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Zinc Beam Flux Dependence of MBE-ZnO Growth

Hiroyuki Kato, Michihiro Sano, Kazuhiro Miyamoto and Takafumi Tao[1]

Stanley Electric Co., Ltd., Research & Development Center
1-3-1 Eda-Nishi, Aoba-ku, Yokohama 225-0014, Japan
Phone: +81-45-911-1111 Fax: +81-45-911-0057 E-mail: h.kato@yrd.stanley.co.jp
[1]Tohoku University, Intitute for Materials Research
2-1-1 Katahira, Aoba-ku, Sendai 980-8579, Japan

1. Introduction

Zinc oxide (ZnO) is one of attractive materials for high-efficiency ultraviolet laser diodes (LD) and light-emitting diodes (LED) because ZnO has a direct energy gap of 3.37 eV with a large excitonic binding energy of about 60 meV at room temperature (RT). Optically pumped RT excitonic lasing from ZnO has been reported [1,2] and excitonic stimulated emission has been observed at temperature up to 550°C [3].

Stoichiometry control in compound semiconductors is important for obtaining high-quality crystals. Molecular beam epitxy (MBE) growth of Zn chalcogenides such as ZnSe, ZnTe and ZnS can be obtained stoichiometry in epilayers by controlling the suitable VI/II ratio [4]. However, systematic studies on O/Zn ratio in ZnO growth have been insufficient yet. In this study, the O/Zn ratio in ZnO growth was varied by adjusting the Zn beam flux (V_{Zn}) under fixed oxygen condition. Here, we report the dependence of the V_{Zn} on the growth and crystalline quality of ZnO epilayers grown by plasma-assisted MBE. High-quality ZnO was obtained under stoichiometric condition, namely, when the O/Zn ratio was optimal. We have demonstrated for the first time that stoichiometric ZnO showed minimal dislocation density and highest electron mobility, compared with non-stoichiometric ZnO.

2. Experimental procedure

ZnO epilayers were grown on *c*-plane sapphire substrates with ZnO/MgO double buffer layers under various V_{Zn} by plasma-assisted MBE. The molecular beam sources were elemental zinc (7N), elemental magnesium (7N) and oxygen radio frequency (RF) plasma (O_2 gas with 6N grade). A substrate was degreased by ultrasonic cleaning in dichloromethane and acetone, and then was etched in a chemical solution of H_3PO_4:H_2SO_4=1:3 at 110°C for 30 min. ZnO epilayers were grown by the following five steps. Step 1 is thermal cleaning of the substrate, where the substrate was cleaned by heating at 800°C for 30 min under an atomic hydrogen irradiation in the growth chamber. The atomic hydrogen was generated by a thermal cracking of molecular hydrogen (2.0 sccm) on a heated tungsten filament at 1800°C. Step 2 is MgO buffer growth, where MgO buffer of about 1-nm thick was grown on the cleaned substrate at 800°C. Step 3 is low-temperature (LT) ZnO buffer growth, where LT-ZnO buffer layer of about 10-nm thick was grown on the MgO buffer at 500°C. Step 4 is buffer annealing, where the buffer was annealed at 900°C for 3 min to improve the surface smoothness of the buffer layer. Step 5 is high-temperature (HT) ZnO growth, where undoped ZnO layers were grown on the annealed buffer under various V_{Zn} from 2.2 to 8.3 Å/s at 700°C for 3-5 h. During the HT-ZnO growth, the oxygen flow rate was 3.0 sccm the RF power was 300 W. X-ray diffraction (XRD) and Hall effect measurements were used to characterize these ZnO layers.

3. Results and Discussion

Fig.1 plots the growth rate of ZnO layers against the V_{Zn}. ZnO growth was limited by Zn beam flux when V_{Zn} < 5.1 Å/s, and by oxygen radical flux when V_{Zn} > 5.1 Å/s. Therefore, ZnO layer was grown under stoichiometric condition when V_{Zn} = 5.1 Å/s.

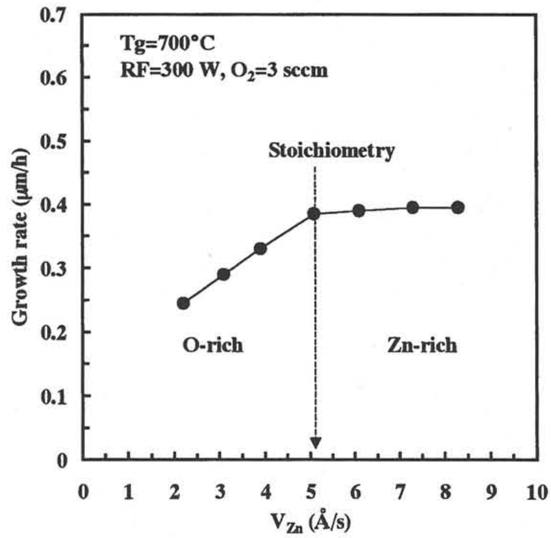

Fig. 1 Growth rate of ZnO layers as a function of Zn beam flux V_{Zn}.

