

Origin of Strain in GaN Thin Films

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ABSTRACT

Photoluminescence measurements are used to determine the strain in GaN thin films grown by Molecular Beam Epitaxy. The strain which originates from growth on lattice mismatched substrates and from differences in thermal expansion coefficients is found to be greatly relaxed. Residual strains are shown to depend on the thickness of GaN buffer layers and the III/V flux ration during main layer growth. The results strongly suggest that the residual biaxial strain caused by the post-growth cooling can be modified by the incorporation of point defects during the main layer growth which introduce an additional hydrostatic strain field. The effect allows for strain engineering of GaN crystals.

GaN thin films are typically grown on lattice mismatched substrates with thermal expansion coefficients that differ from those of the films. Consequently, many of the typically 1-5 μm thick GaN films are strained homogeneously and physical properties such as the band gap energy or even the chemical composition may be altered because of the strain. Experimentally, such strain related phenomena have been accessed by performing Photoluminescence (PL), Raman spectroscopy and x-ray diffraction measurements [1,2,3]. A consistent description of the experiments has been given which links the shift of the E_2 Raman mode and the shift of donor bound excitonic PL-lines with the strain obtained by lattice parameter measurements [3]. The conversion of the strains into stresses suffers from a poor knowledge of the anisotropic elastic constants of GaN. Within the limits of an isotropic approximation, however, it was demonstrated that a bulk modulus $B = 200$ GPa and a Poisson ratio $\nu = 0.23$ would cause a shift the near band edge luminescence by 27 ± 2 meV/GPa and a shift of the E_2 Raman mode by 4.2 ± 0.3 cm^{-1} GPa $^{-1}$ [3].

The experimental results obtained up to now [1,2,3] showed that the strain in samples grown by various methods (MOCVD, MOVPE, MBE) depends on the choice of the substrate material. Surprisingly, the thermal strain can almost completely be removed by the growth of proper buffer layers. Also, it was revealed that the chemical composition of the samples can modify the strain; the effect was modeled to be caused by a coexistence of a biaxial and a hydrostatic strain field that can be present in the GaN thin films because of the post-growth cooling and because of the introduction of point defects during growth [3]. It is the purpose of this paper to present a systematic study that reveals the magnitude of the described strain related effects in GaN thin film heteroepitaxy.

The GaN films were grown on sapphire (0001) planes by MBE at 1000 K. Reactive

nitrogen was provided by a Hollow Anode Source. The lattice mismatch is 16% in this system and the thermal expansion coefficients differ substantially. The main layers were mostly deposited on GaN buffer layers grown at 773 K; in some cases the growth of a buffer layer was omitted. During main layer growth, the Ga source temperature was kept at 1210 K and the nitrogen flow was varied between 5 and 80 sccm. The resulting growth rate was $\sim 0.5 \mu\text{m/h}$. The films were characterized by Rutherford Backscattering (RBS), x-ray diffraction and Hall effect measurements. They were typically n-type ($n \leq 10^{19} \text{ cm}^{-3}$) and the x-ray rocking curves exhibited a full width at half maximum of ~ 9 arcmin. RBS indicated stoichiometric growth, though deviations from a stoichiometric composition below $\sim 1\%$ cannot be detected by this method.

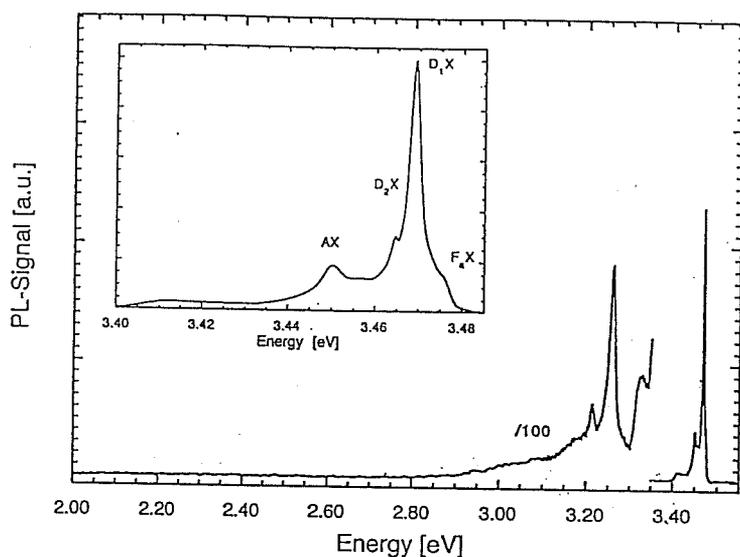


Figure 1: Representative PL spectrum of the GaN films

Here, we report on PL spectroscopy that was used to determine the strain in the samples. The 4K PL was excited at 325 nm by a HeCd laser, analyzed by a double monochromator and detected by a lock-in amplifier. Figure 1 shows a PL spectrum obtained from our films. In the near band edge region free excitons, two donor bound and an acceptor bound exciton can be seen. The yellow luminescence at 2.3 eV is very weak or absent in our samples. PL lines as

