Coexistence of type-I and type-II band line-ups in 1-2 monolayer thick GaN/AlN single quantum wells

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Abstract. GaN/AlN quantum wells (QWs) with varied nominal thickness of 0.5-4 monolayers have been studied by time-resolved photoluminescence (PL) spectroscopy. The structures demonstrate an emission peak with the thickness-dependent wavelength in the range 225-320 nm. The observed temporal behavior of PL between 225 and 280 nm can be described as a superposition of fast and slow decaying components with characteristic decay time constants of the order of 0.1-0.7 ns and 7-30 ns, respectively. The fast PL component with the decay time smaller than 1 ns dominates in the thicker GaN insertions and tends to vanish in the thinnest ones, where the slow PL component becomes progressively longer. These observations imply formation in the GaN/AlN monolayer-thick layers of an inhomogeneous excitonic system involving both direct and indirect in space excitons.

1. Introduction

GaN/AlN (or GaN/AlGaN) quantum wells (QWs) have been recently considered as a promising active region of light-emitting devices operating in mid- and deep-ultraviolet regions [1, 2]. Wavelength of emission from such QWs can be varied from ~320 to ~220 nm due to strong quantum confinement by varying the QW thickness from 4 to 1 monolayer (ML) and thinner. There are several advantages of using such ultrathin GaN/AlN QWs comparing with a conventional design. First, more conventional AlGaN-based QWs with the thickness of several nanometers, grown on c-sapphire, usually suffer from intrinsic electrostatic fields, which reduce an electron-hole overlapping as a result of the quantum-confined Stark effect (QCSE). Decreasing the QW thickness results in the reduction of the QCSE that was observed and theoretically described for several ML thick GaN/AlN QWs [3-5]. Another advantage is efficient light extraction from the c-plane of the GaN/AlN QWs, which resulted from TE-polarization of the emitted light (electric field is perpendicular to the c-axis) [6]; that is because the lowest quantized hole energy level in such structures originates from a heavy hole band [4, 5]. On the contrary, light extraction from the c-plane AlGaN with high Al content is hampered due to inherent TM-polarization of the emitted light [7, 8].

In this work, we represent growth of GaN/AlN QWs with nominal thickness of 0.5-4 ML and study of their electronic properties by means of time-resolved photoluminescence (TR PL) spectroscopy.
2. Results and discussion

The samples were grown on c-sapphire by plasma-assisted molecular beam epitaxy (PA MBE) using a Compact 21T Riber setup. Metal-rich conditions and a maximum substrate temperature $T_s=780^\circ C$ were used for the growth of a 65 nm thick AlN nucleation layer by migration enhanced epitaxy and a 1.5-μm-thick AlN buffer layer by metal-modulated epitaxy. The buffer layer comprised four strained 3.5 nm thick GaN insertions, whose incorporation aimed at decreasing density of threading dislocations in the QW region [9, 10]. Then, 3 ML of AlN, 0.5-4 ML of the GaN QW, and 5 nm of an upper AlN barrier were formed at $T_s=700^\circ C$. Finally, a 35 nm thick AlN cap layer was grown by standard PA MBE at $T_s=770-780^\circ C$. The samples with 1 ML, 2 ML, and 4ML thick QWs were fabricated without rotation during the growth. Also, similar samples with the GaN QW nominal thickness of 0.5 and 1 ML were fabricated with or without rotation during the growth of the QW that resulted in a gradient of the QW thickness along a certain direction on the sample surface. Further we will refer to the samples grown with or without rotation as R or N, respectively, appending the value of the QW nominal thickness in MLs.

For PL excitation, we used a fourth harmonic of a femtosecond Ti-sapphire laser with the emission wavelength 210 nm and pulse frequency 76 MHz. The PL decay curves were measured using a fast photomultiplier operating in a time-correlated single photon counting mode with temporal resolution ~145 ps. Additionally, samples R2 and R4 were studied with the excitation by a third harmonic of the Ti-sapphire laser (260 nm) and TR PL images were obtained with overall resolution ~25 ps using a Hamamatsu streak camera. The high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) analysis has been carried out on FEI Titan 80-300 TEM with spatial resolution of 1.3 Å.

