

# Improved Electrical Properties in ZnO Semiconductor Films Grown by Radical Source MBE

K. Iwata, P. Fons, A. Yamada, K. Matsubara, K. Nakahara\*, H. Takasu\* and S. Niki  
Electrotechnical Laboratory 1-1-4 Umezono, Tsukuba, Ibaraki, JAPAN 305-8568

\*ROHM Corporation, 21 Mizosaki-cho Saiin, Kyoto, JAPAN 615-8585

Fax: 81-298-61-5612, e-mail: iwata355@etl.go.jp

We have grown high quality ZnO epilayers on a-plane sapphire substrates by RS(radical source)-MBE. A flat and smooth surface has been obtained for ZnO grown under Zn rich condition with initial growth done using a low temperature buffer layer. RHEED pattern showing (3x3) surface reconstruction was observed during growth. A high Zn flux is required to grow ZnO at high temperature. High temperature ZnO growth has made possible improvement in ZnO electrical properties. ZnO epilayers with electron mobilities of over  $\sim 120 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and electron concentrations of  $< 6 \times 10^{16} \text{ cm}^{-3}$  have been grown.

**Key words:** ZnO, Zinc oxide, electron mobility, MBE, Radical source MBE, Epitaxial film

## 1 INTRODUCTION

ZnO device applications are numerous for example, blue-violet optical emission devices, wide bandgap high power devices, SAW (surface acoustic wave) devices and ferro-electric memories, among others. If it were possible to combine all of those applications monolithically, semiconducting ZnO will play an important role in their fabrication. Semiconducting ZnO has thus gathered much attention as a hub for monolithic multi functional devices as well as for optical device applications due to its 3.4 eV direct bandgap, and large exciton binding energy of 60 meV.[1] For device applications, however, p-type ZnO must be realized.[2, 3] In order to investigate p-type doping mechanisms, intrinsic high quality ZnO single crystal thin films are necessary.[4] In 1999, high quality ZnO bulk crystal becomes commercially available in large part due to fine control of impurity levels.[5] Purity control is also an important factor in obtaining high quality semiconducting ZnO. [6] MBE has the advantage of in-situ RHEED observations which can be used to provide immediate feedback on epilayer quality. In this paper, we report on improvement of ZnO electrical properties based upon the optimization of growth kinetics.

## 2 EXPERIMENTAL

ZnO layers were grown by RS (radical source)-MBE using a RF (radio frequency) radical cell with an electrostatic ion trap operated at  $\sim 300 \text{ V}$  onto a-plane sapphire substrates. The sources used were elemental Zn with a purity of 7N and O<sub>2</sub> gas of 6N purity.[1, 7] The Zn flux was measured by an ion gauge at the sample position and was varied from  $7 \times 10^{-7}$  to  $4 \times 10^{-6}$  Torr. The oxygen flow rate was 0.3 SCCM. (1120) (a-plane) sapphire substrates were used for ZnO growth making possible uniaxial

locked growth (ULG) as reported in Ref.[8] and [9]. ZnO layers were grown at 550°C after growth of a low temperature ZnO buffer at 350°C. The RF power of the O<sub>2</sub> radical source during growth was 300 W. Sapphire a-plane substrates were heated in a load lock chamber before growth at 400°C to remove contamination and thermally cleaned at above 700°C for 15 min in the growth chamber without plasma-enhanced oxygen irradiation from the radical source just prior to the growth of the ZnO low temperature buffer. The growth rate of the ZnO layer was 0.25-0.50  $\mu\text{m/hr}$  and the thickness of the as-grown films was 0.4-0.9  $\mu\text{m}$ . The substrate temperature was measured by an infrared optical pyrometer calibrated by the melting point of an Al-Ge eutectic (420°C) and Al (660°C). The crystalline quality of the ZnO layers was determined by reflection high energy electron diffraction (RHEED), AFM(atomic force microscopy) surface observation and X-ray diffraction (XRD) pole figures using Cu K $\alpha_1$  radiation. Photoluminescence (PL) measurements were conducted at 1.4 K using a He-Cd laser (325 nm, 19 mW) as an excitation source. Carrier concentration, resistivity and carrier mobility were measured by the Van der Pauw method.

## 3 RESULTS AND DISCUSSION

### 3.1 In situ observation during growth

The surface of the final ZnO film as grown by RS-MBE using a low temperature ZnO buffer layer exhibited a (3x3) reconstruction. A photograph of the (3x3) reconstructed surface observed by RHEED is shown in Fig.1. This reconstruction is present when ZnO is grown under Zn rich conditions.

