Interplay of Confinement, Strain, and Piezoelectric Effects in the Optical Spectrum of GaN Quantum Dots

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We theoretically investigated excitonic states, energy and oscillator strength of optical transitions in GaN quantum dots characterized by different size, shape, interface, and substrate. On the basis of our multi-band model we determined that the piezoelectric field-induced red shift of the ground state transition, observed in recent experiments, can manifest itself only in strained GaN/AlN dots with the dot height larger than 3 nm. It was also established that the oscillator strength of the red-shifted transitions is small (<0.05) and decreases fast with increasing the dot size, while the strength of ground state transitions in c-GaN/c-AlN and GaN/dielectric dots is large (~ 0.4–0.7) and almost independent of the dot size.

Keywords: GaN Quantum Dots, Confinement, Strain, Piezoelectric Effect.

RESEARCH ARTICLE

1. INTRODUCTION

Recently, GaN quantum dots (QDs) have attracted attention as promising candidates for applications in optical and electronic devices. Progress in GaN technology has led to many reports of fabrication and characterization of different types of GaN QDs.[1–8] Stranski-Krastanov growth of wurtzite GaN/AlN QDs has been reported in Refs. 1 and 2. Deposition of a small amount of Si on $Al_xGa_{1-x}N$ prior to GaN has led to the growth of wurtzite GaN/$Al_xGa_{1-x}N$ QDs.[3,4] The polar [0001] axis in the above-mentioned QDs is parallel to the growth direction. Self-organized zincblende c-GaN/c-AlN QDs have been grown along the nonpolar [001] axis as well.[5,6] Ref. 7 describes fabrication of GaN nanocrystals by pulsed laser ablation of pure Ga metal in N_2 gas. By sequential ion implantation of Ga^+ ions followed by N^- ions into dielectrics, wurtzite GaN/dielectric QDs have been prepared.[8]

Despite this large number of reports of fabrication and optical characterization of GaN QDs, there has been very little theoretical investigation of confined electronic states or optical transitions in such nanostructures. However, it has been shown[9,10] that a strong piezoelectric field in wurtzite GaN/AlN QDs influences the optical properties and makes them different from those in conventional semiconductors, such as GaAs, Si, Ge, etc.

In this letter we theoretically investigate the interplay of confinement, strain, and piezoelectric effects on the optical spectrum of GaN QDs. To elucidate the role and relative strength of each of these effects, we apply our theoretical model to GaN QDs characterized by different crystal structures (wurtzite vs. zincblende) and different shapes: truncated hexagonal pyramid, disk, truncated square pyramid, and sphere. Each of the types of QDs considered corresponds to a real structure reported in the literature, which permits us a direct comparison with experiment. In our model we do not simplify the QD shape and properly take into account differences in material parameters (elastic and dielectric constants, effective masses, etc.) at the QD interface. The results of these calculations can be used for the interpretation of photoluminescence and electroluminescence data measured for GaN quantum dots.

2. THEORETICAL DETAILS

In this investigation we start with calculating strain and piezoelectric fields for each QD type and shape, then find electron and hole states, calculate exciton states, and, finally, determine the oscillator strength of optical transitions. A calculation of the strain field in the vicinity of QD is done according to the elasticity theory for zincblende[11] and wurtzite[12] QDs by minimizing the free energy on a three-dimensional (3D) grid with a finite-element method. In general, both induced polarization due to elastic strain and spontaneous polarization contribute to the built-in piezoelectric field. We use the finite-difference method (FDM) to obtain the corresponding piezoelectric potential from the Poisson equation.[10]

To calculate carrier states in zincblende QDs, we have recently developed a multiband envelope function model.[13,14] An analogous model has been applied to wurtzite QDs. It represents a generalization of the strain-dependent multiband envelope-function model for planar

