GaN film growth on LiNbO₃ surfaces using molecular beam epitaxy

Man Hoai Nam¹, ³, Son Chul Goo², Moon Deock Kim² and Woochul Yang¹

¹ Department of Physics, Dongguk University, Seoul 100-715, Korea
² Department of Physics, Chungnam National University, Daejeon 305-764, Korea
³ Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

E-mail: wyang@dongguk.edu

Abstract. GaN has been used for high power, high frequency electronic and optoelectronic devices such as light emitting diodes and laser diodes. Most of the GaN films grow on sapphire (0001) and silicon (111) substrates. In these work, we are trying to grow GaN films on lithium niobate (LiNbO₃) substrates using molecular beam epitaxy (MBE). As a ferroelectric materials, LiNbO₃ has a spontaneous polarization which may provide excellent control of polarity of GaN. The growth of GaN films on LiNbO₃ has been performed after the LiNbO₃ substrates was annealed in air at 1000°C for 2 hours. The annealed substrates allowed us to prepare atomically flat surfaces and improve adhesion of GaN on LiNbO₃. The AlN buffer layer was deposited to get a smaller lattice mismatch with the GaN films. Compared with GaN films grown without a AlN layer, the crystal qualities of GaN films with AlN buffer layers are extremely improved. The surface morphology of LiNbO₃ substrates and the grown GaN films were characterized by atomic force microscopy (AFM), and the crystal structures were studied by X-ray diffraction (XRD).

Keywords: Lithium niobate, gallium nitride, molecular beam epitaxy, polarity.

1. Introduction
Gallium nitride (GaN) and its related compounds have attracted much attention because of their excellent optical and electrical properties for device applications such as light emitting diodes, laser diodes, and high power devices [1-3]. However, it is well known that the epitaxial growth of GaN films suffers from the formation of a high density of crystalline defects. The defects are attributed to the large mismatch of 16.1% between the lattice constants of GaN (a = 0.3189 nm) and sapphire (a = 0.4765 nm), which is widely used for substrates. To solve this problem, the use of an alternative substrate that exhibits a smaller lattice mismatch with GaN is highly desirable [4–10]. Since the (0001) plane of lithium niobate (LiNbO₃) has a lattice mismatch of 6.8% with respect to GaN (0001) plane, we might expect to grow higher-quality GaN films on LiNbO₃ substrates.

LiNbO₃ has a rhombohedral atomic structure, the c-plane surface atomic arrangement of LiNbO₃ (LN) has a hexagonal symmetry in an unit cell with a-axis and c-axis dimensions of [12] and 3.8631 Å, respectively [18]. The surface of (+z) - LN has hexagonal symmetry in structure similar to sapphire, while LN has different surface oxygen bond lengths around the hexagonal oxygen sub lattice. There
are two bonds each of length 2.719, 3.362, and 2.879 Å for LN. Thus, LN has average surface oxygen-oxygen spacing of 2.981 Å, and have a lattice mismatch to GaN $a = 3.185$ Å of 6.8% [12]. A similar analysis of LN mismatch to AlN $a = 3.1114$ Å results in a lattice mismatch of 4.4%.

In addition, the use of LiNbO$_3$ substrates is attractive because large-diameter wafers (> 4 inch) are commercially available at reasonable cost. It should be noted that LiNbO$_3$ has also been used for optoelectronic applications such as optical switching devices and second harmonic generators due to its large nonlinear-optical coefficients [11]. Hence, the successful epitaxial growth of GaN on LiNbO$_3$ could lead to the fabrication of optoelectronic integrated circuits that utilize both GaN lasers and LiNbO$_3$ optical switches [15]. Although Doolittle et al [12-16] have succeeded in the epitaxial growth of GaN films on LiNbO$_3$ (0001) substrates, the diffusion of Li atoms into the GaN films and the formation of LiNb$_3$O$_8$ were observed at the interface between GaN and LiNbO$_3$. The interfacial LiNb$_3$O$_8$ layers leads to some degradation of the electrical and optical properties of the GaN [15]. To probe the formation of the LiNb$_3$O$_8$ layer, a reduction in growth temperature and the use of an AlN buffer layer are highly desirable [14]. The other advantage of using an AlN buffer layer lies in its smaller lattice mismatch (4.4%) with LiNbO$_3$ (0001).

