Properties of GaN grown at high rates on sapphire and on 6H–SiC

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Thick GaN films were deposited with growth rates as high as 250 μm/h by the direct reaction of ammonia and gallium vapor at 1240 °C. The characteristics of our films are comparable to those of typical thin films grown by metal organic chemical vapor deposition or molecular beam epitaxy. Grown under identical conditions, films on (0001) sapphire and on (0001) 6H–SiC were compared in terms of their structural and optical properties. Considering x-ray rocking curve full width at half-maximum (FWHM: 420 arcsec), photoluminescence linewidths of the excitons (FWHM: 3 meV at 6 K and 100 meV at 300 K), free electron concentration, defect related luminescence, and the homogeneity of these properties, we find superior values for films grown on SiC. For both substrate materials we find an optimum growth rate window of 40–80 μm/h. © *1996 American Institute of Physics.* [S0003-6951(96)01944-4]

Considerable progress in the growth of wide band-gap nitrides, especially GaN, has been achieved employing highly developed growth techniques like metal organic chemical vapor deposition (MOCVD)[1,2] and molecular beam epitaxy (MBE).[3,4] The technique of hydride vapor phase epitaxy (HVPE) has been proven to deliver thick GaN films of high quality.[5] Currently, bulk GaN crystals with dimensions of only a few millimeters can be obtained with high pressure synthesis.[6] All the mass produced light emitting diodes are fabricated using thin film deposition techniques. However, nitride films sufficiently thick to exhibit bulk properties are required for obtaining a better understanding of the underlying physics. The growth and characterization of thick GaN films obtained with high temperature vapor phase epitaxy at high growth rates are presented. The structural and luminescence characteristics of our thick films are comparable to those of thin films produced by other growth techniques.

The key to high quality epitaxy is a matching substrate in terms of crystal structure and lattice constant at all temperatures. Any remaining stress is expected to strongly affect the segregation of In in GaInN alloys. Consequently, bulk GaN would be the most promising substrate material for obtaining the highest quality of homoepitaxial films. At present α-sapphire or the more expensive 6H polytype of silicon carbide are used because GaN substrates are not available. To overcome the lattice mismatch between GaN and the heterosubstrates, AlN (Ref. 7) or GaN (Ref. 8) buffer layers have been utilized.

An alternative solution has been demonstrated by the use of thick GaN templates obtained by HVPE at a high growth rate of $\sim$60 μm/h.[9] For this purpose, typically low growth rates <1 μm/h for MOCVD and MBE are not acceptable. Recently, we reported on even higher growth rates of up to 300 μm/h that were achieved through a modification of the sublimation sandwich method (SSM).[10] In SSM,[11,12] typically employed for the epitaxy of SiC, a powder or polycrystalline material is evaporated, transported across a small gap by a thermal gradient and recrystallized on a substrate. We demonstrate here that evaporation of metallic Ga in an ammonia ambient is a very convenient alternative to growing thick, high quality GaN films. This technique has all the characteristics of a vapor phase epitaxy performed at an unusual high temperature. We more appropriately name this process high temperature vapor phase epitaxy (HTVPE). Typical vapor phase techniques for GaN (MOCVD, HVPE) operate around 1000 °C, whereas HTVPE requires considerably higher temperatures near or above 1200 °C. We present the properties of GaN layers grown by HTVPE from metallic Ga and gaseous NH_3 on (0001) sapphire and (0001) 6H–SiC substrates.

A schematic of the horizontal flow quartz reactor is given in Fig. 1. The cylindrical graphite crucible consisting of two parts is heated inductively by a 450 kHz radio frequency source. The lower part of the crucible contains the metallic Ga source. The substrate measuring 1×1 cm^2 is mounted on the upper part facing the Ga source at a very small distance of only a few millimeters. A net flux of Ga towards the substrate is obtained by a perpendicular temperature gradient of several degrees K/cm. N is provided by a stream of NH_3 injected into the gap between the Ga source and the substrate.

At the beginning of the growth cycle the system is precleaned with a 520 °C, 20 min vacuum bakeout. At this temperature, the Ga vapor pressure is 10^{-2} Pa and can be neglected. To initiate GaN growth, the flow of NH_3 is started at 22 cm^3/min and the temperature is raised to 1240 °C within about 2 min. After equilibrium is reached a total pressure of 1.5×10^3 Pa is measured outside the crucible. To stop growth, the NH_3 flow is interrupted and 2 l/min of N_2 are used during the cooldown phase that lasts about 1 h. A po-

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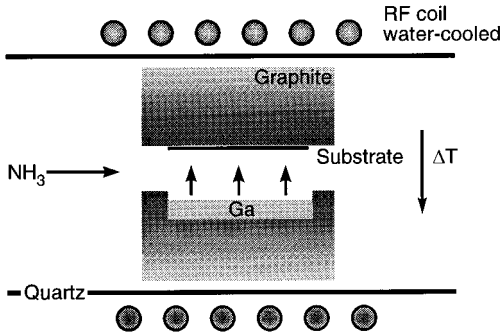

FIG. 1. Schematic of the high temperature vapor phase epitaxy reactor. The graphite crucible containing the metallic Ga and the substrate is heated inductively via a water-cooled coil. Ga vapor is transported over a short gap of a few millimeters.

