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Influence of Well-Width Fluctuations on the Electronic Structure of $GaN/Al_xGa_{1-x}N$ Multiquantum Wells with Graded Interfaces

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Experimental and computation results based on chemical composition assessment of metal-organic chemical vapour deposition grown undoped $GaN/Al_xGa_{1-x}N$ multiquantum well structures in the low composition limit of $x = 0.07$ and wide wells demonstrate composition fluctuations in the barrier layers which lead to large-scale nonuniformities and inequivalence of the different wells. As a consequence the experimental photoluminescence spectra at low temperature show a double peak structure indicative of well-width fluctuations by one lattice parameter (2 monolayers).

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1. Introduction

An important effect that influences optical properties of III-nitride multiquantum wells (MQWs) is the well/barrier interface roughness which results in well-width fluctuations. When it is commensurate with the width of the QW, it should be taken into account in calculating the exciton confinement energy and wave function distributions in the wells. Because of the small exciton Bohr radius

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of 3 nm in GaN the transition energies are quite sensitive to well width fluctuations corresponding to a full c-vector (two monolayers, 2 ML = 0.52 nm), and/or to a $\pm c/2$-vector (1 ML = 0.26 nm). The problem becomes more pronounced in the presence of the inherent polarization fields, due to the spatial separation of the electrons and holes by the field that pushes them closer to the interfaces. The internal electric fields in the MQWs affect the oscillator strengths of the excitons and the position of the corresponding photoluminescence (PL) peaks [1]. The quantum confinement Stark effect (QCSE) is manifested in red-shifted QW transition energies, in contrast to the carrier confinement that blue-shifts them [2].

Local well-width fluctuations could be produced by alloy composition fluctuations when the barrier constituent of the MQW is a ternary compound. The growth at relatively high temperatures permits intermixing at the interfaces. Usually, barrier composition fluctuations are regarded as a reason for inhomogeneous broadening of the excitonic recombination line widths. The residual line width observed in undoped samples is interpreted as due to the hole localization at interface roughness on a scale smaller than the hole Bohr radius. On the contrary, interface disorder (or chemical disorder) on a large-scale is observed to produce separate localization states or PL peak splitting. Such discrete peaks should be observed if the constant well-width areas are larger than the extent of the exciton wave function.

These problems have met extensive research on GaN/AlGaN MQWs structures in recent years [1–4]. The question about the interface quality and how it affects the confined exciton gas is still less studied in some extreme conditions such as relatively wide wells and low Al composition, which is difficult to quantify.

In this work we study the specific localization by interface fluctuations in $GaN/Al_xGa_{1-x}N$ MQWs. The dependence of the excitonic transition energies on the well-width fluctuations in GaN QW of $L_w = 4.5$ nm nominal thickness is calculated in the presence of internal polarization fields. The calculations are performed in the frames of the envelope function approximation. An aluminium fraction of $x = 0.07$ is considered, well below the compositions mostly examined [4]. The well thickness of 4.5 nm appears above the thickness of $L_0 \approx 26$ Å (near 10 GaN MLs) reported in Ref. [4], where transition energies are found nearly independent of the barrier composition. The case considered is less sensitive to confinement because of the low x value and large L_w, and mostly sensitive to the Stark field and well-width fluctuations. By fitting experimental photoluminescence spectra we attempt to estimate the influence of the two effects, the interface roughness and the polarization field, on the PL peak splitting and broadening.

Additionally, interface fluctuations are estimated in a real structure by electron microscopy techniques with nanometer resolution and sensitive to elemental composition, transmission electron microscopy (TEM) in low and high resolution, electron energy loss spectroscopy (EELS) and annular dark field (ADF) imaging, sensitive to the atomic number (z).

2. Calculation and experimental details

The examined GaN/AlGaN MQWs are grown undoped by metal-organic chemical vapour deposition (MOCVD) on (0001) sapphire [5]. The structure consists of five periods of GaN wells $L_{\mathrm{w}} = 4.5$ nm thick, separated by $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}$ barriers of $L_{\mathrm{b}} = 7$ nm. We determine the exciton confinement energy by calculating $E1$ and $HH1$ ground-state confinement energies for electrons and heavy holes in the wells using the formalism of the envelope function approximation. Then the excitonic transition energies are

$$h\nu = E_{\mathrm{g}}(\mathrm{GaN}) - E_{\mathrm{w}}L_{\mathrm{w}} + |E_1| + |HH_1| - E_{\mathrm{exc}}. \tag{1}$$