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heterostructures.[15] Special care has been taken for proper operator ordering in multiband Hamiltonians,[13] which is essential for an accurate description of heterostructures. After the piezoelectric potential is found, the FDM is used again to find carrier eigenstates in each type of GaN QD. Furthermore, exciton states have been computed following Ref. 14. Finally, we calculated the oscillator strength f of exciton transitions from the definition

$$f = \left\langle \left| \int \delta(\mathbf{r}_e - \mathbf{r}_h)(\mathbf{e}\hat{\mathbf{p}}_h)\Psi_{exc}(\mathbf{r}_e, \mathbf{r}_h)\, d\mathbf{r}_e\, d\mathbf{r}_h \right|^2 \right\rangle \Big/ P^2 \quad (1)$$

where $\mathbf{e}$ is the polarization of light, $\hat{\mathbf{p}}_h$ is the hole momentum operator, $\Psi_{exc}(\mathbf{r}_e, \mathbf{r}_h)$ is the exciton wave function, P is the interband momentum matrix element for GaN, such that $P = (2P_{||} + P_{\perp})/3$ for wurtzite GaN, $P_{\perp}$ and $P_{||}$ are momentum matrix elements along the [0001] axis and in the perpendicular direction, and $\langle \ldots \rangle$ denotes averaging over all light polarizations. According to this definition, the maximum value of $f = 1$ is achieved when electron and hole densities are identical.

In our simulation we used material parameters of GaN (AlN) from Refs. 16–19. A linear interpolation of GaN and AlN material parameters was used for $Al_xGa_{1-x}N$. Figure 1 shows the shape of each GaN QD with the height $H = 3$ nm and isosurfaces of probability density 0.8 of electron and hole ground states. Specifically, Figure 1A and E shows the shape of GaN/AlN QDs. The thickness of the wetting layer is assumed to be $w = 0.5$ nm, the ratio of QD height above the wetting layer $h \equiv H - w$ to the QD bottom diameter D_B is 1:5, and the ratio of the QD top diameter D_T to h is 1. This QD corresponds to those reported in Refs. 1 and 2. Figure 1B and F shows the shape of a GaN/$Al_xGa_{1-x}N$ QD with $h/D_B = 1/3$ like those in Refs. 3 and 4. The shape of c-GaN/c-AlN QDs is given in Figure 1C and G. This QD has $w = 0.5$ nm and the ratios $h/D_B = 1:10$ and $D_T/h = 8.6$, which correspond to QDs in Refs. 5 and 6. Figure 1D and H shows the shape of GaN/dielectric QDs after Refs. 7 and 8.

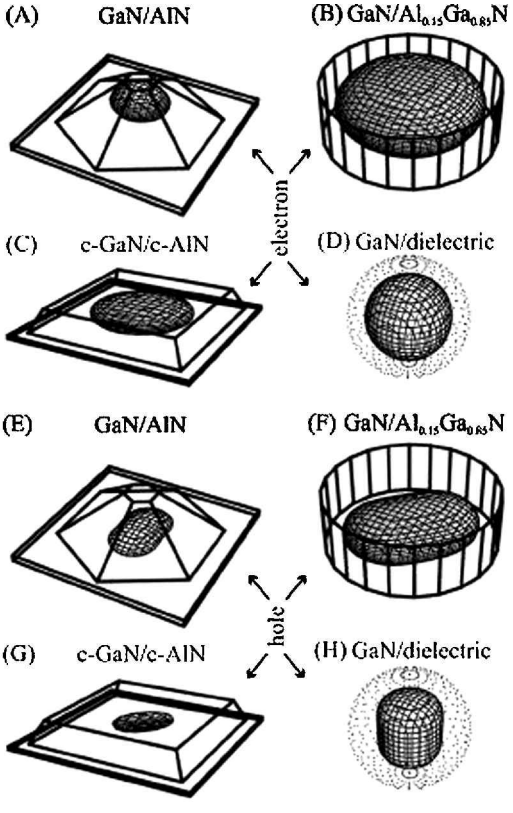

Fig. 1. Shape of GaN QDs of four different types and isosurfaces of probability density 0.8 for electron and hole ground states in QDs with height $H = 3$ nm.

