Extended Abstracts of the 2012 International Conference on Solid State Devices and Materials, Kyoto, 2012, pp1059-1060

Direct heteroepitaxial growth of ZnO over GaN crystal in aqueous solution

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1. Introduction

Zinc oxide (ZnO) has a direct wide band gap, high thermal and electrical conductivities, and a high refractive index, these properties of which are very promising for optoelectronic applications. Moreover, ZnO has the same crystalline symmetries as GaN, with lattice mismatches of only 1.8% and 0.4% for the *a*-axis and *c*-axis, respectively. Therefore, it is expected that ZnO is a most suitable material for GaN-based high power optical devices i.e a transparent electrode [1] for light emitting diodes (LEDs) and an optical confinement layer [2] for laser diodes (LDs).

Generally, ZnO films on GaN-based optical devices have been prepared by vapor phase growth such as metal organic chemical vapor deposition (MOCVD) [1]. To obtain high-quality ZnO films, high temperature growth and/or thermal annealing is essential for vapor phase growth. However, high temperatures above 500˚C easily induce an intermediate layer of Zn, Ga and O with high resistivity such as $ZnGa_2O_4$ [1]. In contrast, an aqueous solution process has the advantage of being able to grow ZnO at a low temperature with inexpensive manufacturing equipment. The low temperature growth prevents the intermediate layer. The formation of an ohmic contact is expected at the ideal ZnO/GaN junction.

Recently, Kim et al. [3] demonstrated ZnO heteroepitaxial growth on GaN by hydrothermal synthesis at 90˚C using two-step process. In the first step, a discontinuous ZnO thin film was deposited on GaN as a seed layer. In the second step, a dense and continuous ZnO film was grown on the seed layer. The ZnO film [3] showed n-type conduction with a carrier concentration of 3.5×10^{18} cm^{-3} and a relatively low electron mobility of 10.3 cm^2/Vs. In this study, we focused on the direct growth of ZnO films on GaN without a seed layer to achieve the ideal ZnO/GaN junction. The epitaxial ZnO films were successfully grown on GaN by aqueous deposition under atmospheric pressure at a low temperature of 70˚C. We also demonstrated the excellent structural and electrical properties of the ZnO films.

2. Experiment and results

In our previous report [4], the ZnO homoepitaxial films were grown by chemical bath deposition (CBD) on Al_2O_3 substrates using a ZnO seed layer prepared by MOCVD. In this study, the ZnO films were grown directly over GaN by the CBD. Commercial n-GaN/Al_2O_3 (0001) (TDI, Inc.) was used as a substrate. The thickness of the Si-doped n-GaN layers was 5 μm, and the carrier concentration was determined to be (1-3) $\times 10^{18}$ cm^{-3} by capacitance-voltage (*C-V*) characteristics with a mercury probe. The growth solution was prepared by dissolving 0.1 mol/L zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and 0.1 mol/L hexamethylenetetramine (HMT, $(CH_2)_6N_4$) in deionized water. The substrates were immersed in the growth solution. The ZnO growth was carried out by heating the growth solution at 70˚C for 3 h. After ZnO growth, the samples were rinsed in deionized water and dried at 105˚C for 10 min.

We characterized the film structures with X-ray diffraction (XRD). Only a single phase of wurtzite-type ZnO and GaN was observed from ω-2θ scans. Both the ZnO film and the GaN layer were highly oriented along the *c*-axis. We evaluated the crystal quality from the ω-scans for the (0006) diffraction peaks of ZnO and GaN. The full width at half maximum (FWHM) of the (0006) diffraction peaks were 0.22˚ and 0.10˚ for ZnO and GaN, respectively. Figure 1 shows the in-plane, φ-scan orientation relationship between the ZnO film and the GaN layer using ZnO and GaN (20-22) reflections. Clear six-fold symmetry was observed, indicating that the ZnO film was epitaxially grown on the GaN layer with an orientation relationship of $(0001)[11\text{-}20]_{ZnO} \| (0001)[11\text{-}20]_{GaN}$. These results indicate that the high-quality epitaxial ZnO film on the n-GaN/Al_2O_3 substrate was obtained by CBD under atmospheric pressure and at a low temperature of 70˚C.

The cross-sectional profiles of the ZnO films were observed with a scanning electron microscope (SEM), as shown in Fig. 2(a). Continuous and highly dense ZnO films were obtained. Grain boundaries in the ZnO films were not observed. The thickness of the ZnO films was 500 - 700 nm. The surface morphology was evaluated with an atomic force microscope (AFM). Figure 2(b) shows an AFM image of the ZnO film in a 5 × 5 μm^2 area. The surface of the ZnO film was smooth with root-mean-square roughness (R_{rms}) values of 6 nm. Furthermore, we observed the interface between the ZnO and GaN with a transmission electron microscope (TEM), as shown in Fig. 3. Crystal lattice fringes were clearly observed. The lattice plane spacing was 0.52 nm, corresponding to the ZnO (0001) planes. We determined the steepness of the interface between the ZnO and GaN without an intermediate layer.

