Single-crystal hexagonal and cubic GaN growth directly on vicinal (001) GaAs substrates by molecular-beam epitaxy

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(Received 29 October 1999; accepted for publication 10 March 2000)

Single-crystal hexagonal and cubic GaN thin films have been grown by radio-frequency nitrogen plasma source molecular beam epitaxy directly on vicinal (001) GaAs substrates, misoriented by 2° toward [100], without using an incident As beam during oxide desorption or the following stages of growth. Both the GaAs nitridation and GaN growth conditions were found to control the structure of the layers. Cubic layers could be grown only without nitridation and under stoichiometric N/Ga flux ratio conditions. N-rich conditions favored the growth of hexagonal layers, which exhibited significantly higher photoluminescence intensities compared to cubic ones. Hexagonal single crystalline GaN films were grown with (1012) planes and presented characteristic surface roughness striations along a (110) substrate direction. On the contrary, a stepped surface morphology was observed for cubic GaN. © 2000 American Institute of Physics.

S0003-6951(00)04818-X]

The realization of device quality GaN layers on GaAs substrates is very interesting, since it could offer several unique advantages: (i) use of well developed GaAs substrates for GaN technology, (ii) monolithic integration of GaN and GaAs devices, and (iii) exploitation of any superior physical or technological properties of the cubic GaN material that can be grown on (001) GaAs1–5 or (001) Si.6,7 Most of the GaN-on-GaAs work has been concentrated on the growth of cubic material. In the molecular beam epitaxy (MBE) method,1–5 an optimization of the GaAs (2×4) surface (by growing a GaAs buffer layer) always proceeded the cubic GaN growth.

In this letter, we present results showing that both hexagonal (h-GaN) and cubic (c-GaN) single-crystal GaN material of excellent optoelectronic quality can be achieved by direct MBE growth of GaN on vicinal (001) GaAs substrates under the appropriate growth conditions. Contrary to previous MBE work, we have not employed an As beam either during oxide desorption or during GaN nucleation and growth and no GaAs buffer layers were introduced.

Thin films of 1.2–1.8 μm GaN were grown by plasma-assisted MBE using a radio-frequency (rf) nitrogen plasma source. The operating power of the rf-plasma source was 400 W at N2 flux of 1 standard cubic centimeter per minute (sccm). The N2 flux was kept constant in all experiments, while the Ga flux was varied within a short range around that required for 0.6 μm/h growth rate. Semi-insulating GaAs substrates, misoriented by 2° from (001) toward [100], have been used.

Initially, GaAs oxide desorption was carried out in the growth chamber at vacuum better than 10−10 Torr. The substrate temperature, measured by a noncontact thermocouple, at oxide desorption was considered to correspond to 600 °C actual substrate temperature and it was used as reference for the following work. The reflected high-energy electron diffraction (RHEED) patterns were generally characterized by modulated line intensity, weak ×2 reconstruction along the [110] azimuth, and faceting along the [110] azimuth. During preparation of the N2 rf-plasma source, the substrate was kept at 450 °C and was turned far from the incident nitrogen beam. After the rf-plasma source was stabilized, two different approaches were compared for initiating the GaN deposition at 540 °C: (i) the GaAs surface was exposed to the N-plasma beam, as the substrate temperature was increased from 450 to 540 °C, (ii) the GaAs surface was exposed simultaneously to the N2 plasma and Ga flux at 540 °C. A two-step GaN growth was then followed with initial growth of few GaN monolayers at 540 °C and a final growth temperature (Tc) of 600–630 °C, without growth interruption.

During growth, the surface of the layers was monitored by RHEED. The crystallinity of GaN was analyzed by x-ray diffraction (XRD) with a powder diffractometer using Cu Kα radiation source. Microstructure was revealed by transmission electron microscopy (TEM), for which cross-sections were prepared by ion milling. The optical properties of the GaN layers were studied by photoluminescence (PL) measurements at 15 and 300 K, using a He–Cd laser excitation at 325 nm, 35 mW. The surface morphology of the layers was studied by atomic force microscopy (AFM).

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GaN growth always started with the formation of polycrystalline material, as shown by RHEED. The polycrystalline RHEED patterns, however, completely disappeared after growing a few monolayers of GaN and single crystal hexagonal or cubic GaN could be grown. RHEED exhibited spotty patterns for hexagonal material and streaky 1131 patterns for cubic GaN, with a weak 32 reconstruction occasionally visible along (110) after growth completion.

The most important condition for growing cubic GaN was found to be the elimination of the exposure of the GaAs surface to N plasma before initiating the GaN deposition. However, for both initial exposure approaches, an amorphous RHEED observation characterized the first moments of N-plasma incidence on the GaAs surface. Our observations indicate that sufficient GaAs nitridation up to 540 °C favors the nucleation of hexagonal GaN material.