A phase map of the observed surface reconstructions as a function of Zn flux is shown in Fig.2. This is similar to that present in GaN growth un-

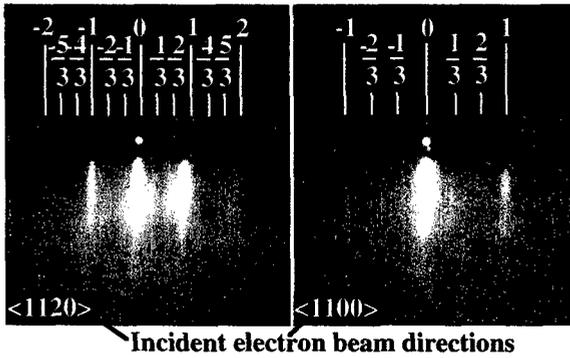


Figure 1: In situ RHEED observations of ZnO (3x3) reconstruction surface during growth.

der a Ga excess.[10] For growth conditions typically used, the growth rate is exclusively determined by the oxygen flux. In this case, it is possible to define a steady-state free Zn surface coverage  $\theta_{Zn}$ . The temperature dependence of  $\theta_{Zn}$  is expected to be a Boltzman-like or

$$\theta_{Zn} = A \exp(-E_a/kT_s) \quad (1)$$

where  $T_s$  is the growth temperature,  $E_a$  is a thermal activation energy and the pre-exponential factor  $A$  is assumed to be temperature independent.[11]

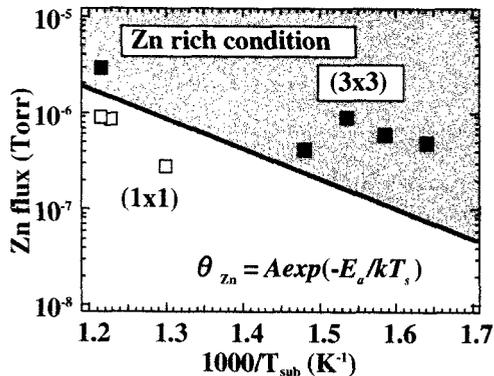


Figure 2: The boundary line between the (3x3) and the (1x1) reconstruction indicating the ZnO surfaces grown under oxygen rich and Zn rich conditions, respectively.

The boundary between the (3x3) and (1x1) reconstruction is given by the curve shown in Fig.2. This is consistent with the surface reconstructions reported in the literature in which sample surfaces were thermally cleaned without the presence of a Zn flux [12, 13, 14]. The ZnO growth rate in the presence of a (3x3) surface reconstruction is limited by the amount of radical oxygen supply. It is speculated that Zn rich conditions lead to a Zn excess and an oxygen poor surface and this surface composition change lead to the formation of the (3x3) reconstruction.

### 3.2 Optical property

PL spectra obtained from ZnO samples grown un-

der Zn rich conditions are shown in Fig.3. Strong near band edge excitonic emissions are observed with no deep emissions at 2.2 eV.

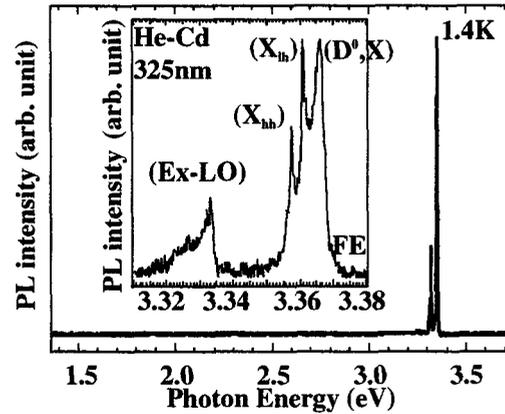


Figure 3: PL spectra of ZnO on a-plane sapphire substrate with near band edge excitonic emission at 3.38 eV with no deep emission at 2.2 eV.

In addition, many sharp peaks were observed around near band edge. A free exciton (FE) PL peak at 3.377 eV is visible. The PL peaks at 3.366 eV, 3.3610 eV and 3.357 eV represent donor-bound-exciton transitions ( $D^0, X$ ) while the emissions at 3.333 eV, 3.326 eV and 3.317 eV are due to LO phonon replicas.[15] These PL spectra indicates improved quality of the ZnO layers.

### 3.3 Electrical property

Figure 4 shows the room temperature electrical properties of ZnO thin films.

