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Citation: Appl. Phys. Lett. **75**, 3449 (1999); doi: 10.1063/1.125292
View online: http://dx.doi.org/10.1063/1.125292
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v75/i22
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Optical spectra of nitride quantum dots: Quantum confinement and electron–hole coupling

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(Received 15 April 1999; accepted for publication 5 October 1999)

We calculate the optical properties of nitride-based quantum dots by taking into account quantum confinement as well as electron–hole interaction. We analyze model structures simulating $In_xGa_{1-x}N$ dots in $In_yGa_{1-y}N$ layers with different alloy compositions. We discuss the trends with the dot size and show that quantum confined excitations exist for a broad range of sizes down to the smallest observed dots. Our results allow us to identify the strong role of Coulomb correlations in the optical spectra and to predict a strong influence of photoexcitation power on selection rules in polarized samples. The signature of quantum confinement can be utilized for a critical interpretation of measured optical spectra. © *1999 American Institute of Physics.* [S0003-6951(99)03448-8]

$In_xGa_{1-x}N$ wide-band-gap semiconductors have been exploited for the successful fabrication of solid-state blue lasers. However, there are still many unresolved issues concerning the lasing mechanism and efficiency. Despite the huge number of threading dislocations arising from strain relaxation in heteroepitaxial growth, the nitride-based devices are very efficient. A clear understanding of the basic physical reason is still lacking. It has been argued that the dislocations are electrically inert because of mutual annihilation. An alternative suggestion is that the carriers in the active region of the device are captured in confined levels rather than in defect states related to dislocations.[1] Such confinement could be associated with three-dimensional self-assembled quantum dots (QDs).[2]

In this letter we show that specific clear-cut features are relevant for characterization, and expected to arise in the optical spectra of the fabricated devices if QD confinement is indeed present. To this purpose, we develop an accurate theoretical description of the linear and nonlinear optical properties of nitride QDs, that was previously not available. We consider $In_xGa_{1-x}N$ dots in $In_yGa_{1-y}N$ layers for different dot sizes and for two alloy compositions that correspond to different regimes of strain distribution and piezoelectric polarization: $(x,y)=(1,0)$[3] and $(x,y)=(0.42,0.10)$.[4] This choice is motivated by experimental studies that suggested compositions close to these values for nitride structures interpreted as QDs.[3,4]

Our results show that Coulomb correlation has an important effect both in the linear regime and in the regime of high photoexcitation typical of optoelectronic device operation. A typical signature of quantum confinement that we predict in strained QDs, where polarization fields exist,[5] is the quenching of some optical transitions for increasing photoexcitation intensity. Our calculations allow us to identify the microscopic nature of the quenching in terms of breaking and recovering of selection rules for allowed optical transitions.

In our calculations for QDs, the initial input is the single-particle properties that are obtained by solving the 3D Schrödinger equation within the envelope-function and effective-mass approximations, by means of a plane-wave expansion with periodic boundary conditions.[6] The single-particle states are used to compute the optical matrix elements within the dipole and rotating-wave approximations, and the Coulomb matrix elements by neglecting interband Auger-type processes. Our description of the optical properties is based on the density-matrix approach at the level of the one-particle density matrix $\rho_{nn'}=\langle \psi_n^\dagger, \psi_n \rangle$.[7,8] The brackets denote the statistical ensemble average, and the field operators $\psi_n^\dagger$ create an electron in the conduction ($n=c$) or valence band ($n=v$). The matrices ρ_{cc} and ρ_{vv} contain the distribution functions and the intraband polarizations; ρ_{cv} accounts for the interband polarizations, which play a central role in the description of the coherent optical response. The time evolution of ρ follows from the Liouville–von Neumann equation:

$$\hbar\dot{\rho}=-i[h_0+h_{\rm op}(t)+\overline{V}[\rho],\rho]+\hbar\dot{\rho}|_{\rm env}. \tag{1}$$

