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In situ X-ray diffraction monitoring during metalorganic vapor phase epitaxy growth of low-temperature-GaN buffer layer

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ABSTRACT

We investigated *in situ* X-ray diffraction (XRD) monitoring during the growth of low-temperature (LT)-GaN buffer layers on the (0001) *c*-plane sapphire substrates. The *in situ* XRD monitoring made it possible to observe the crystalline structures during their growth. We investigated the temperature dependence of LT-GaN buffer layers by *in situ* XRD monitoring during the thermal annealing of the LT-GaN layers. We clearly observed the evolution process, in which an LT-GaN buffer layer grown at 535 °C was crystallized into a hexagonal structure by thermal annealing at temperatures of up to 1090 °C. We also found that the LT-GaN buffer layer was transformed into nano size hexagonal single-crystal islands upon annealing by atomic force microscopy. The crystalline quality of the subsequent GaN layer strongly depended on the growth temperature of the LT-GaN buffer layer.

1. Introduction

High-performance violet- and blue-light-emitting diodes (LEDs) and violet-laser diodes (LDs) based on group III nitrides have been commercialized as a result of several breakthroughs in metalorganic vapor phase epitaxy (MOVPE). Specifically, GaN with high crystalline quality on a (0001) *c*-sapphire substrate has been obtained by a two-step growth process [1,2]. It had previously been difficult to grow a GaN layer with high crystalline quality on a (0001) *c*-plane sapphire substrate owing to the markedly different lattice constants and thermal expansion coefficients of GaN and the sapphire substrate. An AlN or GaN buffer layer grown at a low temperature (500–600 °C) greatly improves the crystalline quality of the subsequent GaN layer [1,2]. An low-temperature (LT) buffer layer annealed at a high temperature (~1000 °C) is transformed into crystal islands enabling the subsequent growth of GaN [3–7]. Therefore, the growth and annealing processes of LT buffer layers are very important in achieving subsequent GaN layers with high crystalline quality and a smooth surface morphology. In general, crystal growth has been monitored by *in situ* optical reflectometry, where the optical *in situ* monitoring system obtains information on the evolution of the surface, growth rate, and wafer curvature [8,9]. However, *in situ* optical reflectometry cannot obtain information on the crystalline structure of epitaxial layers. On the other hand, in previous reports, *in situ* X-ray diffraction (XRD) monitoring has revealed information on the thermal expansion coefficient, residual strain, and dislocation behavior in layers grown by molecular beam epitaxy and MOVPE, leading to further understanding of the mechanisms of crystal growth [10–12]. In this study, we demonstrated that the evolution of the crystallization of LT-GaN buffer layers can be monitored by *in situ* XRD monitoring during MOVPE. The effect of the growth temperature of the LT-GaN buffer layer on its crystallization is discussed on the basis of the results of *in situ* XRD monitoring.

2. Experiments

GaN layers were grown on a (0001) *c*-plane sapphire substrates by MOVPE in a face-down 2″ × 3 horizontal flow reactor (TNEMC: GRC-203). Trimethylgallium (TMGa) and ammonia (NH_3) were used as the sources of Ga and N, respectively. Hydrogen (H_2) was used as the carrier gas. The sapphire substrates were thermally cleaned in H_2 ambient at approximately 1050 °C. After that, LT-GaN buffer layers with a thickness of approximately 20 nm were deposited at various temperatures between 485 and 635 °C (stage I). The LT-GaN buffer layer was annealed by ramping up the temperature to 965 °C for 3 min (stage II), to 1090 °C for 3 min (stage III), then holding the

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temperature at 1090 °C for 3 min (stage IV) in H_2, N_2, and NH_3 ambient. After the annealing process, a 2 μm-thick GaN layer was grown on the annealed LT-GaN layer at 1090 °C. All the samples were monitored by *in situ* symmetric (0002) XRD at the end of stages I, II, III, and IV. The incident X-ray beam was focused on the stationary sample surface using a Johansson curved crystal mirror, and the diffracted X-ray beam was detected by a one-dimensional charge-coupled device array [10,11]. *In situ* XRD spectra can be measured similarly to typical XRD spectra for 1 s and can indicate the tilt components of a crystal and the distribution of the lattice constant *c* [10,11]. The X-ray monitoring system used in this study was supplied by Rigaku Corporation. The crystalline quality of the GaN layer was also evaluated by an *ex situ* X-ray rocking curve (XRC). The full widths at half maximum (FWHMs) of symmetric (0002) and asymmetric (10–12) reflection were measured. The surface morphologies of annealed LT-GaN buffer layers with different growth temperatures were observed by atomic force microscopy (AFM).

3. Results

Fig. 1 shows typical *in situ* XRD spectra with symmetric (0002) diffraction of as-grown LT-GaN buffer layers grown at (a) 485, (b) 535, and (c) 635 °C (stage I), and the annealed LT-GaN buffer layers (stages II–IV). The *in situ* XRD peak intensities of the LT-GaN buffer layers immediately after growth increased with increasing growth temperature of the LT-GaN layers, as shown in Fig. 1 (stage I).