The solid line in Fig.4 indicates the theoretical calculated value for electron scattering in ZnO, which can be used as a guide for improving ZnO electrical properties. The total electron mobility  $\mu_{total}$  is given by;

$$\frac{1}{\mu_{total}} = \sum \frac{1}{\mu_i} = \frac{1}{\mu_{pop}} + \frac{1}{\mu_{acp}} + \frac{1}{\mu_{iis}} \quad (2)$$

where  $\mu_{pop}$  is electron mobility due to polar optical photon scattering,  $\mu_{acp}$  is that due to acoustic phonon scattering and  $\mu_{iis}$  is that due to ionized impurity scattering as given by the Brooks-Herring approximation. The electron mobility of  $\mu_{pop}$ ,  $\mu_{acp}$  and  $\mu_{iis}$  are given by;

$$\mu_{pop} = \frac{0.199(T/300)^{1/2} (e/e_c^*)^2 (m_0/m^*)^{3/2}}{(10^{22} M)(10^{23} v_a)(10^{-13} \omega_0)} (e^z - 1)G(z) \quad (3)$$

$$G(z) = 2 \times 10^{-5} z^6 + 8.5 \times 10^{-4} z^5 + 1.4 \times 10^{-2} z^4 - 0.1z^3 + 0.5z^2 - 0.7z + 1.0$$

$$z = \hbar\omega_0/k_B T$$

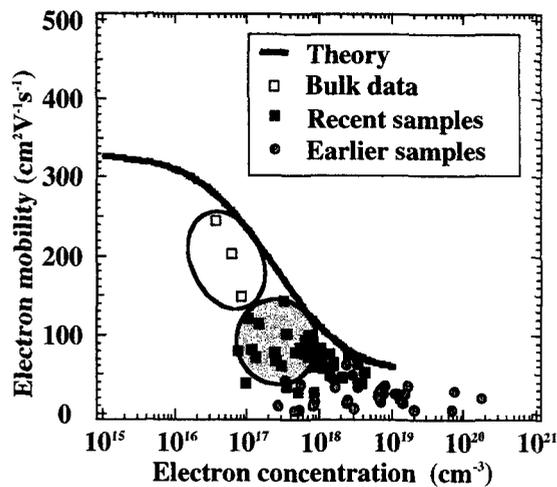


Figure 4: Calculated values for electron mobility in ZnO. Bulk single crystal results are shown as open squares and thin films results on a- and c-plane sapphire substrates are shown as filled squares and circles, respectively.

$$\mu_{acp} = \frac{2^{2/3} \pi^{1/2} e \hbar^4 \rho_l^2}{3(m^*)^{5/2} (k_B T)^{3/2} E_l^2} \quad (4)$$

$$\mu_{iis} = \alpha \frac{k_s^2 T^{3/2}}{N_i (m^*/m_0)^{1/2}} \left[ \ln(1+b) - \frac{b}{1+b} \right]^{-1} \quad (5)$$

$$\alpha = 3.284 \times 10^{15}$$

where  $e_c^*$  is the Callen effective charge,  $M$  is the reduced mass,  $v_a$  is the unit cell volume,  $\omega_0$  is the angular frequency of the zone-center LO phonons,  $E_l$  is the deformation potential,  $\rho$  is the mass density and  $k_s$  is the static dielectric constant.[16] Recently high quality ZnO bulk crystals have been fabricated by the Eagle-Pitcher Corporation in U.S.A. These bulk crystals have the best reported electrical properties at present and the mobility and the carrier concentration values of these samples are plotted in Fig.4. The electrical properties for our samples are also shown in Fig.4. The electrical properties of these recent ZnO samples are now approaching the Eagle-Pitcher results.

### 3.4 Resistivity control of n-ZnO

Figure 5 shows the resistivity dependence on n-type ZnO carrier density at room temperature. ZnO resistivity can be varied over a wide range from  $2 \times 10^{-4} \Omega \text{cm}$  to  $4 \times 10^3 \Omega \text{cm}$ . We used two dopants to obtain low and high resistivity ZnO. Ga was used for low resistivity and Nitrogen for high resistivity samples. Ga is a suitable dopant for MBE.

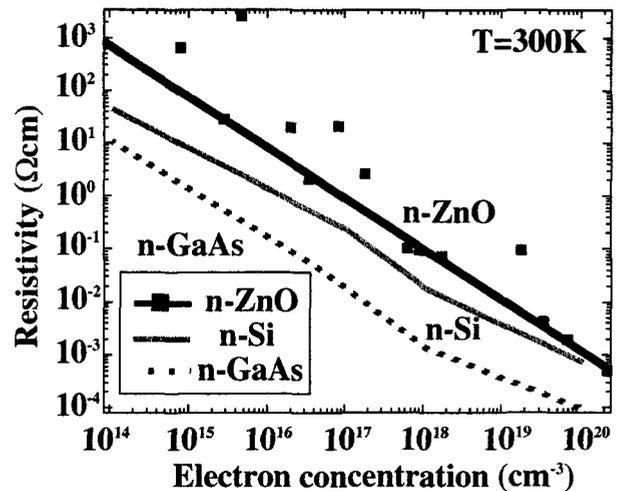


Figure 5: Resistivity dependence on n-type ZnO carrier density. Dopant for low and high resistive ZnO is Ga and Nitrogen, respectively.

