Photoreflectance spectroscopy of thick GaN layers grown by hydride vapour phase epitaxy technique

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The room temperature photoreflectance (PR) spectroscopy was used to investigate thick GaN epitaxial layers. The GaN layers were grown by hydride vapour phase epitaxy (HVPE) technique and compared to thin GaN layer grown by metalorganic vapour phase epitaxy (MOVPE) technique on AlN buffer layer. We observed energy red shift of the PR resonance for HVPE GaN layers compared with MOVPE GaN layer. This blue shift is due to reduction of the strain in HVPE layer. In addition, weak PR features related to Franz–Keldysh oscillations (FKO) have been observed. The electric field determined from the FKO period is 28 and 71 kV/cm for MOVPE and HVPE layers, respectively.

Keywords: GaN, photoreflectance, photoluminescence, electric field.

1. Introduction

GaN and related nitrides are attractive materials for fabrication of semiconductor devices such us visible–ulraviolet light emitting diodes and visible–ultraviolet detectors, and high temperature and high frequency transistors [1, 2]. Due to the lack of lattice and thermal matched substrates GaN epilayers are usually grown on foreign substrates with a large lattice mismatch with GaN. This is believed to cause a strains and a huge density of crystal defects and tends to deteriorate optical and electrical properties of GaN-based devices. Much improved device performance could be facilited by the development of high quality free-standing GaN substrates with tailored electrical properties. So far, the homoepitaxy of GaN layers on GaN substrate grown at high temperatures and high hydrostatic pressures has been applied to obtain high-quality GaN layers [3, 4]. However, other faster and cheaper methods of growth are still sought. One of the rapidly advancing sources of thick, free-standing GaN

wafers is hydride vapour phase epitaxy (HVPE) [5]. The thick GaN layers prepared by HVPE technique after separation from the sapphire by laser-induced lift-off [6, 7] are excellent as a substrate for (Al)GaN based structures.

In this paper, optical properties of Ga-face GaN layers grown by HVPE and MOVPE techniques are investigated using room temperature photoreflectance (RTPR) and room temperature photoluminescence (RTPL) spectroscopies. Based on the analysis of RTPR spectra we are able to estimate the position of excitonic-like transitions in GaN layers. We show the reduction of strain build-in HVPE GaN layer in comparison with MOVPE one. The photoreflectance (PR) spectroscopy is a kind of modulation spectroscopy and has a derivative-like character of optical spectra. It allows the energy position of optical transitions to be determined very precisely even at room temperature. We show that PR spectroscopy is an excellent tool for investigation of the optical quality of semiconductor layers due to contactless character and high sensitivity.

2. Experimental setup

The HVPE layers were deposited by HVPE on a GaN buffer layer which was grown on a *c*-plane sapphire substrate in a vertical flow MOVPE system at atmospheric pressure [8, 9]. The MOVPE growth was carried out in a home-made MOVPE system with horizontal quartz reactor (atmospheric pressure) with radio-frequency heating. The thickness of GaN buffer layer was about 2 μm. The thick GaN layers were grown in a conventional HVPE system: three-temperature zone furnace and horizontal quartz reactor. Nitrogen (6N) was used as a carrier gas. GaCl was formed by reaction of gaseous HCl (6N) and liquid Ga (6N) at 920°C. A two-step deposition method was applied. The first step was the growth of GaN with small amount of HCl (approx. 4 ml/min). In the second step of growth was faster with the flow of HCl being 10ml/min. The thickness of HVPE GaN layer was ~40 μm. In addition, a 2 μm thick GaN grown on ~20 nm low temperature AlN buffer was taken as a reference GaN layer. This reference structure was grown by MOVPE technique.

The PR measurement was performed in so-called bright configuration where the sample was illuminated by white light from a halogen lamp (150 W) serving as a probe beam source at near normal incidence. The reflected light was dispersed through a 0.55 m focal length single grating monochromator and detected by R647P Hamamatsu photomultiplier. For photomodulation of 300 nm line an Ar^+ laser was used as a pump beam, which was mechanically chopped at the frequency of 266 Hz. The signal was recorded by a model SR830 DSP lock-in amplifier. More details about PR setup can be found elsewhere [10]. The PL measurement was performed using the same apparatus and Ocean Optics HR4000 high-resolution spectrometer with CCD camera. The spectral resolution was kept on the level of meV. All measurements were done at room temperature.

