Short-period superlattices of $AlN/Al_{0.08}Ga_{0.92}N$ grown on AlN substrates

S. A. Nikishin,[a] B. A. Borisov, A. Chandolu, V. V. Kuryatkov, and H. Temkin
Department of Electrical and Computer Engineering and Nano Tech Center, Texas Tech University, Lubbock, Texas 79409-3102

M. Holtz
Nano Tech Center/Department of Physics, Texas Tech University, Lubbock, Texas 79409

E. N. Mokhov, Yu. Makarov, and H. Helava
The Fox Group Inc., 1154 Stealth Street, Livermore, California 94550

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High-quality short-period superlattices of $AlN/Al_{0.08}Ga_{0.92}N$ have been grown by gas-source molecular-beam epitaxy with ammonia on Al face of AlN (0001) substrates. A significant reduction was achieved in the dislocation density, down to 3×10^8 cm^{-2}. Complete removal of residual Al_2O_3 surface oxide is needed in order to obtain low dislocation density in homoepitaxy on AlN. We show that the presence of Al_2O_3 islands with the surface coverage as low as 0.2% results in increased dislocation density. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1815056]

Layers of AlGaN with high content of AlN suffer from high dislocation densities that reduce quantum efficiency and lifetime of light emitting diodes (LEDs) and solar blind photodetectors. Short period superlattices (SPSLs) of $AlN/Al_{0.08}Ga_{0.92}N$, with an average AlN content of 0.60–0.70, used for the preparation of ultraviolet (UV) LEDs and photodetectors operating in the range of 260–290 nm (Refs. 1–4) also show dislocation densities in the 3×10^9–1×10^{10} cm^{-2} range.[5] Close lattice match between bulk AlN and these SPSL layers makes AlN substrates very attractive for use in devices. Metalorganic chemical vapor deposition (MOCVD) of high quality epitaxial AlN,[6,7] $Al_{0.5}Ga_{0.5}N$,[6] multiple quantum wells of $AlN/Al_{0.5}Ga_{0.5}N$,[8] and $Al_{0.5}Ga_{0.5}N/Al_{0.42}Ga_{0.58}N$,[9] and AlGaN-based LEDs[10] on AlN substrates have been reported recently.

In this letter, we describe the structural and optical properties of short period superlattices consisting of AlN barriers and $Al_{0.08}Ga_{0.92}N$ wells grown on (0001) oriented AlN substrates. A significant reduction in the dislocation density, as low as 3×10^8 cm^{-2} compared with 9×10^9 cm^{-2} obtained on sapphire substrates, is demonstrated with only 100 well/barrier pairs. Our experiments also show the importance of complete removal of residual Al_2O_3 from the surface of AlN. Even submonolayer coverage of Al_2O_3 results in significant increase in the dislocation density of homoepitaxial layers. Epitaxial growth was investigated using *in situ* reflection high energy electron diffraction (RHEED).

The Al-face AlN substrates[11] were nominally (0001) oriented, with diameter 1.25 cm and thickness 0.3 mm. The asymmetrical reciprocal space map (RSM) for the $(11\bar{2}4)$ reflection of the AlN substrate is shown in Fig. 1. In addition to the main peak, labeled (1), two subsidiary maxima, labeled (2) and (3), are observed in the $\Delta(2\Theta-\omega)-\Delta\omega$ plot. The presence of these local intensity maxima is characteristic of the mosaic nature of the AlN substrate. The tilt in the mosaic blocks, and the inability of these misoriented blocks to have the optimum x-ray scattering condition at the same time, produces these intensity maxima. The analysis of the central peak of the RSM shows a high degree of lateral coherence of $\sim44\ \mu$m with an average tilt value of ~135 arcsec, consistent with excellent quality of the AlN substrate. This is further corroborated by the narrow linewidths, at full width half maxima, of the symmetric (0002) and asymmetric $(11\bar{2}4)$ ω scans of 100 and 221 arcsec, respectively. From the (0002) linewidth the screw dislocation density is calculated to be $3.5\times10^7/\text{cm}^2$.