narrow as 2.4 meV were detected in the samples which is why their energetic position could be determined accurately. In a previous study it was shown that the measured displacements of the dominant donor bound exciton is caused by strain. This was confirmed by Raman measurements and by x-ray diffraction [3]. A zero strain calibration was provided by homoepitaxial growth on bulk GaN substrates where the donor bound exciton was observed at 3.467 eV [4]. The stresses in the samples can be calculated from the displacement of the donor bound excitonic transitions from this zero strain position using the numerical values given in the introduction.

Figure 2 summarizes the results of our measurements. In figure 2a it can be seen that the largest residual strain is present in films that contain no or a thin ($< 15 \text{ nm}$) buffer layer. Increasing the buffer thickness to 31 nm leads to a complete relaxation of the residual strain. The observed displacement of the donor bound exciton by 2.5 meV reveals a stress relaxation of about 100 MPa. A similar effect was observed for GaN growth on AlN buffer layers [2]; however, the AlN buffer layer thickness had to exceed 200 nm to relax the strain. From figure 2b it can be seen that an increasing nitrogen flux decreases the excitonic line position by 1.5 meV which indicates a stress relaxation by about 50 MPa. A

dependence of the strain on the III/V flux ratio can be understood if it is attributed to the incorporation of point defects into the film because of non-stoichiometric growth. In this case the films are biaxially strained by the substrate material and hydrostatically compressed

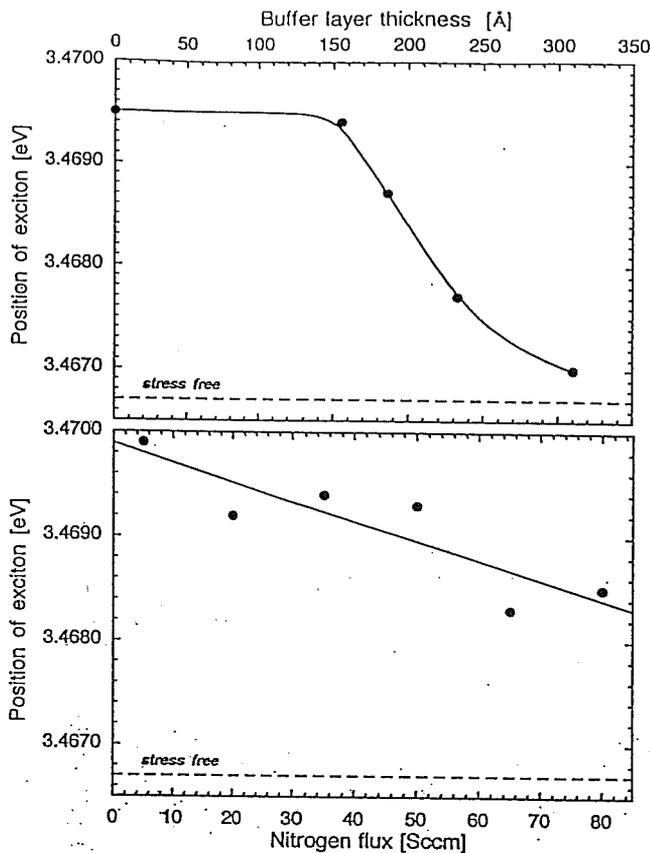


Figure 2: Strain relaxation in GaN films:
a (top): Nitrogen flux = 35 sccm
b (bottom): Buffer layer thickness = 20 nm

or expanded by the presence of point defects. The strain in the layer caused by such coexisting biaxial and hydrostatic strain fields has recently been estimated to be [3]:

$$\epsilon_c = (1 - b C) (1 - 2 \nu \sigma_a / E) - 1 \quad (1a)$$

$$\epsilon_a = (1 - b C) (1 + (1 - \nu) \sigma_a / E) - 1 \quad (1b)$$

where E is the Young Modulus, ν is the Poisson ratio, σ_a is the biaxial stress, C is the point defect concentration, ϵ_c and ϵ_a are the strains along the c and a -axis of the GaN film and b is an expansion (contraction) coefficient given by:

$$b = 1/3 [1 - (r_s / r_h)^3] N^{-1} \quad (2)$$

Here, N is the concentration of lattice sites of the host matrix ($8.8 \cdot 10^{22} \text{ cm}^{-3}$ Ga + N sites in GaN), r_h is the covalent tetrahedral radius of host atoms and r_s is the radius of solute atoms. Equations 1 and 2 allow to estimate the strain in the GaN films for varying biaxial stress if point defects of a given concentration are present. They neglect relaxation effects and the ionicity of the constituents. In the particular case studied here a concentration of native point defects such as vacancies or

antisite defects in the range 10^{18} - 10^{19} cm^{-3} can account for the observed effect. It is remarkable that this defect concentration is well comparable with the carrier concentrations in our samples that is commonly attributed to the presence of native point defects.

Finally, we compare the magnitude of measured stresses in GaN films grown on sapphire with the stress that is expected from the difference in the thermal expansion coefficient which were measured between 300 K and 750 K [5]. We extrapolated these data to our growth temperature of 1000 K and assumed that no strain is present during the growth process. The stresses are calculated isotropically from the strain by use of the mentioned elastic constants. Result are depicted in figure 3. It can be seen that the observed stresses in our films are only a small fraction of the expected thermal stress. Also, the largest stresses reported in films grown by MBE under different conditions or by MOVPE on an AlN buffer layer [3] even cannot account for the thermal stress as indicated in the

figure. Since we did not observe cracks in our films, it is concluded that either plastic relaxation occurs during the post-growth cooling process or/and that the films were strained during growth (in contrast to our assumption made for calculating the thermal stresses). Recent temperature dependent Raman measurements support the latter argument [6].

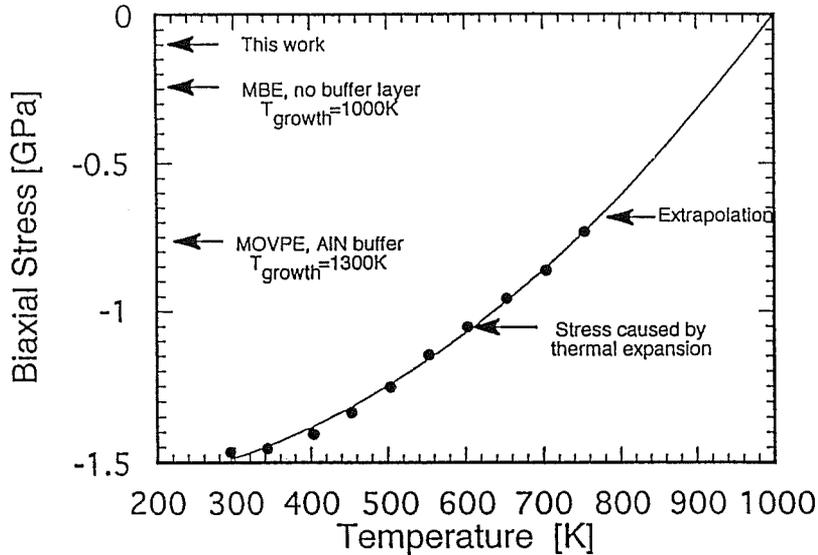


Figure 3: Comparison of the thermal stress expected from the different thermal expansion coefficients of GaN and sapphire with measured stresses in GaN films.

layer and the III/V flux ratio during the main layer growth. The effect is attributed to a the coexistence of a biaxial and a hydrostatic strain field caused by a temperature dependent lattice mismatch and by the presence of point defects, respectively. From the unusual large difference of the tetrahedral covalent radii of the Ga (0.126 nm) and the N atom (0.07 nm) that influences the hydrostatic strain in case of defect formation we expect that GaN thin films can be strain engineered to an extent that is uncommon in other compound semiconductor systems. This strain has to be taken into account in all studies of optoelectronic properties of heteroepitaxially grown films of GaN and related compounds.

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In conclusion we find that the thermal strain in GaN films grown on sapphire substrates is either relaxed plastically and/or that the growth itself proceeds under a substantial strain. LT-GaN buffer layers are found to relax strain more efficiently in comparison with published data on AlN buffer layers. The amount of residual strain can be determined by the thickness of the buffer