3. Results

Figure 1 shows a comparison of RTPR spectra measured for sample S1 and S2. In order to determine energies of the optical transitions, the PR spectra were fitted by the low-field electromodulation Lorentzian line shape functional form [11, 12]:

$$\frac{\Delta R}{R} = \text{Re}\left[\sum_{j=1}^{n} C_j \exp(i\Theta_j)\left(E - E_j + i\Gamma_j\right)^{-m_j}\right] \tag{1}$$

where n is the number of optical transitions and spectral functions used in the fitting procedure, C_j and Θ_j are the amplitude and phase of the line shape, and E_j and Γ_j are the energy and the broadening parameter of the transition, respectively. The exponent m_j is a characteristic parameter, which equals 2.5 and 2 for a three-dimensional interband transition and an excitonic transition, respectively.

The RTPR spectrum of sample S1 reveals two well-resolved PR features near 3.42 eV. We found that a fit with $m_j = 2$ simulates experimental data better than a fit with $m_j = 2.5$. This suggests that PR features have excitonic rather than band-to-band character. The weak oscillation-like structure below the energy of 3.41 eV has been neglected in our analysis of PR data. Such an oscillation is associated with the light interference and/or electrooptic effects within the GaN layer [13]. The energy position
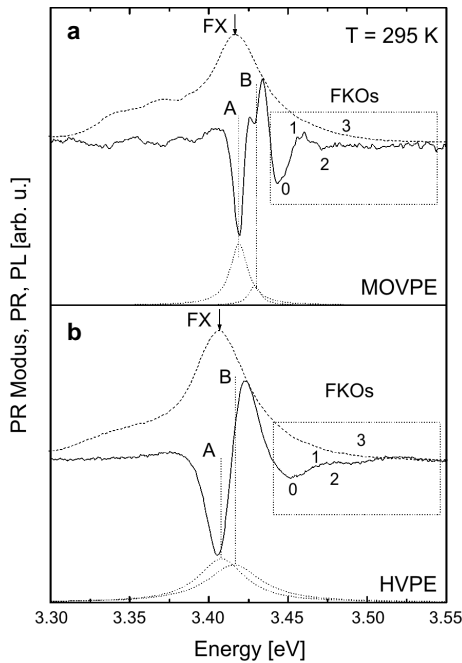

Fig. 1. Room temperature photoreflectance (solid line) and photoluminescence (dashed line) spectra of MOVPE (**a**) and HVPE GaN layers (**b**). The dotted lines represent the modus of *A* and *B* exciton transition.
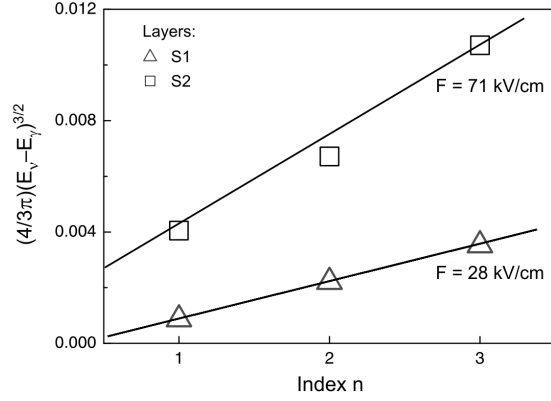
Fig. 2. Built-in electric field for the MOVPE (S1) and HVPE (S2) GaN layers extracted from FKO period.

of A and B lines extracted from the fitting procedure are 3.419 and 3.429 eV, respectively. These lines are related to absorption between Γ_9^V and Γ_7^C bands (A line) and absorption between Γ_7^V (upper-band) and Γ_7^C bands (B line) of wurtzite GaN [14]. The transition related to absorption between Γ_7^V (lower-band) and Γ_7^C bands was neglected due to its low intensity and interference with Franz–Keldysh oscillations (FKO) features. The FKO appears in the higher energy range of PR spectrum (see the dashed rectangle in Fig. 1). This suggests that observed FKO features can influence the excitonic resonance. A plot of $(4/3\pi)[(E_n - E_g)/\hbar]^{3/2}$ [11, 15] against the extreme number n should be a straight line as can be seen in Fig. 2. From the slope of this line it is possible to obtain the electrooptic energy $\hbar\Theta$ of an electron with mass equal to the interband reduced effective mass μ ($\mu = 0.2m_e$ for GaN [16]) in the direction of electric field F. The electrooptic energy is defined as

$$(\hbar\Theta)^3 = \frac{e^2\hbar^2 F^2}{2\mu}. \tag{2}$$

The electric field determined for S1 sample is $F = 28$ kV/cm. This explains why we observe well resolved PR features related to the A and B exciton transitions even at existing electric field. This is due to a high value of A and B exciton energy dissociation ($E_b = 26$ meV). The ionization field associated with dissociation energy for GaN exciton is 100 kV/cm [17, 18]. It is three times higher than the value of the electric field determined for this sample.