Figure 1 shows a typical XRD pattern of the single crystalline hexagonal GaN films, where the (002) and (004) Bragg peaks from the substrate are used as reference. The main peak due to the GaN layer could be identified as the (1012) Bragg reflection at about 2θ=48.2° of the hexagonal GaN, while the hexagonal (0002) and cubic (002) reflections could be hardly detected. This implies that the hexagonal layers are grown with the (1012) planes, rather than the (0001), parallel to the surface. Taking into account that the angle between the hexagonal (1012) and (0001) GaN planes is 43°, the XRD pattern can be understood assuming that the layer is grown with the [0001] direction (c axis) inclined to the surface normal by 43°. This is clearly proved by the high-resolution TEM image of the h-GaN/GaAs interface [Fig. 2(a)]. The above-calculated angle between the c axis and the surface normal can be measured in Fig. 2(a).

The N/Ga flux ratio (R) was also found to be a critical parameter for controlling the final crystal structure of cubic or hexagonal GaN on vicinal GaAs. Single crystalline cubic GaN layers were grown only under stoichiometrical R values and when nitridation of the GaAs surface was not used. N-rich growth conditions always favored the growth of hexagonal GaN.

The XRD patterns of cubic GaN layers were characterized by the (002) Bragg reflection of cubic GaN at 2θ =40°. This reflection exhibited a full width at half maximum (FWHM) of 0.5° (θ–2θ scanning) which is rather good compared to 0.1° of the GaAs substrate. Figure 2(b) shows a high resolution TEM image of the cubic GaN layer following the orientation of the substrate.

A typical 15 K PL spectrum of the cubic 1.8 μm GaN film, grown without a pre-exposure of GaAs to N-plasma (nitridation) and under stoichiometric flux ratio conditions, is shown in Fig. 3. Two emission lines were observed at 3.26 and 3.15 eV, with FWHM of 33 and 39 meV, respectively. These two peaks are attributed to the cubic phase and have been assigned to bound exciton and donor–acceptor (D–A) transitions, respectively. The room temperature PL spectrum of cubic GaN showed a strong band edge emission at 3.21 eV with 58 meV FWHM and no emission signals were recorded above 3.30 eV, which correspond to hexagonal GaN.
GaAs. The results suggest a high quality of the grown cubic films.

A strong peak at 3.40 eV, probably related to a D–A transition and a weak donor–bound exciton peak at 3.46 eV characterized the 15 K PL of hexagonal GaN grown at high N/Ga flux ratio. A remarkable feature in these samples was the absence of the yellow luminescence band and this may suggest that the density of defects being responsible for the yellow peak was low.

The typical surface morphologies of the single crystalline cubic and hexagonal GaN films are shown in the AFM images of Figs. 4(a) and 4(b), respectively. Smoother surfaces were obtained for cubic GaN [Fig. 4(a)]. The stepped surface morphology of Fig. 4(a) was typical for all the cubic films, indicating a step-flow growth mechanism. The rms roughness of the layers was at around 3.5 nm. The hexagonal GaN films were characterized by roughness striations aligned along a (110) GaAs direction, as shown in Fig. 4(b). The rms roughness of these layers was significantly higher than that of the cubic ones and a value of approximately 9 nm was determined for a GaN film, of similar thickness.

Our results indicate that both hexagonal and cubic single-crystal GaN can be grown by MBE on vicinal (001) GaAs, with a “nonconventional” growth procedure (direct growth on GaAs and high growth rate). The details of the initial exposure of the GaAs surface to N plasma and the N/Ga flux ratio were found to control the crystal structure of the layers. The N/Ga flux ratio (R) dependence is in agreement with previous studies of the growth of GaN on (001) GaAs substrates.1–3

In general, it has been considered impossible to grow cubic GaN on a vicinal GaAs surface or a nonoptimally flat GaAs (001) surface. We have shown, here, that both hexagonal and cubic single-crystal material can be grown easily on a vicinal (001) GaAs surface, without using a GaAs buffer to optimize the surface quality. Our approach initially starts with the growth of a polycrystalline-mixed phase material but the selected growth and nitridation conditions obviously favor the subsequent domination of one crystalline phase orientation. We consider very important the use of vicinal substrates for the successful completion of this process. The surface step array should provide a preferential direction for the growth of different GaN crystals, under different conditions, assisting in the eventual overgrowth of a single domain thin film material. Evenmore, our approach, without the use of As in the beginning of the growth, is more suitable for future exploitation, but most importantly it excludes As from the growth chamber, which may have degrading effects, as impurity, in the material’s luminescence properties.1

Summarizing, we have presented an approach of controlled MBE growth for synthesis of single-crystal cubic or hexagonal GaN on vicinal (001) GaAs, misoriented by 2° toward [100], without any growth pretreatment using an As beam. The pre-exposure of the vicinal (001) GaAs surface to N-plasma, prohibits the growth of cubic GaN. However, when the GaAs surface is exposed simultaneously to the N plasma and Ga beams, a hexagonal or cubic crystal phase may be selected by the adjustment of the N/Ga flux. Both GaN crystal phases presented promising luminescence properties for the development of GaN devices on (001) GaAs substrates.

Research programs of the GSRT, Hellenic Ministry of Development and a research grant of University of Crete have supported this work. OTKA project No. T030447 is also acknowledged for financial support and author B.P. thanks the University of Oxford, Department of Materials, for providing the HREM facility.