In this study, we report on the first successful epitaxial growth of GaN films on ferroelectric materials of lithium niobate (LiNbO$_3$) substrates.

2. Experimental

The GaN film was grown on LiNbO$_3$ substrates with a AlN buffer layer by plasma-assisted molecular beam epitaxy (MBE). The system is equipped with reflection high energy electron diffraction (RHEED) for monitoring the growth. In order to obtain atomically flat substrates, the as-received Lithium niobate (LiNbO$_3$) substrates are cleaned with de-ionized (D.I) water, then the LiNbO$_3$ were put on a quartz board and annealed in the air at 1000°C for two hours in quartz tube of furnace system. On the cleaned substrate backside (-z surface), Ti (2000 Å in thickness) was deposited by sputtering to enhance radiation absorption from the heater.

After Ti deposited, LN substrates were cleaned with organic solvents EKC 830 (Posistrip positive photoresist remover filtered to 10 microns) and rinsed with de-ionized D.I water again. Next, the samples were outgassed in vacuum at 200°C for 1 hour in a preparation chamber before being loaded into the growth chamber of the MBE system. Prior to growth of GaN, a AlN buffer layer of 100 nm in thickness [11, 12] was grown on (+z)-LN substrates at 600°C with 0.8 SCCM (standard cubic centimeter per minute) nitrogen at nitrogen plasma power of 250 W, that will provides for predominantly Ga-polar GaN films. The GaN bulk film was grown at 650°C with 0.5 sccm nitrogen. The thickness of the grown GaN film was ~ 400 nm. During the growth, a reflection high energy electron diffraction (RHEED) pattern was monitored to examine the film growth mode. Each sample was analyzed ex situ by atomic force microscopy (AFM) and x-ray diffraction measurement using a Phillips X’pert Pro MRD to investigate surface morphology and structure.

3. Results and discussions

As-received lithium niobate (LN) substrate has a lot of surface damages such as scratches and corrugations in the nanometer scale range due to mechanical polishing, which decrease the adhesion of GaN to the substrate, as shown in figure 1(a). To produce atomically flat surfaces, furnace annealing at 1000°C in dry air environment [11, 12, 14, 18] have been performed. After annealing, the surface damages of LiNbO$_3$ have been drastically changed.
Figure 1. AFM images of the LiNbO$_3$ substrate (a) as-received substrate (without annealing), (b) after 2 hours of annealing (10 µm x 10 µm, scaled view), and (c) after 2 hours of annealing (2 µm x 2 µm, scaled view).

Figure 1 shows AFM images of LiNbO$_3$ substrate surfaces of an as-received and after furnace annealing at 1000°C. Figure 1a shows many scratches on the surface of the as-received LiNbO$_3$ that are not suitable for GaN growth. The surface roughness was 0.32 nm in root mean square (rms), for a 2µm x 2µm area. The AFM image of LiNbO$_3$ substrate after 2 hours of annealing at 1000°C in air was shown in the figure 1b. It showed that, all the surface damage was removed, indicating a unit-cell height step and terrace structures on the surface after annealing at high temperature. The step terrace width is about 380 nm, and the surface roughness is 0.19 nm, for a 2µm x 2µm area, in figures 1b and 1c.

Figure 2. AFM images of the surface of LiNbO$_3$ substrate (5 µm x 5 µm scaled view): (a) after 3 hours of annealing), (b) after 4 hours of annealing, and (c) after 6 hours of annealing.

However, longer annealing produces a facet coarsening surface which might increase surface roughness. Figure 2 shows the AFM images of the LiNbO$_3$ surfaces after annealing at various times. After 3 hours annealing the surface is very similar to one annealed for 2 hours. The LiNbO$_3$ substrate produces atomically flat terraces of 400 nm width, and the surface roughness of 0.49 nm, as shown in figure 2a. However, after annealing for 4 hours and 6 hours, the surface shows a slightly porous morphology that increases surface roughness, as shown in the figure 2b and figure 2c. The surface roughnesses are 0.65 nm, and 0.51 nm for annealing samples for 4 hours and 6 hours, respectively. From these results, we can conclude that 2–3 hours annealing gives the best surface smoothness.

