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MOVPE growth of GaN and LED on (1 1 1) $MgAl_2O_4$

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Abstract

The growth of wurtzite GaN by low-pressure metalorganic vapor-phase epitaxy on (1 1 1) magnesium aluminate ($MgAl_2O_4$) substrates have been studied. The morphological, crystalline, electrical and optical properties are investigated. A p–n junction GaN LED was fabricated on the $MgAl_2O_4$ substrate.

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Keywords: GaN; $MgAl_2O_4$; MOVPE; LED

1. Introduction

III–V nitride is one of the most promising materials for fabricating light-emitting devices in the green, blue and ultraviolet region as well as high-temperature and high-power devices. High-brightness blue and green light-emitting diodes (LED) have already been made commercially available [1]. Recently, the room-temperature continuous-wave operation of InGaN multi-quantum-well structure laser diodes have been reported [2]. When a GaN-based laser diode is fabricated on a (0 0 0 1) Al_2O_3 substrate, an optical cavity is usually formed using dry-etching. It is well known that the cleaved facet generally makes a superior cavity mirror because of its flatness and verticality. Cleavage can be obtained when the $(1\,1\,\bar{2}\,0)$ Al_2O_3 substrate is used. However, the cleaved face $(1\,\bar{1}\,0\,2)$

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of the Al_2O_3 substrate is different at an angle of 2.4° from the cleaved face (1 $\bar{1}$ 0 0) of GaN. Therefore, the search for a substrate not only having a closer lattice match to GaN than Al_2O_3, but also having the same cleavage direction as the epilayer is being actively pursued.

Cubic $MgAl_2O_4$ has a spinel-type structure. The (1 1 1) substrates having threefold symmetry would promote wurtzite GaN growth. The substrates have a smaller lattice mismatch ($\Delta d/d = 9\%$) and a smaller thermal expansion coefficient mismatch with GaN than sapphire. With this substrate cleavage is easy, we therefore feel that the use of (1 1 1) spinel-deposited films should favor the realization of GaN–AlGaN-based electrically pump UV-blue laser [3–5].

In this paper we report the growth of GaN and a p–n junction GaN LED on magnesium aluminate.

2. Experimental procedure

GaN epilayers were grown in a horizontal MOVPE reactor at 50 mbar [6]. TMGa, NH_3 and CP_2Mg were used as Ga, N and Mg precursors, respectively. The sources were mixed at the entrance of the reactor in order to suppress parasitic reaction. The substrates used in this study were (1 1 1)-oriented $MgAl_2O_4$ with mechanically polished surfaces on both sides. The substrate was first degreased with organic solutions and etched in a hot $H_2SO_4 : H_3PO_4 = 3:1$ mixture. Before growth, the substrate was heated to 1100°C in a H_2 stream for 10 min followed by a nitridation treatment in an NH_3 flow. The films were grown using a two-step process. First a thin (~ 20 nm) GaN buffer layer was grown at 550°C, then GaN film growth was carried out at 1050°C. Typical TMGa molar flow rate was 25 μmol/min. The input V/III ratio was 4500. The growth conditions yielded a growth rate of 1.8 μm/h.

Several analytical techniques were employed to characterize the grown layers. The crystalline quality was measured by X-ray diffraction (XRD) and three-crystal X-ray diffraction (TXRD). Transmission electron microscopy (TEM) and atomic force microscopy (AFM) image were also used. The carrier concentration and mobility were characterized by the Van der Pauw technique. Photoluminescence (PL) measurements were performed at 10 K. Cathodoluminescence (CL) measurements

