Normalized reflection spectra in GaAs/$In_xGa_{1-x}As$ single quantum wells: Structure characterizations and excitonic properties

A. D'Andrea and N. Tomassini
Istituto Metodologie Avanzate Inorganiche, Consiglio Nazionale delle Ricerche, I-00016 Monterotondo Stazione (Rome), Italy

L. Ferrari, M. Righini, and S. Selci
Istituto Struttura della Materia, Consiglio Nazionale delle Ricerche, Via Enrico Fermi 38, I-00044 Frascati (Rome), Italy

M. R. Bruni, M. G. Simeone, and N. Gambacorti
Istituto di Chimica dei Materiali, Consiglio Nazionale delle Ricerche, I-00016 Monterotondo Stazione (Rome), Italy
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A systematic study of GaAs/$In_xGa_{1-x}As$ single quantum wells is performed in two sets of samples with different alloy concentrations (namely, $x=9\%$ and 18.5%) and well thicknesses ranging from 15 to 250 Å. These samples are grown by the molecular-beam-epitaxy facility and characterized by "normalized reflection spectroscopy." Accurate calculations of exciton energies are computed in the effective-mass approximation by a variational wave function expanded in electron-hole subbands taking into account the four-band Lüttinger Hamiltonian and strain tensor energy. Maxwell's equations of the system are exactly solved in order to compute the optical response in polaritonic framework. Model calculations well compare in energies and line shapes with normalized reflectivity for quantum-well thicknesses lower than 70 Å. For larger samples it is necessary to hypothesize a certain degree of strain relaxation and nonhomogeneous indium concentration in the sample in order to explain some discrepancies between theory and experiments.

In recent papers,[1-3] exciton binding energies and the optical response in single quantum wells of *II-VI* ($Cd_xZn_{1-x}Te/CdTe$) and *III-V* ($In_xGa_{1-x}As/GaAs$) strained materials were computed by an accurate variational exciton model in the effective-mass approximation, expanded in electron and hole subband products. The Luttinger Hamiltonian[4] and strain tensor energy[5] are embodied in the model[2] and the physical parameter values adopted, in order to compute the exciton energy states in binary $In_xGa_{1-x}As$ alloy, were obtained from pure material parameters by a "virtual crystal model" interpolation schema.[2,6] These calculations were able to reproduce optical spectra of a large number of experiments quoted in the literature.[2]

In the present paper, a systematic study of the optical response of two sets of $In_xGa_{1-x}As/GaAs$ single quantum wells, with different alloy concentration ($x=9\%$ and 18.5%), is performed. The samples are grown by molecular-beam epitaxy (MBE) under the same growth conditions. The quantum-well thicknesses range from 15 to 250 Å and each sample is composed of two quantum wells of rather different thickness values. Moreover, in order to have no mixing in the spectra among polariton peaks attached to the two different wells, a barrier 1000 Å thick is placed in between.

The samples are routinely characterized by reflection high-energy electron diffraction (RHEED), high-resolution x-ray diffraction (HRXRD), and optically by "normalized reflection spectroscopy."[7] We would like to emphasize that the line shapes of normalized reflection spectra are obtained by an accurate subtraction of the background contribution; this procedure (explained in some details in the next section) gives a sort of "normalized reflectivity" that is sensitive to exciton properties (energies, oscillator strength,...) and also to the thicknesses of the different zones of the samples (barriers, wells, buffer, and substrate), due to the Fabry-Perot interference effect.

The optical response, computed in the polariton framework, well compares with experimental results for thin quantum wells (lower than 70 Å), while for thicker ones, a nonhomogeneous indium concentration and a partial relaxation of the strain must be considered in order to explain the systematic redshift of the experimental polaritonic peaks, with respect to the theoretical ones. The good agreement between theory and experimental spectra for thin quantum wells supports the conclusions that in this range of dimensions, indium concentration is homogeneous in the well thickness.

The growth of the samples and the experimental apparatus for normalized reflectivity are explained in some details. Exciton envelope functions in quantum wells are computed in the four-band framework and the Maxwell's equations are exactly solved for exciton polaritons. Experimental and numerical results are compared and discussed and conclusions are given.

