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Crystal Morphology and Optical Emissions of GaN Layers Grown on Si(111) Substrates by Molecular Beam Epitaxy

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Crystal morphology of GaN layers grown on Si(111) evolves from whisker-like microcrystals to compact films as a function of the III/V ratio. Small changes in the III/V ratio (from Ga-rich to N-rich) during the growth of a compact layer result in the appearance of microcrystals on the top of the layer, indicating a sharp transition between the two growth regimes.

Four different morphologies are obtained by increasing the III/V ratio: a) completely columnar whisker-like samples exhibiting a pair of intense excitonic emissions at 3.471–3.478 eV; b) a mixture of compact regions with columnar microcrystals showing two pairs of excitonic emissions; c) compact layers with very small microcrystals on the top surface with a weaker dominant transition at 3.415 eV (±5 meV) and, d) full compact and smooth layers with a single dominant excitonic emission at 3.466 eV. A combination of PL measurements with SEM photographs and CL imaging reveals that both pairs of emissions in samples b) come from the columnar microcrystals. The high energy pair (3.471–3.478 eV) is attributed to the free-exciton A and a donor-bound exciton while the low energy pair (3.452–3.458 eV) is assigned to acceptor-bound excitons associated to valence bands Γ_{9v} and Γ_{9v}. Power and temperature dependence together with time-resolved data show that the dominant peak at 3.415 eV (±5 meV) present in samples c) correspond to a donor-acceptor transition. CL measurements as a function of electron beam energy (depth) also indicate that this emission is more intense towards the interface between the layer and the sample. Finally, the excitonic emission in samples d) is shifted to lower energies due to residual biaxial tensile strain of thermal origin.

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Magneto-Optical Studies of Shallow Donors in MOCVD Grown GaN Layers in FIR

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Far infrared magnetooptical investigations of shallow donors in epitaxial MOCVD GaN layers show two types of shallow donors. In relaxed layers, a donor with an ionization energy of 35 meV was found. In strained, undoped and Si doped samples, a donor with ionization energy 32.5 meV was observed. From the p state splitting in magnetic field, the cyclotron effective mass for conduction electrons was found to be $m^* = 0.222\ m_0$.

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Luminescence and ESR Spectra of GaN:Si Below and Above Mott Transition

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Investigations of luminescence and ESR of silicon doped GaN layers are presented. The room temperature electron concentration in the investigated layers ranged from 1.7×10^{17} cm^{-3} to 7×10^{18} cm^{-3}. The layer with the highest electron concentration has metallic conductivity. The ESR investigation revealed the presence of a characteristic asymmetric resonance whose intensity grows with increasing silicon impurity concentration. This resonance, corresponding to perpendicular $g = 1.985$ and parallel $g = 1.983$ has been observed in Si doped layers with electron concentration below the Mott transition. It seems that the ESR resonance is due to isolated Si donors. It has been found that the total PL emission increases with the silicon concentration, and is strongest in the layer with metallic conductivity. This indicates that silicon impurities eliminate non-radiative recombination centers or they create a new path of radiative recombination. The AFM and low temperature PL measurements indicate that strain relief via creation of pinholes may be responsible for the increase of radiative emission in GaN: Si epilayers.

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Threshold Currents of Nitride Vertical-Cavity Surface-Emitting Lasers With Various Active Regions

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A detailed threshold analysis of room-temperature pulsed operation of GaN/AlGaN/AlN vertical-cavity surface-emitting lasers (VCSELs) is carried out. The model takes advantage of the latest results concerning gain in active regions, material absorption in the cladding layers, as well as cavity diffraction and scattering losses. The simulation showed that although VCSELs with single (S) or multiple (M) quantum-well (QW) active regions exhibit lower threshold currents, they are much more sensitive to any increase in optical losses than their bulk counterparts. In particular, decreas-

ing the active region radius of gain-guided QW VCSELs below 5 μm (which increases diffraction losses) or increasing dislocation densities (which, in turn, raises scattering losses) gives an enormous rise to their threshold currents. Therefore small-size GaN VCSELs should have an index-guided structure. In the case of MQW VCSELs, the optimal number of quantum wells strongly depends on the reflectivities of resonator mirrors. According to our study, MQW GaN lasers usually require noticeably lower threshold currents compared to SQW lasers. The optimal number of QW active layers is lower in laser structures exhibiting lower optical losses. Although the best result occurred for an active region thickness of 4 nm, threshold currents for the various sizes differ insignificantly.