SPSLs consisting of AlN barriers [3 monolayers (ML) thick] and $Al_{0.08}Ga_{0.92}N$ wells (3 ML thick) were grown by gas source molecular beam epitaxy (GSMBE) with ammonia.[12] Growth conditions were similar to those used in the growth on sapphire substrates, as described previously.[1–4] A 40 nm thick nucleation layer of AlN was grown first to prepare a two-dimensional (2D) Al-polar surface. A buffer layer of $Al_{0.6}Ga_{0.4}N$ was grown next. In growth on sapphire substrates this layer, with a thickness of ~500 nm, was needed to reduce the dislocation density in overgrown SPSL.[4] It was retained in the growth on AlN substrates for the purpose of comparison. SPSLs of $AlN/Al_{0.08}Ga_{0.92}N$ with 100 pairs were grown next.

The evolution of RHEED patterns illustrating the growth of AlN and $Al_{0.6}Ga_{0.4}N$ buffer layers and the SPSL itself is shown in Fig. 2. Figure 2(a) illustrates the state of the surface of AlN substrate below 700 °C. The positions of the (00), (01), and (−01) reflections from the (1×1) AlN surface reconstruction are indicated by solid arrows. We assume, as

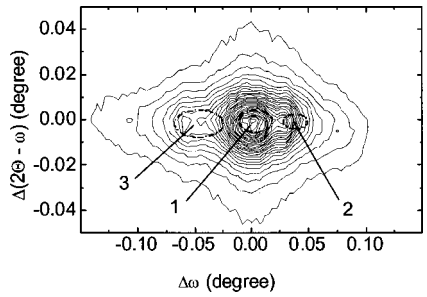

FIG. 1. Reciprocal space map for the $(11\bar{2}4)$ reflection of an AlN substrate. Regions labeled (1)–(3) are indicative of mosaic structure of the wafer.

[a]Author to whom correspondence should be addressed; electronic mail: sergey.nikishin@coe.ttu.edu

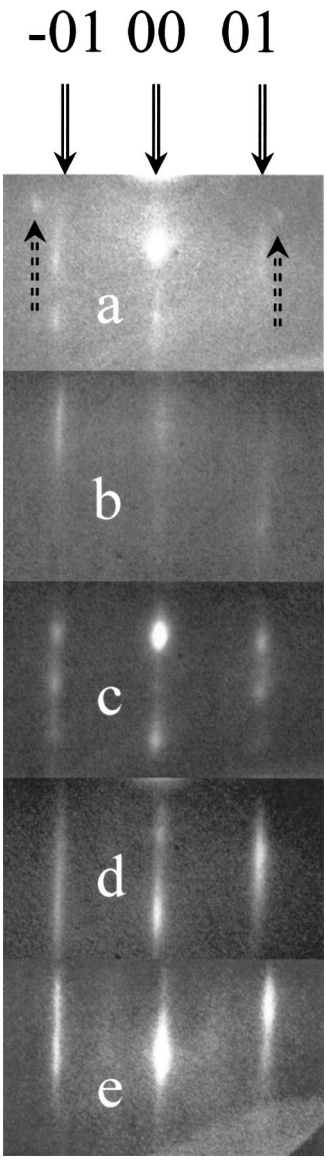

FIG. 2. Evolution of RHEED patterns for different stages of GSMBE: (a) the surface of AlN substrate at $T<700\,°C$. The positions of the (00), (01), and (−01) reflections from the (1×1) AlN surface are indicated by solid arrows. Reflections from crystalline Al_2O_3 islands are indicated by dashed arrows; (b) (1×1) surface structure of AlN exposed to ammonia; (c) formation of 3D islands on 10 nm thick AlN epitaxial layer; (d) 2D growth of $Al_{0.6}Ga_{0.4}N$ buffer with the corresponding streaky pattern; (e) formation of a (2×2) surface structure after deposition of about 20 pairs of SPSL.