Two sets of double quantum well at a different indium concentration ($x=9\%$ and 18.5%) were grown in GaAs(001) substrate, using a computer controlled Varian GenII MBE Machine. The substrate preparation was carry on by a standard wet etching procedure; the resulting surface oxide film was removed by heating at 580–600 °C under an arsenic flux. A buffer layer of GaAs (0.5 μm) was grown between substrate and wells. The substrate temperature, during the growth, was taken fixed at 530 °C. The V/III pressure ratio was kept from

27 to 35 atoms depending on the indium concentration. The growth rate was 1.02 μm/h for GaAs and 0.637–1.12 μm/h for $In_xGa_{1-x}As$ alloy.

The ternary alloy composition and the thickness of sublayers were measured *in situ* by RHEED. Moreover, the samples were characterized by a D5000 Siemens x-ray diffractometer in the conventional symmetrical reflection geometry.

The samples were grown with two barriers of large thickness (1000 Å) between vacuum and well and between the two different wells. Notice that the well with smaller thickness is always placed close to the buffer.

The optical experimental setup is basically a cross double beam reflectometer.[7] The reflected spectra are detected by an optical multichannel analyzer (OMA) equipped with a EG&G linear array. This arrangement allows an almost simultaneous record of the different techniques like normalized reflectivity spectra (RS), photoluminescence (PL), and photoreflectance (PR), and the present spectroscopy cannot be confused with other techniques.[8] Because of unneeded grating repositioning, a direct comparison of the absolute positions of RS, PL, and PR structures can be made within instrument resolution ($\Delta E \sim 0.16$ meV@2800 nm).

The OMA Spectrograph is a triple turret, 0.25-m Monospec 27 (by Jarrel-Ash), with a 25 μm entrance slit, and a EG&G 1453A linear array at the exit position. The accessible optical range is between 180 and 1100 nm. Two moveable gratings, of 1200 g/mm and 150 g/mm rulings, coupled with the fixed size of the array (1024 photodiode elements, 25 μm wide) allow a detailed or enlarged view of the interested zone. The optical sources are a 150 Watt Tungsten lamp, a He-Ne 5-mW Laser, or alternatively, a 0.5 Watt Ar^+ Laser.

Normalized spectra, $RS=I_{sample}/I_{ref}$, take into account source variation, the whole optical transfer function, the different gain of single photodiodes, and also the large scale contribution of the substrate reflectivity, showing an absolute reflectively spectrum of quantum well and bulk excitonic structures. Sometimes the temperature difference between the studied and reference samples leads to spurious features that are difficult to remove. In this case, RS are obtained with a mirror instead of a substrate as a normalization sample. The spectrum is then an overposition of sharp structures, related to the bulk and the quantum-well excitonic lines, and a smooth background due to the substrate reflectivity. This background has to be evaluated and removed to obtain an absolute RS.

Let us consider a multiple quantum wells of $In_xGa_{1-x}As/GaAs$ grown along z-axis on a buffer of GaAs (001). The total exciton Hamiltonian results in a 3×3 matrix,

$$\mathbf{H}_{ex}=\mathbf{T}_v(-i\nabla_h)+\mathbf{S}_v+\mathbf{E}_g(x) +[T_c(i\nabla_e)+S_c+V_{Coul}(|\mathbf{r}_e-\mathbf{r}_h|)+V_{im}(\mathbf{r}_e,\mathbf{r}_h)]\mathbf{I}\ , \tag{1}$$

where $\mathbf{T}_v$ is valence Luttinger Hamiltonian, $\mathbf{S}_v$ is strain matrix of the valence band, $\mathbf{E}_g(x)$ is a diagonal matrix that embodies the alloy unstrained energy gaps from the top of the valence bands (Γ_8 and Γ_7) and the bottom of the conduction band (Γ_6), T_c and S_c are, respectively, kinetic and hydrostatic energy of electron in conduction band, while V_{Coul} and V_{im} are, respectively, Coulomb interaction and image potential of the exciton, and $\mathbf{I}$ is the 3×3 unitary matrix.

