Critical size for localization of the *L*-like conduction states in InAs quantum dots grown on GaAs

J. A. Prieto,^{a)} G. Armelles, J. M. García, L. González, A. San Paulo, and R. García
*Instituto de Microelectrónica de Madrid (C.N.M., C.S.I.C.), Isaac Newton 8,
 28760 Tres Cantos, Madrid, Spain*

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The localization of the *L*-like conduction states is found to change from the islands to the substrate in InAs quantum dots grown on GaAs as the island-size decreases. This is due to a size-induced modification of the strain state of the islands. The critical size should correspond to dislocation formation. As a result, small InAs islands coherently strained to GaAs exhibit optical properties markedly different from those of bulk InAs. © 2000 American Institute of Physics.
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A great variety of materials exhibit physical properties that depend on size in the nanometer range.¹ Such physical properties often experience an abrupt change at a *critical size*, as is the case, for instance, of the metal–nonmetal transition in Hg² or Fe³ clusters. Also, semimetal C turns into semiconductor⁴ and nonmagnetic Rh becomes magnetic.⁵ This has attracted much attention both from fundamental and technological points of view since nanometer-sized particles form a new class of systems, with features really different from those of the constituent materials, just below the critical size.

Semiconductors also exhibit size effects in their electrical and optical properties as a consequence of carrier localization.¹ Practical applications of semiconductor nanoparticles or quantum dots (QDs) usually require a host. Nevertheless, the host may modify the behavior of QDs drastically. It has been predicted that free-standing InP QDs must have a direct gap.⁶ However, small enough InP QDs coherently embedded in GaP should exhibit an indirect gap due to the modification of the conduction energy levels caused by strain.⁷ In this letter we present experimental evidence of a change in the localization of the *L*-like conduction states in InAs QDs grown on GaAs as the island-size decreases. The position probability density moves from the islands to the substrate because of a type-I–type-II crossover in real space related to a size-induced modification of the strain state of the islands, with a critical size given by dislocation formation. As a result, small coherent islands, in contrast to large relaxed ones, exhibit no *E*₁-like transition. Not expected in free-standing QDs, our results also point out the dramatic influence of the host in the optical properties of semiconductor nanoparticles.

A series of (001)-oriented uncapped QD structures, with nominal InAs deposition between 2 and 6 monolayers (ML), was grown under identical conditions via molecular-beam epitaxy. InAs was supplied by pulses of 0.15 ML with 2 s interruption at 500 °C and under an As₄ pressure of 1.6×10^{-6} Torr. The reflection high-energy electron-diffraction pattern indicated formation of QDs in all the cases. After cooling down under arsenic atmosphere, the

samples were removed from the growth chamber. Then, their surface morphology was studied using an atomic-force microscope. InAs deposits below 4 ML [Fig. 1(a)] result in a rather uniform distribution of small individual islands. The higher the amount of InAs the larger the island density. However, above 4 ML [Fig. 1(b)] large individual islands appear as well, in agreement with previous results.⁸ Typical dimensions are $20 \times 20 \times 5$ and $50 \times 50 \times 20$ nm³. The bimodal island size distribution characteristic of InAs deposits in excess of 4 ML is evident in Fig. 2, where the histograms of island height corresponding to the samples of Fig. 1 are shown.

Small and large islands exhibit extremely different optical properties in the photon energy region of the *E*₁ transition of bulk InAs, as revealed by photorefectance (PR) measurements carried out at 80 K (Fig. 3). Samples with solely small islands exhibit no InAs-related signal. On the contrary, those with large islands display a feature, near 2.63 eV,

FIG. 1. Atomic-force microscopy images of two (001)-oriented uncapped InAs/GaAs quantum dot structures with 2 (a) and 6 (b) ML of nominal InAs deposition.

^{a)}Electronic mail: josea@imm.cnm.csic.es

FIG. 2. Histograms of island height of the samples shown in Fig. 1: (a) 2 ML; (b) 6 ML. The scale corresponding to the large islands (in light gray) has been magnified 20 times as they contain a considerable portion of the InAs deposition. Gaussian fits (dashed lines) are included as a guide to the eye.

which the intensity rises with the InAs deposition. Samples with less than 2 ML of InAs but grown on InP clearly show island-related transitions in the spectral range considered.⁹ Hence, the feature around 2.63 eV should be regarded to the large islands. The absence of a contribution from the small islands is surprising not only by comparison with the results reported in Ref. 9, but also because features associated with the E_0 transition have been observed by PR, even at room temperature, in similar samples.¹⁰ The spectral structure due to the E_1 transition is expected to be stronger, as occurs in massive material, because of the larger joint density of states at the L point of the Brillouin zone.