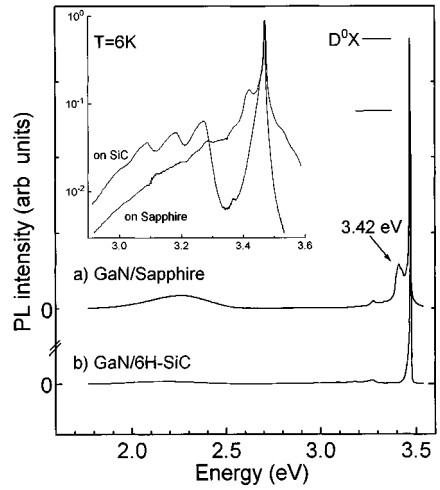

FIG. 2. Photoluminescence spectra recorded at 6 K for GaN grown on (a) sapphire and (b) 6H–SiC. The films on sapphire exhibit an additional luminescence band around 3.42 eV that is absent in the films on 6H–SiC. The spectra were normalized to be the donor-bound exciton emission and displaced vertically.

tentially advantageous feature of the growth process described here is the very high growth rate of GaN. We have achieved rates of up to 250 μm/h by optimizing the temperature gradient between the Ga source and the substrate. Smooth films of constant thickness and homogeneous optical, structural, and defect properties across the entire substrate were found at an optimum temperature difference between 10 and 20 K over a gap of 7 mm, resulting in growth rates of 40–80 μm/h for both SiC and sapphire. We found that the growth rate is more stable when SiC is used as a substrate instead of sapphire. Homogeneous films of a thickness of up to 20 μm could be obtained within a total growth cycle of only 100 min. No special buffer layers were used for these growth cycles.

The epitaxial GaN films were almost transparent and exhibit smooth surfaces on a length scale of 100 μm in the optical microscope. The films were also characterized by x-ray diffraction and photoluminescence (PL). θ–2θ scans and x-ray rocking curve measurements of the (0002) GaN peak were recorded with a four crystal high resolution x-ray diffractometer. The PL was excited with the 325 nm line of a 40 mW HeCd laser and the emitted light was detected using a photomultiplier and standard lock-in techniques. The spectra were taken at 6 K as well as at room temperature.

Thick (0001) oriented GaN films were obtained on both substrates as proven by θ–2θ x-ray scans, which revealed the GaN (0002) and (0004) diffraction peaks. The film quality along the growth direction was assessed by a rocking curve measurement of the (0002) peak. Depending on the growth rates, rocking curve FWHM of 420–1000 arcsec were observed for the (0001) 6H–SiC based material and 1000–1250 arcsec for the films on (0001) sapphire. The higher values were observed for the higher growth rates. This indicates a lateral transport limitation of the gaseous precursors on the growth surface. Results obtained by counting line defects in a cross-sectional view of a high resolution transmission electron micrograph indicate a density of dislocations in the range of 10^9 cm^{-2} in the GaN films grown on sapphire.[13] They are highly oriented perpendicular to the substrate and their density is similar to values found in other reports.[14]

PL spectra of films grown on both types of substrates taken at 6 K are displayed in Fig. 2. The luminescence of all films is dominated by the recombination of excitons bound to neutral donors (D^0X) with a typical line width of 3–5 meV. The line position coincides with the transition in bulklike material at 3.472 eV (300 μm HVPE film[5]). We find this value independent of the film thickness and for both substrates investigated. This observation stands in contrast to other reports where considerable deviations of the peak positions are observed (HVPE,[5] MOCVD[15]). These differences are typically attributed to biaxial stress in the films due to a mismatching substrate or due to the thermal mismatch introduced during the cooldown phase directly after the growth. From the fact that we find identical peak positions for GaN on 6H–SiC (compressive stress) and GaN on sapphire (tensile stress), we conclude that HTVPE films have no substrate induced stress at low temperatures (6 K).

