Oscillator strengths for optical band-to-band processes in GaN epilayers

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We investigated the evolution of the relative oscillator strengths of the A, B, and C excitons in α-GaN epilayers grown along the [0001] direction on sapphire, 6HSiC, and ZnO substrates by metalorganic vapor phase epitaxy and molecular-beam epitaxy. A universal model was found to account for the observed spectroscopic features regardless of the substrate employed. In addition, we found that, due to the small value of the spin-orbit interaction compared to the stress-induced modifications of the interlevel splitting, C and B lines may undergo a strain-induced exchange of their oscillator strengths when strain field in the epilayers varies from biaxial tension towards biaxial compression. Moreover, we can account for the strain-induced distribution of radiative recombination rates in high-quality GaN epilayers. [S0163-1829(96)05832-8]

Gallium nitride is a semiconductor that is likely to receive a good deal of attention in the foreseeable future; it can be produced with n-type and p-type conductivities with the quality required by doping devices. Already, commercial light emitting diodes have been realized with a plethora of other devices in development.[1] Unfortunately, this compound, which has a remarkable stability at high temperatures and is relatively insensitive to chemical aggressions, has not yet been easily obtained in large-scale bulk ingots. High-pressure synthesis methods lead to pieces of material rarely extending a few square millimeters and, to date, are for academic interest, or may be of value for niche applications of homoepitaxial depositions.[2,3] Large-area GaN epilayers can be obtained using metaloraganic vapor phase epitaxy (MOVPE), hydride vapor phase epitaxy (HVPE), and molecular-beam epitaxy (MBE) methods on a variety of substrates among which are Al_2O_3, 6H-SiC, and ZnO, to cite a few examples.[4,6] These substrates are not only lattice mismatched to GaN but also have very different thermal expansion coefficients. Therefore, the resulting GaN epilayers are subjected to temperature-dependent strain. The changing temperature may cause strain relief via dislocations with severe consequences in devices performance and lifetime. Concerning quantum wells based on nitride compounds, strain field may be used to influence the dispersion relation relative to the in-plane hole motion in the valence bands.[7] This was extensively utilized in the (Ga,In)As-GaAs system to improve hole mobility[8] and/or reduce Auger recombination in quantum wells lasers.[9]

The residual strain fields in GaN epilayers are currently under active investigation, using photoluminescence, reflectance, Raman spectroscopy, and x-ray diffraction.[5,10–16] Most of the investigations have so far been devoted to epilayers in wurtzite symmetry deposited on sapphire and the magnitude of the strain was studied in relation to growth conditions, morphology, or nature of the sapphire-GaN interface. Raman spectroscopy provided evidence for hardening of the Raman active modes with an increase of GaN lattice parameter in the [0001] direction, i.e., with an increase of the in-plane deformation.[13–15] Band structure varies more rapidly with strain than lattice frequencies do. Therefore, photoluminescence, reflectance, or absorption techniques where first-order processes are involved, rather than the second-order mechanisms probed by Raman scattering, are extensively used to study strain fields. In the case of α-GaN, the complex structure of the topmost valence band together with the wurtzite symmetry must be simultaneously considered if the evolution of the exciton energies in strained layers is to be correctly interpreted.[10] In this paper, we extend preliminary investigations of strain field in GaN layers deposited on sapphire to samples grown on 6H-SiC and ZnO. We show that layers deposited on ZnO and sapphire are biaxially compressed while biaxial dilatation is likely to be invoked if one is to identify transitions in epilayers grown on 6H-SiC. In addition, we address the stress-induced modification of the oscillator strength, which is unusually important in GaN, due to the small value of the spin-orbit interaction.

Wurtzite symmetry is known to be conserved under oriented-(0001) biaxial stress. Using the nomenclature of group theory adapted to solid state physics, we can say that the fully symmetric linear combinations of nonvanishing components of the strain tensor (here e_{zz} and $e_{xx}+e_{yy}=e_{\perp}$), transform as Γ_1. The most general form in which to write the time-reversal independent valence-band Hamiltonian that describes the crystal-field and strain effects on a system of p electrons being attributed a spin is given by an invariant theory:[10,17]

$$H_V=\sum_{\alpha} \{a_1^{\alpha}+a_2^{\alpha}\boldsymbol{l}_z^2+a_3^{\alpha}\boldsymbol{l}_z\sigma_z+a_4^{\alpha}(\boldsymbol{l}_x\sigma_x+\boldsymbol{l}_y\sigma_y)\}\Xi_{\Gamma_1}^{\alpha}, \tag{1}$$

where the $\Xi_{\Gamma_1}^{\alpha}$ are any time-reversal invariant quantities having C_{6v} symmetry. To each $\Xi_{\Gamma_1}^{\alpha}$ are associated four quantities a_i^{α} with i running between 1 and 4 having particular

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influence on the intimate details of the valence-band physics and defined in Ref. 10. For our purpose, we shall neither consider any stress-induced variation of the spin-orbit interaction parameters, nor include electron-hole exchange interaction, in relation with the nature of experimental data currently available.