Here, h_0 is the single-particle Hamiltonian for carriers confined in the QD and can include an external magnetic field $\underline{B}\|z$; $h_{\rm op}(t)$ is the interaction with an external light field; $\overline{V}[\rho]$ is the Hartree–Fock potential that describes the mutual Coulomb interactions among photoexcited electrons and holes within a mean-field approximation; $\dot{\rho}|_{\rm env}$ accounts for interactions with the environment of the QD (phonons, electrons in the wetting), treated within the relaxation-time approximation. The semiconductor Bloch equations[7,8] result from writing explicitly Eq. (1) for ρ_{cc}, ρ_{vv}, and ρ_{cv}. In quasiequilibrium conditions, the optical absorption spectra are obtained from the Fourier transform of the polarization. Within linear response, the calculation of the absorption spectra is cast in the form of an eigenvalue problem[7,8] whose solutions give the the polarization eigenmodes (excitons) of the system.

Our choice for the material parameters (see Table I) is based on first-principles calculations. The dielectric constant ϵ_0 for InN ($\epsilon_0=14.6$) and GaN ($\epsilon_0=10.3$) is obtained from

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TABLE I. Material parameters used in the calculations for $In_xGa_{1-x}N$ QDs in $In_yGa_{1-y}N$ layers.

	$(x,y)=(1,0)$	$(x,y)=(0.42, 0.10)$
ϵ_0	14.6	12.1
m_e	$0.127m_0$	$0.139m_0$
m_h	$1.457m_0$	$1.299m_0$
E_g	1.89 eV	2.83 eV
CBO	1.18 eV	0.29 eV
VBO	0.43 eV	0.23 eV

Ref. 9. We use a weighted average of the in-plane and out-of-plane effective masses of InN and GaN for both electrons (m_e) and heavy holes (m_h), neglecting valence band mixing.[10] For $In_xGa_{1-x}N$, ϵ_0, m_e, and m_h are interpolated with Vegard's law. The conduction and valence band offsets (CBO and VBOs) for InN/GaN were calculated for materials strained onto an AlN substrate.[11] Because of the 10% lattice mismatch between InN and GaN, we assume that the dots with $(x,y)=(1,0)$ are completely relaxed and we take into account biaxial strain relaxation using deformation potentials[12] to calculate the VBO and the CBO for the relaxed $(x,y)=(1,0)$ dots. To obtain the VBO for the $(x,y)=(0.42, 0.10)$ dots, we fit the data for junctions of alloys with different composition,[13] taking into account biaxial strain up to second order. We then need the band gap E_g to evaluate the CBO. We use $E_g(x)=xE_g(1)+(1-x)E_g(0)+\alpha x(1-x)+\Delta E[e(x)]$, with $e(x)$ the strain; $\Delta E[e(x)]$ is calculated from the deformation potentials and elastic constants for wurtzite crystals,[14] and α is calculated by fitting the band gap values for different alloy compositions.[13] The QD confinement potential is assumed to have a cylindrical shape (height/diameter ratio=1:2.5); this is the simplest choice consistent with the presence of a preferential axis for epitaxially grown nitride devices.[15] For the strained $(x,y)=(0.42, 0.10)$ dots, we approximately take into account the effect of piezoelectric polarization,[6] as discussed below.

Figure 1 shows the electron single-particle energies for InN dots in GaN. With decreasing dot size the energy splitting between bound states of the QD (states with energies below the CBO) increases; few states remain bound.[16] The right panel shows the square of the wave functions for a dot of 2 nm height. Due to the cylindrical symmetry, the angular part of the wave function $[\exp im\phi\ (m=0,\pm1,\pm2,\ldots)]$ factorizes. In Fig. 1, state (a) corresponds to $m=0$, while states (b,b′) and (c,c′) correspond to $m=\pm1$ and $m=\pm2$, respectively.

