M R S Internet Journal Nitride Semiconductor Research

Free excitons in strained MOCVD-grown GaN layers

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(Received Tuesday, November 26, 2002; accepted Monday, February 3, 2003)

GaN layers grown on sapphire substrates were characterized using high resolution optical reflectivity and absorption spectroscopy in the region of ground and excited exciton states. The main exciton parameters are deduced from calculations of reflectivity contours for A and B exciton S-states. The parameters of the Γ_5 state of the A-exciton as well as those of the Γ_5 and Γ_1 states of the B-exciton are determined from a comparative analysis of reflectivity and absorption spectra in thin layers. The influence of strains inherent to MOCVD-grown GaN layers on the exciton parameters including effective masses and longitudinal-transverse splitting is discussed. Electron transitions from the three (Γ_9, Γ_7, Γ_7) upper valence bands to the second E_{c2} conduction band of Γ_3 symmetry were evidenced.

1 Introduction

Gallium nitride and related alloys are attractive materials for various high-temperature high-power electronic applications [1] [2] [3] [4]. Advances in the technology of low temperature epitaxial growth allow one to grow GaN layers of 2 – 10 nm thickness with the smoothness of hetero-interfaces at the order of one atomic layer [3] [4]. When the layer thickness is comparable with the de-Broglie wavelength, the electron and hole energy spectrum depends on the layer thickness due to quantum confinement effects. These effects open new possibilities to control the wavelength of the emitted light through the variation of the quantum well width.

In spite of a great deal of interest in these materials, many features of strained GaN layers, such as the influence of strains on the electron and hole effective masses, longitudinal-transverse exciton splitting, etc., are poorly explored. The study of the impact of strain upon material characteristics is important since the growth of GaN layers on sapphire and 6H-SiC substrates is a common practice due to the lack of suitable GaN substrates. Strains in GaN layers are caused by large lattice and thermal mismatches between GaN and the substrate materials.

In this work, we investigate optical properties of GaN layers grown on sapphire substrates and compare optical parameters of these strained layers with the data published on non-stressed material.

2 Experimental

The GaN layers used in our experiments were grown by low-pressure MOCVD on (0001) c-plane sapphire using trimethylgallium (TMGa) and ammonia (NH_3) as source materials [5]. The carrier gas was Pd-cell purified hydrogen (H_2). Heating was accomplished by RF induction of the graphite susceptor. A buffer layer of about 25-nm thick GaN was first grown at 510 °C. Subsequently n-GaN layers were grown at 1100 °C. The concentration of free electrons in the top n-GaN layer was 1.7×10^{17} cm^{-3}.

Photoreflectivity and absorption spectra were measured using the light from a halogen lamp. The white light reflected from the sample (in reflectivity experiments) or passed through the sample (in absorption experiments) was analysed through a double spectrometer with 1200 lines/mm gratings assuring a linear dispersion of 0.8 nm/mm. The signal from an FEU-106 photomultiplier with SbKNaCs photocathode working in a photon counting mode was introduced in an IBM computer via the IEEE-488 interface for further data processing. The spectral resolution was better than 0.5 meV. The samples were mounted on the cold station of a LTS-22-C-330 workhorse-type optical cryogenic system.

https://doi.org/10.1557/S1092578300000442 Published online by Cambridge University Press

3 Results and discussion

It is known from numerous experiments on Cu_2O and II-VI compounds that exact values of the exciton bound energy (R) and bandgap (E_g) are determined from the energy position of n = 2, n = 3, etc. exciton excited states. The errors in calculating the R and E_g values are higher in the case when only the n = 1 and n = 2 states are observed, since the screening of the Coulomb electrostatical potential influences the energy position of the n = 1 line. The strains inherent to GaN layers grown on sapphire or SiC substrates due to large lattice and thermal mismatches between GaN and these materials strongly influence the energy position of exciton lines [6] [7] [8] [9]. According to our measurements and literature data the shift of the ground (n = 1) exciton states can reach several tens of meV, while the shift of this state due to the screening of the Coulomb electrostatical potential is several meV (an order of magnitude less). Apart from that, according to the literature data [10] [11] [12], strains lead to a shift of all exciton lines, but practically do not influence the exciton binding energy.