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Properties of GaN Epilayers Grown on Misoriented Sapphire Substrates

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Three silicon-doped 3 μm thick GaN epilayers were grown simultaneously by metalorganic chemical vapour deposition on (0001) sapphire substrates misorientated by 0°, 4° and 10° toward the m-plane (100). A comparative study of these epilayers was undertaken using photoluminescence (PL) spectroscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), cathodoluminescence (CL) imaging, CL spectroscopy and Hall effect measurements. Low temperature PL of the 0° and 4° epilayers shows donor bound exciton (BE) emission between 3.47 and 3.48 eV and a low level of yellow band emission. The peak intensities of both emission bands are a factor of 2 higher for the 4° layer. In the 10° epilayer, the BE band is 3× stronger than in the 0° epilayer but there is no discernible yellow band. However, a number of additional bands appear at 3.459, 3.417, 3.362, 3.345, 3.309, and 3.285 eV. These bands, some of which are acceptor related, may be attributed to the presence of structural defects in this epilayer, pointing to an abrupt degradation of its structural quality compared to the others. This degradation is confirmed by AFM studies. On a 20 μm × 20 μm image the 0° and 4° epilayers exhibit smooth surface morphologies, while the 10° epilayer shows a high density of hexagonal pits. Finally, SEM images reveal the surface of the 10° epilayer to be "streaked" and pitted. Low temperature CL images at 3.48 eV (bound exciton region) show random spotty emission, while those at 3.28 eV and 3.41 eV exhibit a streaky appearance similar to the SEM image. This suggests that these luminescence bands are indeed associated with structural defects.

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Schottky Diodes on MOCVD Grown AlGaN Films

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Au Schottky diodes were prepared by vacuum evaporation or by plasma sputtering on n-AlGaN(Si) films with Al mole fractions of 0, 0.11 or 0.23. The barrier heights were deduced from C-V and I-T measurements. The difference between the C-V and I-T results was less than 0.1 eV for the barriers deposited at 300°C on HF etched samles with prior in situ heating at 450°C. For low deposition temperatures (about 150°C) C-V and I-T methods give results differing by some tenths of an eV. For deposition temperatures exceeding 450°C the diodes were very leaky. The barrier heights were 0.8 eV, 0.9 eV and 1.1 eV for AlGaN with compositions of 0, 0.11 and 0.23. For plasma sputtered diodes on GaN and AlGaN (x = 0.11) samples, the difference in C-V and I-T results was quite considerable and admittance spectroscopy indicated the presence of deep electron traps at 0.12–0.14 eV that were absent in vacuum evaporated diodes. For similar diodes on AlGaN(x = 0.23) samples the results of C-V and I-T measurements were very close and no traps at 0.12–0.14 eV could be detected. This difference is most likely due to damage caused by low energy ions. More Al-rich films are less susceptible to such damage. Persistent photocapacitance was observed in n-AlGaN Schottky diodes after illumination at 85 K.

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GaN-Based Materials for Blue Emitting Device Structures Grown in Multiwafer Planetary® Reactors

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Using optimised growth processes for an AIX 2000 HT Planetary® Reactor a high material quality and high potential device yield are demonstrated. Doping levels for GaN single layers from $1 \cdot 10^{20}$ cm^{-3} free electrons to semi-insulating to $1 \cdot 10^{18}$ cm^{-3} free holes with state-of-the-art layer resistance uniformities especially for n-type layers are shown. Both AlGaN and GaInN with composition homogeneities of better than 1 nm photoluminescence peak-wavelength standard deviation are displayed. Finally, examination of optically pumped laser action in simple double-hetero structures is quoted to prove the quality of the material.

