Electronic-grade GaN(0001)/Al_2O_3(0001) grown by reactive DC-magnetron sputter epitaxy using a liquid Ga target

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Electronic-grade GaN (0001) epilayers have been grown directly on Al_2O_3 (0001) substrates by reactive direct-current-magnetron sputter epitaxy (MSE) using a liquid Ga sputtering target in an Ar/N_2 atmosphere. The as-grown GaN epitaxial films exhibit low threading dislocation density on the order of $\leq 10^{10}$ cm^{-2} determined by transmission electron microscopy and modified Williamson–Hall plot. X-ray rocking curve shows narrow full-width at half maximum (FWHM) of 1054 arc sec of the 0002 reflection. A sharp 4 K photoluminescence peak at 3.474 eV with a FWHM of 6.3 meV is attributed to intrinsic GaN band edge emission. The high structural and optical qualities indicate that MSE-grown GaN epilayers can be used for fabricating high-performance devices without the need of any buffer layer. © *2011 American Institute of Physics*. [doi:10.1063/1.3576912]

Gallium nitride (GaN) is a wide band gap semiconductor material, used in optoelectronic devices due to its direct band gap of 3.4 eV and it is attracting an exceptional interest due to its suitability as a base for cost-effective high performance optoelectronic devices.[1–7] In the past two decades, reports on GaN films grown by chemical vapor deposition (CVD) or molecular beam epitaxy (MBE) have dominated thanks to the relative ease of achieving electronic-grade epitaxial films.[3,4,6] A few groups have demonstrated band edge photoluminescence (PL) in GaN films, grown by radio-frequency and direct-current (DC) magnetron sputter epitaxy (MSE).[8,9] However, despite some unique and attractive features of the MSE technique, it has not been further pursued for exploitation of electronic grade GaN. The reason is mainly due to unresolved problems leading to, e.g., sputtering process instabilities, nonstoichiometry, and high-defect-densities, etc.[6,8,9]

DC-MSE has the potential of electronic-grade GaN epilayer synthesis at low temperatures thanks to the inherent flux of low energy process gas ions that promote adatom mobility during growth. However, for reactive sputter deposition of electronic-grade GaN there are difficulties in obtaining stable growth conditions, mainly caused by nitridation of the target surface and the low melting point (29 °C) of metallic Ga. For example, a liquid Ga (*l*-Ga) sputtering target needs to be kept horizontal in a cooled trough and sputtering gas can be trapped in the *l*-Ga with bubble bursts in the source as a consequence. On the other hand, mastering reactive sputtering from a liquid target can give clear process advantages such as; elimination of target erosion effects, and a possibility of continuous supply of source material. DC-MSE can also easily be scaled up for deposition over large areas while maintaining excellent control over impurity incorporation.

In this letter, we report the growth of high quality GaN (0001) epitaxial films directly on Al_2O_3 (0001) at 700 °C by a single step DC-MSE growth process with a *l*-Ga target and N_2 gas as sources. A narrow process window is found that balances the sputtering and nitridation of the target. Electronic-grade epilayers are evidenced by time of flight elastic recoil detection analysis (ToF-ERDA), transmission electron microscopy (TEM), high-resolution x-ray diffraction (HRXRD), and PL spectroscopy.

MSE means sputtering under as pure conditions as in MBE, i.e., using very low base pressure and ultrahigh purities of the source materials.[10] A type-II unbalanced magnetron configuration was used to extend the plasma to the substrate vicinity. GaN was grown on (0001) oriented c-plane Al_2O_3 substrates in a UHV chamber having a base pressure of 1.0×10^{-8} Torr. Liquid Ga (99.999 99% pure), contained in a horizontal water cooled stainless steel trough of 50 mm diameter, was used as the magnetron sputtering target. A mixture of Ar (99.999 999% pure) and N_2 (99.999 999% pure) was used as working gas at partial pressures of 2.5 mTorr and 2 mTorr, respectively. Ga was initially sputtered at 20 W for 2 min where after the power was reduced to 10 W. The films were grown with the substrate kept at 700 °C and at floating potential (−20 V). These conditions yielded a growth rate of 1.5 Å/s. It should be pointed out that this is an unexpectedly high growth rate considering the moderate power that is applied to the 50 mm cathode in this process. The growth per energy is 0.15 Å/J, which is about two orders of magnitude higher than for MSE of AlN from a solid Al target under similar conditions[11] and about one order of magnitude higher than InN.[12] This encouragingly high deposition rate of GaN by DC-MSE has not been previously reported and subject to a separate study.