Significant effects of the two types of substrates are observed in PL (Fig. 2) only at low temperatures. In contrast to films on SiC (spectrum b), GaN films on sapphire (spectrum a) exhibit a strong additional luminescence band centered around 3.42 eV. Its apparent optical localization energy of 80 meV indicates the presence of an impurity with a strong central cell interaction. The partially resolved fine structure of this peak suggests the participation of the nondegenerate valence band. This supports a recent assignment of an oxygen related donor-to-valence band transition.[16] In bandstructure calculations of GaN it has been shown that the low lying $3d$ shells of gallium interact with the shallow lying electrons of the small nitrogen core.[17] A similar interaction should then also be expected for the very low mass oxygen impurity in GaN. As films on both types of substrates were grown under identical conditions, the sapphire substrate must be considered to be the source of oxygen.

At energies around 3.27 eV, zero phonon lines of band–acceptor and donor–acceptor pair transitions are observed (see logarithmic plot in the inset of Fig. 2). These transitions have been reported repeatedly and indicate the presence of a common acceptor. We recently pointed out that carbon is a very likely candidate.[18] The splitting of the band–acceptor and donor–acceptor pair transitions is strongly affected by

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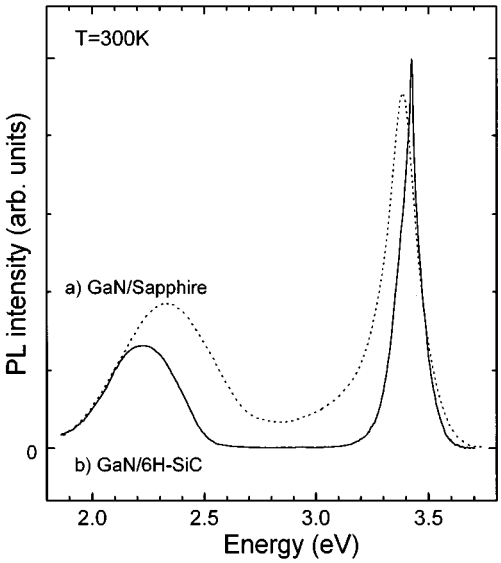

FIG. 3. Photoluminescence spectra recorded at room temperature for GaN grown under identical conditions on (a) sapphire and (b) 6H–SiC.

the impurity concentration and allows for an approximate determination of the major dopant concentrations.[19,18] We find a donor concentration near 10^{17} cm^{-3} for the films grown on SiC and higher concentrations near 10^{18} cm^3 for films grown on sapphire. The corresponding free electron concentrations in this range were confirmed in Raman experiments using the A_1(LO) phonon–plasmon coupled mode.[20] We do not report results based on transport measurements (Hall effect, resistivity) because these were found to be unreliable and very sensitive to structural defects such as microcracks.

A weak PL contribution at 3.36 eV is found for GaN grown on SiC (inset Fig. 2). Due to its low intensity, this feature is obscured in the films grown on sapphire. It was shown recently that this line can be attributed to strongly localized excitons associated with structural defects.[21]

In addition, the frequently reported luminescence around 2.2 eV is observed. Comparing the peak spectral intensities, we find that the near-band-edge emission strongly dominates in films grown on both SiC and sapphire. In a recent study such a dominance was correlated with a small ratio of group III and group V atomic fluences at the growth surface.[22] It is not clear what mechanism would lead to such a correlation.

Room temperature PL data are presented in Fig. 3. Luminescence of the films on SiC is still dominated by the near-band-edge transitions at 3.426 eV (300 K) at a FWHM of only 100 meV. The peak maxima of the films on sapphire are found at smaller energies (3.38 eV at 300 K). This energy corresponds to the defect related band at low temperatures (3.42 eV at 6 K).[23] Comparing the relative luminescence intensities of those two lines at room temperature with the corresponding ratio at low temperature, we find a strong decrease of the 3.426 eV near-band-edge transition in GaN on SiC. A smaller decrease is found for the defect related band in GaN on sapphire. This is a direct consequence of the difference in their respective binding energies. It should be mentioned that the defect related luminescence band coincides with the reported emission energy of stimulated emission in GaN.[24] This defect, which previously has been associated with oxygen,[16] could therefore be a critical factor in device optimization.

In summary, growth of GaN films on sapphire and 6H–SiC at very high growth rates by high temperature vapor phase epitaxy is reported. Significant differences are observed depending on the substrate used. We find a higher structural and optical quality for films grown on (0001) SiC than on (0001) sapphire. We relate this to the reduced lattice mismatch and a better thermal stability of SiC. The observation of the 3.42 (6 K) defect band in combination with a higher free electron concentration in the films grown on sapphire suggests unintentional doping with oxygen from the sapphire. The high quality of the material and the high growth rates of 40–80 μm/h make HTVPE a suitable technique for the growth of thick GaN films that subsequently could be used as templates for homoepitaxial GaN.

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