discussed below, that the weak additional reflections, indicated by dashed arrows, arise from *ex situ* formation of crystalline Al_2O_3 islands on the AlN surface. These islands cannot be removed by baking of the AlN substrate at high temperatures. Instead, we attempted to nitridate the surface layer by exposing to the flux of ammonia. At a substrate temperature of 800 °C and the ammonia flux of 10 sccm formation of a pure (1×1) surface structure was observed, as shown in Fig. 2(b). This (1×1) structure was stable up to the beginning of epitaxial growth of the AlN nucleation layer, at 900 °C. The 40 nm thick layer was grown with a rate of 300 nm/h. On sapphire, these conditions result in two-dimensional (2D) growth mode after about 2 min of growth.[1–4,13] Surprisingly, the 2D growth mode in homoepitaxy of AlN on AlN substrates could not be reached. Figure 2(c) illustrates the state of the surface after the growth of

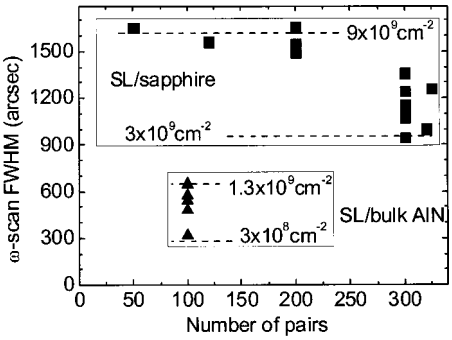

FIG. 3. X-ray linewidth (FWHM) in omega scan plotted as a function of the number of pairs for SPSLs grown on AlN (triangles) and sapphire (squares) substrates. The horizontal dashed lines indicate calculated dislocation densities.

10 nm of AlN. The spots appearing in the RHEED pattern reflect formation of 3D islands of AlN. It is known that addition of Ga facilitates transition to the 2D mode[14] and AlGaN was grown next. Growth of $Al_{0.6}Ga_{0.4}N$, with the growth rate of 450 nm/h, produced the 2D transition in 10–15 min. The corresponding streaky RHEED pattern is shown in Fig. 2(d). The entire $Al_{0.6}Ga_{0.4}N$ layer was grown in the 2D mode and well defined streaky RHEED pattern was maintained during the growth of SPLSs. Formation of a (2×2) surface structure could be seen after deposition of about well/barrier 20 pairs, as shown in Fig. 2(e). The layers were very flat, with the surface roughness (rms) of less than 1 nm as measured by $1\times1\ \mu m^2$ atomic force microscopy scans.

Figure 3 plots the x-ray diffraction linewidth, full width at half maximum (FWHM), of the (0002) peak measured as a function of the total number of SPSL pairs grown on AlN (triangles) and sapphire (squares) substrates. In samples grown on sapphire the linewidth decreases with increasing SPSL thickness, down to ~1000 arcsec for 300 pairs. For 100 pairs the best linewidth was ~1500 arcsec. In samples grown on AlN the FWHM was as narrow as 300 arcsec, for 100 pairs. In SPSLs grown on sapphire the density of screw dislocations was estimated at $9\times10^9\ cm^{-2}$ for less than 200 pairs. In SPLSs grown on AlN substrates screw dislocation density as low as $3\times10^8\ cm^{-2}$ could be obtained, a reduction of over one order of magnitude. However, this dislocation density is consistently higher than that measured in AlN substrates.

Room temperature cathodoluminescence measurements (CL) were carried out at an emission current of 0.1 mA, with the beam diameter of 5 mm. The electron beam voltage of 3 kV was used, resulting in the penetration depth of ~100 nm. The total thickness of SPSL was about 150 nm. Typical CL spectra of representative SPSLs grown on sapphire (dashed line) and AlN (solid line) are shown in Fig. 4. Band-edge emission at 272 nm (4.56 eV) dominates the spectra. This emission wavelength is consistent with the well and barrier thicknesses of these SPSLs.[4] The band-edge intensity of structures grown on AlN is consistently higher, by factors of 2–3, than that grown on sapphire substrates. The emission at ~320 nm is visible in structures grown on either substrate. Its origin is not well understood. The improved CL intensity is attributed to lower dislocation density. In GaN, a reduction in the dislocation density, from 10^9 to $10^8\ cm^{-2}$, is expected to result in radiative recombination and lumines-

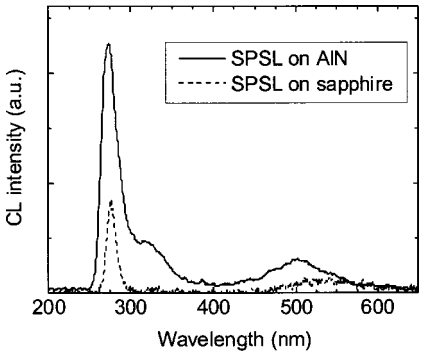

FIG. 4. CL spectra comparing SPSL grown on AlN (solid line) and sapphire (dashed line).

cence efficiency increasing by about a factor of 4,[15] consistent with our results.

