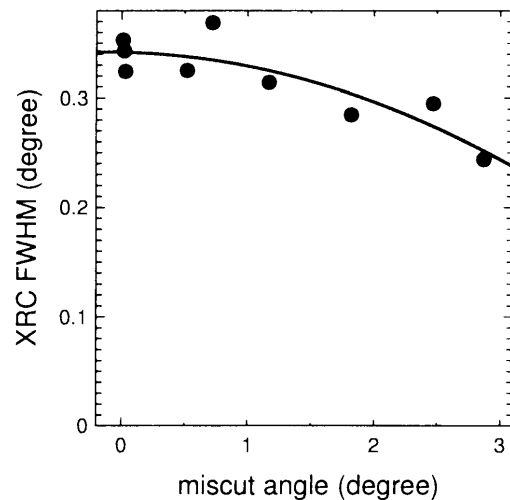


Figure 3.27: FWHM of XRC as a function of miscut angle of substrate from c plane.

angles larger than 2.5 deg. For these samples, RHEED patterns showed streaks after the growth, and their surfaces were smooth. FWHM of ZnO (0002) peak of XRC decreased with larger miscut angles (Fig.3.27). No significant difference was seen by the direction of miscutting (toward a -axis, or toward c -axis).

From these results, it was shown that miscut angles can improve the morphology of ZnO epilayers on c plane sapphire substrates. Miscutting of the substrate increases the density of steps and kinks on substrate surface [11]. As discussed in section 3.7.2, in the case of c -plane sapphire substrates, existence of microscopic steps or kinks on substrate surface was preferred for better morphology of ZnO epilayers. Considering together, the above results indicate that steps and kinks on the c plane sapphire surface promote $+c$ oriented growth of ZnO at the initial growth stage, while growth on flat terraces provokes $-c$ oriented growth and surface faceting.

3.8.2 On a -plane

Growth on a -plane sapphire substrates, intentionally miscut to c - or m -axis direction with a maximum miscut angle of 8.95 degrees, was examined. The growth temperature was $T_{gr}=600$ °C, and the pressure of Zn was 1.5×10^{-6} Torr. The flow rate of oxygen was 0.25sccm, and the RF power was 400W. The growth time was 2 h.

c -axis oriented ZnO films were obtained, with their c -axis tilted to align with the a -axis of the substrates (Fig.3.28). Also, emergence of hexagonal hillocks was observed at film surfaces. FWHM of ZnO (0002) peak of XRC was best for samples with small miscut angles, and constant for samples with miscut angles larger than 2 degrees (Fig.3.29). Both the miscut towards c - and m -axis gave similar results. As far as investigated, use of miscut a -plane sapphire substrates simply deteriorated the quality of the ZnO film.

Considering the above results, miscut angle of a -plane sapphire substrate is very likely to have a tendency to degrade the quality of the ZnO epilayer. This can be ascribed to the already-small mismatch between just-oriented a -plane sapphire and c -oriented ZnO, as described in section 3.6. The miscut angle apparently promotes mismatch between the substrate and epilayer in the a -plane case, which is in strong contrast with the c -plane case. Thus miscutting of a -plane sapphire substrates is not recommended for ZnO epitaxy.

3.9 Optimized results

Utilizing the results obtained in this chapter, the characteristics of ZnO films were improved as shown in Table 3.9.

Parameter	preliminary values	best values
XRC FWHM (ZnO(0002); arcsec)	> 3600	< 360
Growth rate (nm/h)	< 100	300 ~ 400
PL DL/NBE intensity ratio (RT)	~1	~ 150
Donor concentration (cm ⁻³)	1×10^{18}	5×10^{17}
Carrier mobility (cm ² /Vs)	~ 1	~ 15

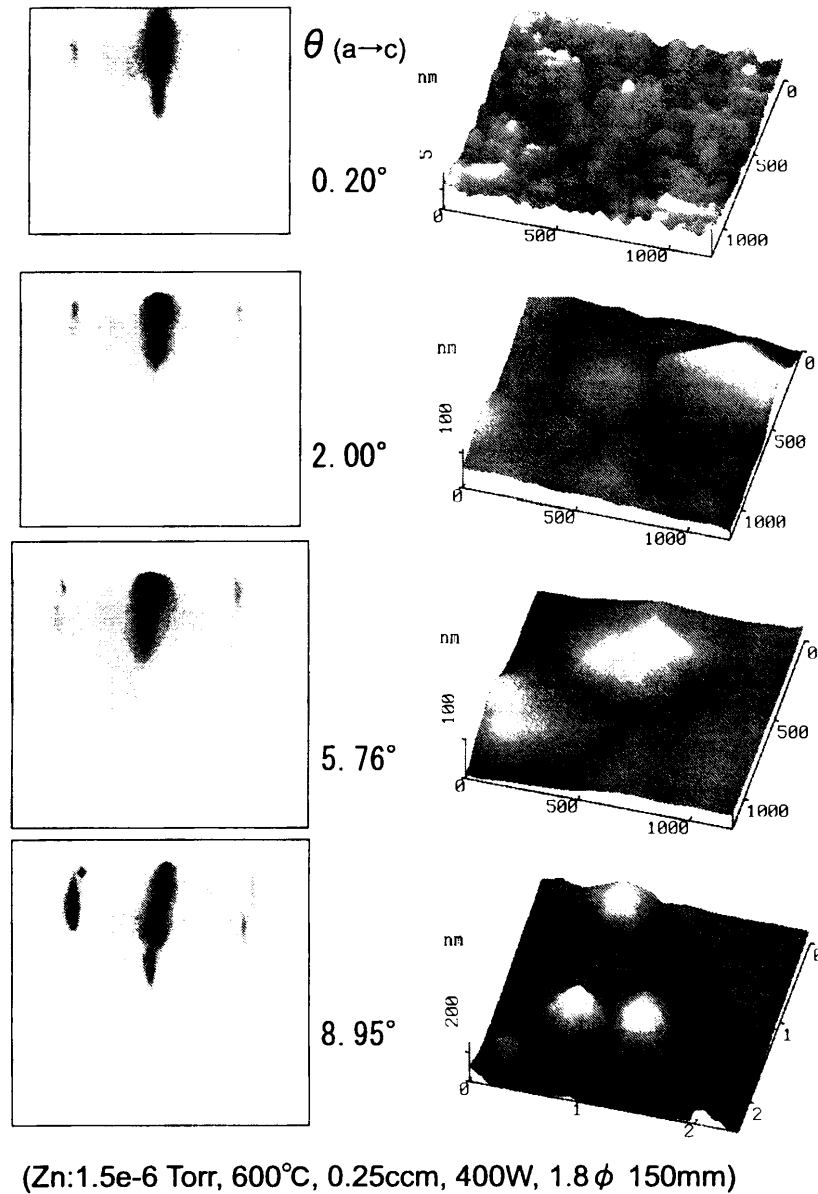


Figure 3.28: RHEED and AFM images of ZnO grown on miscut *a* plane sapphire substrates. Tilted growth and emergence of hexagonal hillocks were observed.

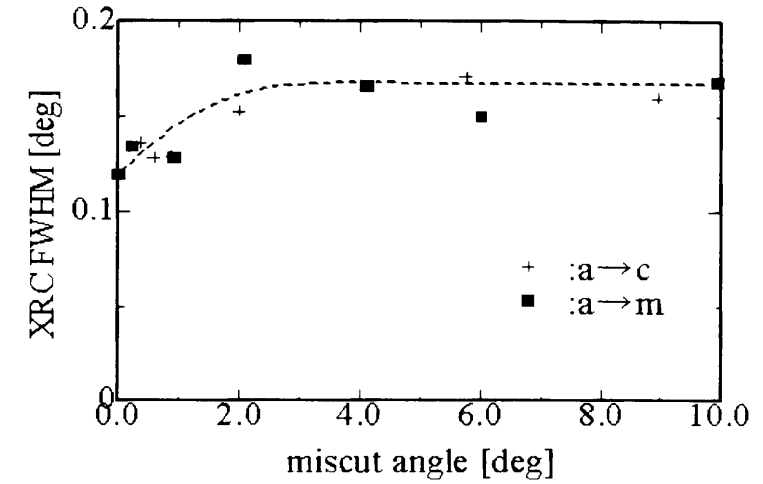


Figure 3.29: FWHM of ZnO(0002) XRC peak as a function of substrate miscut angle from *a* plane sapphire.

Judged from the FWHM of XRC ZnO(0002) peak, the crystallinity was significantly improved by applying the developed techniques. Also, the growth rate has largely increased, fast enough for future device fabrication.