The n = 1 lineshape in high quality crystals is determined by exciton polaritons sensitive to the longitudinal-transverse (ω_{LT}) splitting and the damping parameter (γ). The dielectric function in the region of exciton resonance is written as:

$$\varepsilon(\omega,k)=\varepsilon_0+\frac{2\varepsilon_0\omega_{LT}\omega_0}{\omega_0-\omega+\frac{\hbar^2k^2}{2M}\omega_0-i\gamma\omega} \quad (1)$$

The reflectivity from an isotropic crystal in the case of normal incident light is determined by:

$$R=\left|\frac{\left(\frac{1-n_0}{1+n_0}\right)+\left(\frac{n_0-n^*}{n_0+n^*}\right)e^{i2kn_1t}}{1+\left(\frac{1-n_0}{1+n_0}\right)\left(\frac{n_0-n^*}{n_0+n^*}\right)e^{i2kn_1t}}\right|, \quad (2)$$

where $n_0=\sqrt{\varepsilon_b}$, $n^*=\frac{n_1n_2+\varepsilon_b}{n_1+n_2}$, ε_b is the background dielectric constant, t is the dead-layer thickness, k is the exciton wave-vector, n_1 and n_2 are longitudinal and transverse components of the refractive index determined from:

$$n_{1,2}^2=\frac{1}{2}\left(\left(\varepsilon_b+\frac{2Mc^2(\omega-\omega_0)}{\hbar\omega_0^2}\right)\pm\left(\left(\frac{2Mc^2(\omega-\omega_0)}{\hbar\omega_0^2}-\varepsilon_b\right)^2+\frac{8Mc^2\varepsilon_b\omega_{LT}}{\hbar\omega_0^2}\right)^{1/2}\right) \quad (3)$$

An oscillating structure due to the Fabré-Perot interference is observed in the reflectivity and absorption spectra of GaN layers in the energy region E < 3.46 eV. The spectral dependence of the refractive index at photon energies approaching the exciton energy can be drawn from this interference pattern (Figure 1). At photon energies E > 3.47 eV the interference structure in spectra taken from a GaN layer of d = 1.5 μm thickness is practically absent. Instead, evident excitonic features are observed in this spectral range (Figure 2). The maxima in the reflectivity spectrum at 3.4870 and 3.4970 eV are due to the n = 1 states of A and B excitons, respectively. The weak feature at 3.5220 eV is attributed to the n = 1 state of the C exciton. A weak band at 3.5062 eV (associated with n = 2 state of the A exciton) as well as two weak features at 3.5120 and 3.5170 eV (associated with n = 2 state of the B exciton) are observed at the long-wavelength side of the n = 1 state of the C exciton. A value of 25.2 meV is deduced for the A exciton binding energy from the energy position of the n = 1 and n = 2 states. As mentioned above, the ground state energy is affected by the screening of the effective interaction between electrons and holes. Recently, it was shown that anisotropy, intersubband coupling and polaron corrections should be also taken into account when estimating ground and first excited exciton states in GaN [13]. Therefore, the calculation of the effective Rydberg from the experimentally observed separation between the n = 1 and the n = 2 exciton states in the simplest hydrogen-like model is only a first approximation.

The simulation of the reflectivity contours for the n = 1 resonance of the A and B excitons in terms of a model taking into account the spatial dispersion, the presence of a dead-layer and the additional Pekar boundary conditions is illustrated by the dotted-line in Figure 2. The best fit to the experimental spectrum is achieved using ε_b = 9.3 and the following exciton parameters: transverse exciton energy E_0^A = 3.4870 eV, E_0^B = 3.497 eV; longitudinal transverse splitting E_{LT}^A = 1.5 meV, E_{LT}^B = 2.2 meV; damping parameter γ^A = 3.6 meV, γ^B = 2.2 meV; and exciton mass $m^A = 1.2\ m_0$, $m^B = 0.65\ m_0$.

One should note that the values obtained for the damping parameters of A and B excitons are too high. This could be a consequence of the strains our layers

https://doi.org/10.1557/S1092578300000442 Published online by Cambridge University Press

experience. According to the literature data, the damping parameter in strained GaN layers is higher than that inherent to non-stressed layers [8] [9] [14]. In order to check if the obtained values are not a mistake of simulation, we have applied our method for the calculation of spectra presented in Ref. [14] for non-stressed GaN layers (Figure 3). We have obtained the following parameters as a result of simulation: ε_b = 9.9, E_0^A = 3.4770 eV, E_{LT}^A = 1.25 meV, m^A = 1.2 m_0, γ^A = 0.001 meV for the A exciton and E_0^B = 3.4814 eV, E_{LT}^B = 1.15 meV, m^B = 0.45 m_0, γ^B = 0.02 meV for the B exciton. These values are in excellent agreement with those deduced in Ref. [14].