The "tailoring" of the band gaps along the z axis and the physical properties of a multiple quantum well of $In_xGa_{1-x}As/GaAs$ are computed following the lines of Ref. 2. All the calculations are performed at 80 K, and energy gap is given by the following interpolation formula:

$$\mathbf{E}_g(x,T)=\mathbf{E}_g(0,0)+ax+bx^2-(c+dx)\frac{T^2}{T+(ex+f)}\ , \tag{2}$$

where the GaAs energy at 0 K is $\mathbf{E}_g(0,0)=1.5192$ eV and a, b, c, d, e, f parameter values are $a=1.597$ eV, $b=0.5$ eV, $c=5.408\times10^{-4}$ eV/K; $d=-9.470\times10^{-4}$ eV/K, $e=183$ K, $f=204$ K. The valence-band offset: $Q_v=\Delta E_v/\Delta E_g=[E_v(x)-E_v(x=0)]/[E_g(x=0)-E_g(x)]$ is taken from those quoted into the literature ($Q_v=0.3$). Finally, in order to simulate a quasicontinuum of states outside the wells, the sample (barriers, wells, and buffer) is confined in a box of thickness L_{Box}, imposing the so-called "no-escape boundary conditions"[9,10] at the surfaces. In order to compute optical response in a multiple-quantum well, we solve the Maxwell's equation for S polarization at normal incidence along the line of Ref. 2.

The exciton model adopted for the calculations, Eqs. (1) and (2), is able to describe the optical response of Wannier exciton in heterostructures of strained semiconductor materials. The model is free from fitting parameters in the sense that the calculations use the physical parameter values of pure materials. Unfortunately, different sets of parameter values are present in the literature for the system $In_xGa_{1-x}As/GaAs$. Then, in a previous paper,[2] two of the present authors have tried to reproduce a large set of experimental results[11–18] in order to perform a sensible choice. A very good agreement in the exciton energy values and in line shapes was obtained between theory and the experimental results when the parameter values coincide with those given by Landolt-Börnstein.[19]

In Figs. 1 and 2 are shown typical normalized reflectivity spectra for two single quantum wells of $In_xGa_{1-x}As/GaAs$, grown in doped silicon GaAs substrate with thicknesses 35 Å ($S113$) and 80 Å ($S27$) and indium concentration 9.5%, and 11%, respectively ($T=80$ K). In the same figures are also reproduced the reflectivity spectra computed by four-band model at the same temperature. For the thin quantum well ($L_w=35$ Å), we obtain a good agreement between theory and experiment (about 1 meV in the energy peak position) and for thick quantum well ($L_w=80$ Å), we must redshift the computed spectrum about 20 meV. The same results were obtained for a large set of samples growth by MBE facilities and not reported here. Note, that the large value of theory-experiment energy disagreement (≥ 20 meV), present in large quantum wells, cannot be justified

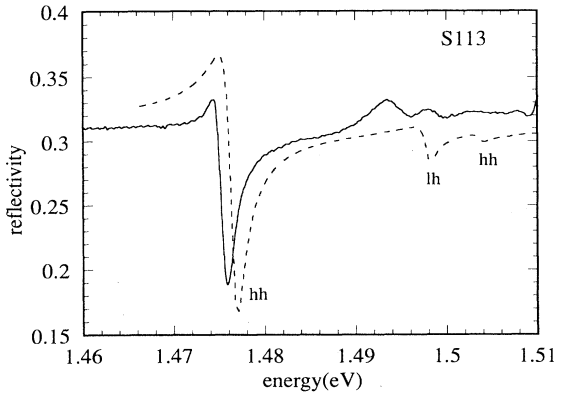

FIG. 1. Normalized reflectivity in the single quantum well ($S113$) of thickness $L_w = 35$ Å and indium concentration $x = 9.5\%$ (solid curve). Reflectivity computed by the four-band model for the sample is also shown (dashed curve). Parameter values are given in Ref. 2.