PL spectra were free of deep-level luminescence, and excitonic peaks were clearly visible at low temperatures (Fig.3.30). The PL spectra at low temperatures were dominated by neutral donor-bound excitonic peaks[12], with presence of free excitonic peak. However, compared to bulk ZnO crystals[13], excitonic peaks were not clear in absorbance spectra, which means that further improvement in optical quality is required. The electrical properties needed to be improved, as the donor concentration was still too high for p type conduction control, and the carrier mobility was still much lower than those of bulk crystals ($> 200 \text{ cm}^2/\text{Vs}$). These problems may be ascribed to insufficient crystallinity, which is still far from the best data of epitaxial ZnO ($\sim 10 \text{ arcsec}$)[8]. And possibly, small amount of incorporation of impurities from the assembly parts of

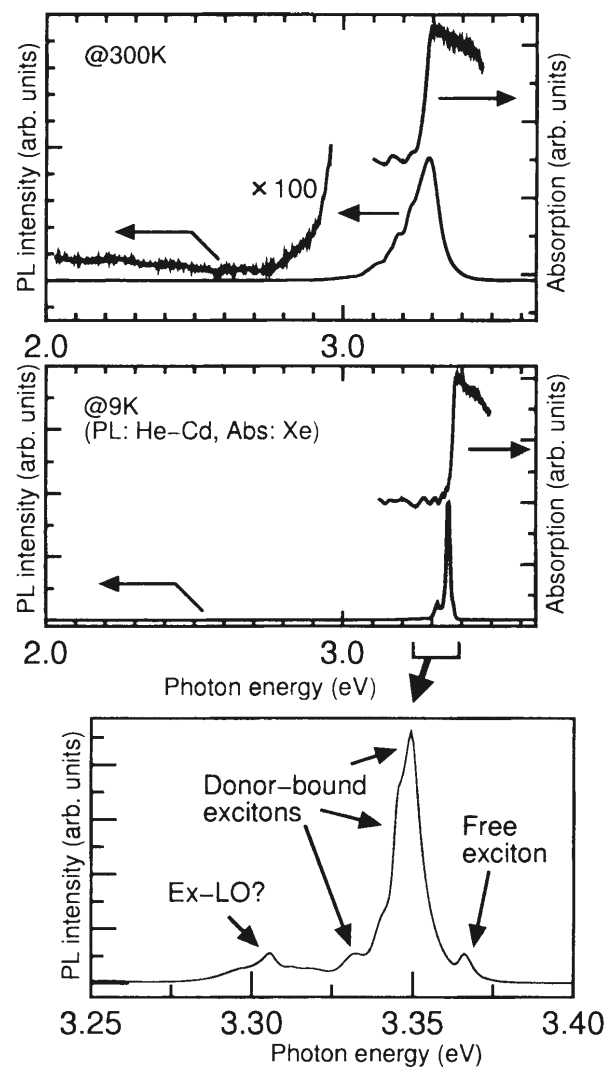


Figure 3.30: Typical optical characteristics of ZnO film grown by RSMBE method. PL spectra are free of deep luminescence. However, excitonic peaks are not clear in absorbance spectra.

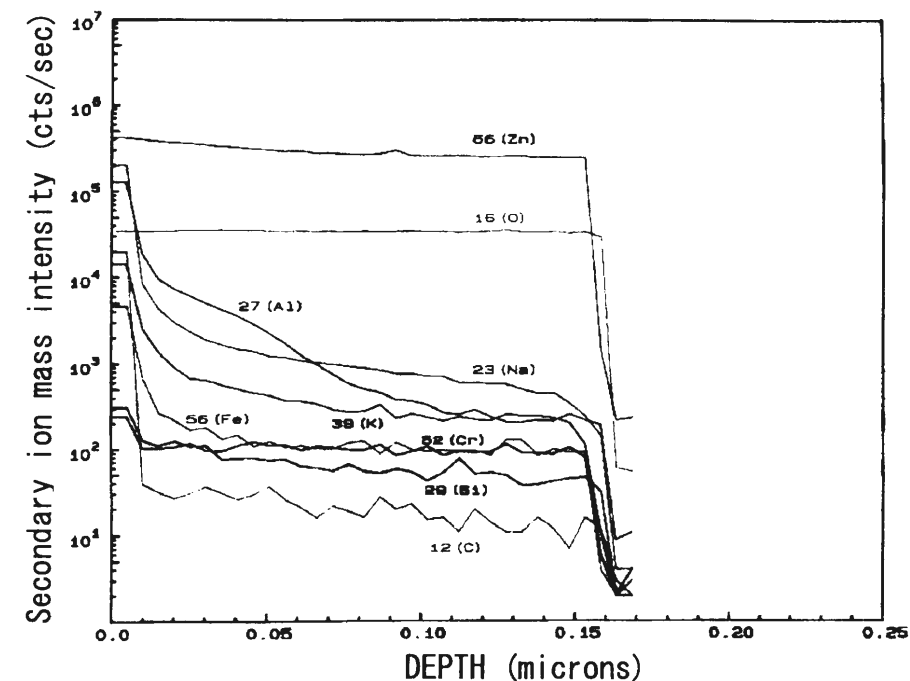


Figure 3.31: SIMS depth profile of a typical ZnO film grown by the RSMBE system. Contamination was greatly reduced. However, Fe, Cr, Al, possibly sputtered from the structures of the radical oxygen cell, were needed to be further reduced from this early result.

the radical cell, such as iron, chromium from Inconel or stainless steel parts, or aluminum from alumina insulators [14] used for the CPE, which was confirmed by SIMS measurements (Fig.3.31). Though the contamination level was significantly suppressed than the samples obtained in the previous chapter, further reduction of the impurities would be required.

3.10 Summary

In this chapter, effects of each growth parameter on radical source MBE (RSMBE) growth of ZnO were described. Examined parameters include the growth temperature, Zn pressure, oxygen flow, RF power applied to the radical cell, orifice size and distance of the radical cell, substrate vendor, miscut angle of sapphire substrate.

The following achievements were described:

1. Effects of fundamental growth parameters of ZnO were evaluated by the crystallinity and optical characteristics of the ZnO films. Each growth parameter were roughly optimized.
2. Specific type of surface roughening was shown to be strongly promoted by excessive oxygen supply, and this roughening was shown to be related to the direction of c -axis of ZnO. This surface roughening was mainly determined at the initial growth stage. It was found to be also heavily dependent on substrate configuration, such as the surface smoothness or miscut angles, and preferable configurations were found.
3. a -plane sapphire substrate was shown to be suitable than c -plane sapphire substrate for RSMBE ZnO growth, reducing a specific type of twinned growth of ZnO.
4. It was found that the use of miscut substrates can improve the crystallinity of ZnO films on c -plane sapphire substrates. On the other hand, in the case of a plane substrates, it degraded the quality of ZnO films in their crystallinity and morphology.
5. Utilizing the techniques developed in this chapter, the obtained ZnO films at optimized conditions clearly showed excitonic peaks in PL spectra, with improved growth rate, enhanced crystallinity and smooth surface morphology.

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Chapter 4

Growth and characterization of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ films

4.1 Introduction

For larger energy gap for confinement, and for wider applicable range in wavelength, both widening and narrowing of bandgap by alloying are desirable. For this purpose, MgO and CdO are candidate materials for alloying with ZnO (Fig.4.1). Alloying with MgO was previously reported to widen the bandgap up to 4.0eV[1]. On the other hand, alloying with CdO ($E_g=2.3\text{eV}$ [2]) had been reported to narrow the bandgap for $\sim 200\text{meV}$ by PLD method[3], but no further reports on bandgap narrowing have been made. Also, the luminescence peak still remained at 3.2eV, at the edge of UV region.

One reason that further investigations were not conducted by PLD on ZnCdO was possibly from the difficulties in supplying sufficient amount of Cd, which has a relatively high vapor pressure and thus requires large amount of supply during growth. Another reason was that CdO has a bond-length ($2.35\text{\AA}$) largely different from that of ZnO ($1.99\text{\AA}$). This would make replacement of Zn atoms with Cd atoms from ZnO crystal unstable, thus promoting phase separation between ZnO and CdO. Using the delta lattice parameter (DLP) model[4], the calculated max-

