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MOCVD Equipment for Recent Developments Towards the Blue and Green Solid State Laser

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For the growth of an electrically pumped lasing nitride emitter, the development of the MOCVD equipment and the process are mutually dependent. Most important is the implementation of the rapid temperature changes that are required between the growth of the different layers of a device structure. Equally important is to provide a reaction chamber that develops a stable gas phase at all growth temperatures used in the process. In this paper we will give insight in the technology and the relationship between processes and equipment. The development of the reaction chamber was supported by mathematical modeling that formed the basis for the selection of appropriate process parameters for growth of group-III nitrides. The modeling consists of the numerical solution of the Navier-Stokes equations coupled with heat transfer and mass transport of the chemical species. The modeling of radiative heat transfer takes into account the effect of changing surface radiative properties. These changes result from the coating of the reactor inner surfaces during the growth run. Coupled flow dynamics and chemistry including homogeneous and heterogeneous reactions play an important role for predicting growth rate distributions on the susceptor area. At the practically used high temperatures, group-III metalorganics turn out to be almost entirely decomposed and it is the mass transport of these decomposition products to the growing layer that is assumed to control the growth rate in accordance with experimental observations.

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Temperature Distribution in the Chamber used for Crystal Growth of GaN under High Pressure of Nitrogen

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The theoretical analysis of high pressure influence on the conditions of crystal growth of GaN is presented. High pressure influence on the transport and equilibrium properties of nitrogen is estimated using scaling approach. Nitrogen gas properties are used in the finite element calculation of the thermal conditions in the high pressure chamber. The temperature distribution during GaN growth in the vertical temperature-gradient configuration is obtained.

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ECR RIE-Enhanced Low Pressure Plasma Etching of GaN/InGaN/AlGaN Heterostructures

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A room temperature (RT) plasma etch process has been developed to non-selectively etch GaN/InGaN/AlGaN structures, grown on sapphire substrates, using an electron cyclotron resonance (ECR) plasma source with RIE enhancement. The process chemistry chosen was Cl_2/CH_4 based in order to facilitate the formation of volatile etch by-products, typically to form group III halides and group V hydrides, although indium is more likely to form an organometallic compound as opposed to a chloride. A characteristic of this process is the very smooth sidewall features obtained and the controllability of the etch profile via ECR power, table bias and/or gas flow ratio. Typical results obtained using a RT process were etch rate above 100 nm/min, selectivity to resist mask above 30:1 and smooth anisotropic profile at low ion-energies (below 100 eV). The process etch rate showed a characteristic increase with increasing table bias (above 130 nm/min) with only small changes in the relative etch rate of each compound (i.e., selectivity maintained at roughly 1:1), however, this etch does rely upon competing etching and deposition mechanisms and thus too large a variation in one parameter without a corresponding compensation with another leads to a rough surface and a more selective etch. The process has also been demonstrated using a metal mask (e.g., Ni) and present work is progressing onto other gas combinations and the use of high temperature electrodes.

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GaN Based *p-n* Structures Grown on SiC Substrates

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Wide bandgap nitrides (InN, GaN, AlN) have been considered promising optoelectronics materials for many years. Recently two main technological problems in the nitrides were overcome: (1) high quality layers have been grown on both sapphire and SiC substrates and (2) *p*-type GaN and AlGaN material has been obtained. These achievements resulted in the

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fabrication of bright light emitters in the violet, blue and green spectral regions. First injection laser has been demonstrated. This paper reviews results obtained over the last few years on nitride *p-n* junctions, particularly on GaN based *p-n* junctions grown on SiC substrates. We will consider GaN *p-n* junctions, AlGaN *p-n* junctions, GaN and AlGaN *p-i-n* structures, and, finally, GaN/SiC *p-n* structures.