We carried out Hall measurements of the ZnO films on insulating i-GaN/Al_2O_3 substrates with a high resistivity greater than 1×10^6 Ωcm. The electrical property of the ZnO film exhibited n-type conduction with a carrier concentration of 6.9×10^{18} cm^{-3}, an electron mobility of 41 cm^2/Vs, and a resistivity of 2.2×10^{-2} Ωcm. In spite of a higher residual carrier concentration, the electron mobility of the ZnO film in this study was four times that of the ZnO film [3] grown by hydrothermal synthesis at 90°C. This is probably due to high-crystalline quality of ZnO films formed on the GaN, as mentioned above.

We also evaluated the specific contact resistance (ρ_c) of the ZnO/n-GaN junction by circular transmission line model (CTLM) [5]. The inner radius of the CTLM pad was 50 μm, and the distance (d) between the inner and the outer pads was 20 - 70 μm. Figure 4 shows the typical *I-V* characteristic at the ZnO/n-GaN interface with d = 50 μm. We calculated the ρ_c from the linear region (-0.5 to 0.5 mA) in the *I-V* curves with d = 20 - 70 μm. The ρ_c was 4.3×10^{-3} Ω cm^2 between the as-grown ZnO film and the n-GaN. This low ρ_c value indicates that the ZnO and the n-GaN formed a well-connected junction.

3. Conclusions

We successfully fabricated continuous ZnO films on n-GaN/Al_2O_3 substrates without seed layers by CBD at a low temperature of 70°C. From XRD patterns and TEM observation, it was found that single-crystalline ZnO films were grown on GaN layers directly. Furthermore, the ZnO films exhibited n-type conductivity with a relatively low resistivity even in unintentionally doped material. A low specific contact resistance of 4.3×10^{-3} Ω cm^2 was obtained at the ZnO/n-GaN junction. These results indicate that ZnO thin films grown by CBD can be potential candidates for application to GaN-based high power optical devices.

Acknowledgements

The authors would like to thank Dr. Daisuke Ueda for his continuous support, encouragement, and insightful comments. The authors are also indebted to Dr. Kaoru Inoue for his helpful suggestions and discussions.

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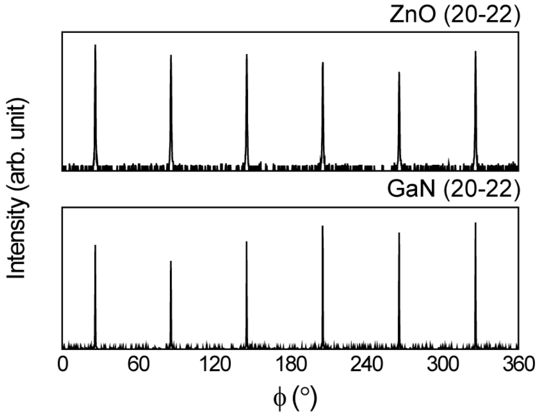

Fig. 1 XRD in-plane diffraction patterns of the ZnO film on n-GaN/Al_2O_3 substrate.

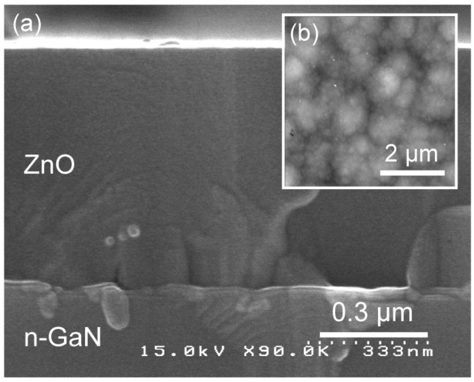

Fig. 2 (a) Cross-sectional SEM profile and (b) surface AFM morphology of the ZnO film on n-GaN/Al_2O_3 substrate.

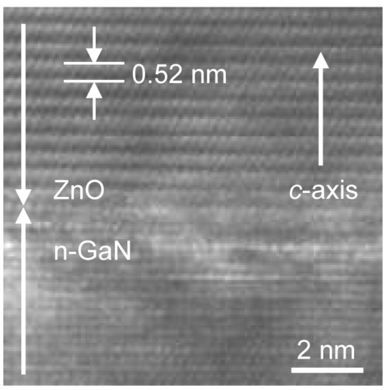

Fig. 3 TEM image of the ZnO/n-GaN interface.

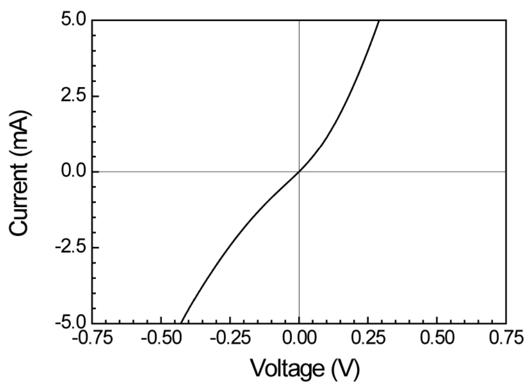

Fig. 4 *I-V* characteristic at the ZnO/n-GaN junction.