Several causes can lead to an increase in the dislocation density in homoepitaxially grown layers. Surface impurities, such as carbon from organic solvents used for cleaning may contaminate the surface and result in 3D growth mode of epitaxial layer with a dislocation density higher than of the substrate. Such problems are well known in epitaxy of GaAs on GaAs[16] but we do not believe carbon contamination is a problem in our case. The Al-terminated surface of AlN is also known to be unstable in air, as determined by thermodynamic considerations.[17,18] The presence of residual native oxide on AlN, may elevate the dislocation density in the subsequently grown AlN layer. We believe that the complex structure observed by RHEED even before any growth is attributable to the presence of islands composed of Al_2O_3. Such an oxide may form by exposure to air, by the reaction: $2AlN+3H_2O \rightarrow Al_2O_3+2NH_3$.[17,18]

From RHEED images we obtain the ratio $a_{island}/a_{AlN(0001)}=0.886\pm0.013$, where a_{island} is the lattice constant determined from the separation between weak reflection seen in Fig. 2(a). This compares to $a_{sapphire(0001)}/a_{AlN(0001)}=0.883$ obtained from standard values of lattice constants of sapphire and AlN.[19] The RHEED images are thus consistent with the presence of islands of Al_2O_3 on the surface of AlN. The effects of this oxide on AlN growth are reduced using a nitridation step, a key feature of growth on sapphire. In our nitridation of AlN, by exposure to ammonia, the RHEED features attributed to the presence of surface Al_2O_3 indeed disappear. The disappearance of these reflections, however, cannot be taken as a proof of complete nitridation of Al_2O_3 islands. While the Al_2O_3 reflections vanished from RHEED screen when the substrate was exposed to ammonia at the high temperatures, one cannot affirm that all islands of Al_2O_3 were nitridated completely. We believe that Al_2O_3 islands are responsible for formation of additional dislocations in subsequently grown AlN layer. Indeed the AlN grown on the top of Al_2O_3 islands should have a similar dislocation density as AlN grown on sapphire.

The smallest ratio for $a_{sapphire(0001)}:a_{AlN(0001)}=0.2747\ nm:0.3112\ nm$ is close to the "magic" ratio of 8:9.[19] A close match and strain relaxation between bulk sapphire and AlN can be obtained by introducing one edge dislocation in every eight surface atoms of nitrogen of AlN.[19] In a monolayer of AlN grown on sapphire this mismatch results in dislocation density of $D_1=1.6\times10^{11}\ cm^{-2}$. Dislocation density in our SPSLs grown on bulk AlN substrates varies from $D_2=3\times10^8$ to $D_2=1.3\times10^9\ cm^{-2}$. Assuming that the entire increase in SPSL dislocation density, over that of $(1-3)\times10^7\ cm^{-2}$ of AlN substrates, is due to the presence of Al_2O_3 islands, the degree of oxidation is given by a ratio of $D_2/D_1\sim(2-8)\times10^{-3}$. Thus, the residual Al_2O_3 islands with surface concentration of 0.2% could increase the dislocation density in homoepitaxial films by over an order of magnitude. The surface coverage of ~0.2% is close to the detection limit of Auger electron spectroscopy or x-ray photoelectron spectroscopy, making direct detection of the Al_2O_3 difficult. This suggests that improvements of homoepitaxial growth of AlN rely on either a surface cleaning process, or more effective nitridation.

In summary, we describe GSMBE growth resulting in high quality $AlN/Al_{0.08}Ga_{0.92}N$ SPSLs on bulk AlN substrates. These SPSLs have lower dislocation density and higher radiative recombination efficiency than similar structures grown on sapphire.

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