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Electronic Structure of Biaxially Strained Wurtzite Crystals GaN, AlN, and InN

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We present first-principles studies of the effect of biaxial (0001)-strain on the electronic structure of wurtzite GaN, AlN, and InN. We provide accurate predictions for the valence band splittings as a function of strain which greatly facilitates the interpretation of data from samples with unintentional growth-induced strain. The present calculations are based on the total-energy pseudopotential method within the local-density formalism and include the spin-orbit interaction nonperturbatively. For a given biaxial strain, all structural parameters are determined by minimization of the total energy with respect to the electronic and ionic degrees of freedom. Our calculations predict that the valence band state Γ_9 (Γ_6) lies energetically above the Γ_7 (Γ_1) states in GaN and InN, in contrast to the situation in AlN. In all three nitrides, we find that the ordering of these two levels becomes reversed for some value of biaxial strain. In GaN, this crossing takes place already at 0.32% tensile strain. For larger tensile strains, the top of the valence band becomes well separated from the lower states. The computed crystal-field and spin-orbit splittings in unstrained materials as well as the computed deformation potentials agree well with the available experimental data.

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Theoretical Model for Analysis and Optimization of Group III-Nitrides Growth by Molecular Beam Epitaxy

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A theoretical model which accounts for a physisorption precursor of molecular nitrogen is proposed for the analysis of group III-nitride growth by molecular beam epitaxy (MBE). The kinetics of nitrogen evaporation are found to be an essential factor influencing the MBE growth process of group III-nitrides. The high thermal stability of nitrides is explained to be related to the desorption kinetics resulting in a low value of the evaporation coefficient. The values of the evaporation coefficients as functions of temperature are extracted from the experimental Langmuir evaporation data of GaN and AlN. Using the revised thermodynamic properties of the group III-nitrides, and the obtained values of the evaporation coefficient, the process parameter dependent growth rate and transition to extra liquid phase formation during the GaN MBE are calculated. The theoretical results are compared to the available experimental data.

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Growth of GaN Films on (0 0 1) and (1 1 1) GaAs Surfaces by a Modified MBE Method

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Films of GaN have been grown using a modified MBE [molecular beam epitaxy] method in which the active nitrogen is supplied from an rf activated plasma source. Wurtzite films grown on (001)-oriented GaAs substrates show highly defective, ordered polycrystalline growth with a columnar structure; the (0001) planes of the layers being parallel to the (001) planes of the GaAs substrate. Films grown using a coincident As flux, however, have a single crystal zinc-blende growth mode. They have better structural and optical properties. To improve the properties of the wurtzite films we have studied the growth of such films on (111)A- and (111)B-oriented GaAs substrates. The improved structural properties of such films, assessed using x-ray and TEM methods, correlate with better low temperature PL performance.

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Correlation Between Surface Morphologies and Crystallographic Structures of GaN Layers Grown by MOCVD on Sapphire

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GaN layers deposited by MOCVD [metalorganic chemical vapor deposition] on sapphire have been characterized by transmission electron microscopy (TEM). Two substrate orientations were used, (0001) and $(2\bar{1}\bar{1}0)$.We determine the crystallographic structures (defect content and layer polarity) of three different types of GaN layers with different surface morphologies. Convergent beam electron diffraction studies were particularly important to determine the polarity of the GaN layers. We find that polarity and surface diffusion are the factors that control the different growth modes. Unipolarity is obtained thanks to the annealing of the low temperature buffer layer or/and thanks to the nitridation of the sapphire substrate.

Hexagonal pyramids and flat tops are formed when the material has a dominant N-polarity. The pyramids contain many tiny hexagonal columnar inversion domains (IDs). These pyramids are formed when the tiny Ga-polar IDs grow faster than the surrounding N-polar matrix. Flat GaN layers are unipolar, with a Ga polarity. Rough grainy layers which are unipolar (Ga-polarity) are obtained when surface diffusion is not high enough.

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In-depth Analysis of the Impurities in GaN

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GaN epitaxial films were analyzed by secondary ion mass spectrometry (SIMS). Standard implanted samples were used to determine the appropriate analytical conditions for analysis of impurities. The dose and energy of implantation for selected elements (Mg, Al, Si, Zn, Cd, H, C, and O) were chosen so the maximum impurity concentration was not more than 10^{20} atoms/cm^3. The optimum analysis conditions were ascertained from the standards for each element, and the detection limits were deduced from the background levels of the implantation profiles. We demonstate that lower detection limits of 10^{15} atoms/cm^3 with a dynamic range 10^3–10^5 are possible. Zn and Cd have low ion yields, so the minimum detection level for these elements is the background level of the detector. The detection limits of the other elements are determined by the contamination of an initial GaN matrix.

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