Related to the $\{|\Phi\Gamma_9\rangle, |\Phi\Gamma_7\rangle^1, |\Phi\Gamma_7\rangle^2\}$ basis set, we write down the following matrix:

$$\begin{pmatrix} |\Phi\Gamma_9\rangle & |\Phi\Gamma_7\rangle^1 & |\Phi\Gamma_7\rangle^2 \\ \langle E_0^v\rangle+\Delta_1+\Delta_\parallel+C_1e_{zz}+C_2e_\perp+C_3e_{zz}+C_4e_\perp & 0 & 0 \\ 0 & \langle E_0^v\rangle+\Delta_1-\Delta_\parallel+C_1e_{zz}+C_2e_\perp+C_3e_{zz}+C_4e_\perp & \sqrt{2}\Delta_\perp \\ 0 & \sqrt{2}\Delta_\perp & \langle E_0^v\rangle+C_1e_{zz}+C_2e_\perp \end{pmatrix}. \quad (2)$$

The evolution of the conduction band is given by two deformation potentials as

$$E_c=\langle E_0^c\rangle+D_1e_{zz}+D_2e_\perp . \quad (3)$$

The band-to-band transition energies are obtained by the difference between conduction and valence energies. The oscillator strengths for these processes are obtained from the eigenvectors associated with each of the eigenenergies. In σ polarization, where the electric field is normal to the c axis of the crystal, if we attribute a value of 0.5 to the strength to the transition involving the $|\Gamma_9\rangle$ state, the strengths of the transitions involving the other two levels are half of the square of the modules of the contribution of $|\Gamma_7\rangle^1$ in the eigenvectors produced by resolution of Eq. (2). In a cubic symmetry, we would obtain $\frac{1}{2}$, $\frac{1}{6}$, and $\frac{1}{3}$ as relative values for the oscillators strengths of A, B, and C transitions, respectively. Concerning the π polarization, when the electric field of the incident photon is collinear with z, the transitions between conduction band and $|\Gamma_9\rangle$ are forbidden while the strengths of the two other processes are proportional to the square of the modules of the contribution by $|\Gamma_7\rangle^2$ in the eigenvectors of Eq. (2). The values of oscillator strength obtained in cubic symmetry corresponding to A, B, and C transitions are 0, $\frac{2}{3}$, and $\frac{1}{3}$, respectively.

In a previous paper,[10] we have shown that the optical transitions detected in reflectance of GaN and labeled as A, B, and C can be quantitatively related to strain fields present in the film with an extremely good accuracy, using the following parameters: $\Delta_{cr}=10\pm0.1$ meV, $\Delta_\parallel=6.2\pm0.1$ meV, and $\Delta_\perp=5.5\pm0.1$ meV. In addition, the relation between the four spin-independent deformation potentials $(Di-C_i)$, were also obtained. We, therefore conclude that the most convenient presentation conducive to the analysis of the data is one where the transition energies are plotted versus energy of the A line.[10] Previous similar studies[10–12] were restricted to epilayers deposited on sapphire. We note that, similar to what happens for MOVPE-grown samples (full circles),[11,12] MBE-grown samples (open circles) agree very well with the model as shown in Fig. 1, where the data were restricted to one sample grown by MBE on sapphire.[18] To emphasize the universality of the model, we now include in the figure data taken on SiC (Refs. 4 and 19) and ZnO (Ref. 20) substrates. Again the agreement between theory and experiment is remarkably good.

The biaxial stress in GaN layers is of a tension and compression nature for 6HSiC and ZnO substrates, respectively. We also note that C line is not observed in the case of growth on ZnO, which can be ascribed to the following: The growth on ZnO substrates has not been yet optimized. The distribution of the oscillator strength between B and C exciton levels is stress dependent, which we have previously observed.[11,12] We now more concretely quantify it in Fig. 2 where we plot the evolution of the strengths of B and C transitions with respect to the energy of the A line, in σ polarization. In particular, we note that, in the case of strong biaxial compression, the C line tends to disappear while B strengthens. Due to the ~20-meV value of the binding energy for the A exciton, line C becomes degenerate with conduction to $|\Gamma_9\rangle$ continuum of states, with ramifications to its strength and width. Both effects have not been included in our model.