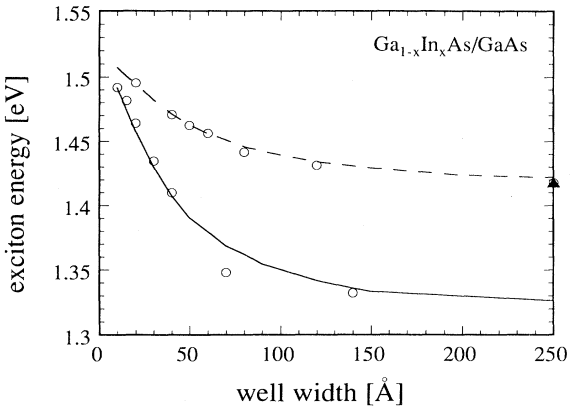

FIG. 3. Heavy-hole exciton transition energies computed by the four-band variational model for two different indium concentration, namely, $x = 9\%$ (dashed curve) and 18.5% (solid curve). Experimental results are also reported.

by the uncertainty on the physical parameter values adopted in the calculations.[2]

In order to go a bit deeper in understanding this phenomena, we have performed a systematic study in two different sets of samples "*ad hoc*" growth by MBE facilities on undoped GaAs(001) substrates. The goal of this study is to point out the influence of the partial strain relaxation and nonhomogeneous indium concentration on normalized reflection spectra. In Fig. 3 are reported the exciton transition energies for the lowest exciton level ($n = 1$), as a function of well width for the two sets of samples with nominal indium concentrations $x = 9\%$ and 18.5%.

The observed theory-experiment disagreement in optical response for large quantum wells (≥ 70 Å) can be due to three different effects, namely: (a) the band bending of the sample at the surface (vacuum barrier) or at the interfaces (barrier well), (b) the indium concentration in the well is spatially nonhomogeneous, and (c) the strain of the sample is partly relaxed (this is the so-called "plastic phase" between strained and dislocated materials). Point (a) is ineffective since the dopant concentration in these samples (5×10^{-11} cm^{-3}) gives a Debye length of about 10 μm, thus the energy shift is essentially due to the structural properties of the strained sample [points (b) and c)]. Let us consider a single quantum well with indium concentration $x = 9\%$ and well thickness 250 Å. Since the polariton experimental peak ($E_{\text{exp}} = 1.4177$ eV) is redshifted with respect to the theory ($E_{\text{theor}} = 1.4209$ eV) of 13.2 meV, we hypothesized that this effect is due to the nonhomogeneous indium concentration into the well. In fact, in Fig. 4, the x-ray-diffraction spectra for this sample is shown and a good fit of the experimental data, also reported in the picture, is obtained by a linear interpolation of indium concentration x inside the well from 5% to 10%. Notice that the graded concentration of indium decreases the gap between valence and conduction bands and gives, in this case, a perfect agreement between theory and experiment ($E_{\text{theor}} = 1.4170$ eV).

Samples with nominal indium concentration $x = 9\%$

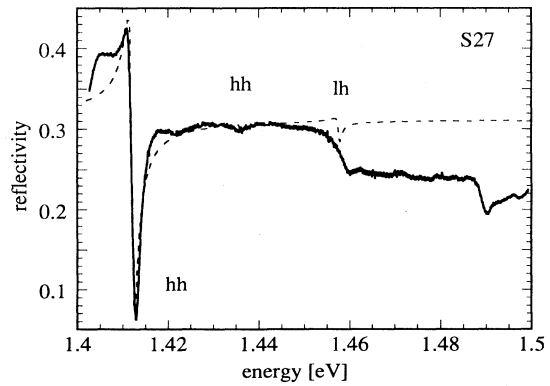

FIG. 2. Normalized reflectivity in the single quantum well ($S27$) of thickness $L_w = 80$ Å and the indium concentration $x = 11\%$ (solid curve). Reflectivity, computed by the four-band model for the same sample is also shown (dashed curve). Parameter values are given in Ref. 2.