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Pinholes, Dislocations and Strain Relaxation in InGaN

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We analyse by means of transmission electron microscopy (TEM) and atomic force microscopy (AFM) the strain relaxation mechanisms in InGaN layers on GaN as dependent on the In content. At the experimentally given thickness of 100 nm, the layers remain coherently strained, up to an In concentration of 14%. We show that part of the strain is reduced elastically by formation of hexagonally facetted pinholes. First misfit dislocations are observed to form at pinholes that reach the InGaN/GaN interface. We discuss these results in the framework of the Matthews-Blakeslee model for the critical thickness considering the Peierls force for glide of threading dislocations in the different slip systems of the wurtzite lattice.

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Localized Epitaxy of GaN by HVPE on Patterned Substrates

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We report ongoing experiments on the growth of GaN by hydride vapor phase epitaxy (HVPE), using a newly designed Aixtron horizontal reactor. Growth was carried out on c-plane Al_2O_3 substrates on which a thin GaN layer had been predeposited by MOVPE and patterned using a dielectric mask. The mask pattern was designed to give information on the growth rate and morphology along different directions, and contained both a star-shaped pattern and arrays of parallel stripes of various widths and orientations. All growths were performed at atmospheric pressure and ~1050°C deposition temperature. For the range of experimental conditions investi-