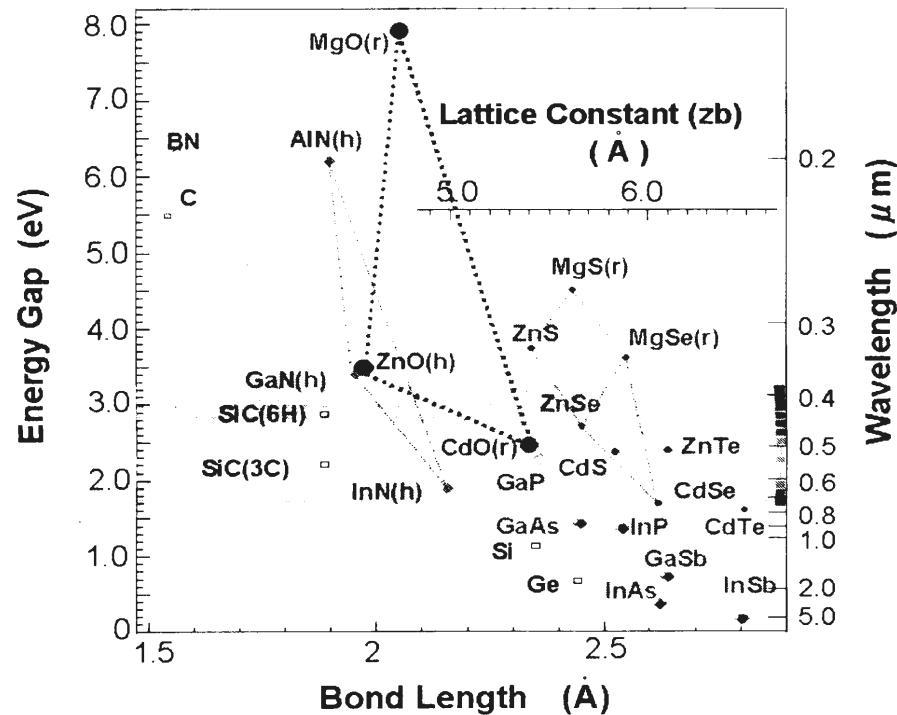


Figure 4.1: Bond length and energy gaps of various semiconductor materials.

imum composition of CdO that the ZnCdO crystal can be meta-stable is 3.3% at 873K, and lower for lower temperatures. However, in analogy of the InGaN case, the phase separated regions may work as confinement structures that enhance the stability of excitons [5]. Moreover, as RSMBE method can dynamically vary the flux of metallic source materials, it can supply larger amount of Cd during growth than usual PLD method.

In this chapter, under expectation of further narrowing of the bandgap of ZnO or utilizing phase separation between ZnO and CdO , alloying of CdO with ZnO by RSMBE method was examined. Also, unexpected blue luminescence was found in PL spectra of films grown at specific conditions, and this blue luminescence was extensively investigated.

4.2 RSMBE growth of ZnCdO films

4.2.1 Procedures

ZnCdO films were grown in the RSMBE system, which was basically same to the system used in Chapter 3. Metallic zinc, metallic cadmium, and radical oxygen were used as source materials. A Knudsen cell (K-cell: Eiko MB-3000D) was added to the system as Cd source. This K-cell had two sets of heaters around the 40cc PBN crucible, with one of the heaters placed densely at the exit edge of the crucible. As the partial pressure of Cd during growth was extremely high (2×10^{-5} Torr at maximum), no orifice was attached to the crucible, in order to avoid the crucible from choking up¹. The temperature of the Cd cell was controlled by two temperature controllers (REX-P300) connected to two sets of heaters and thermocouples. The temperature of the exit edge was kept higher than that of the source material to avoid condensation. The operation condition of the radical cell was fixed to certain parameters, due to its inherent complexity observed in the previous chapter. The

¹Note: this would have made supply of Cd rather unstable, compared to that of zinc (= with orifice).

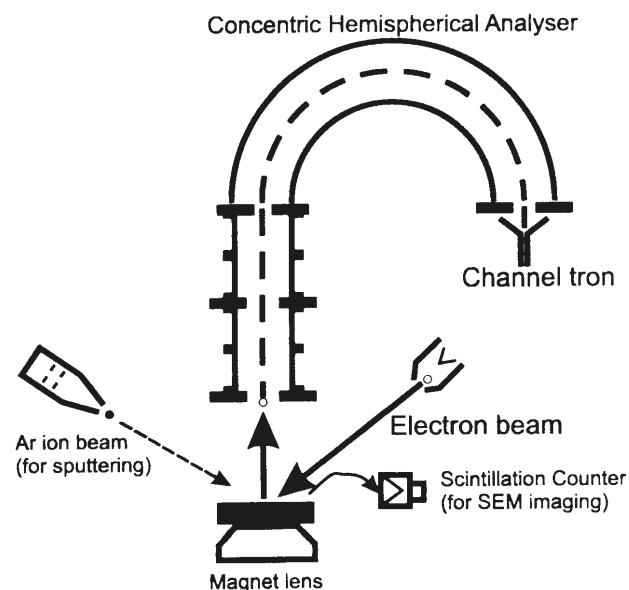


Figure 4.2: Schematic diagram of the AES system (Kratos AXIS-165S).

distance between the oxygen radical cell and the substrate was 150mm, and the orifice size of the radical cell was 1.8mm ϕ . Oxygen flow was 0.25sccm, and the RF power applied to the radical cell was 400W,

Prior to growth, *a*-plane Kyocera sapphire substrates were degreased and thermally cleaned at 700°C for 15min. Epitaxy of ZnCdO films under various partial pressures of zinc and cadmium was conducted for 2 hours. The growth rate was 200 - 400 nm/h. The partial pressures of zinc and cadmium were systematically varied between 3.1×10^{-7} - 2.3×10^{-6} Torr and 3.0×10^{-7} - 1.4×10^{-5} Torr, respectively. Growth temperature (T_{gr}) was varied between 400 - 600 °C. For comparison, growth of pure CdO was also conducted at a Cd pressure of 1.4 - 1.5×10^{-6} and $T_{gr} = 600$ °C.

The properties of grown films were characterized by photoluminescence (PL) excited by a He-Cd laser, optical absorption, Auger electron spectroscopy (AES; Kratos AXIS-165S; see Fig.4.2), atomic force microscopy (AFM) and X-ray diffraction (XRD).

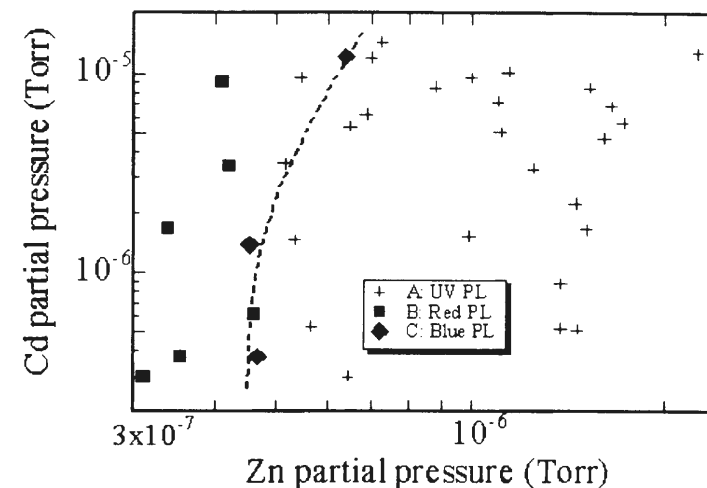


Figure 4.3: Categorization of the ZnCdO films grown with varied Zn and Cd pressures. The obtained films could be categorized in three types, each of them close to either pure ZnO or pure CdO . These samples were grown at 600°C.

4.2.2 Results

The obtained films were categorized into three types, as shown in Fig.4.3. At relatively high Zn pressure, the film was transparent (type-A), same as pure ZnO films. At low Zn pressure, the film color turned to half-transparent red (type-B), similar to that of pure CdO films. At intermediate Zn pressure of approximately 4 - 7×10^{-7} Torr, transparent or slightly yellow films were obtained (type-C), which showed distinctive optical properties, as described later in section 4.3.

The macroscopic composition and the growth direction of the films were investigated by AES and XRD (Fig.4.4). The electron beam size of AES was large, and no microscopic composition fluctuation was observed. For type-A films, ZnO -related peaks dominated the XRD and AES spectra. The growth direction was $\text{ZnO}(0001)$, suggesting that these films are essentially identical to $\text{ZnO}(0001)$ crystals, though a small amount of Cd

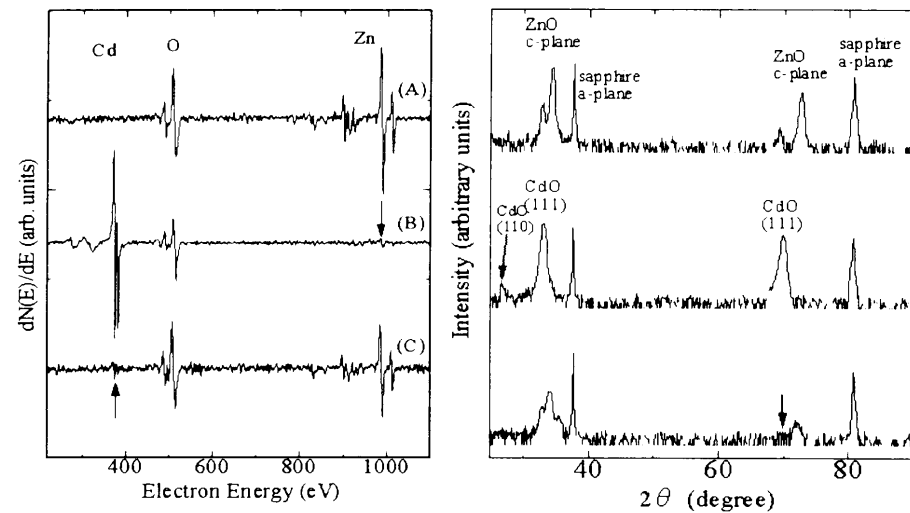


Figure 4.4: Typical AES spectra and XRD patterns of each type of ZnCdO films.

may be incorporated below the detection limit. For type-B films, CdO related peaks dominated the XRD and AES spectra, which was similar to pure CdO films. The observed XRD peaks were dominated by $\text{CdO}(111)$, and weak signals from $\text{CdO}(110)$ were also observed in some samples.