Given the dot geometry, the confinement potential for electrons and holes is almost identical. The consequent similarity of electron and hole wave functions imposes restrictions on the optical transitions: Within the envelope-function approximation, the interband matrix elements are of the form $\int d\mathbf{r}\phi_h^{\nu_h}(\mathbf{r})\phi_e^{\nu_e}(\mathbf{r})$,[6] with $\phi_e^{\nu_e}(\phi_h^{\nu_h})$ the wave function for electrons (holes) with quantum number ν. Owing to wave function orthogonality, the optical transitions are thus allowed only between electron and hole states of opposite (or zero) quantum number m. Optical absorption spectra are shown in Fig. 2 for two different sizes of InN QDs in GaN. The energy splitting between different peaks is on the order of the splitting of the corresponding electron levels in Fig. 1 (the correction due to hole confinement is one order of magnitude smaller). The spectrum of Fig. 2(b) shows that, in a cylindrical InN/GaN dot of 2 nm height and 5 nm diameter, the two lowest absorption peaks are split by ~ 300 meV. Figure 2(a) shows that such splitting is decreased to ~ 75 meV for the larger dots considered. These values give a reference for the energy of the confinement related peaks in absorption spectra if quantum dot behavior in a device structure is indeed present. A closer inspection of the differences between solid and dashed lines in Fig. 2 indicates that Coulomb interactions are important for a quantitative description of the spectra. Three pronounced effects are present: (i) a redshift of the transition energies (exciton binding energy) due to the attractive Coulomb interaction between electrons and holes; (ii) a size dependence of the exciton binding energy, which is about 30 meV for the larger dots and 60 meV for the smaller dots; (iii) the appearance of additional peaks, caused by the coupling between optically allowed and forbidden transitions. The level coupling induced by Coulomb interactions results in a transfer of oscillator strength to the lower energy excitations (Fig. 2).

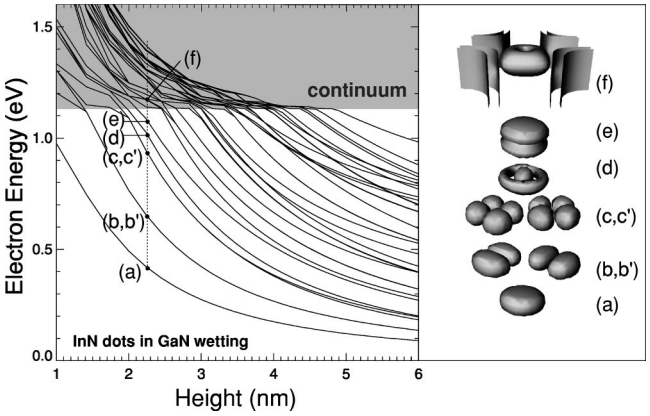

FIG. 1. Electron single-particle energies (left panel) for InN dots GaN $[(x,y)=(1,0)]$ as a function of the dot size (60 lowest energy levels); a cylindrical confinement potential is assumed (height/diameter ratio of 1:2.5). The right panel shows the square of the wave functions.

Our calculations reveal that the magnetic-field dependence of the optical transitions is negligible in the strong confinement regime: a significant diamagnetic shift can be observed for large dots with a confinement length $\gtrsim 30$ nm. In this sense magneto-optics, successfully employed for arsenide-based nanostructures,[17] is not expected to be a powerful characterization tool for the small self-assembled

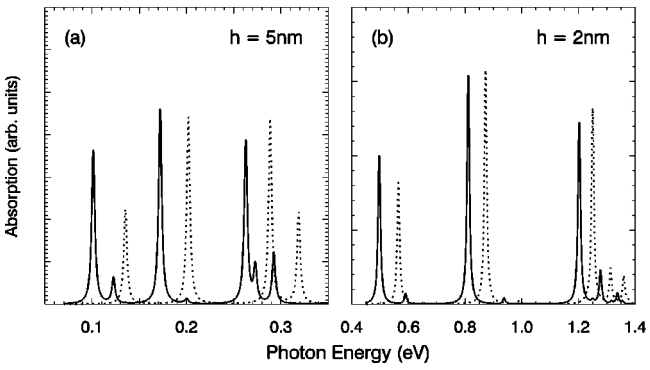

FIG. 2. Optical absorption spectra for a dot height of 5 nm (a) and 2 nm (b) (same QD geometry as in Fig. 1). Photon energy zero is set at the band gap. Solid (dashed) lines: electron–hole interaction included (neglected).