It is speculated that acceptors induced by Nitrogen compensate donors in the high resistivity region. The thin and dot lines in Fig.5 indicate the case of n-type Si and GaAs, respectively. A comparison of the values shown in Fig.5 indicates that the n-ZnO is already practical for fabrication of majority carrier devices.

## 4 CONCLUSIONS

We have grown high quality ZnO crystal on a-plane sapphire substrates. A Zn rich surface composition leads to a (3x3) reconstructed surface. The control of surface composition and lattice polarity of ZnO growth by in situ RHEED observation have made possible the improvement of ZnO electrical properties. ZnO electron mobilities of  $120 \text{ cm}^2/\text{Vs}$  and electron concentrations of  $7 \times 10^{16} \text{ cm}^{-3}$  were obtained. It has been varied ZnO resistivity widely from  $2 \times 10^{-4} \Omega \text{cm}$  to  $4 \times 10^3 \Omega \text{cm}$ . These results are promising for fabrication of ZnO devices.

### Acknowledgements

The authors would like to express their thanks to Dr. H. Shibata, Dr. M. Watanabe and Dr. H. Yajima for useful discussions.

## References

- [1] K. Iwata, P. Fons, A. Yamada, K. Matsubara, K. Nakahara, H. Takasu and S. Niki, *Phys. Stat. Sol. (a)* 180, 287 (2000).
- [2] M. Joseph, H. Tabata and T. Kawai, *Jpn. J. Appl. Phys.* 38, L1205 (1999).
- [3] K. Minegishi, Y. Koiwai, Y. Kikuchi, K. Yano, M. Kasuga and A. Shimizu, *Jpn. J. Appl. Phys.* 36, L1453 (1997).

- [4] K.Iwata, P.Fons, S.Niki, A.Yamada and K.Matsubara , *J.Cryst.Growth.* 209 , 526 (2000).
- [5] D.C.Look, D.C.Reynolds, J.R.Sizelove, R.L.Jones, C.W.Litton, G.Cantwell and W.C.Harsch , *Solid State Communications.* 105, 399 (1998).
- [6] K.Iwata, P.Fons, A.Yamada, K.Matsubara, K.Nakahara, T.Tanabe, H.Takasu and S.Niki, *J.Cryst.Growth.* 214/215, 50 (2000).
- [7] P.Fons, K.Iwata, S.Niki, A.Yamada and K.Matsubara , *J.Cryst.Growth.* 201/202, 627 (1999).
- [8] P.Fons, K.Iwata, A.Yamada, K.Matsubara and S.Niki, *J.Cryst.Growth.* 209 , 532 (2000).
- [9] P.Fons, K.Iwata, A.Yamada, K.Matsubara and S.Niki, *Appl.Phys.Lett.* 77, 1801 (2000).
- [10] K.Iwata, H.Asahi, S.J.Yu, K.Asami, H.Fujita, M.Fushida and S.Gonda , *Jpn.J.Appl.Phys.*, 35, L289 (1996).
- [11] P.Hacke, G.Feuillet, H.Okumura and S.Yoshida , *Appl.Phys.Lett.* 69, 2507 (1996).
- [12] S.H.Overbury, P.V.Radulovic, S.Thevuthasan, G.S.Herman, M.A.Henderson and C.H.F.Peden , *Surface Science* 410, 106 (1998).
- [13] M.Galeotti, A.Atrei, U.Bardi, G.Rovida, M.Torrini, E.Zanazzi, A.Santucci and A.Klimov , *Chemical Physics Letters* 222 , 349 (1994).
- [14] M.Sambi, G.Gwanozzi, G.A.Rizzi, M.Casarin and E.Tondello , *Surface Science* 319, 149 (1994).
- [15] D.C.Reynolds, D.C.Look, B.Jogai, C.W.Litton, T.C.Collins, W.C.Harsch and G.Cantwell , *Physical Review B* 57, 12 151 (1998).
- [16] J.D.Wiley, R.K.Willardson, A.C.Beer , *Semiconductors and Semimetals* 10, 91-174 (1975).

(Received December 8, 2000; Accepted December 27, 2000)