For type-C films, ZnO -related peaks dominated both AES and XRD spectra. The Cd solid compositions estimated from AES signal intensities were lower than 5%. XRD peaks were dominated by $\text{ZnO}(0001)$. XRD peaks from CdO was not observed in many type-C samples, but some samples showed $\text{CdO}(111)$. These results showed that type-C films mainly consisted of $\text{ZnO}(0001)$ crystals, containing a small amount of CdO . Though many of the type-C samples did not show CdO peaks in XRD spectra, phase separation in these films was strongly suggested.

The surface morphology of the films was studied by AFM. The surface morphology of type-A films was dependent on the total pressure of Cd and Zn: smoother for higher pressure and rougher for lower pressure, which agrees with the results obtained for pure ZnO films in section

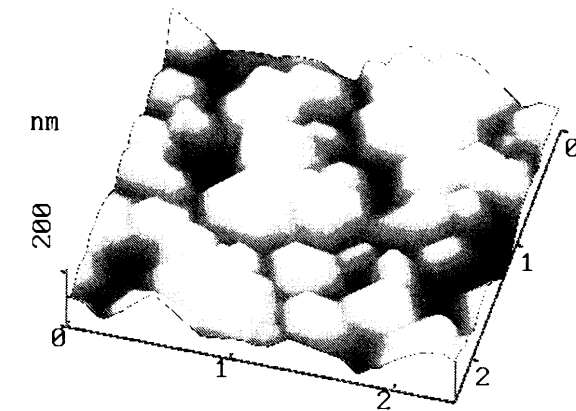


Figure 4.5: AFM image of a typical blue-luminescent ZnCdO film.

3.5.4. All of the type-C films, which was grown under relatively oxygen-rich conditions, had rough surfaces covered with hexagonal hillocks, as shown in Fig.4.5. The surface structures of type-C films were similar to those of type-A films with rough surfaces.

The optical properties of films were investigated by PL and absorption measurements. Type-A films clearly showed banded luminescence in the UV region, and no deep level luminescence was observed. Type B films showed deep level peaks only, and their intensities were extremely weak. Type-C films showed a distinct blue luminescence, as described in section 4.3.

The bandgaps of the type-A and type-C films were quite close to that of pure ZnO ($\sim 3.3\text{eV}$ at RT), as shown in Fig.4.6. Judged from the shift of the absorption edges, the bandgap narrowing of ZnCdO films was smaller than $\sim 50\text{meV}$ for the transparent films obtained in this investigation.

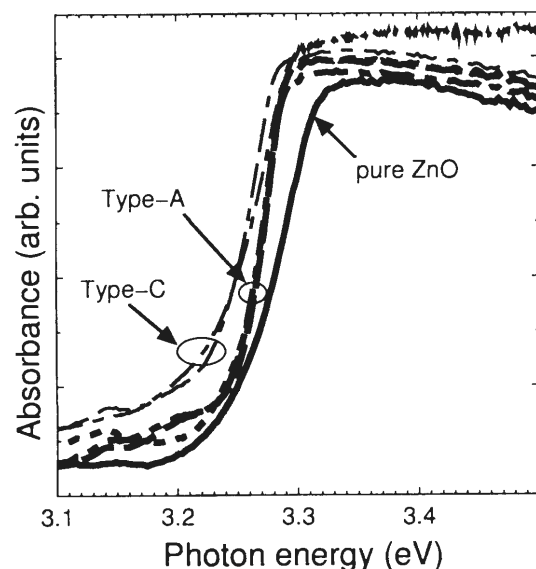


Figure 4.6: Absorption spectra of type-A and type-C films measured at RT, using a xenon lamp as light source. The absorption edge of type-A and type-C films were quite close to that of pure ZnO, with a maximum shift of $\sim 50\text{meV}$.

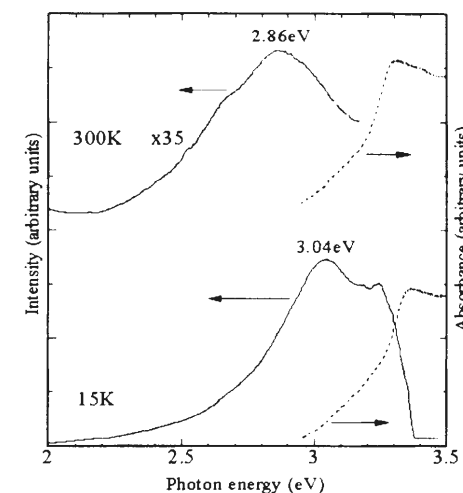


Figure 4.7: PL and absorption spectra of a typical type-C (blue-luminescent) ZnCdO film. Distinct blue luminescence with a large Stokes shift was observed.

4.2.3 Discussion

As foreseen from the large difference in bond-lengths, alloying of CdO into ZnO showed a tendency to provoke phase separation at a very low CdO composition. Under the growth conditions applied in this work, the critical composition of CdO estimated from the signal intensity of AES spectra was 3~5%. This value is much higher than the predicted solubility limit, suggesting occurrence of phase separation. As the observed shift of bandgap was quite small, materials other than CdO should be preferable for bandgap narrowing, except the blue luminescence described in this section.

4.3 Blue luminescence from ZnCdO films

Blue luminescence from a typical type-C ZnCdO film is shown in Fig.4.7. This blue luminescence peak (I_{blue}) was located at 2.65~2.80 eV at RT

under weak irradiation of He-Cd laser (325nm), and was clearly visible to naked eyes. And, as the absorption edges of these films remained close to that of pure ZnO (Fig.4.6), a large Stokes shift up to $\sim 500\text{meV}$ was observed between the luminescence peak and the absorption edge for type-C films. To the best of our knowledge, this was the first time that pure blue luminescence was discovered for both ZnO and CdO. This blue luminescence is interesting as a candidate method for applying ZnO for visible light emitting devices. Therefore, extensive investigation on this blue luminescence was conducted, as described below.

4.3.1 Dependence on temperature and excitation intensity

The temperature dependences of spectra and integrated intensity of PL are shown in Fig.4.8 and Fig.4.9. At low temperatures, both the luminescence peaks at near-bandedge(NBE) and in the blue region were observed. The NBE peaks disappeared at higher temperatures, while the blue peak remained relatively strong in intensity. The intensity ratio (R_i) of the integrated luminescence intensity between low ($\leq 15\text{K}$) and room ($\sim 300\text{K}$) temperatures was $R_i = 5.7 \sim 35$, which was much lower than the case of pure ZnO films ($R_i > 100$). Supposing all of the carriers radiatively recombine at low temperatures, the internal quantum efficiency at RT was estimated to be $1.5\% \sim 17.3\%$, much higher than the case of pure ZnO films ($< 1\%$). PL spectra under varied excitation intensities are shown in Fig.4.10. With larger excitation power, blueshift of I_{blue} was observed, and the NBE peak was gradually enhanced. This suggested that the state density of levels corresponding to I_{blue} was low, and was filled up at high excitation densities.

Considering that phase separation would have occurred in this film, the relatively independent behaviors of NBE peaks and I_{blue} suggested existence of two kinds of regions in the film; regions that have characteristics close to that of pure ZnO, and regions that are blue-luminescent.