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gated the maximum ratios of lateral to vertical growth velocities of around 2 and coalescence of the layer after approximately 10 μm of growth were observed for stripes oriented along the <100> direction.
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http://nsr.mij.mrs.org/3/41/
300°C GaN/AlGaN Heterojunction Bipolar Transistor
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A GaN/AlGaN heterojunction bipolar transistor has been fabricated using Cl_2/Ar dry etching for mesa formation. As the hole concentration increases due to more efficient ionization of the Mg acceptors at elevated temperatures (> 250°C), the device shows improved gain. Future efforts should focus on methods for reducing base resistance, which are briefly summarized.
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Macro- and Microstrains in MOCVD-Grown GaN
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Undoped and Si-doped GaN films were grown by low pressure MOCVD on (0001) sapphire substrates. The angular distribution of the X-ray diffraction corresponding to the (0002), (0004), $(10\bar{1}0)$, $(20\bar{2}0)$, and $(11\bar{2}4)$ reflections has been measured by means of double- and triple -crystal diffractometry with Mo $K\alpha_1$ and Cu $K\alpha_1$ radiation under conditions of symmetrical and asymmetrical Bragg- and Laue-geometry. In our experiments a non-coplanar geometry was also applied. On the basis of the performed studies, five independent components of the tensor of microdistortion were evaluated and the average grain-size in two directions was determined. The type, position, and density of dislocations were established as well. The role of dislocations in strain relaxation and their influence on the optical and electrical properties are discussed.
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Nucleation of AlN on the (7×7) Reconstructed Silicon (1 1 1) Surface
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The (7 × 7) reconstructed (1 1 1) surface of silicon is found to be an excellent surface for the nucleation of epitaxial aluminum nitride, despite the +23.4% misfit in the AlN/Si system. AlN nucleated above the (7 × 7) to (1 × 1) transition temperature (830°C) is found to contain 30° misoriented grains, while films nucleated below the transition temperature are single orientation. Optimized aluminum nitride films grown on (7 × 7) silicon surfaces make excellent substrates for GaN heteroepitaxy.
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The Emission Properties of Light Emitting Diodes Using InGaN/AlGaN/GaN Multiple Quantum Wells
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Luminescence spectra of Light Emitting Diodes (LEDs) with Multiple Quantum Wells (MQWs) were studied at currents J = 0.15 μA-150 mA. A high quantum efficiency at low J is caused by a low probability of the tunnel current J (which is maximum at $J_m \approx 0.5–1.0$ mA). J(V) curves were measured in the range $J = 10^{-12}–10^{-1}$ A; at $J > 10^{-3}$ A they may be approximated by a sum of four parts: $V = \phi_k + mkT\cdot[\ln(J/J_0)+(J/J_1)^{0.5}] + J\cdot R_s$. The part $V \sim (J/J_1)^{0.5}$ is the evidence of a double-injection into i-layers near MQWs. Their presence is confirmed by capacitance measurements. An overflow of carriers through the MQW causes a lower quantum efficiency at high J. A model of a 2D-density of states with exponential tails fits the spectra. The value of T in the active layer was estimated. A new band was detected at high J; it can be caused by non-uniformity of In content in MQWs.
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Paramagnetic Defects in GaN
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In this work, paramagnetic defects in wurtzite GaN crystals were systematically studied using the Electron Spin Resonance (ESR) technique and using electrical measurements. Three different resonance signals were found. The first had $g_{||} = 1.9514 \pm 0.0005$ and $g = 1.9486 \pm 0.0005$, a commonly observed defect in n-type crystals ascribed to the shallow donor of GaN. The second ESR signal, an anisotropic line of $g_{||} = 2.0728 \pm 0.0015$ and $g = 1.9886 \pm 0.0015$, was observed only in Mg-doped p-type GaN layers, and was assigned to the Mg acceptor. The last ESR resonance signal, an isotropic line with $g = 2.0026 \pm 0.0005$ was observed only in AMMONO GaN crystals after thermal annealing, as well as in Mg-doped GaN epitaxial layers. It was tentatively identified as due to a deep acceptor.
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X-Ray Reciprocal Lattice Mapping and Photoluminescence of GaN/GaAlN Multiple Quantum Wells; Strain Induced Phenomena
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Structural properties of GaN/GaAlN multiple quantum wells (MQW) grown by nitrogen plasma assisted MBE on MOCVD-grown GaN/sapphire (GaN pseudosubstrates) have been characterised by X-ray reciprocal lattice mapping to determine the strain and composition of ternary alloys. The results clearly demonstrate that the barriers of GaAlN with up to 17% of aluminium content grown by plasma assisted MBE on GaN are fully strained. Optical properties have been characterised by low temperature photoluminescence. Photoluminescence emission peaks corresponding to the GaN/GaAlN MQW structures revealed strong red-shift with respect to the GaN energy gap. This can be explained by a strong internal electric field present in the QW's which is attributed to a transfer of piezoelectric field due to Fermi-level alignment.
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GaN Single Crystal Habits and Their Relation to GaN Growth Under High Pressure of Nitrogen
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In the growth of GaN from nitrogen dissolved in Ga under high N_2 pressure, two main habits are observed: plate-like and needle-like. The plate-like crystals can be divided into those having (0001), $(000\bar{1})$ and $\{10\bar{1}0\}$ faces and those with the additional $\{10\bar{1}1\}$ and $\{10\bar{1}2\}$ faces. The needle-like crystals belong to three classes: with or without (0001) faces and a third with unusual, star-like needles. The plate-like and needle-like habits and transformation between these habits are discussed in greater detail. It is shown that it is possible to evaluate the relative growth rates corresponding to such transitions.
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Native Defects and Carbon Impurity in Cubic BN

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Using the Green's function technique based on the linear muffin-tin orbital method in the atomic-spheres approximation we study the electronic structure of native defects and substitutional carbon impurities in cubic BN. To include the lattice relaxation effects a supercell approach in connection with the full-potential linear muffin-tin-orbital method is applied.

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Growth on GaN and GaAs on Fianite by MOCVD Capillary Epitaxy Technique

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Heteroepitaxial GaN and GaAs films were grown by both conventional two-step MOCVD and the new "capillary epitaxy" technique on (001) and (111) fianite (YSZ) substrates. The capillary epitaxy technique was investigated for the example of GaAs films growth on a YSZ substrate. This technique allows both the reduction of the minimum thickness and the improvement of the quality of III-V films. PL spectra of undoped GaN films on YSZ were studied.