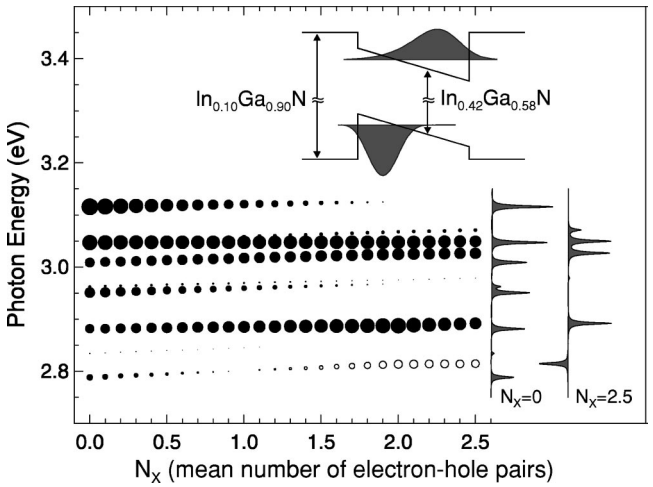

FIG. 3. Optical absorption spectra for a strained QD $[(x,y)=(0.42, 0.10)]$ with 4 nm height as a function of exciton concentration: full (open) circles denote absorption (gain); two typical spectra are shown in the right panel. The inset sketches the confinement potential along the z direction (shaded areas: square of the electron and hole wave functions).

InGaN QDs (few nanometers large[18]), unless high fields are used. It may be of relevance for intentionally grown GaN QDs, whose size is in the range of tens of nanometers.[19]

We next turn to the case of strained dots with $(x,y)=(0.42, 0.10)$: The effect of piezoelectric polarization[5] is expected to play an important role. To gain insight into the major qualitative features expected for strained nitride QDs, we consider an electric field of -0.15 V/nm in the z direction. Magnitude and sign of the field are chosen on the basis of the calculated value for strained InN/GaN quantum wells[5] and assuming a reasonable average of a nonconstant electric field along the height of the dot: this approximately takes into account the effect of dot shape on the polarization field. See the inset of Fig. 3 for a schematic representation of the polarization field: the smallest band offsets are chosen according to Table I. The linear absorption spectrum is shown on the right of Fig. 3 $(N_X=0)$. The main effect of an internal field is that electrons and holes are spatially separated. Thus, the optical matrix elements for the energetically lowest transitions decrease and the selection rules no longer apply. To inquire into the consequences of piezoelectric field screening by injected carriers, we compute the Hartree–Fock ground state self-consistently from Eq. (1) for a given concentration of electron–hole pairs, and we then obtain the optical absorption spectra through a diagonalization procedure.[6,7] Because of the reduced phase space and of the resulting suppression of scatterings, such an approach is approximate in the case of QDs.[20] Figure 3 shows the optical absorption spectra for different carrier concentrations: the size of the circles corresponds to the height of the respective absorption peak. State filling changes the character of the lowest transition from absorption to gain.[6,7] The screening of the piezoelectric field has the following consequences: First, with increasing N_X the overlap of the electron and hole wave functions increases, which leads, e.g., to an enhancement of the peak at ~ 2.88 eV. Second, the orthogonality relations are partially recovered, which results in the disappearance of some peaks. The observation that some of the optical transitions are quenched, while others are unaffected when the photoexcitation intensity increases (due to screening of the piezoelectric fields and recovery of selection rules), can therefore be taken as a signature of quantum confinement.

In conclusion, we have shown that the optical spectra of nitride-based quantum dots exhibit effects that allow us to gain insight into their confinement properties. (i) Confined states exist for a broad range of sizes down to the experimentally observed dimensions of few nanometers. (ii) Coulomb coupling is essential for a quantitative description and gives exciton binding energies as large as 60 meV for InN dots in GaN. (iii) In strained nitride QDs strong additional signatures of quantum confinement must arise in the nonlinear optical spectra due to piezoelectric-field effects. The effects discussed above should be considered for a critical interpretation of optical spectra.

The authors thank Angela Rizzi for helpful discussions. This work was supported by the EC TMR Network ''Ultrafast Quantum Optoelectronics'' and by the MURST program ''Physics of nanostructures.'' U.H. acknowledges support by the EC through a TMR Marie Curie Grant.

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