3. RESULTS AND DISCUSSION

Figure 2 presents electron and hole ground-state energy as a function of the QD height for each type of GaN QD. Electron (hole) energy is given with respect to the unstrained conduction (valence) band edge of bulk GaN. As seen from Figures 1A and 2A, both confinement and piezoelectric field affect the electronic state in GaN/AlN QDs. The dependence of the electron energy on the QD height is nonlinear, whereas linear dependence is expected in the case of the piezoelectric field effect only. The electron is pushed to the top of the QD, and its energy drops below the bulk conduction band edge for QDs higher

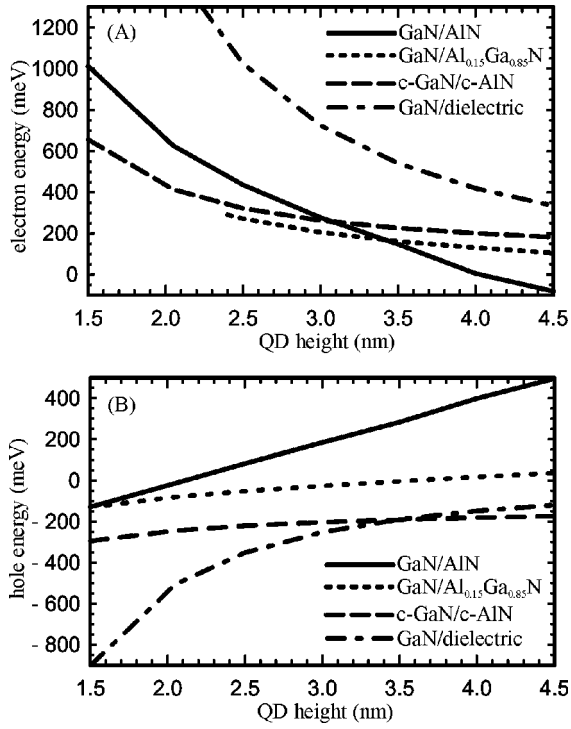

Fig. 2. Electron (A) and hole (B) ground-state energy levels as functions of the QD height for four different types of GaN QDs. The thickness of the wetting layer is included in the QD height. Electron (hole) energy is counted from the unstrained conduction (valence) band edge of the bulk GaN.

than 4 nm. Figures 1E and 2B indicate that the piezoelectric field effect is the dominant one for holes in GaN/AlN QDs. The hole is pushed to the wetting layer, and its energy depends almost linearly on H. The hole energy is above the bulk valence band edge for $H > 2$ nm. Piezoelectric fields are much weaker in GaN/$Al_{0.15}Ga_{0.85}N$ QDs. Correspondingly, confinement plays the dominant role for electrons and strongly affects hole states (see Fig. 1B and F). Figure 1C and G illustrates the interplay of deformation field and confinement effects in c-GaN/c-AlN QDs. Although confinement makes a large contribution to the electron state, the hole is mainly influenced by the deformation field. The extent of electron density is noticeably larger than that of a hole. Both strain and piezoelectric fields are absent in GaN/dielectric QDs. Thus, carrier states are defined by confinement only, the charges are not separated, and the particle energies are proportional to $1/H^2$.

To sum up, piezoelectric fields and quantum confinement affect the carrier energy differently. Depending on which contribution is stronger in a given QD, the QD height dependence of the energy levels varies from linear (pure piezoelectric effect) to the inversely proportional to the square of the QD height (pure confinement effect).