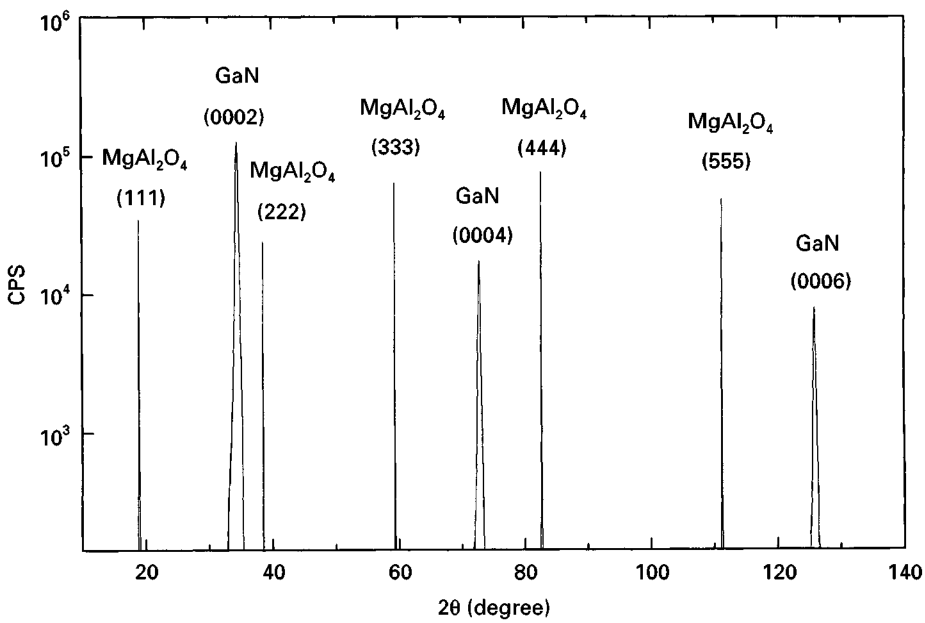

Fig. 1. XRD patterns of $GaN/MgAl_2O_4$.

were performed at room temperature. Raman measurements were carried out in backscattering from the epilayer surface at room temperature.

3. Result and discussion

According to our quasi-thermodynamic equilibrium model and phase diagram for the MOVPE growth of GaN [7], we select the growth condition as described above. The growth condition is located in a single condensed phase region, in which high quality of GaN film is expected. The surface morphology of GaN is smooth and mirror-like. The Hall electrical data at room temperature show that the unintentionally doped GaN films grown at 1050°C demonstrate n-type conduction with a mobility of 10–18 $cm^2 V^{-1} s^{-1}$. Some as-grown GaN samples over $MgAl_2O_4$ are highly insulating, but the reason is not clear at present. Sun et al. also reported a similar result in Ref. [4].

GaN grown on (1 1 1) $MgAl_2O_4$ has a hexagonal wurtzite structure. The XRD from (0 0 0 2), (0 0 0 4) and (0 0 0 6) diffraction of GaN grown on $MgAl_2O_4$ is shown in Fig. 1. All other peaks in Fig. 1 are attributed to the substrate. The full-width at half-maximum (FWHM) of (0 0 0 4) diffraction for the conventional rocking curve is 9.78 arcmin ($\Delta\theta$). We made further measurements of the sample by TXRD in ω-mode and $2\theta/\theta$-mode. The FWHM of (0 0 0 4) diffraction of these two modes are 9.18 arcmin ($\Delta\theta_1$) and 0.69 arcmin ($\Delta\theta_2$), respectively. The superposition rule, $\Delta\theta = \Delta\theta_1 + \Delta\theta_2$, holds roughly in the sample, where $\Delta\theta_1$ represents misorientations of the GaN grains, $\Delta\theta_2$ represents variation of the lattice spacing. We found that the $\Delta\theta_2$ is about one order of magnitude smaller than $\Delta\theta$ in the sample, which means the Mosaic structure is dominant. It is the main reason for the broad X-ray diffraction line.

The cross-sectional TEM images of 3 μm GaN epilayer are studied. The TEM images show: (1) at the $GaN/MgAl_2O_4$ interface there is a 5 nm thick island layer with hexagonal structure; (2) the buffer layer contains column structures, indicating the three-dimensional growth mode; (3) the dislocation density decreases markedly from the interface

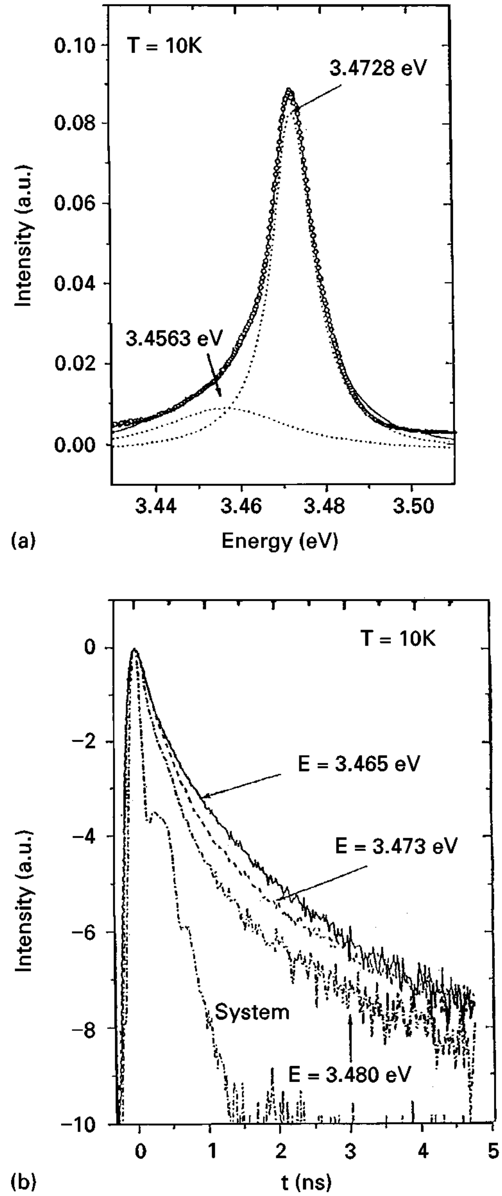

Fig. 2. spectrum of $GaN/MgAl_2O_4$ at 10 K. The solid line is the fit of the experimental data (o) for two individual peaks (the dotted lines). (b) Time-resolved emission spectra of GaN. The instrument response to laser pulses is indicated as system.