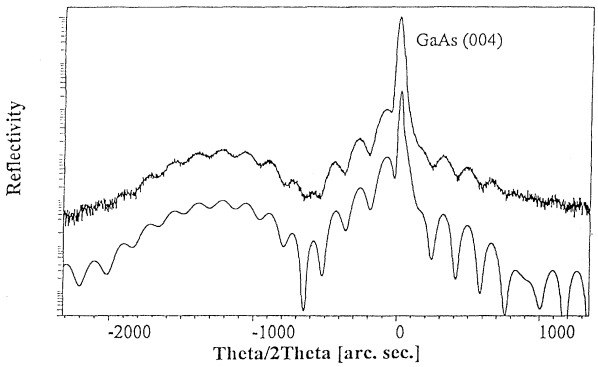

FIG. 4. X-ray-diffraction spectrum for a quantum well of thickness $L_w = 250$ Å and nominal indium concentration $x = 9\%$ (upper curve). The x-ray-diffraction simulation (lower curve) is obtained by introducing a linear gradient composition in the well.

show an average disagreement between theory and experiments of about 3 meV, but this discrepancy results lower than 1 meV for well thicknesses lower than 70 Å. Samples with $x=18.5\%$ show a greater disagreement (≈ 7 meV), but this is also strongly reduced (≈ 3 meV) for thin wells (<70 Å). Moreover, the large disagreement (≈ 19 meV) shows by the sample $S144$ ($L_w=70$ Å) should be due to a partial relaxation of the strain [point (c)], since x-ray-diffraction spectra (not reported here) point out homogeneous indium concentration for this sample.

In conclusion, "moderate" disagreement in exciton energy between theory and experiment in a large well can be due to a graded indium concentration, while larger energy disagreement in a thin quantum well can be explained only by a partial strain relaxation of the samples.[5]

In Fig. 5 is shown typical normalized reflection spectra in a double well sample for indium concentration $x=9\%$ and well thicknesses 80–40 Å. Computed line shapes, also reported in the picture, are in sound agreements with experiments. Notice that in principle, for the same exciton localization in the wells and $L_w \leq a_B$, thin quantum well must show greater oscillator strength than the large one.[9] In the present case, accurate calculations point out the same localization (about 75%) for the exciton in 40 and 80-Å well widths. In Fig. 5, theoretical optical spectra for the 80–40-Å sample is shown taking into account that the thinner well is placed close to the buffer. The spectrum is computed by noninteracting wells, using in the calculations a static dielectric constant with a small imaginary part ($\varepsilon_B=13.2+i1.2$).

A systematic optical study in two sets of single quantum wells, "*ad hoc*" grown by MBE facilities on different substrates and with different thicknesses and indium concentration, is performed. While computed spectra in thin quantum wells ($L_w<70$ Å) compare well with experiments, a systematic energy redshift is observed for large quantum wells ($L_w>70$ Å), and this effect increases, increasing the indium concentration. Moreover, in large quantum wells, graded indium distribution is pointed out and a partial relaxation effect (plastic phase) in samples that show large disagreement between theory and experiments (>20 meV) is hypothesized.

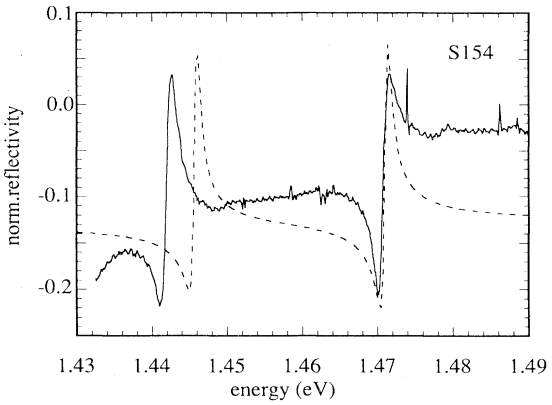

FIG. 5. Normalized reflectivity in the double quantum well of thicknesses, respectively, $L_w=40$ and 80 Å and indium concentration $x=9\%$ (solid curve). Reflectivity (dashed curve) computed by two noninteracting quantum wells of thicknesses 40 and 80 Å, indium concentration $x=9\%$ and static dielectric constant $\varepsilon_B=13.2+i1.2$.

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