The energy shift of exciton ground-state energy with respect to the bulk GaN energy gap is presented in Figure 3A as a function of H. The plot also shows reported experimental data points for the corresponding GaN QD type: boxes are Widmann et al.;[2] diamonds are after Ramval et al.;[4] triangles are after Daudin et al.;[6] and stars are after Leppert et al.[7] As one can see, our results are in agreement with available experimental data. The red shift with respect to bulk GaN energy has been found only in GaN/AlN QDs. This is in line with our calculations, since the piezoelectric effect is the strongest in such QDs. Based on our calculations, we can also state that to have a red-shifted transition one needs QDs with $H > 3$ nm. The oscillator strength of the excitonic ground-state transitions in each of the four QD types is plotted in Figure 3B as a function of QD height H. The piezoelectric field in GaN/AlN and GaN/$Al_{0.15}Ga_{0.85}N$ QDs pushes electrons and holes apart, thus decreasing f. With increasing H, the piezoelectric field increases, and, therefore, f decreases. The oscillator strength of red-shifted transitions in GaN/AlN QDs is extremely small and decreases fast with increasing H. Weaker charge separation in GaN/$Al_{0.15}Ga_{0.85}N$ QDs leads to somewhat larger f. In the absence of piezoelectric fields, the oscillator strength is rather large and almost independent of QD height, which is the case for GaN/dielectric and c-GaN/c-AlN QDs. The c-GaN/c-AlN QDs have smaller f than GaN/dielectric QDs because the hole in the former QDs is located in the deformation potential trap.

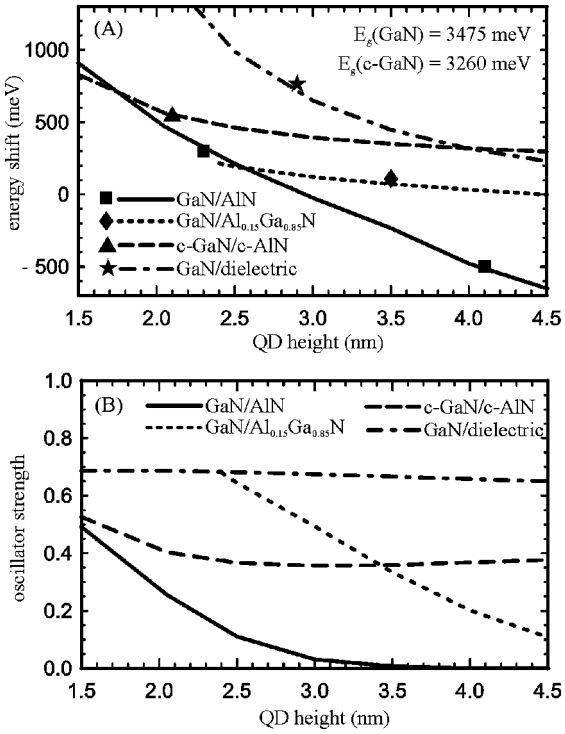

Fig. 3. (A) Energy shift of the exciton ground-state energy level as a function of the QD height for four types of GaN QDs. The energy shift in GaN/$Al_{0.15}Ga_{0.85}N$ QDs is shown only for the QD heights that allow both electron and hole discrete energy levels. The legend shows the bulk energy gaps of hexagonal and cubic GaN. Experimental points are after Widmann et al.[2] (■); Ramval et al.[4] (♦); Daudin et al.[6] (▲); Leppert et al. [7] (★). (B) Oscillator strength of the excitonic ground-state transition as a function of the QD height for the same QD types. Note that the oscillator strength of the red-shifted transition rapidly decreases with the QD height, whereas that of blue-shifted transitions is nearly independent of the QD height.

4. CONCLUSIONS

We have carried out an investigation of confinement, strain, and piezoelectric field effects on the optical spectrum of GaN QDs on the basis of a rigorous theoretical model that takes into account the exact shape, interface, and material parameters of the QD and barrier regions. To separate the effects and elucidate their relative strengths, we applied our model to four different types of GaN QDs, which have been reported in the literature. We have shown that the interplay of quantum confinement and piezoelectric field allows one to fine-tune the energy and strength of optical transitions in GaN QDs by a smart choice of interface and the QD shape. The results of these calculations can be used for the interpretation of photoluminescence data measured for different types of GaN quantum dots.

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