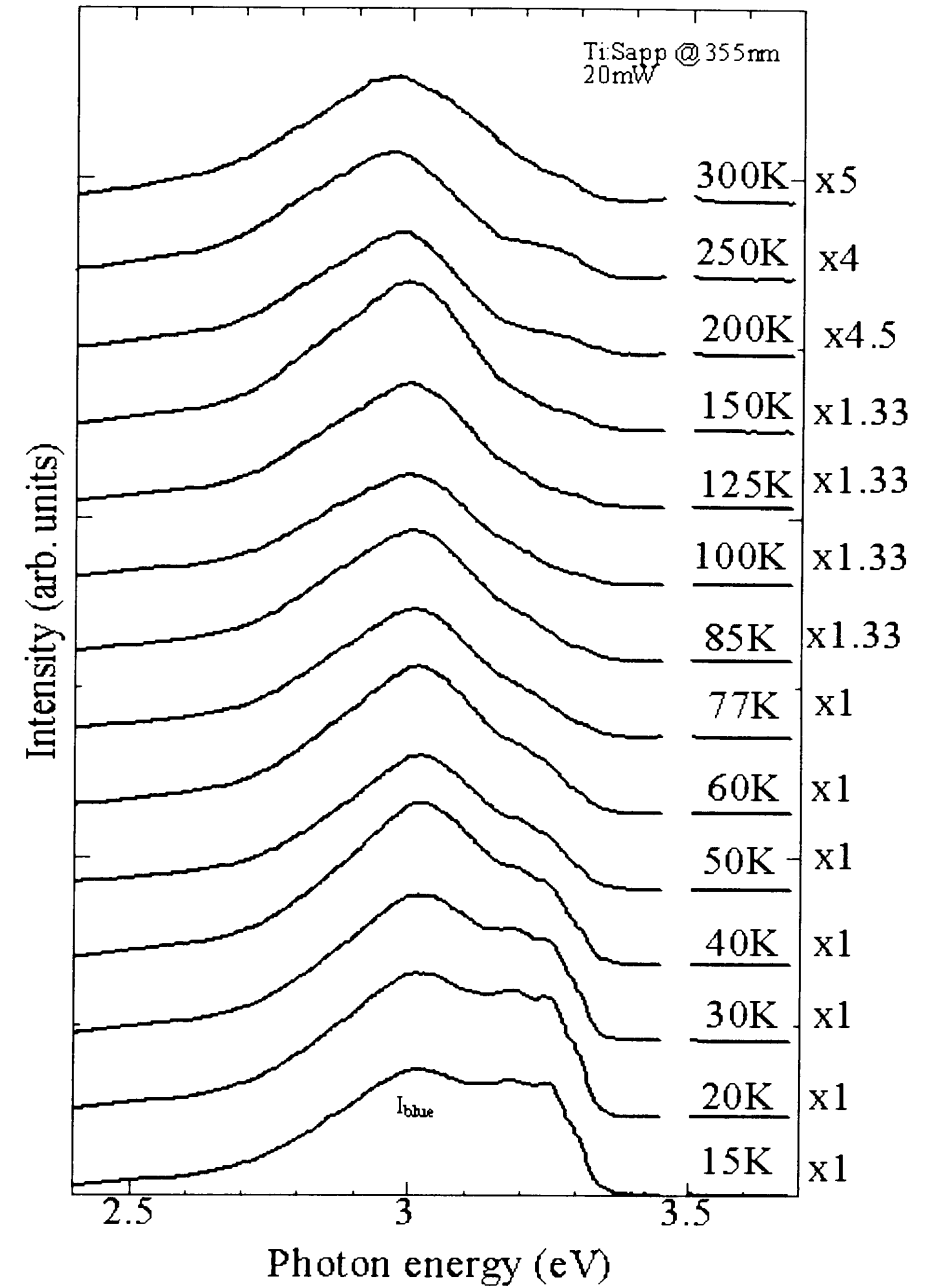


Figure 4.8: PL spectra of a typical type-C (blue luminescent) ZnCdO film. The peak at the near-bandedge significantly decreased at higher temperatures, while I_{blue} remained visible to naked eyes.

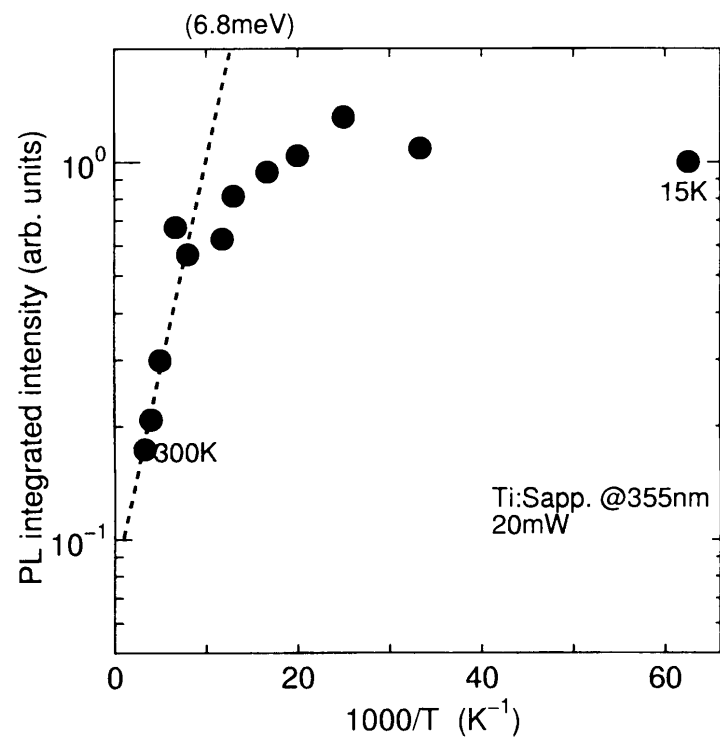


Figure 4.9: Integrated intensity of PL as a function of temperature, measured on a type C ZnCdO film. The intensity at RT is $\sim 17.3\%$ of that at 15K.

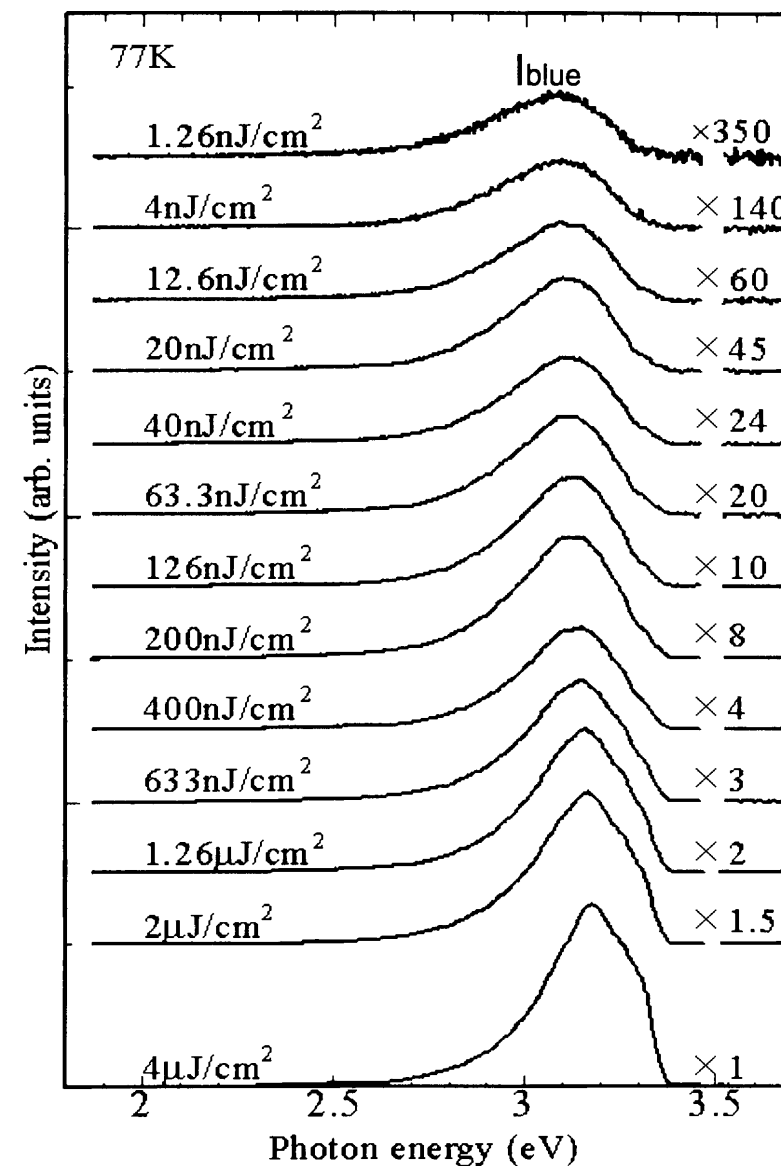


Figure 4.10: PL spectra of a typical type-C ZnCdO film, taken under varied excitation intensities. SHG of Ti:sapphire laser operated at 355nm was used for excitation. The pulse width and frequency was 1.5ps, 80MHz. With stronger excitation, blueshifts were observed.