When the LiNbO$_3$ substrate was annealed at high temperature, the topmost surface is thermodynamically unstable and is transformed to the equilibrium crystal surface by the rearrangement of the surface atoms [14]. The improvement of LiNbO$_3$ surface quality has been attributed to diffusion and re-growth processes, leading to atomic flatness and removal of scratches from the surface.
To check the presence of ferroelectric inversion domains on LiNbO$_3$, a chemical etching was performed using HF for 15 minutes. Before high temperature thermal treatment, as-received (+z)-cut LiNbO$_3$ was not etched, indicating a single domain. However, after high-temperature thermal treatment at 1000°C in air followed by etching, (+z)-cut LiNbO$_3$ shows faceted pits, indicating repolarization on the surface, as shown in figure 3b. Therefore, high-temperature thermal treatment gives a trade-off between adhesion and control of polarity of GaN epitaxial layer on LiNbO$_3$.

During the GaN growth, the *in situ* RHEED pattern was monitored. Figures 4a and 4b show the RHEED patterns of LiNbO$_3$ substrates at high temperatures. The RHEED patterns of LiNbO$_3$ substrate at 200°C is a dim. However, when the substrate temperature increases to the growth temperature at 500°C, the pattern degrades and exhibits transmission features. The RHEED patterns were streaky and clearly, as shown in figure 4b. This indicates that the corrugation of the surface has increased significantly, suggesting initiation of LiNbO$_3$ is decomposing at high temperature.

The RHEED patterns during the growth of the AlN buffer layer consists of streaks and spots, as shown in figures 4c and 4d, which indicates that single-crystal AlN grows epitaxially on LiNbO$_3$, and that the surface morphology is slightly roughened, probably due to stress in the film. Careful interpretation of the RHEED pattern allows us to conclude that AlN (0001) grows on LiNbO$_3$ (0001) with an in-plane epitaxial alignment.
The structural quality of the GaN/AlN/LiNbO₃ was assessed by X-ray diffraction study. Figure 5 shows the omega–two theta X-ray diffraction spectrum for a GaN film on lithium niobate. The dominant peak of GaN (0002) is located at 34.56 degrees of two theta, indicating alignment of the GaN (0001) direction along the (0001) direction of lithium niobate substrate. This result shows the growth of a well-oriented GaN film on the LiNbO₃ substrate. The peaks at 20 = 36.124 degrees and 20 = 39.1 degrees are due to the reflections of AlN buffer layer and LiNbO₃ substrate, respectively. The additional peak is found to be located at two theta of 38.3 degrees, which peak is related to lithium triniobate, LiNb₃O₈, a stable monoclinic phase in the lithium oxide/niobate oxide system resulting from preferential desorption of LiO₂ near the sample surface [15]. This preferential desorption results in an imbalance state in the lithium oxide/niobium oxide ratio which becomes 1:3 LiO₂:Nb₂O₅ in the near surface regions.

Figures 6a and 6b show the surface morphology of GaN epitaxial layer grown on LiNbO₃ without AlN buffer layer and GaN films with a AlN buffer layer of 100 nm thickness, respectively. For a GaN film grown on LiNbO₃ without AlN buffer layer, the surface roughness is 28.40 nm, while for the GaN film grown on LiNbO₃ with AlN buffer layer, the surface roughness is 1.22 nm. The surface roughness of GaN/AlN/LiNbO₃ is much smoother than GaN/LiNbO₃. It is inferred that the AlN buffer layer was used to get a smaller lattice mismatch with the GaN films surface. Therefore the surface of GaN films with AlN buffer layers is extremely improved.

4. Conclusions
LiNbO₃ can be a promising substrate for the growth of GaN film due to its slightly lattice mismatch and the structural similarity between GaN and LiNbO₃. The high temperature thermal treatment has been used to obtain atomically flat surface and to remove the surface damage from mechanical polishing. The different annealing conditions gave rise to different of surface smoothness. The
annealing at 1000°C for 2 hours produces the optimal surface smoothness for adhesion of GaN to LiNbO3 substrates. We have first successfully epitaxial growth of decent quality GaN layer on lithium niobate (LiNbO3) substrates by molecular beam epitaxy. The surface morphology was also improved by the insertion of the AlN buffer layer of 100 nm thickness, it gives the better surface smoothness compared with GaN film grown on LiNbO3 without AlN buffer layer.

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Acknowledgments
This work is supported by the Korea Research foundation grant funded by the Korean Government (KRF-2007-331-C00082).