The exciton binding energy E_{exc} is approximately 26 meV, corrected according to [6] by its variation in dependence of the well-width fluctuations in the range of 15–20 ML and under electric field. The term $E_{\mathrm{w}}L_{\mathrm{w}}$ accounts for the decrease due to the QCSE. The electric fields in the well and the barrier are calculated as in [7] and are $E_{\mathrm{w}} = -4.2 \times 10^5$ V/cm, and $E_{\mathrm{b}} = 2 \times 10^5$ V/cm. These large internal fields are considered to modify the potential profile of the MQW needed for the computing of $E1$ and $HH1$. Due to the different signs of E_{w} and E_{b}, the electric field slopes the potential profile in different directions for the barrier and well regions. Further, the confinement potential profile of the 5 well/barrier structures for the nominal well width (4.5 nm) and for widths corresponding to fluctuations of one, two, and four MLs, is used for calculating the ground-state $E1$ and $HH1$ confinement energies and wave function distributions for the finite barrier triangular well case.

An estimation of the composition fluctuations was conducted on a JEOL 2010F FEG TEM/STEM analytical microscope and EELS using inelastically scattered electrons with energy losses characteristic of the Ga and Al elemental species. The changes in Al content are inferred using the Al $L_{2,3}$-edge across the interface (line scan with steps ≈ 8 Å) to obtain the composition profiles of the MQW and consequently the real well-width fluctuations. The Al composition profile is used to build the real potential profile of the structure. Again the bound state energies are calculated in the two cases with and without electric field.

3. Experimental results and discussion

The computation results for 2 K in Fig. 1a show a nearly linear behaviour of the well-width dependence of the ground-state excitonic transition energy as expected for wide wells [4]. As illustrated by the results, the well-width fluctuations of $\pm$ one c-vector under the QCSE lead to a change in the bound states energy of ≈ 25 meV. The difference in the transition energies is large enough to cause residual broadening or even PL peak splitting. We have compared the calculated energies with the experimentally obtained PL spectrum [8] shown in Fig. 1b. The spectrum reveals a doublet which could be assigned to two localization states. The FWHM of the main PL peak is small enough (< 20 meV) to allow the spectral

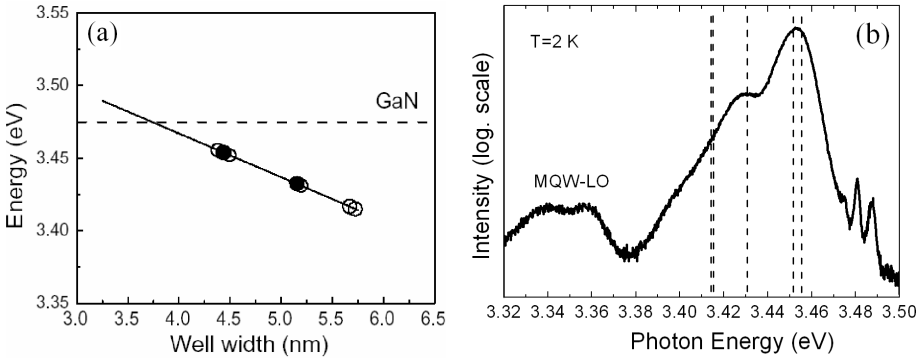

Fig. 1. (a) Calculated well-width dependence of excitonic transition energies for $GaN/Al_{0.07}Ga_{0.93}N$ MQW (solid line); experimental PL doublet peak positions of the 4.5 nm MQW (black spots) and excitonic transition energies computed from the chemical composition profile of the same MQW (white spots); bulk GaN exciton energy (dashed line); (b) PL spectrum of the 4.5 nm MQW, showing doublet peaks, and the transition energy positions calculated from the chemical composition profile marked with dashed lines. The (strained) GaN buffer layer excitonic transitions appear at 3.478 eV and 3.485 eV, respectively.

