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Strain analysis of a GaN epilayer grown on a c-plane sapphire substrate with different growth times

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Abstract The strain analysis of a GaN epilayer with different growth times on a c-plane sapphire substrate via a two-step growth method, using low-pressure, metalorganic chemical vapor deposition, was conducted based on the precise measurement of the lattice parameters, using high-resolution X-ray diffraction. The high-temperature growth time was changed at a fixed growth condition. The c- and a-lattice parameters were measured, followed by the out-of-plane and in-plane strains. Then, the biaxial and hydrostatic components were extracted from the total strain values obtained, and were discussed in this paper as functions of GaN growth time.

Introduction

Gallium nitride (GaN) and the related nitride compound semiconductors are interesting as they can be applied in light-emitting diodes (LEDs); laser diodes (LDs), particularly in the green to the ultraviolet (UV) regions; and high-temperature electronic devices [1–4]. The GaN epilayer is widely grown mainly on a c-plane sapphire substrate, through metalorganic chemical vapor deposition (MOCVD), despite the large mismatch between the epilayer and the sapphire substrate in the lattice constants and the thermal-expansion coefficients, because of the lack of other suitable substrates [2–4]. The GaN epilayer on a c-plane sapphire substrate is widely grown with the use of the two-step MOCVD growth method, employing an AlN buffer layer [5] or a low-temperature GaN buffer layer [6].

Kisielowski et al. [7, 8] reported that a biaxial strain and a hydrostatic strain could coexist in the GaN epilayer. The external biaxial strain originates from the lattice mismatch and from post-growth cooling due to the different thermal-expansion coefficients of the GaN epilayers and the substrate. The additional internal hydrostatic strain was shown to have been introduced by the presence of point defects, which can be compressive or expansive depending on the size of the involved point defects. Harutyunyan et al. [9] reported a high-resolution X-ray diffraction (HRXRD) strain-stress analysis of a GaN/sapphire heterostructure grown through molecular beam epitaxy (MBE), particularly in the deformation state, depending on the relative content of N in the $Ga_{1-x}N_x$ buffer layer.

In this study, a residual-strain analysis of GaN/(0001) sapphire heterostructures with increasing growth time, using MOCVD, was conducted by measuring the c-lattice and a-lattice parameters using HRXRD. A two-step growth condition was used via a low-pressure MOCVD in a horizontal flow reactor, and the growth time of the high-temperature GaN epilayer was then changed. The process pressure of the horizontal MOCVD reactor (300 Torr), the growth condition of the low-temperature GaN, and the other process variables were fixed for each growth time of the high-temperature GaN.

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Experiment

An undoped GaN epilayer was grown on a c-plane sapphire substrate in a horizontal MOCVD reactor at a low pressure of 300 Torr, as described in the authors' previous papers [10, 11]. In all the experiments, a two-step growth method of GaN—consisting of the deposition of the low-temperature GaN buffer layer and the high-temperature GaN epitaxial growth—was employed. The growth time of the high-temperature GaN was changed from 1 to 15 min so that the time evolutions of the high-temperature GaN growth during the two-step MOCVD growth can be studied. The V/III ratios were 2,740 and 1,370 for buffer growth and the main high-temperature growth, respectively. The growth rate had been fixed at 0.07 μm/min; as such, the thickness of GaN that was grown for 15 min was estimated to be 1.1 μm.

The c-lattice and a-lattice parameters of the GaN epilayers were measured with a ω–2θ scan of wurtzite GaN through triple-axis, high-resolution X-ray diffraction (HRXRD), to obtain precise measurements (PANalytical X'Pert PRO MRD). The diffracted peak positions were corrected based on the reference positions of the single sapphire crystal. The c-lattice parameter of the wurtzite GaN epilayer was determined from the detected ω–2θ scan diffraction spectra for the Bragg symmetrical setup. The a-lattice parameter of the wurtzite GaN epilayer was extracted using the above c-lattice parameters as well as the interplanar spacing from the diffraction peaks of the asymmetrical reflections.

Results and discussion

Table 1 shows the obtained values of the c-lattice and a-lattice parameters, with increasing growth time, of the wurtzite GaN epilayer on a sapphire (0001) substrate grown using a two-step growth method that employs low-pressure MOCVD.

Table 1 The measured values of the c-lattice and a-lattice parameters of the GaN epilayers, with increasing growth time, on a (0001) sapphire substrate grown using a two-step growth method that utilizes a low-pressure MOCVD

Sample (min)	Measured c-lattice parameter (nm)	Measured a-lattice parameter (nm)
1	0.52541	0.31348
2	0.51886	0.31815
5	0.51869	0.31811
10	0.51782	0.31805
15	0.51869	0.31777

The unstrained c-lattice and a-lattice parameters, which were obtained from a reference, were used to measure the out-of-plane and in-plane strain components. Leszczynski et al. [12] reported the lattice parameters of the homoepitaxial GaN layers using high-resolution X-ray diffraction. The unstrained c-lattice and a-lattice parameters were 0.51850 and 0.31878 nm, respectively [12].