The degree of strain of small and large islands must be different,¹¹ which may explain their distinct behavior. To investigate this, Raman scattering spectra were taken at 80 K in the vicinity of the transversal and longitudinal optical vibration modes (TO and LO phonons, respectively) of bulk InAs, using distinct lines of an Ar⁺ ion laser as optical excitation. The parallelism with the PR results is obvious (Fig. 4). Only the specimens with large islands display an InAs-related signal which the intensity rises with the InAs depo-

FIG. 3. 80 K photoreflectance spectra of the samples shown in Fig. 1: dotted line, 2 ML; solid line, 6 ML. E_1^L and E_1^S denote, respectively, features related to the L -derived states of the large islands and the L states of the substrate. Downloaded 26 Feb 2010 to 161.111.180.191. Redistribution subject to AIP license or copyright; see <http://apl.aip.org/apl/copyright.jsp>

FIG. 4. 80 K Raman scattering spectra of the samples shown in Fig. 1: dotted line, 2 ML; solid line, 6 ML. Peaks A, B, and C are associated with dispersion through phonons localized in the large islands, whereas TO_s and LO_s correspond to the transversal and longitudinal optical vibration modes of the substrate.

sition. Such a signal consists of three peaks located at 225, 239, and 254 cm⁻¹ (labeled A, B, and C, respectively) that resemble Raman scattering through the InAs-like TO and LO (peaks A and B) and GaAs-like LO (peak C) phonons of an unstrained Ga_xIn_{1-x}As alloy with a Ga content around 10%.¹² The large islands seem to be comprised of Ga_{0.1}In_{0.9}As rather than InAs, probably because of the annealing process.¹³ Moreover, they should be relaxed, as expected, via formation of misfit dislocations. Ga content around 10% (Ref. 14) and absence of strain are in agreement with the energy position of the PR feature since quantum confinement is negligible due to the considerable size of the large islands as well as the high effective masses at L . Small islands, coherently strained to the substrate, do not contribute to the spectra. Nevertheless, dispersion through LO-like phonons localized in InAs islands grown on InP has been reported.⁹

Strain modifies the electronic structure of semiconductors. Figure 5 shows a simple calculation of the alignment between the energy levels corresponding to the L states of bulk GaAs and the L -derived states of relaxed (a) and coherently strained (b) InAs QDs. Lineup (a) is obtained from the unstrained valence band offset at Γ (Ref. 15) and the energies of the InAs and GaAs band edges at L ;¹⁶ lineup (b) computing, within the deformation potential theory, the strain-induced modification of the energies of the conduction L states [$\Delta E(L_c)$] and the E_1 transition (ΔE_1) of bulk InAs.¹⁷ We have considered the effect of the hydrostatic part of strain concentrated on the conduction band edge,¹⁸ using

FIG. 5. Energy level lineup for the L states of bulk GaAs and the L -derived states of relaxed (a) and coherently strained (b) InAs islands. The case of a pseudomorphic InAs layer (c) is also shown.

the deformation potentials of GaAs¹⁷ instead of those of InAs as a first approach. Mean values of the strain components in coherent surface islands were obtained from Ref. 19. Figure 5 also displays the case of a pseudomorphic InAs layer (c) for the sake of completeness. Discrepancy between experiment and calculation may be expected given that the latter one assumes InAs islands. However, the degree of strain in coherently strained Ga_{0.1}In_{0.9}As islands should not be significantly different [it is only 10% lower in the case of a dislocation-free quantum well (QW)]. On the other hand, a low Ga content does not alter the E_1 gap.¹⁴ Consequently, our treatment should describe the situation within an error due mainly to the compositional variation of the band gap, less than 0.1 eV.¹⁴

Whereas a type-I lineup confines both conduction and valence states to the large islands, the type-II lineup characteristic of the small ones keeps the conduction state mainly localized in the substrate. As a well-defined size demarcation exists between relaxed and coherently strained islands, the critical size for such a type-I–type-II crossover in real space should correspond to dislocation formation. The result is a weak overlap of the L -derived wave functions and, in consequence, the quenching of the island-related E_1 transition. Without resonant conditions for optical excitation, Raman scattering is not observable.⁹ Both facts are in accordance with the experiment. Notice that a pseudomorphic InAs layer also exhibits a conduction type-II lineup [Fig. 5(c)]. As a matter of fact, there are no publications concerning either the E_1 resonance or Raman scattering through optical phonons in dislocation-free InAs/GaAs QWs.

One of the most desirable effects of size reduction in semiconductors is the concentration of oscillator strength into narrow regions of the optical spectrum.¹ This may be unattainable if QDs are embedded in a semiconductor host, as the quenching of the island-related E_1 transition in InAs/GaAs QD structures presented here illustrates. Nevertheless, our results also suggest the possibility of hopefully adjusting the electronic structure and, therefore, the physical properties of semiconductor nanoparticles through the proper choice of the matrix. As emphasized in Ref. 9, InAs islands grown on InP exhibit a type-I lineup at the L -like critical point. In contrast, the size-induced modification of the strain state of the islands causes, when the substrate is GaAs, a type-I–type-II crossover in real space. Consequently, below disloca-

tion formation the behavior of (coherent) InAs/GaAs QDs differs from that of InAs/InP ones considerably. Moreover, such heterostructures indeed form a new class of systems since the E_1 transition has a pronounced contribution to the optical spectrum of bulk InAs. The importance of the host may not be exclusive of semiconductors, but characteristic of several materials, such as the magnetic elements.²⁰

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