Numerous studies on exciton spectroscopy have shown that the energy position of the transverse exciton excited states are determined much more accurately from the absorption spectra. Figure 4 presents the reflectivity and absorption spectra of a GaN layer with d = 0.5 μm thickness. The simulation of the reflectivity contour of this layer by application of the method discussed above gives the following parameters: ε_b = 9.3, E_0^A = 3.4853 eV, E_{LT}^A = 1. 5 meV, m^A = 1.2 m_0, γ^A = 3.3 meV for the A exciton and E_0^B = 3.4950 eV, E_{LT}^B = 2.2 meV, m^B = 0.65 m_0, γ^B = 2.0 meV for the B exciton. One can observe that the parameters obtained for the 0.5 μm thick layer are very close to those of the 1.5 μm thick layer. This means that these layers are equally stressed in spite of the existence of an intermediate buffer layer. While the influence of biaxial strain on the energies of excitons in GaN layers is well documented [15], experimental data on the stress-induced variation of the longitudinal-transverse splitting and exciton masses are practically absent. Using the data presented in Figure 18 of Ref. [15], we estimated the strain in our layers to be of about 10 kbar. Comparing the values of E_{LT} deduced above for stressed and non-stressed layers, one can conclude that the LO-TO splitting of the A-exciton is practically unaffected by the stress, while this parameter increases from 1.25 meV to 2.2 meV for the B-exciton when the stress increases from 0 to 10 kbar. These observations are in fairly good agreement with the results of calculations presented in Figure 24 of ref. [15]. On the other hand, the m^A exciton mass in our layers coincides with that of non-stressed layers, while the m^B exciton mass is increased by a factor of 1.4. These data are consistent with the results of theoretical analysis of GaN layers subjected to biaxial strain [11]. On the basis of the obtained m^A and m^B exciton masses and the known electron effective mass ($m_{\hat{a}}^* = 0.22\text{-}0.24m_0$) [6] [7] [8] [9] one can calculate the $M^*_{v1} = (1\pm0.1)m_0$ and $M^*_{v2} = 0.39m_0$ effective masses of the valence bands split due to the crystal field and spin-orbital interaction.

A maximum at 3.4945 eV corresponding to the ω_{tB} transversal B exciton frequency can be seen in the absorption spectrum. Two other maxima at 3.4910 and 3.4865 eV are observed on the long-wavelength side of this band. Taking into account the C_{6v} symmetry of the wurtzite GaN, one can conclude that Γ_5 and Γ_6 excitons are formed as a result of interaction between a hole from Γ_9 valence band and an electron from Γ_7 conduction band. The Γ_5 excitons are active in σ polarization, while Γ_6 excitons are inactive in dipole approximation [16]. The weak feature at 3.4865 eV in the absorption spectrum differs by 1.2 meV from the $\omega_t^{\Gamma_5}$ (3.4853 eV) determined from the reflectivity spectrum. This feature is either due to the Γ_5 exciton or due to the Γ_6 exciton appearing as result of breakdown of the selection rules caused by the biaxial strain. In the last case, the 1.2 meV value characterizes the exciton splitting due to the short-range exchange interaction.

The B exciton series is formed by the Γ_7 valence band and the Γ_7 conduction band. A Γ_1 exciton active in π polarization, a Γ_5 exciton active in σ polarization, and a Γ_2 exciton forbidden in both π and σ polarizations are formed as a result of this interaction. Taking this into account one can suppose that the absorption peak at 3.4945 eV is related to the transverse $\Gamma_5(\omega_t)$ exciton. The absorption peak at 3.4910 eV is due to the transverse $\Gamma_1(\omega_t)$ exciton. According to theoretical evaluations [16], the intensity of the Γ_1 exciton in π polarization is lower than that of Γ_5 exciton in σ polarization. We suppose that the weak features at 3.5115 and 3.5153 eV are caused by the n = 2 excited state of the Γ_1 and Γ_5 excitons, respectively. In such a case, from the ground and the first excited exciton states one can deduce the binding energy for the Γ_1 and Γ_5 excitons: 27.1 and 27.6 meV respectively.

The n = 1 line of the C exciton forms a doublet at 3.5220 and 3.5250 eV which is supposed to be related to the Γ_1 and Γ_5 excitons, respectively. The weak feature at 3.5415 eV can be attributed to the n = 2 state of the C exciton. The binding energy of the C exciton deduced from this assignment equals 26.0 meV.

Three absorption bands at 3.5829, 3.5939 and 3.6110 eV were evidenced in the high-energy spectral range (Figure 5). We attribute these bands to transitions from Γ_9, Γ_7, and Γ_7 valence bands to the second E_{c2} band of Γ_3 symmetry. The splitting of the $\Gamma_1(E_{c1})$ and

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$\Gamma_3(E_{c2})$ bands at k = 0 is estimated then to be around 100 meV, which is in rather good correlation with theoretical prediction [17] [18].

ACKNOWLEDGMENTS

This work was supported by CRDF and MRDA under Grant # ME2-3013.