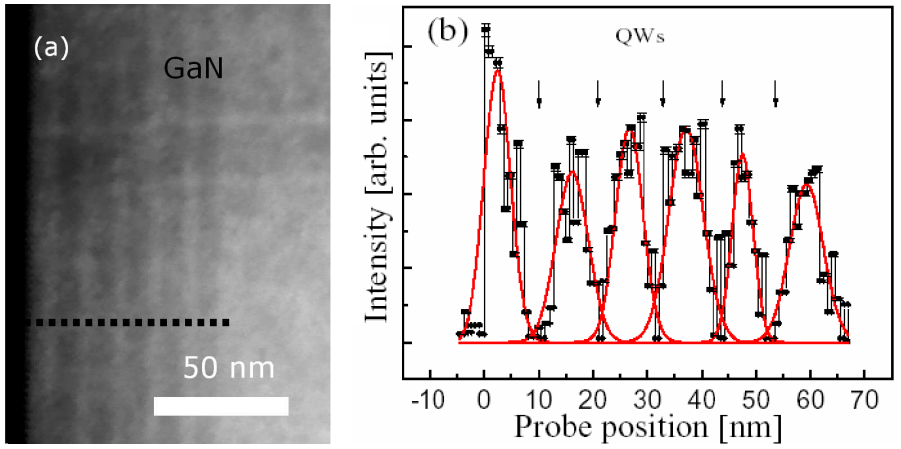

Fig. 2. (a) A cross-section ADF image of the 4.5 nm 5 well/barrier structures; (b) line--scan across the MQW stack representing the integrated intensity of the Al $L_{2,3}$ edge. The concentration in the barriers is fitted by six Gaussian functions.

effect from large area well-width variations to be resolved. The two peak positions are included in the theoretical plot in Fig. 1. Accordingly, these states correspond, respectively, to the areas, where the QW width is near 4.5 nm (higher energy 3.454 eV) and 4.5 nm + 2 MLs (lower energy 3.432 eV).

As an estimation of the roughness of the interfaces and the composition fluctuations, Fig. 2a presents a cross-section ADF image of the structure. It shows a general picture of the 5 periods with a slightly changed contrast in some regions that reflects the z-variations in the well/barriers. The figure also illustrates the Al concentration profile across the MQW stack, produced by EELS (line scan shown in Fig. 2a, dashed line). A non-uniform distribution of Al in the barrier layers is observed leading to graded interfaces. The statistical distribution of the concentration in the barriers is fitted by six Gaussian functions. The results inevitably show an inequivalence of the 5 QWs. Depending on the concentration fluctuations the real MQW structure consists of 5 wells with different widths fluctuating around the nominal width of 4.5 nm. Accordingly, different transition energies are calculated for the 5 wells, grouped around three energy positions. They are fitted to the linear plot and spectrum in Fig. 1a, b. It appears that two of the wells (3.452 eV and 3.456 eV) contribute to the main peak at 3.454 eV. The energy shifts for these states are less than several meV, which is within the experimental error and could be regarded as equivalent to the nominal well. One well contributes to the lower peak at 3.432 eV and corresponds to a well-width variation of one c-vector. The other two computed positions (3.414 eV and 3.415 eV) are red-shifted and we consider their contribution to the peak broadening around 3.415 eV corresponding to a variation of $2c$-vectors. We could speculate that it contains an unresolved overlap of contributions from well-width fluctuations. Because of the lower contribution to the intensity it seems that they are rarely met, also the overlapping of the envelope functions is lower. As it is seen, the calculated energies are in good agreement with the PL experimental results. The line-scan gives the variation in the Al concentration between the wells with nearly a nanometer resolution. We should mention that the chemical composition in the low x value limit is very difficult to quantify experimentally and our results are not integrated over a larger area of the sample, but the signal intensity represents an average of the excited volume depending on the sample thickness along the incident electron beam which could be typically ≤ 100 nm. It seems to be a reasonable assessment of the degree of interface disorder and its influence on the spectral properties of the MQWs. We can assume that excitons are localized in specific interface regions due to the intrinsic chemical barrier disorder. The characteristic length of the alloy disorder is ≈ 2 MLs. These observations are consistent with recently published investigations [8] on the well-width fluctuations in similar structures by PL mapping across the sample surface with different excitation spot size. Long-range variation of the PL peak position across the sample is explained in terms of corresponding variations in Al composition in the barriers. Micro-PL spectra confirm that the areas of constant well width are of an extent $< 1\ \mu\mathrm{m}^2$, much larger than the exciton Bohr radius, allowing the observation of discrete PL peaks.

The coincidence of the microscopic chemical analysis and the PL results could be an indication that this type of interface disorder is typical of the growth

mode. Kinetic growth processes such as segregation and atom migration lead to an intermixing of atoms at interfaces between layers of different materials — not fully understood at present.

4. Conclusion

On the basis of assessment of the composition fluctuations in the barrier layers we can assume that excitons are localized by large-scale interface fluctuations of the order of two MLs and leading to the inequivalence of the respective wells in the specific case of wide wells and low Al composition.

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