Note from Figs. 1 and 2 that crystal field splitting can be offset by biaxial dilatation if growth occurs on 6HSiC. Also note that almost a perfect match with values of cubic symmetry ($\frac{1}{3}$ and $\frac{1}{6}$, respectively) is then found for oscillator strengths of C and B lines. The agreement should be per-

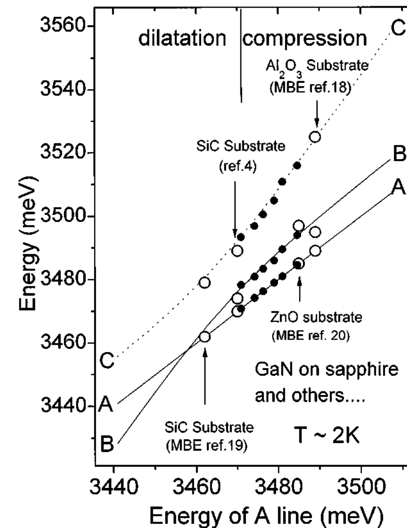

FIG. 1. Evolution of the three main peaks of GaN epilayers versus strain (position of A line). Full circles are data from MOVPE grown samples, open circles are samples grown by MBE.

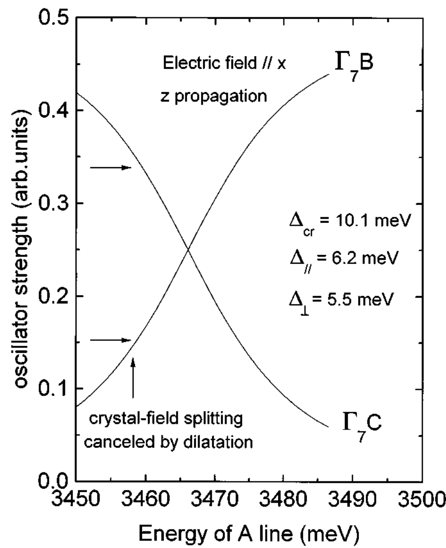

FIG. 2. Plot of the band-to-band oscillator strengths for B and C transitions in σ polarization. Intensity of A equals 0.5 in this model.

fectly realized in case of an isotropy of the spin-orbit interaction.

For the sake of completeness, we now consider data taken for SiC and published by other groups[4,19] in detail. In contrast to their interpretation, we attribute the line they labeled as B to C. In addition, the well resolved doublet with observed 4-meV split, named A in Ref. 4, most likely represents the A and B lines. This assignment is more consistent with our calculation of the variation of different energy levels reported in Fig. 1. The authors of Ref. 4 have attributed the doublet structure to a longitudinal-transverse splitting of the Γ_5 exciton. Even for the experimental configuration of Ref. 4, i.e., the reflectivity spectra were taken with incident angle of 45°, this assignment is in contrast with the predictions of group theory, relative to internal structure of the Γ_5 exciton created from the $|\Gamma_9\rangle$ hole, and its optical activity in π polarization, when photon propagates along the z direction.[17] It is worth noticing that the increase of the ratio between the strength of the line we assign to C and the strength of the low-energy doublet is in good agreement with the calculations of oscillator strengths reported in Fig. 2.

We now turn our attention to the agreement between radiative recombination rates and the inverse of oscillator strengths we calculate. Time-resolved spectroscopy investigation of GaN epilayers is currently being pursued. The measured values of lifetimes are scattered[21–25] due to sample-dependent competition between radiative and nonradiative processes. Recent investigations in the high-quality epilayer—giving the free exciton A line at 3.483 eV at 2 K—performed at low temperature before recombination becomes dominated by nonradiative processes indicate that the *radiative lifetime* of the B exciton is larger than that of A.[25] Their finding is consistent with our calculation, which gives $\tau_A/\tau_B \sim 0.85$ for this strain situation. This simplified model reveals the weak efficiency of the nonradiative interband thermalization processes via interaction of free exciton with the acoustic phonon field, and predicts the radiative lifetimes of B and C excitons to be extremely sensitive to strain.

In conclusion, we have shown that the properties of GaN epilayers grown on 6HSiC, Al_2O_3, and ZnO can be universally qualified in terms of optical quality and residual strain using a simple description derived from group theory and a few *ad hoc* parameters it requires. The model is valid for biaxial compression and dilatation.

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