The strains and biaxial stresses in the GaN epilayers of the same samples as those in Table 1 were measured and extracted. Table 2 shows the strains and biaxial stress in the GaN epilayers. A convention—that the strains are negative if the epilayer is under compression and positive if it is under tension—was used. The GaN epilayer on the (0001) sapphire substrate exhibits in-plane isotropic elastic properties, and its in-plane deformation state can be described by one strain component [9].

The measured strain in the c-direction ε_c corresponds to the out-of-plane strain component, and the measured strain in the a-direction ε_a corresponds to the in-plane strain component. The obtained values of ε_c and ε_a are both superpositions of the biaxial strain components $\varepsilon_c^{(b)}$ and $\varepsilon_a^{(b)}$, and of the hydrostatic strain component ε_h [7–9].

$$\varepsilon_c = \varepsilon_a^{(b)} + \varepsilon_h \tag{1}$$

$$\varepsilon_a = \varepsilon_a^{(b)} + \varepsilon_h \tag{2}$$

The hydrostatic strain ε_h can be determined from the Poisson ratio, ε_c, and ε_a The Poisson ratio, on the other hand, can be determined from the elastic constants C_{13} and C_{33} [9]. The values of the elastic constants of GaN, $C_{13} = 106$ GPa and $C_{33} = 398$ GPa, were referenced from a previous Brillouin scattering measurement [13], resulting in the Poisson ratio of 0.210317460.

The Poisson ratio and the elastic constants cited in the previous report were then used to extract the biaxial and hydrostatic strain components of each sample. Table 2 also shows the out-of-plane (in the c-direction) and in-plane (in the a-direction) biaxial strain components $\varepsilon_c^{(b)}$ and $\varepsilon_a^{(b)}$, as well as the hydrostatic strain ε_h.

The in-plane biaxial stress in the GaN epilayer σ_f can be calculated from the following relationship:

$$\sigma_f = M_f \varepsilon_a^{(b)} \tag{3}$$

where M_f is the biaxial elastic modulus [9]. The elastic constants of wurtzite GaN, C_{ij}, from the Brillouin scattering measurement [13], were used as

Table 2 Strains and biaxial stress in the GaN epilayers, with increasing growth time, on a (0001) sapphire substrate grown using a two-step growth method that utilizes the low-pressure MOCVD used in Table 1

Sample (min)	Measured strain in c-direction ε_c	Measured strain in a-direction ε_i	Hydrostatic strain ε_h	Biaxial strain in c-direction $\varepsilon_c^{(b)}$	Biaxial strain in a-direction $\varepsilon_a^{(b)}$	Biaxial stress σ_f (GPa)
1	1.33×10^{-2}	-1.66×10^{-2}	2.92×10^{-3}	1.04×10^{-2}	-1.95×10^{-2}	–9.35
2	6.94×10^{-4}	-1.98×10^{-3}	-2.34×10^{-4}	9.28×10^{-4}	-1.74×10^{-3}	–0.83
5	3.66×10^{-4}	-2.10×10^{-3}	-4.91×10^{-4}	8.58×10^{-4}	-1.61×10^{-3}	–0.77
10	-1.31×10^{-3}	-2.29×10^{-3}	-1.65×10^{-3}	3.40×10^{-4}	-6.38×10^{-4}	–0.31
15	3.66×10^{-4}	-3.17×10^{-3}	-8.62×10^{-4}	1.23×10^{-3}	-2.31×10^{-3}	–1.11

C_{11} = 390 GPa, C_{12} = 145 GPa, C_{13} = 106 GPa, and C_{33} = 398 GPa, respectively, resulting in the biaxial elastic modulus M_f, or 478.5 GPa [9]. The biaxial stress component in the crystallographic b-direction equals the component in the a-direction, whereas the biaxial stress component in the c-direction equals zero [9].

As can be seen in Table 2, for all the different growth times in the main GaN epilayers grown in this study, which made use of the two-step MOCVD method, both the measured (i.e., total) and extracted biaxial in-plane strains are of the compressive type. Moreover, the absolute magnitude of the measured in-plane strain was always greater than that of the hydrostatic strain. Both the measured and biaxial out-of-plane strains were of the tensile type, except for the value obtained for the 10-min sample. The absolute magnitude of the biaxial in-plane strain was always greater than that of the hydrostatic strain, except for the 10-min sample.