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FIGURES

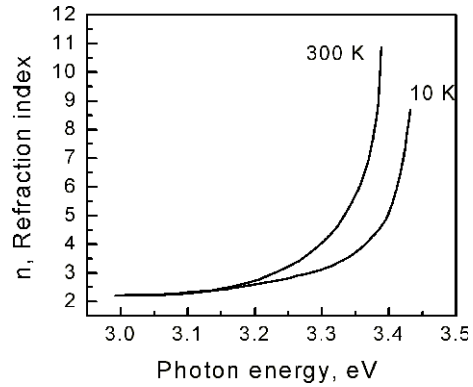

Figure 1. The spectral dependence of the refractive index calculated from the interference pattern in the reflectivity and absorption spectra of a GaN layer at 10 K and 300 K.

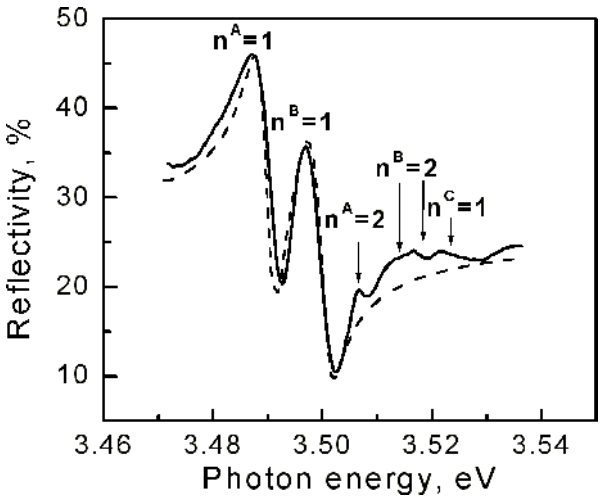

Figure 2. Experimental (solid curve) and calculated (dashed curve) spectra of 1.5 μm thick GaN layer. T = 10 K.

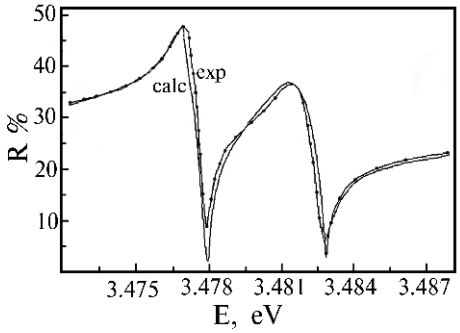

Figure 3. Experimental spectrum reproduced from Ref. [14] for a non-stressed GaN layer (dots) and the result of calculations (solid curve).

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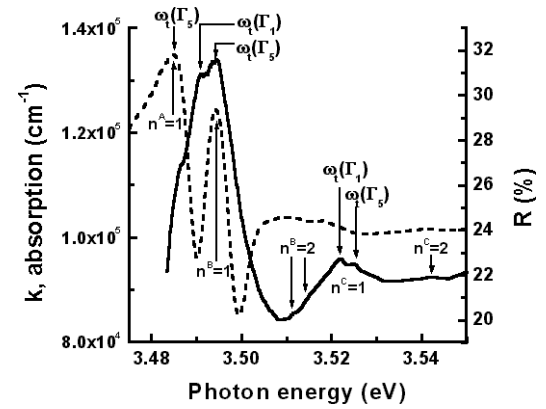

Figure 4. The reflectivity (dashed curve) and absorption (solid curve) spectra of a 0.5 μm thick GaN layer. T = 10 K.

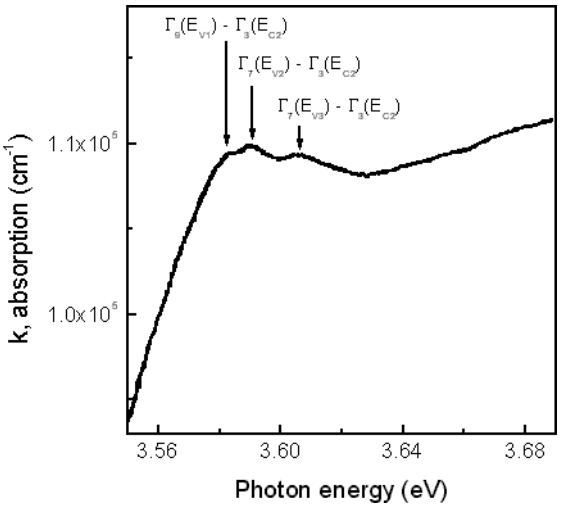

Figure 5. The absorption spectrum of a 0.5 μm thick GaN layer measured in the high-energy spectral range. T = 10 K.

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