An initial series of experiments revealed a narrow process window in terms of partial pressures. With a slight increase in Ar partial pressure, the films became metallic and a slight increase in N_2 partial pressure lead to deteriorated structural quality as well as a significant drop in growth rate due to target poisoning, evident by formation of a solid nitride scale on the target surface. Films grown at the optimum conditions were found to be N-face by means of a KOH selective etching experiment.[13]

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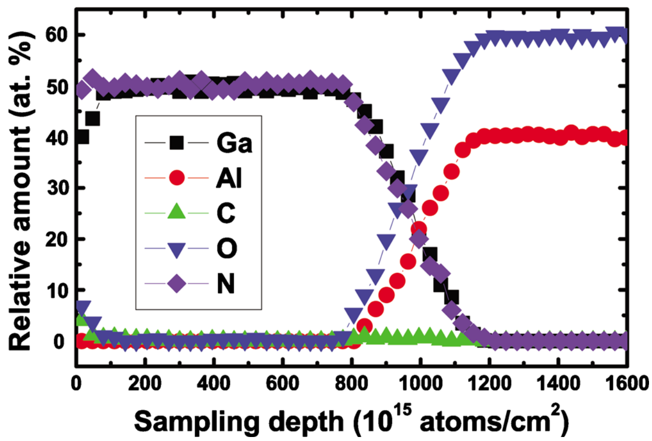

FIG. 1. (Color online) Elemental depth profile of a ∼200 nm thick GaN film obtained by ToF-ERDA.

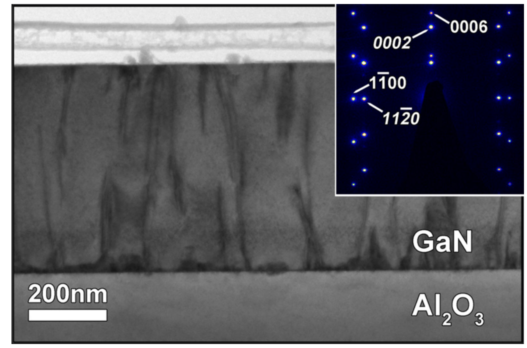

FIG. 2. (Color online) XTEM micrograph and selected area electron diffraction pattern of film and substrate. In the SAED pattern, indices in italic font represent the film and nonitalic fonts represent the substrate. The zone axis is $[11\bar{2}0]$ in the GaN crystal.

A compositional depth profile obtained by ToF-ERDA from a ∼200 nm thick GaN epilayer is shown in Fig. 1. The film demonstrates excellent stoichiometry and purity in its interior, where Ga and N concentrations are 49.7(±1) at. % and 50.1(±1) at. %, respectively. The O content is lower than 0.2 at. % with a slight increase toward the surface and C could be traced also at the film substrate interface. The origin of the increased C-signal at the surface and the interface is unknown, but may stem from hydrocarbons physisorbed at the surface prior and after the growth. Possible sources of O are postgrowth surface oxidation and in-diffusion along threading defects.

A cross-sectional TEM (XTEM) image of the GaN layer is shown in Fig. 2 along with the corresponding selected area diffraction (SAED) pattern, recorded along the $[11\bar{2}0]_{GaN}$ zone axis. The SAED pattern is characteristic of a single crystal GaN epilayer on sapphire with the epitaxial relation: $[11\bar{2}0]_{GaN} \| [1\bar{1}00]_{Al_2O_3}$ and $(0001)_{GaN} \| (0001)_{Al_2O_3}$. As can be seen, the surface is very flat, indicating a two-dimensional growth mode. At the vicinity of the substrate/film interface, a high defect density region is found with features protruding 10–20 nm into the epilayer introducing a certain degree of relaxation at the initial stages of growth. A region of irregular strain contrast is also found to extend into the substrate at the interface which is typical for partially relaxed epilayers. Threading dislocations are observed to appear at the interface and progress with a near constant density throughout the film. Assuming a specimen thickness of 125(±25) nm in the beam direction, the dislocation density is estimated to $\sim 8(\pm 1) \times 10^9$ cm^{-2}.

HRXRD was performed using a Philips X'Pert MRD diffractometer equipped with a hybrid mirror monochromator and an asymmetric channel-cut Ge-analyzer crystal. Reciprocal space maps (RSMs) around the GaN 0002 and $10\bar{1}5$ reflections, recorded at the same azimuth, are shown in Fig. 3. The maps show well defined peaks and their positions yield the *a* and *c* lattice parameters to be 3.187 Å and 5.190 Å, respectively, which corresponds to a 0.047% isotropic lattice expansion combined with a 0.11% biaxial basal plane compression, if compared to the relaxed parameters.[14] The isotropic expansion indicates the presence of point defect in the film, which may be generated through the exposure of the surface to the sputtering plasma during growth. The biaxial strain component can be explained by the thermal expansion coefficient mismatch between GaN and the sapphire substrate. The rocking curve full-width at half maximum (FWHM) of the 0002 peak is 1054 arc sec, which is comparable to what is obtained by other growth techniques directly onto Al_2O_3,[15,16] indicating a relatively high crystal quality. The broadening direction of the $10\bar{1}5$ reciprocal lattice point is somewhat inclined from the lateral direction (‖ surface) toward the direction perpendicular to the Q-vector (ω-direction) (see Fig. 3), which is typical for films exhibiting a small mosaic tilt and a limited lateral domain size.[17] The size, shape, and inclination of the $10\bar{1}5$ reciprocal lattice point are similar to high-quality films grown to the same thickness by CVD and MBE.[6,15,16] The density of the threading screw dislocation was calculated by the use of a modified Williamson Hall plot of the broadening of 0002, 0004, and 0006 rocking curves[18,19] which gave a screw dislocation density of 1.6×10^9 cm^{-2}. This is about 20% of the total thread-