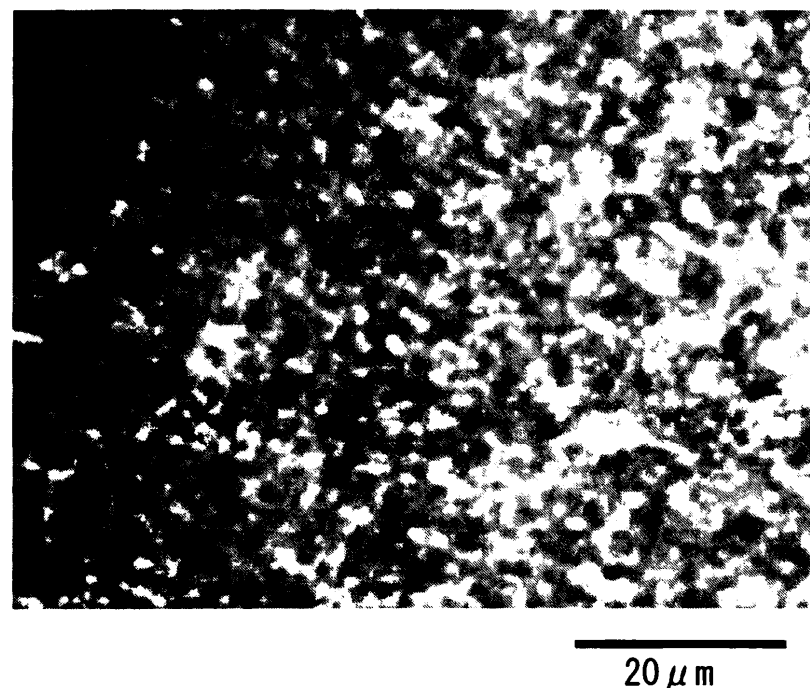


Figure 4.11: Plan-view FL microscopy image of a typical type-C ZnCdO film at RT, excited by a mercury lamp. The contrast in the image reflects the difference in luminescence intensity.

4.3.2 Spatial distribution

Spatial distribution of luminescence was investigated by FL microscopy at RT. On type-C films, the entire area was blue luminescent, while the luminescence intensity was spatially nonuniform. Figure 4.11 is a typical example, where differences in PL intensity appeared as clear contrasts. As all of the type-C films had rough surfaces, the surface roughness could be considered as one cause of this nonuniformity. However, in the case of type-A (=UV luminescent) films, the luminescence intensity was relatively uniform than the type-C case. This difference between type-A and -C films suggested that the blue luminescent regions are nonuni-

formly distributed in type-C films, resulting in distinctive nonuniformity in luminescence intensity. The luminescence was fluctuated both macroscopically and microscopically ($<1\mu\text{m}$). The microscopic fluctuation was supposed to be related to the hexagonal grains of the films. However, even at the highest magnification ($\times 400$), the microscopic nonuniformity in the image were below the resolution of the equipments, and their structures could not be determined in detail.

Considering that the luminescent regions were estimated to be nonuniformly distributed, spatial composition fluctuation was investigated by micro energy dispersive X-ray spectroscopy (μEDX) measurements linked with transmission electron microscopy (TEM) observations. A typical type-C sample was lapped flat, and measured by μEDX with a in-plane resolution of $<5\text{nm}$. Hexagonal grain structure of the film was clearly observed by plan-view bright field image of scanning TEM (STEM), as shown in Fig.4.12. From the μEDX measurements linked with TEM observations, the solid composition of Cd was found to be spacially distributed, being concentrated at the grain boundary regions.

4.3.3 Discussion

The origin of blue luminescence is unknown, but multiple models of blue luminescence can be assumed. For example:

1. CdO dot-like regions: This model can be crossed out, as the blueshift of the luminescence peak ($2.3\text{eV} \rightarrow \sim 2.8\text{eV}$) is way too large for a dot with a barrier bandgap of 3.2eV .
2. ZnCdO with narrowed bandgap: This is also unlikely, because the blue luminescent films were obtained only under very narrow and strict growth conditions, and the luminescence peak did not shift gradually with varied growth conditions.
3. Unknown deep level of ZnO : This model is the most acceptable one among the models proposed here. In this case, as the absorbance below the ZnO bandgap was small, the blue luminescent

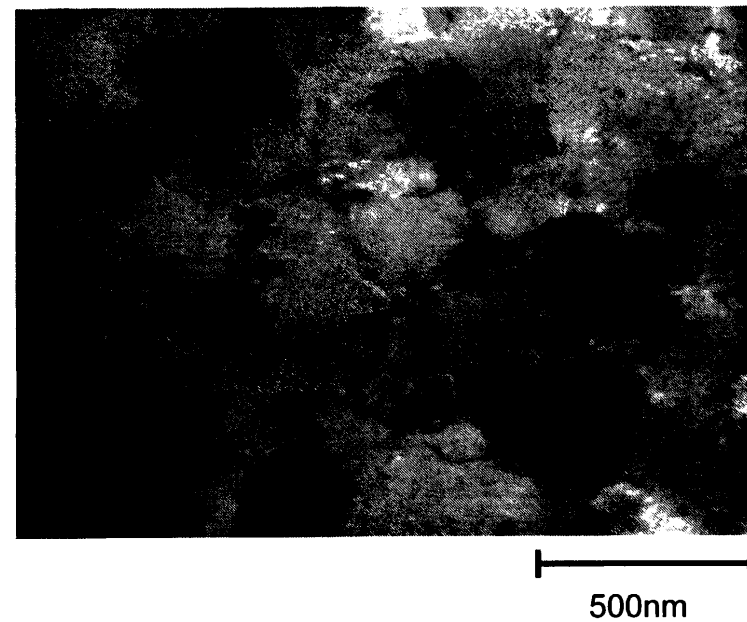


Figure 4.12: Plan-view bright-field STEM image of a typical type-C (blue-luminescent) ZnCdO film. Hexagonal grain structures were clearly observed.

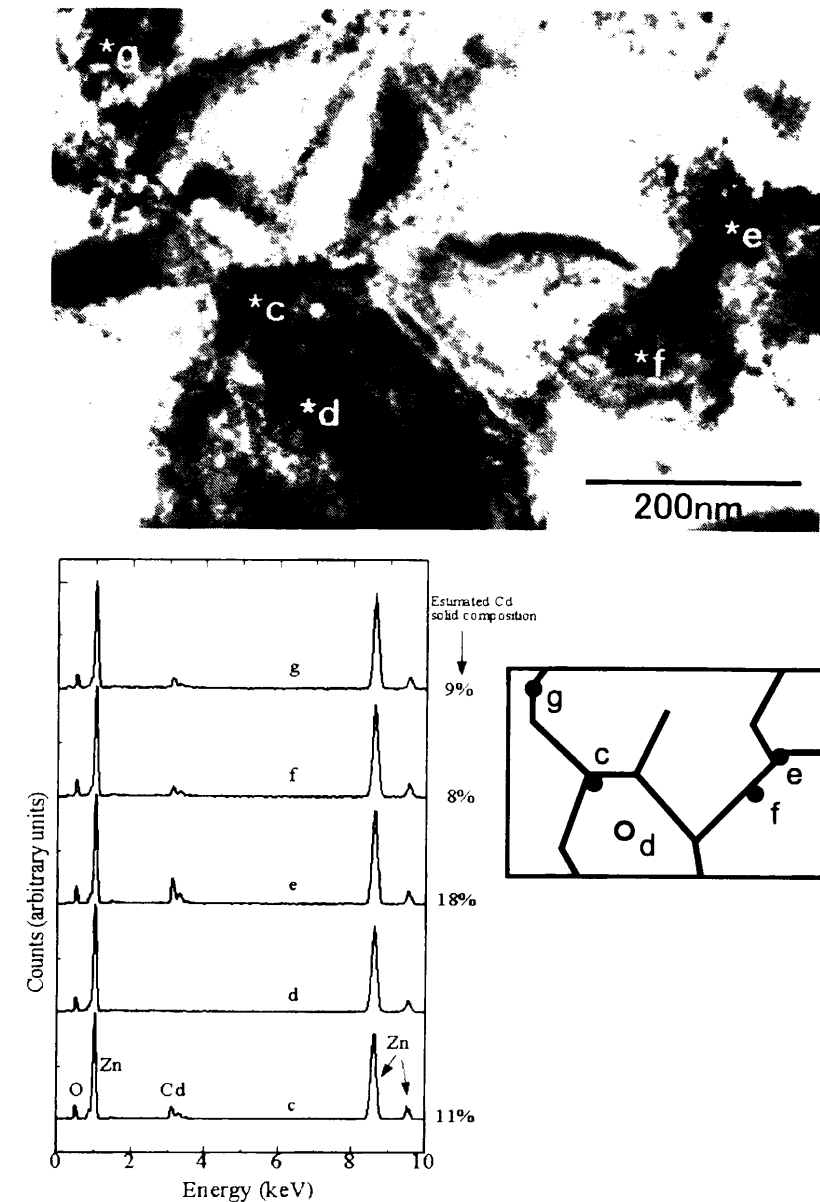


Figure 4.13: Summary of EDX measurements on a type C ZnCdO film. The drawing delineates the grain boundaries and measured points. The CdO composition was found to be concentrated at the grain boundaries. The solid composition of Cd (roughly estimated from EDX signal intensities) varied between 0~18% .