The PL spectra of 4 ML and 2 ML thick GaN/AlN QWs at 77 K demonstrate a multiexponential decay on the time scale ~1.5 ns and a single exponential one with the decay time constant of 0.15 ns, respectively (figure 1). The relation of the PL intensity at 77 K to those at 300 K equals 3 for the 2-ML-QW and 10 for the 4-ML-QW. Both shortening the PL lifetime and improving the internal quantum yield apparently indicates the above mentioned reduction of the QCSE in the thinner QW [3].

![Figure 1](image1.png)

**Figure 1.** TR PL images taken from the 4 ML thick GaN QW in sample R4 (a) and form the 2 ML thick QW in sample R2 (b).

Figure 2 shows HAADF STEM images, measured in two different points of sample N1. Although the STEM images in figure 2 look quite similar, the corresponding PL bands are spectrally separated by~0.7 eV. Integrated STEM profiles of the QWs are presented in figure 3. As can be seen, the QW thicknesses are close to the nominal values. Smaller height of the STEM profiles in the 1-2 ML thick QW in comparison with the 4 ML thick one is probably related to formation of an AlGaN/AlN QW instead of the intended binary GaN/AlN one.
Temporal behavior of the PL emission from the QWs with the nominal thickness ≤ 2 ML can be described by two decay time constants, $\tau_1 \sim 0.1-0.7$ ns and $\tau_2 \sim 10-30$ ns. Spectral positions of the QW PL bands and respective extracted decay time constants are shown in figure 4. A prominent trend of an increase of the time constant $\tau_2$ and a decrease of $\tau_1$, while thinning the QW, is observed for all studied samples. We suppose that the longer PL component results from the formation of type-II band line-ups, when the electron and hole are separated in space.

According to Ref. [5], a type-II band alignment is predicted for sufficiently thin (less or equal to 4 ML) GaN/AlN QWs and corresponds to the situation, when a recombining electron is localized in the GaN insertion whereas a hole from the crystal-field split valence band is located in the surrounding AlN. On the other hand, a type-I band alignment (recombining heavy hole states are localized in the QW) is confidently predicted for thicker QWs. In this way, at a certain average QW thickness both types of transitions may have approximately the same energy, owing to unavoidable QW thickness fluctuations. In terms of this model, the observed increase of $\tau_2$ and vanishing of the fast PL component (see figure 5) can be explained by progressive sinking of the heavy and light hole energy levels in the GaN insertion below the level of the crystal-field split hole level in the AlN barriers with decreasing the average GaN thickness.

An additional confirmation of this model follows from temporal behavior of PL registered in the GaN QWs with thickness ~1.5-2 ML, emitting in the wavelength range 260-280 nm (figure 5 (a) and (c)). We found that the fast and intense PL component detected in these sample is spectrally shifted toward lower energies with respect to the slow one. This appears in the TR PL image as a shift of the
PL peak toward higher energies during first nanoseconds after the excitation pulse (figure 5 (c)). This rather unusual behavior cannot be explained neither by hopping of localized excitons nor by the QCSE screening. We propose that the observed rapidly decaying bright emission corresponds to type-I transitions, which originate from thicker areas of the QW. On the other hand, type-II transitions are most probable for thinner QW areas, and, therefore, they possess higher energy due to stronger quantum confinement of electrons in the thinner part of the QW comparing with the thicker one. That additionally confirms coexistence of type-I and type-II band line-ups in the studied GaN/AlN QW.

![Figure 5](image)

**Figure 5.** TR PL images detected from sample N1 in point 3 (a) and in point 2 (b). Dependence of the PL spectrum on delay time for point 3 (c) and point 2 (d). Respective STEM images are shown in figure 2.

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