The crystalline quality of the ZnO layers was evaluated by measuring symmetric (0002) and skew symmetric (10-10) ω-rocking curves using an X'-pert

MRD system (Philips). The (0002) XRC parallel to the ZnO surface shows the declination of tilt angle, whereas the (10-10) XRC perpendicular to the surface shows the declination of twist angle. In wurtzite GaN with the same crystal structure as ZnO, it is known that the tilt is related to the density of screw threading dislocations (TD) with Burgers vector b = <0001>, while the twist is related to the density of edge TD with b = <11-20> [5]. Fig.2 shows the dependence of full width at half maximum (FWHM) of X-ray rocking curves (XRC) on V_{Zn}. The FWHM of (0002) XRC are 42-78 arcsec which show that ZnO layers have high crystalline quality with high-oriented and low screw-TD densities, independent of V_{Zn}. However, the FWHM of (10-10) XRC strongly depends on V_{Zn}. The FWHM increases with decreasing V_{Zn} from stoichiometric condition (V_{Zn} = 5.1 Å/s), whereas the FWHM is constant or slightly increases when $V_{Zn} \geq 5.1$ Å/s. The narrowest FWHM of (10-10) XRC is 720 arcsec when V_{Zn} = 5.1 Å/s. This shows that ZnO grown under stoichiometric condition has high crystalline quality with low TD densities and O-rich ZnO contains a number of edge-TD densities compared with stoichiometric and Zn-rich ZnO.

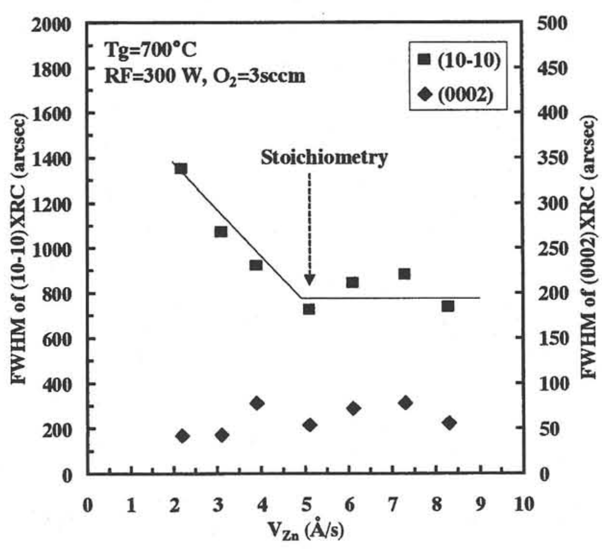

Fig. 2 FWHM of symmetric (0002) and skew symmetric (10-10) XRC as a function of Zn beam flux V_{Zn}.

The electrical properties such as mobility and carrier concentration of the ZnO layers were evaluated by Hall effect measurement using van der Pauw method. Fig.3 shows the dependence of electron mobility and residual carrier concentration on V_{Zn}. The mobility decreases with deviation from stoichiometry and the optimal mobility is 130 cm^2/Vs when V_{Zn} = 5.1 Å/s. We note that the carrier concentration increases at the part of O-rich condition. This increase in carrier concentration would be caused by point defects such as oxygen vacancies and interstitial Zn atoms generated by the distortion around many edge-TD.

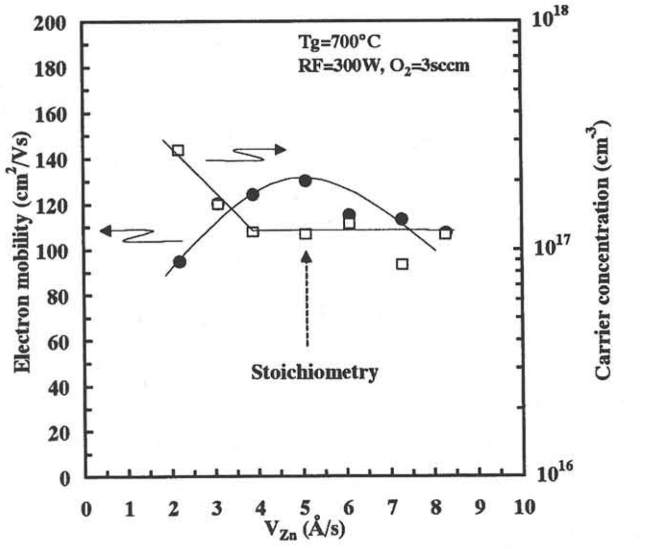

Fig.3 Electron mobility and carrier concentration of ZnO layers as a function of Zn beam flux V_{Zn}.

4. Conclusions

We have investigated the V_{Zn} dependence of ZnO grown by MBE. High crystalline quality of ZnO epilayers grown under stoichiometric condition was confirmed by XRD and Hall effect measurements. The FWHM of (10-10) XRC showed 720 arcsec and optimal electrical properties were electron mobility of 130 cm^2/Vs and residual carrier concentration of 1.2×10^{17} cm^{-3} when V_{Zn} = 5.1 Å/s.

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