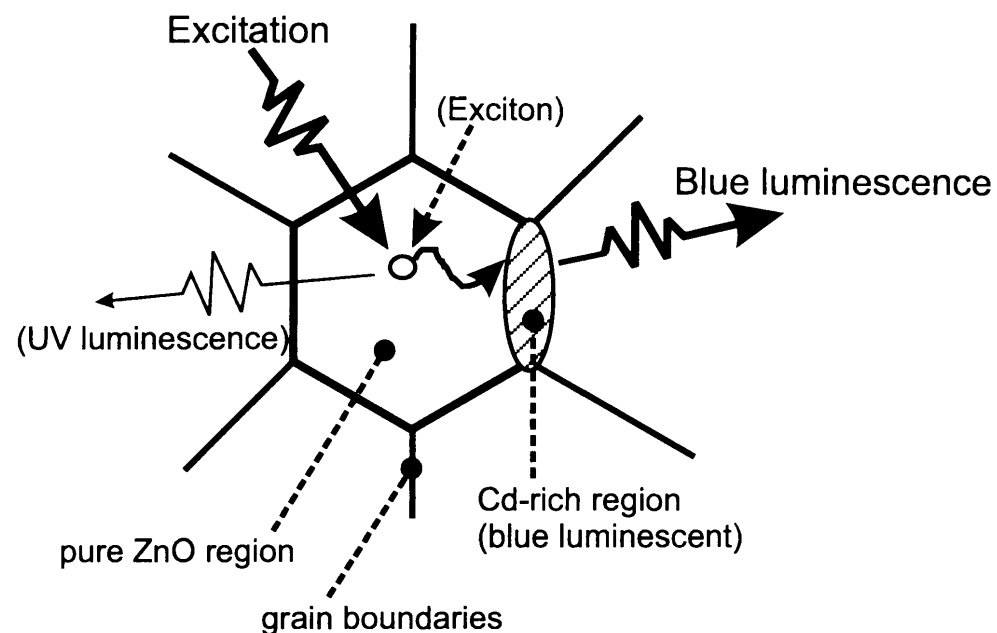


Figure 4.14: The model of spatially fluctuated ZnCdO film. The grain mostly consists of pure ZnO , and Cd is concentrated at the hexagonal boundary regions. The blue luminescent regions, which are small in their area, would be concentrated together at the boundaries. Excitons are trapped in the blue luminescent regions and radiatively recombine.

region must be small in their area. They would possibly be concentrated near the grain boundaries, where Cd atoms are concentrated. The presence of Cd atoms would have induced emergence of radiative recombination centers in ZnO . Recently, blue luminescence centered around $\sim 400\text{nm}$ from $\text{ZnO}:\text{Zn}$ was independently reported[6], which supports this model.

Independent of the above models, the excitons excited at the pure- ZnO region would have moved into the blue luminescent region to make radiative recombination, as sketched in Fig. 4.14. This mechanism agrees with the rapid decrease of NBE luminescence with higher temperatures. This may have supported the blue luminescence at higher temperatures,

where the carriers are expected to diffuse further.

4.4 Summary

In this chapter, alloying of ZnO with CdO by RSMBE, and the characteristics of the obtained $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ crystals was described.

The following achievements were described:

1. The composition of the films was found to have tendencies to be close to either pure ZnO or pure CdO . The properties of grown films changed sharply at the critical Cd composition of $x=3\sim 5\%$.
2. At specific growth conditions, blue photoluminescence was observed from the grown films. They were found to be spatially fluctuated in both luminescence intensity and Cd composition, with Cd concentrated at the hexagonal grain boundaries.
3. The blue luminescent films outwardly showed large Stokes shift of $\sim 500\text{meV}$. This blue luminescence was found to have a high internal quantum efficiency up to $\sim 20\%$.

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Chapter 5

Conclusions

This research work was done for two objectives; to obtain information and knowledge on growth of ZnO for optical device usages, and to exploit the possibility of ZnO-based compound semiconductors. More than half of this work was dedicated to evaluate and improve molecular beam epitaxy (MBE) techniques which were premature as growth methods for ZnO, using gas-source MBE (GSMBE) and radical-source MBE (RSMBE) methods. The rest of this work was dedicated to modify the optical properties and improve the functionality of ZnO by alloying with CdO, using RSMBE method.

In Chapter 2, GSMBE growth of ZnO using NO_2 as oxygen source was described. NO_2 was used for MBE growth of ZnO for the first time. It was shown that ZnO epitaxy occurs by simply irradiating NO_2 gas and Zn on the substrate, without using thermal cracking or activation by plasma. NO_2 and N_2O gases were effectively adsorbed by the liquid nitrogen shroud, and the residual pressure during growth of ZnO was maintained quite lower than the case of radical oxygen. Compared to the case of radical oxygen, the reproducibility was relatively low when NO_2 gas was used as oxidizer. Use of low-temperature buffers was shown to improve reproducibility. From these results, it was shown that use of NO_2 as oxidizer has advantages in GSMBE growth of ZnO under existence of liquid nitrogen shrouds. However, problems specific to the

used equipments obstructed further investigations.

In Chapter 3, in consideration of the results obtained in the previous chapter, RSMBE growth of ZnO was described. Effects and optimization of fundamental growth parameters were described. Growth on bulk ZnO substrates with different polarities was described. A specific type of surface roughening was found to be related to the difference in growth direction of ZnO crystal. Growth on sapphire substrates with different surface orientations was described, and *a* plane substrate was shown to be suitable than *c*-plane substrate for RSMBE growth of ZnO. Also, in the case of *c* plane sapphire, use of substrates with smooth surfaces was found to roughen the morphology of the overgrown ZnO films under the growth conditions applied in this work. Growth on sapphire substrates with different offset angles was described, and it was shown to improve the crystallinity of ZnO on *c*-plane substrate, while it causes tilting of ZnO *c*-axis on *a* plane substrates. These results are the base for extensive researches on MBE growth of ZnO-based compound semiconductors, and will help further improvements on the quality of ZnO crystals.

In Chapter 4, alloying of ZnO with CdO by RSMBE, and the characteristics of the grown $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ crystals were described. It was found that the properties of grown films change sharply around a critical Cd composition of $x=3\sim 5\%$. Near the critical Cd composition, blue photoluminescence at RT was observed for samples grown at a specific growth condition. Large Stokes shift of $\sim 500\text{meV}$ was outwardly observed on blue luminescent ZnCdO crystals. Both luminescence intensity and Cd composition were found to be concentrated at the boundaries of hexagonal grains. The blue luminescence was estimated to have high internal quantum efficiency up to $\sim 17\%$. These results have suggested the possibility of expanding the applicable wavelength range of ZnO based compound semiconductors to the visible region, with high luminescence efficiency.

The results obtained in this study have offered several useful information on ZnO epitaxy and investigation for ZnO based active semiconductor devices, which had been at their very infant stage of development and

still continuing to grow. These achievements would help exploitations on new optical devices utilizing excitons, and enhanced functionality and quality of present ZnO-based devices widely used in the industry.

Further improvement in the quality of ZnO films, especially suppression of donor concentration for conduction type control, is the most major task remaining for future investigations on growth of ZnO by RSMBE method.

Appendix

Table A-1: Comparison of GaN, ZnSe, and ZnO

Compound	ZnO	GaN	ZnSe
E_g (RT) [eV]	3.2~3.3 [1, 2]	3.39 [3]	2.715 [3]
E_g (0K) [eV]	3.43 ~ 3.44 eV [4]		
E_{ex} [meV]	59~63 meV [5, 4]	24 [6]	22 [7]
E_b	15 meV [8]	5.7 [9]	3.5 [8]
r_b	14~18 Å [5, 10]	29	45 [5]
m_e	0.24~0.28 [3, 10]	0.20 ($\parallel$) , 0.18 ($\perp$) [11]	0.15 ~ 0.17 [5]
m_{hh}	1.8 [3]	1.76 [11]	1.14 [3]
ε	8.84(c),8.47(a) [3]	10.4(c),9.5(a)	8.1
ε_{AC}	4.0 [3]	5.80	5.75
Structure	W*	W,ZB	ZB
L.C. [Å]	3.250(a),5.207(c) [12]	3.180(a),5.178(c)	5.667
M.P. [°C]	1970 [10]	1523	1793

*: ZnO: Transforms into rocksalt at > 95kbar [13]

(E_g : bandgap, E_{ex} : exciton binding energy, E_b : bi-exciton binding energy, r_b : bohr radius of exciton, m_e : effective mass of an electron, m_h : effective mass of a heavy hole, ε : relative dielectric constant(DC), ε_{AC} : relative dielectric constant(AC(lightwave region)), W: Wurtzite, R: Rocksalt, ZB: Zincblende, L.C.: lattice Constant, M.P.: melting point)

Table A-2: Bandgap, exciton binding energy, energy level of exciton of ZnO at low temperatures[4]

valence	bandgap [eV]	E_{ex} [meV]	energy level of exciton [eV]
A	3.4410	63.1	3.37785 (1s), 3.4252(2p)
B	3.4434	50.4	3.39296 (1s), 3.4308(2p)
C	3.4817	48.9	3.4327 (1s), 3.4694(2p)