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Current Status of GaN Crystal Growth by Sublimation Sandwich Technique

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The current status of GaN crystal growth using the Sublimation Sandwich Technique is discussed in the paper. We use modeling to analyze gas dynamics in the reactor and the supply of the main gaseous species into the growth cell under growth conditions used in experiments. Important features of growth process—non-equilibrium cracking of ammonia, partial sticking of ammonia at the growing surface and kinetic limitation of GaN thermal decomposition—are taken into account in the model. Growth is carried out on sapphire and 6H-SiC substrates in ammonia atmosphere using a Ga/GaN mixture as the group-III element source. Single crystals of GaN of size 15 × 15 mm and up to 0.5 mm thick are normally grown with the optimized growth rates of 0.25–0.35 mm/h. The GaN crystals are characterized by photoluminescence, by the Color Cathodoluminescence Scanning Electron Microscopy technique, by differential double-crystal and triple-crystal X-ray diffractometry, and by electron paramagnetic resonance. Mechanisms of sublimation growth of GaN and physical limitations of the growth process are discussed.

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Morphology and Optical Properties of Cubic Phase GaN Epilayers Grown on (001) Si

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Optical properties of GaN epilayers of a cubic phase are studied. We show a strong influence of the sample morphology on intensity of the edge emission. Whereas edge luminescence is reduced at the grain boundaries, red emission is spatially homogeneous.

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Raman Study of Resonance Effects in $Ga_{1-x}Al_xN$ Solid Solutions

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The photoluminescence and Raman spectra of several $Ga_{1-x}Al_xN$ layers ($0 \leq x \leq 0.86$) grown on sapphire substrates by metal-organic vapor phase epitaxy have been recorded at room temperature, under an excitation at 244 nm. Using the photoluminescence spectra, the variation of the band gap of these alloys can be followed only up to $x = 0.5$. From resonant Raman scattering, it can be deduced that the band gap energy of the solid solution for x very close to 0.7 corresponds to the incident photon energy (5.08 eV). This result is confirmed by a detailed comparison of the present work with previous experimental data on the $A_1(LO)$ phonon peak position, obtained under visible excitation.

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Aging Mechanisms of InGaN/AlGaN/GaN Light-Emitting Diodes Operating at High Currents

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Changes of luminescence spectra and electrical properties of light-emitting diodes (LED's) based on InGaN/AlGaN/GaN heterostructures were investigated over a long period of operation. Blue and green LED's with InGaN single quantum wells were studied at currents up to 80 mA for 10^2–2.10^3 hours. An increase of luminescence intensity at operating currents of 15 mA was detected at the 1st stage of aging (100–800 hours) and a slow fall was detected in the 2nd stage. Greater changes of spectra were observed at low currents (<0.15 mA). A study of charged acceptor distribution in the space charge region has shown that at the 1st stage their concentration grows, and in the 2nd stage, it falls. The models for the two stages are proposed: 1) activation of Mg due to destruction of residual Mg-H complexes; 2) formation of donor vacancies N. A model of defect formation by hot electrons injected into the quantum well is discussed.

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Phase Separation in Wurtzite $In_{1-x-y}Ga_xAl_yN$

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The wurtzite structure $In_{1-x-y}Ga_xAl_yN$ quaternary system is studied with respect to the unstable region in mixing. The composition in the unstable region is calculated from the free energy of mixing by using the strictly regular solution model. The interaction parameter used in this calculation is obtained by using the delta-lattice-parameter method. Here, the proportionality constant connecting the lattice constants and the band-gap energy is determined by fitting the calculation to the composition data obtained experimentally from InGaN grown by metallorganic vapor phase epitaxy. From this calculation, the ternary alloys of InAlN, InGaN and GaAlN are predicted to always, sometimes, and hardly ever, respectively, have an unstable mixing region. The essential mismatch in thermal equilibrium between the strictly regular solution approximation and the growth conditions in MOVPE is removed by using a fitting calculation and experimental data. Also, the mismatch between the zinc-blende structure and the wurtzite structure is corrected. As a result, this prediction of the phase separation in $In_{1-x-y}Ga_xAl_yN$ becomes more reliable.

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