($\sim$ 400 nm) although high density of threading dislocations still remain in the rest of the epilayer.

Fig. 2a shows the photoluminescence spectrum of a GaN sample grown on $MgAl_2O_4$ measured at

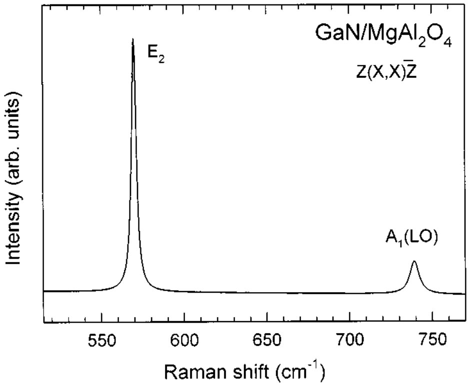

Fig. 3. Raman spectrum of GaN epitaxial layer grown on $MgAl_2O_4$.

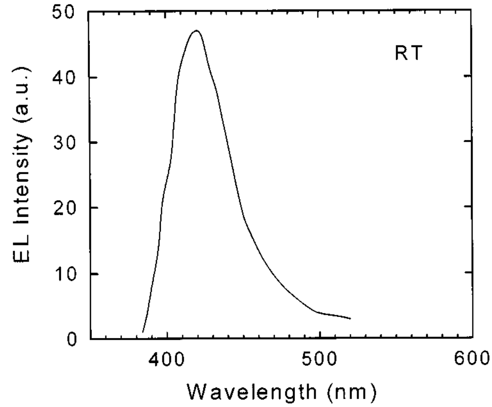

Fig. 4. EL spectrum of a p–n junction GaN LED at RT.

10 K. The PL of GaN is dominated with the narrow I_2 line (neutral donors-bound exciton (D^0, X) transition) at 3.4728 eV with FWHM of 12 meV. On the lower energy side of the I_2 line another emission line at 3.4563 eV can be observed, which is due to the I_1 recombination (neutral acceptor–bound exction (A^0, X) transition). The donor–acceptor pair (D–A) line with a corresponding phonon replica is also observed, which is not show in Fig. 2a. Fig. 2b shows the decay of these I_2 and I_1 lines at 10 K by employing time-resolved emission spectroscopy. The detection system response to the laser pulses is also included and indicated as system, which is about 0.15 ns.

The 488 nm line of an Ar^+ ion laser is used to measure the Raman scattering spectrum. A backscattering geometry, denoted as $Z(XX)\bar{Z}$, with the Z direction parallel to the [0 0 0 1] axis of GaN, is employed. A spectrum recorded at room temperature is shown in Fig. 3. The GaN line modes at 738 and 568 cm^{-1}. These line modes closely correspond to the wurtzite symmetry phonon modes of GaN, labeled A1(LO) and E2 (high), respectively. According to the selection rule for $Z(XX)\bar{Z}$ configuration, A1(LO) and E2 (high) lines are the allowed modes. The FWHM of E2 and A1(LO) are 3.4 and 10 cm^{-1}, respectively. The line modes observed in this study are in good agreement with those grown on sapphire as reported by Kozawa et al. [8].

Cp_2Mg is introduced to the reactor to obtain p-GaN. The molar ratio of Cp_2Mg to TMGa is 0.1. After 700°C annealing for 30 min. the sample shows p-type conductivity. Hole concentration is 3×10^{17} cm^{-3} and hole mobility is 10 cm^2 V^{-1} s^{-1} measured by the van der Pauw method. The CL spectrum of p-GaN doped with magnesium is dominated by donor–acceptor pair recombinations.

A p–n junction GaN LED is fabricated on the $MgAl_2O_4$ substrate. The EL emission peak is 420 nm with FWHM of 45 nm at room temperature as shown in Fig. 4.

4. Conclusion

Single-crystal GaN epitaxial film was obtained on (1 1 1) magnesium aluminate substrate using low-pressure MOVPE. The quality of the GaN epilayers is good. p-GaN was obtained.

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