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List of publications

5.1 Full length papers and letters

1. Keiichiro Sakurai, Daiji Iwata, Shizuo Fujita and Shigeo Fujita
"Growth of ZnO by Molecular Beam Epitaxy Using NO₂ as Oxygen Source"
Jpn. J. Appl. Phys., Vol.38, No.4B, April 1999, 2606-2608.
2. Keiichiro Sakurai, Masahiko Kanehiro, Ken Nakahara, Tetsuhiro Tanabe, Shizuo Fujita and Shigeo Fujita
"Effects of oxygen plasma condition on MBE growth of ZnO"
J. Cryst. Growth, Vol.209, No.2-3, February 2000, 522-525. *Note: directions of ZnO (+c/-c) is reversed in this paper.*
3. Keiichiro Sakurai, Masahiko Kanehiro, Ken Nakahara, Tetsuhiro Tanabe, Shizuo Fujita and Shigeo Fujita
"Effects of substrate offset angles on MBE growth of ZnO"
J. Cryst. Growth, Vol.214/215, June 2000, 92-94.
4. Keiichiro Sakurai, Takeshi Kubo, Daisuke Kajita, Tetsuhiro Tanabe, Hidemi Takasu, Shizuo Fujita and Shigeo Fujita
"Blue Photoluminescence from ZnCdO Films Grown by Molecular Beam Epitaxy"
Jpn. J. Appl. Phys., Vol.39, No.11B, November 2000, L1146-L1148.
5. Keiichiro Sakurai, Takeshi Kubo, Daisuke Kajita, Tetsuhiro Tanabe, Hidemi Takasu, Shizuo Fujita and Shigeo Fujita
"Composition fluctuation and luminescence properties of MBE grown textured ZnCdO films"
Appl. Phys. Lett., to be submitted.

5.2 Proceedings

1. Keiichiro Sakurai, Ken Nakahara, Tetsuhiro Tanabe, Shizuo Fujita and Shigeo Fujita
"Effects of sapphire substrate configurations on MBE growth of ZnO"
Materials Research Society Symposium Proceeding (conf. of 1999 MRS Fall Meeting, Symposium O, Boston, MA, USA), Vol.587 (2000), Session No.O6.2.1.
2. Keiichiro Sakurai, Takeshi Kubo, Ken Nakahara, Tetsuhiro Tanabe, Shizuo Fujita and Shigeo Fujita
"MBE Growth of ZnO on Miscut a-plane Sapphire Substrates"
Proceedings of The Third SANKEN International Symposium, Vol.57, March 2000, 306.

5.3 Papers presented at international conferences and meetings

1. Keiichiro Sakurai, Daiji Iwata, Shizuo Fujita and Shigeo Fujita
"MBE growth of ZnO using NO₂ as oxygen source"
The 17th Electronic Materials Symposium (Session F: 'Optoelectronic Materials'), July 8-10 (1998), Izu-nagaoka, Japan.
2. Keiichiro Sakurai, Daiji Iwata, Shizuo Fujita and Shigeo Fujita
"MBE growth of ZnO using NO₂ as oxygen source"
1998 International Conference on Solid Devices and Materials (Symposium C-7: 'Wide Gap Electronics and Optoelectronics'), September 7-10 (1998), Hiroshima, Japan.
3. Keiichiro Sakurai, Masahiko Kanehiro, Ken Nakahara, Tetsuhiro Tanabe, Shizuo Fujita and Shigeo Fujita
"Effects of oxygen plasma condition on MBE growth of ZnO"
The 7th Intl. Conf. on Chemical Beam Epitaxy and Related Growth Techniques (Session We2: 'Growth Mechanism and Growth Monitoring for Widegap Semiconductors'), July 27-30 (1999), Tsukuba, Japan.
4. Keiichiro Sakurai, Masahiko Kanehiro, Ken Nakahara, Tetsuhiro Tanabe, Shizuo Fujita and Shigeo Fujita
"Effects of substrate offset angles on MBE growth of ZnO"

The 9th International Conference on II-VI Compounds (Session Tu-P), November 1-5 (1999), Kyoto, Japan.

5. Keiichiro Sakurai, Ken Nakahara, Tetsuhiro Tanabe, Shizuo Fujita and Shigeo Fujita
"Effects of sapphire substrate configurations on MBE growth of ZnO"
MRS Fall Meeting (Symp.O6: 'Substrate Engineering'), November 29 - December 3 (1999), Boston, MA, USA.
6. Keiichiro Sakurai, Takeshi Kubo, Ken Nakahara, Tetsuhiro Tanabe, Shizuo Fujita and Shigeo Fujita
"MBE Growth of ZnO on Miscut a-plane Sapphire Substrates"
The Third SANKEN International Symposium (Session P2: 'ZnO and II-VI materials and Devices'), March 14-15 (2000), Osaka, Japan.
7. Keiichiro Sakurai, Ryo Tatsumi, Takeshi Kubo, Ken Nakahara, Tetsuhiro Tanabe, Shizuo Fujita and Shigeo Fujita
"Effects of Substrate Offset Angles on MBE Growth of ZnO (II)"
2000 Electronic Materials Conference (Session AA: 'Novel Materials'), June 21-23 (2000), Denver, CO, USA.
8. Keiichiro Sakurai, Daisuke Kajita, Takeshi Kubo, Ken Nakahara, Tetsuhiro Tanabe, Shizuo Fujita and Shigeo Fujita
"Optical Properties of ZnCdO Films Grown by Plasma-Assisted MBE"
The 2000 U.S. Workshop on the Physics and Chemistry of II-VI Materials (Session: 'ZnO'), October 30 - November 1 (2000), Albuquerque, NM, USA.

5.4 Domestic Meetings (in Japanese)

1. 櫻井啓一郎、岩田大司、藤田静雄、藤田茂夫
「NO₂ を用いた ZnO 薄膜の MBE 成長」
1998 年春期 第 45 回応用物理学関係連合講演会 29a-ZN-5、東京工科大学、1998 年 3 月
2. 櫻井啓一郎、金廣正彦、田辺哲弘、中原 健、藤田静雄、藤田茂夫
「ZnO の MBE 成長における成長温度と表面モフォロジー」
1999 年春期 第 46 回応用物理学関係連合講演会 29p-Q-2、東京理科大学、1999 年 3 月

3. 櫻井啓一郎、田辺哲弘、中原 健、藤田静雄、藤田茂夫
「ZnO の MBE 成長におけるサファイア基板オフ角の影響」
1999 年秋期 第 60 回応用物理学会学術講演会 2a-ZY-7、甲南大学、1999 年 9 月
4. 尾形健一、櫻井啓一郎、藤田静雄、藤田茂夫、松重和美
「MBE 成長 ZnO の熱処理効果」
1999 年秋期 第 60 回応用物理学会学術講演会 2a-ZY-9、甲南大学、1999 年 9 月
5. 櫻井啓一郎、今井大輔、西原隆治、篠原真、田辺哲弘、中原 健、藤田静雄、藤田茂夫
「ZnO の MBE 成長におけるサファイア基板オフ角の影響 (II)」
第 47 回応用物理学関係連合講演会 29a-YL-5、青山学院大学、2000 年 3 月
6. 今井大輔、西原隆治、篠原真、櫻井啓一郎、田辺哲弘、中原 健、藤田静雄、藤田茂夫
「ZnO(0001) エピタキシャル薄膜における 1/2 ユニットステップ構造の評価」
第 47 回応用物理学関係連合講演会 29p-YL-1、青山学院大学、2000 年 3 月
7. 櫻井啓一郎、久保健、梶田大介、田辺哲弘、高須秀視、藤田静雄、藤田茂夫
「MBE 成長 ZnCdO 薄膜の CdO 固溶限界と物性変化」
第 61 回応用物理学会学術講演会 5p-Z-7、北海道工業大学、2000 年 9 月
8. 久保健、櫻井啓一郎、梶田大介、田辺哲弘、高須秀視、藤田静雄、藤田茂夫
「MBE 成長 ZnCdO の光学的評価」
第 61 回応用物理学会学術講演会 5p-Z-8、北海道工業大学、2000 年 9 月
9. 櫻井啓一郎、高木豪士、梶田大介、久保健、田辺哲弘、高須秀視、藤田静雄、藤田茂夫
「青色発光 ZnCdO 薄膜の光物性と発光機構」
第 48 回応用物理学関係連合講演会、明治大学、2001 年 3 月 (発表予定)

5.5 Related publications

1. Jun Suda, Masahiro Ogawa, Keiichiro Sakurai, Yoichi Kawakami, Shizuo Fujita and Shigeo Fujita
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Journal of Crystal Growth, Vol.184/185 (1998) 863-866.
2. Kenichi Ogata, Keiichiro Sakurai, Shizuo Fujita, Shigeo Fujita and Kazumi Matsushige
"Effects of thermal annealing of ZnO layers grown by MBE"
J. Cryst. Growth, Vol.214/215, June 2000, 312-315.

5.6 Award

- Outstanding Student Paper presented at the 2000 U.S. Workshop on the Physics and Chemistry of II-VI Materials, October 30 - November 1 (2000), Albuquerque, NM, USA.