In the case of sample S2, PR spectrum looks differently. The RTPR spectrum is slightly broadened and weak FKO feature is well visible on the high energy side. The fitting procedure with excitonic line shape ($m_j = 2$) gives the energies of A and B transitions of 3.408 and 3.416 eV, respectively. As in the previous sample the transition related to absorption between Γ_7^V (lower-band) and Γ_7^C bands was neglected due to its low intensity. The electric field obtained with the same procedure as for sample S1 is 71 kV/cm (Fig. 2). The higher electric field for the structure S2 influences

the broadening of excitonic transition [17–19]. This explains why we cannot obtain such well resolevd excitonic resonances as in the case of sample S1. Nevertheless, structures S1 and S2 have a very qood optical quality. Only several cases of such sharp and well-resolved excitonic RTPR resonances as for sample S1 have been reported so far [20–22].

The main difference between samples S1 and S2 is the energy of *A* and *B* transitions. PR spectra (Fig. 1) show ~11 meV shift of an *A* exciton transition towards low energy for sample S2 in comparision with S1. Also energy separation between *A* and *B* excitons (E_{AB}) for sample S2 ($E_{AB} = 8$ meV) is smaller than for sample S1 ($E_{AB} = 10$ meV). To date several authors have reported this phenomenon based on PR experiment but at low temperatures [21, 23, 24]. This exciton energy shift is caused by strain relaxation between the GaN film and the substrate. Wurtzite GaN grown on sapphire substrates with GaN or AlN buffer layers always suffers from a certain amount of in-plane biaxial strain because of the mismatch of lattice constants and the thermal expansion coefficients between GaN (and/or AlN) and sapphire [25]. In the case of samples grown by HVPE the strain due to the lattice mismatch is believed to relax relatively fast during the growth with the formation of dislocations [24]. This is clearly confirmed by the broadening of PR resonance.

Room temperature PL spectra of samples S1 and S2 (Figs. 1 and 3) exhibit high intensity peaks denoted by FX at the energy of 3.416 and 3.406 eV with the half widh at half maximum (HWHM) of 42 and 47 meV, respectively. In comparison with the energy position of *A* exciton obtained from RTPR experiment we deduced that FX peak is rather excitonic-like but a contribution of band-to-band recombination to this peak is not excluded. Also previous works have reported the observation of room-temperature free exciton recombination [26–30]. In the case of sample S1, Fig. 2 also shows a broad PL feature centered at the energy of ~2.7 eV. Such a PL band is related to defect states and/or donor–acceptor transitions. Note that the PL intensity of this broad band is significantly smaller than the intensity of FX peak.
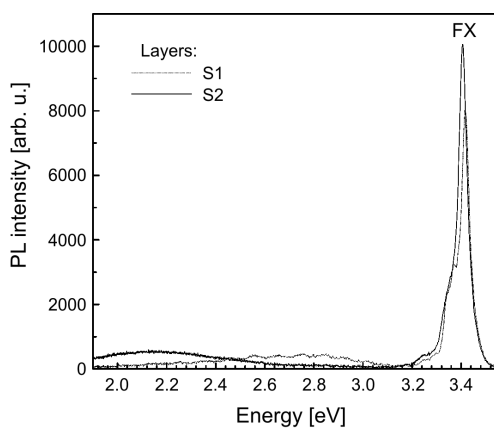

Fig. 3. Room temperature photoluminescence spectra of MOVPE (S1) and HVPE (S2) GaN layers.

In the case of sample S2 this broad band almost disappears but appears another broad band centered at the energy of ~2.15 eV which is related to defect states in the GaN layer. The intensity of this band is significantly smaller than the intensity of FX peak. The observation of free excitonic recombination at room temperature can be explained by high exciton binding energy (~26 meV) and low concentration of defects for both S1 and S2 samples. PL data clearly confirm that samples S1 and S2 have good optical quality.

4. Conclusions

The optical properties of MOVPE and HVPE grown GaN layers have been investigated in this paper. We have found that both samples have good optical quality. The RTPR resonances for both samples are excitonic despite the built-in electric field in the layers (28 and 71 kV/cm for MOVPE and HVPE layers, respectively). We observed shift of energy position towards low energy for HVPE grown sample in comparison with MOVPE one. We attributed such behavior to a strain reduction in the HVPE layer, whereas MOVPE layer remain still significantly strained.

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