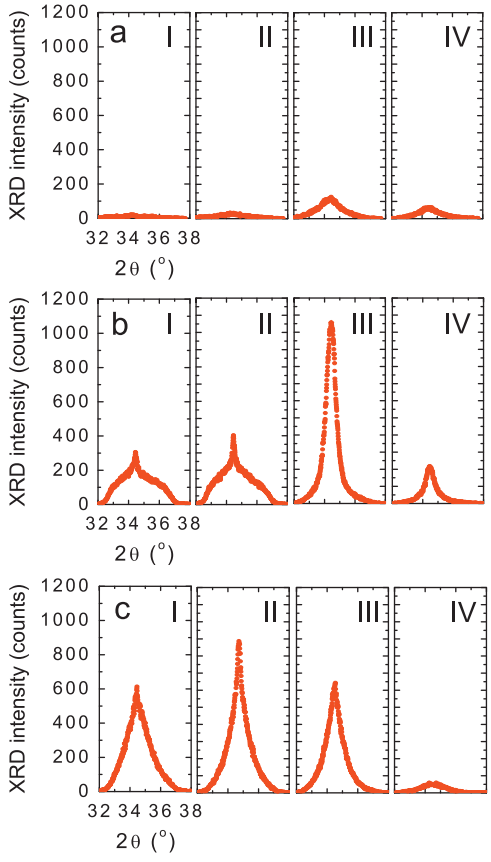

Fig. 1. *In situ* XRD spectra of LT-GaN buffer layers grown at (a) 485 °C, (b) 535 °C, and (c) 635 °C. The *in situ* XRD spectra were obtained from the LT-GaN buffer layers immediately after growth (stage I) and during thermal annealing at 965 °C for 3 min (stage II), 1090 °C for 3 min (stage III), and during holding at 1090 °C for 3 min (stage IV).

This suggests that the crystallization of hexagonal single crystals in the LT-GaN buffer layers before annealing was enhanced with increasing growth temperature. As shown in Fig. 1(a), for the LT-GaN buffer layer grown at 485 °C it is difficult to enhance the transformation of hexagonal single crystals by thermal annealing. In contrast, Fig. 1(b) shows that the *in situ* XRD spectra consist of several peaks. Thus, the crystalline structure before annealing (stage I) and that of the annealed LT-GaN buffer layers (stage II) are composed of hexagonal single crystals. According to previous report [4], these broadened *in situ* XRD spectra also predict that the crystalline structure of the LT-GaN buffer layers is composed a random amorphous-like phase, a cubic phase, or a mixed cubic-hexagonal phase [4]. The *in situ* XRD spectrum of the annealed LT-GaN buffer layer (stage III in Fig. 1(b)) indicated that the effect of thermal annealing of the LT-GaN buffer layer immediately after its growth is to induce the crystallization of hexagonal single crystals. Then, the hexagonal single crystals were evaporated by thermal annealing (stage IV in Fig. 1(b)). Therefore, the *in situ* XRD intensity of the annealed LT-GaN buffer layer markedly decreased. Note that after the annealing process (stage III in Fig. 1(b)), the crystal structure was almost completely transformed into hexagonal single-crystal islands. Fig. 1(c) shows that the crystalline structure of the LT-GaN buffer layer before annealing (stage I) is predominantly composed of hexagonal single crystals with the amount of crystallization increasing with the growth temperature. However, the LT-GaN buffer layer grown at 635 °C was evaporated of the hexagonal single crystals by thermal annealing, and very little crystallization was observed after annealing. In particular, the *in situ* XRD peak of the annealed LT-GaN buffer layer grown at 535 °C clearly narrows with the nucleation of hexagonal single crystals of GaN as shown in Fig. 1(b). Therefore, the crystallization of the LT-GaN buffer layer is essential to be moderately composed the nucleation hexagonal single crystals into the LT-GaN buffer layer before thermal annealing.

Fig. 2 shows a summary of the *in situ* XRD peak intensity and FWHM of the LT-GaN buffer layers during thermal annealing (stages III, IV) as a function of the growth temperature. The figure shows that the *in situ* XRD peak intensity increase and the FWHM of the LT-GaN buffer layer decreases with increasing growth temperature. It was found that the crystalline quality of the hexagonal single crystals in the LT-GaN buffer layers was mainly improved by thermal annealing (stage III). Thus, each LT-GaN buffer layer is appeared to promote evaporation during thermal

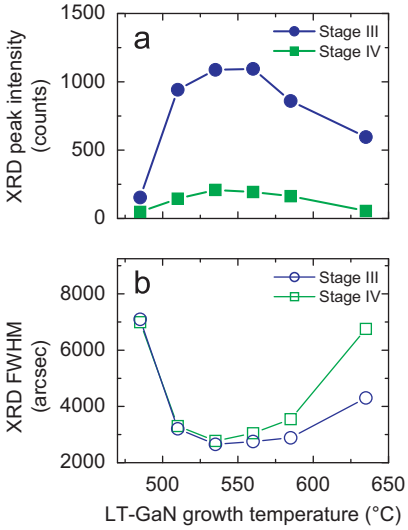

Fig. 2. Dependence of the *in situ* XRD (a) peak intensity and (b) FWHM of LT-GaN during thermal annealing (stages III and IV) at growth temperatures from 485 to 635 °C.