The samples with different growth times showed a negative hydrostatic strain in the GaN epilayer, except for the 1-min sample. The negative hydrostatic strain showed a compressive character and a large absolute value. The covalent radius of the Ga atom is considerably larger than that of the N atom, in tetrahedral covalent bonds (r_{Ga} = 0.126 nm, r_N = 0.07 nm) [9, 14]. Oxygen is one of the most frequent impurities during MOCVD [3, 4], and the covalent radius of the O atom is smaller than that of the N atom in tetrahedral covalent bonds (r_O = 0.066 nm, r_N = 0.07 nm) [14]. Though carbon is also an inherent impurity during MOCVD [3, 4], oxygen was considered a major impurity because the intentionally undoped GaN epilayer was n-type, and because the authors' previous study also showed an n-type character [10, 11]. Oxygen impurity is known to induce the n-type carrier, whereas carbon impurity is known to induce the p-type carrier [4, 5].

Therefore, the compressive hydrostatic strains from the 2-min to the 15-min samples suggest that the relatively dominant point defects are V_{Ga}, V_N, N_{Ga}, and O_N. Interestingly, for 1 min, ε_h showed a positive value, unlike the others. Therefore, the Ga_N, Ga_i, N_i, O_i,, and C_i type defects are thought to have caused a crystal expansion for the 1-min sample.

The external biaxial strain originates from the growth on the lattice-mismatched substrates and from post-growth cooling [7, 8]. The effective a-lattice parameter of GaN is larger than that of sapphire due to the 30° rotation of the epitaxial orientation relationship between wurtzite GaN and the (0001) sapphire substrate [3, 4]. Thus, compressive stress can be induced in the GaN epilayer. Since the thermal-expansion coefficient of GaN (5.6×10^{-6} K^{-1}) is much smaller than that of sapphire (7.5×10^{-6} K^{-1}) [3], compressive stress is also induced in the GaN epilayer. The thermal strain $\varepsilon_{thermal}$ can be calculated from the thermal-expansion coefficients as -2.014×10^{-3}, having originated from post-growth cooling to room temperature from the growth temperature 1,080°C. This value stems from two assumptions: that there is no plastic deformation during cooling, and that the misfit strain is completely relieved at high-temperature growth.

If the lattice mismatch is more than 4% and the layer thickness is not too small, the strain is almost completely relaxed by the generation of misfit dislocations during the epilayer growth through MOCVD [15]. When cooling the layers to room temperature, stresses and strains are also generated due to the different thermal-expansion coefficients.

The measured values of $\varepsilon_a^{(b)}$ in Table 2 do not exactly agree with the value of the calculated thermal strain, such as $\varepsilon_{thermal} = -2.014 \times 10^{-3}$. From the growth time of 2 to 15 min, however, $\varepsilon_a^{(b)}$ showed compressive values with an order of about 10^{-3}, which is the same for the thermal strain $\varepsilon_{thermal}$.

If the thickness of the layer is not sufficiently high, the relaxation of the strain at the growth temperature will be incomplete, and the lattice mismatch strain will persist when it has been cooled to lower temperatures [15]. Additional misfit dislocations may also be generated during the cooling process, partially relieving the thermal strain [15]. Both factors will make the observed biaxial strain $\varepsilon_a^{(b)}$ different from the thermal strain $\varepsilon_{thermal} = -2.014 \times 10^{-3}$, which has been calculated from the thermal-expansion coefficients.

The tendency of $\varepsilon_a^{(b)}$, however, as can be seen in Table 2, is to become closer to the $\varepsilon_{\text{thermal}}$ value with increasing growth time, though some deviating fluctuation and oscillation can be seen. The in-plane biaxial strain seems to have no simple linear tendency to increase or decrease with increasing growth.

On the contrary, the 1-min-growth sample showed much larger values (ε_c, ε_a, ε_h, $\varepsilon_c^{(b)}$, and $\varepsilon_a^{(b)}$), which were larger by one order of magnitude in other values with longer growth items, as can be seen in Table 2. For the 1-min sample, $\varepsilon_a^{(b)}$ is an order of 10^{-2} in a compressive state. The large in-plane strains (both measured and biaxial) and the biaxial stress of the 1-min sample are thought to be evidences of an incomplete relaxation for the initial island stage of high-temperature growth with limited thickness. In the authors' previous paper, the AFM image of the 1-min sample showed 3-dimensional islands that looked like flat-top-shaped islands rather than hillock-type ones [11]. The root-mean-squared (rms) roughness was 28.2 nm for the 1-min sample, and 0.53 nm for the 10-min sample [11]. In this study, a typical two-step growth method was employed using a low-pressure MOCVD. Because of the large difference between the lattice parameters of GaN and the sapphire substrate, the free energy of the system will be lowered if the growth is three-dimensional (3D).

Conclusion

All the samples, which had different growth times, showed compressive in-plane strains of the GaN epilayer on a (0001) sapphire substrate grown using a two-step, low-pressure MOCVD. As the GaN epilayer on the c-plane sapphire substrate thickens, the in-plane biaxial strain seems to approach the thermal strain that originated from the large difference between the thermal-expansion coefficients of GaN and sapphire. At the earliest stage of 3D island formation, the relaxation of the strain from the large mismatch is incomplete, resulting in a much larger in-plane strain.

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