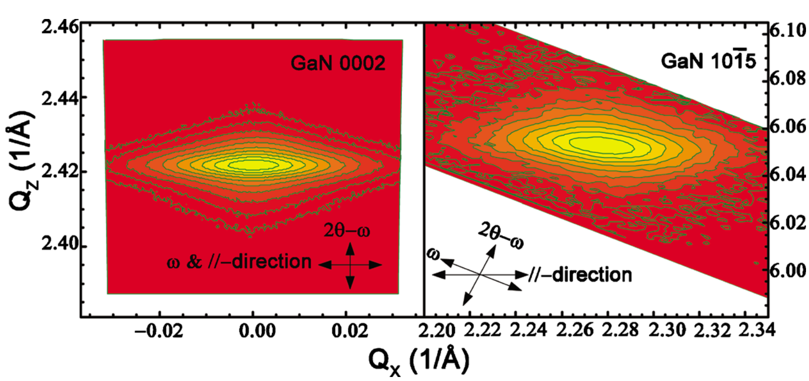

FIG. 3. (Color online) RSMs around the GaN 0002 and $10\bar{1}5$ reflections.

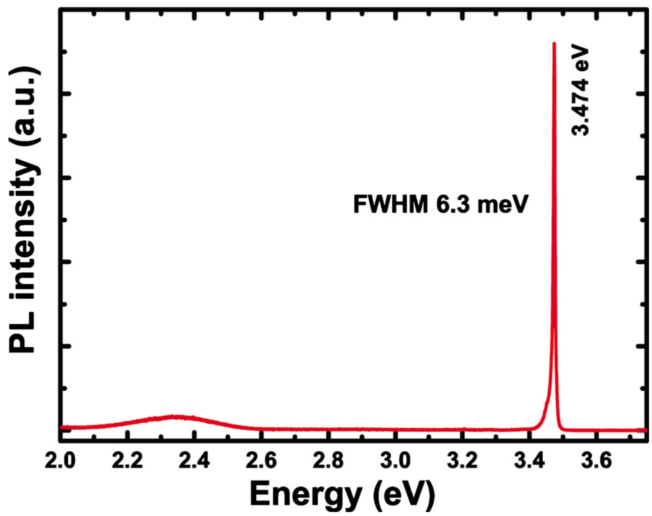

FIG. 4. (Color online) Low temperature (4 K) μ-PL spectrum.

ing defect density estimated from the XTEM micrograph indicating that edge dislocations are the dominant threading defects in these layers.

In both MBE and CVD growth of GaN it is common to use an AlN buffer layer to reduce the defects in the GaN film by trapping them close to the interface and also to reduce the effect of thermal expansion differences to avoid cracking. Also, in conventional GaN growth methods the film thickness is commonly a few micrometers, which is dictated by the need to bury the defects generated in the seed/buffer layer.[20] In the present work no buffer layer was used, yet the defect density is low close to the interface (see Fig. 2) compared to CVD-grown films where low temperature GaN or AlN buffer layers are used to confine most of the defects within the first 200–300 nm.[21] This implies that MSE growth may yield fewer defects at the beginning of the growth of epitaxial GaN film without the need for a buffer or low temperature nucleation layer. A reason for the low defect density during initial growth of MSE-grown GaN can be the higher adatom mobility due to a relatively high kinetic energy of the sputtered atoms and stimulated surface mobility by impinging ions from the sputtering plasma.

To demonstrate the optoelectronic semiconductor properties of the material, microphotoluminescence (μ-PL) was carried out at low temperature (4 K) and also at room temperature, excited with a continuous-wave 266 nm laser.[22] A 4 K μ-PL spectrum, shown in Fig. 4, exhibits a sharp near band edge (BE) emission at 3.47 eV with a narrow FWHM of 6.3 meV. The result indicates a high-purity and high-quality GaN film, in accordance with the TEM and HRXRD results. The FWHM of 6.3 meV is the narrowest reported BE emission from MSE-grown GaN.[9] In addition, our material also reveals strong room-temperature μ-PL BE-luminescence at 3.4 eV with a FWHM of 73.3 meV, although slightly redshifted and broadened due to lattice expansion and carrier thermalization effects. In contrast to the strong band edge emission, a weak and broad yellow luminescence is observed. Such luminescence is widely observed also in CVD and MBE films and is explained by impurity related defect states.[3,5,23]

In conclusion, the epitaxial growth of electronic-grade GaN(0001) onto c-plane Al_2O_3 by reactive DC-MSE from a liquid Ga target is demonstrated at a moderate temperature of 700 °C. The material has excellent structural and optical properties without any buffer layer of AlN or low-temperature GaN nucleation layer. The scalability of magnetron sputtering makes MSE a suitable method for large scale production of electronic grade GaN epilayers onto very large substrates.

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