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Wetting layer states of InAs/GaAs self-assembled quantum dot structures: Effect of intermixing and capping layer

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The authors present a modulated reflectivity study of the wetting layer (WL) states in molecular beam epitaxy grown InAs/GaAs quantum dot (QD) structures designed to emit light in the 1.3–1.5 μm range. A high sensitivity of the technique has allowed the observation of all optical transitions in the QD system, including low oscillator strength transitions related to QD ground and excited states, and the ones connected with the WL quantum well (QW). The support of WL content profiles, determined by transmission electron microscopy, has made it possible to analyze in detail the real WL QW confinement potential which was then used for calculating the optical transition energies. We could conclude that in spite of a very effective WL QW intermixing, mainly due to the Ga–In exchange process (causing the reduction of the maximum indium content in the WL layer to about 35% from nominally deposited InAs), the transition energies remain almost unaffected. The latter effect could be explained in effective mass envelope function calculations taking into account the intermixing of the QW interfaces described within the diffusion model. We have followed the WL-related transitions of two closely spaced QD layers grown at different temperatures, as a function of the In content in the capping layer. We have shown that changing the capping layer from pure GaAs to In0.236Ga0.764As has no significant influence on the composition profile of the WL itself and the WL QW transitions can be usually interpreted properly when based on the cap-induced modification of the confinement potential within a squarelike QW shape approximation. However, some of the observed features could be explained only after taking into consideration the effects of intermixing and InGaAs cap layer decomposition. © 2007 American Institute of Physics. [DOI: 10.1063/1.2711146]

I. INTRODUCTION

In the last years nanometer-sized semiconductor quantum dots (QDs) have become a subject of a rapidly developing area in the semiconductor research. They are used in an ever growing number of applications for building various devices, improving their operation and leading to the decrease of their dimensions. It includes devices for optoelectronics, quantum computing, and quantum cryptography.1–3 In particular, one of the very important issues and challenges is the tuning of the emission wavelength of InAs/GaAs quantum dots to 1.3 and 1.55 μm for developing GaAs based QD laser diodes for telecommunication applications.4,5 Most of the applications concern quantum dots fabricated in the so-called Stranski-Krastanov process.6 This method uses the relief of the elastic energy when two materials with a large lattice mismatch form an epitaxial structure. The deposited material initially forms a thin layer known as a wetting layer (WL), on top of which three dimensional defect-free nanometer-sized islands appear when the critical layer thickness is exceeded.

Most of the studies focus on the properties of the dots, whereas relatively few of them regard the properties of the wetting layer. On the one hand, the WL is assumed to be just a thin layer (about one to two monolayers thick) which, from the electronic structure point of view, is usually imagined as an ultranarrow rectangular-like quantum well (QW). However, on the other hand, it is well known that all the growth-assisted or postgrowth processing-induced intermixing effects (such as In–Ga atom exchange or interdiffusion) affect not only the dots, but the WL as well.7,8 It would mean that the WL confinement potential well shape might become strongly nonrectangular and should change significantly as a function of the growth conditions or after the postgrowth processing. This, however, seems to remain in contradiction to some experimental observations regarding energies of the optical transitions reported by different authors, concerning, for instance, the InAs/GaAs WL QWs.9–16 They are very similar in many reports and are usually in satisfactory agree-

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ment with the calculations assuming a rectangular well shape and its fractional thickness of about 1.5 monolayer.\textsuperscript{17–19}

In this paper we aim at presenting a more detailed discussion of the optical transitions related to the existence of the wetting layer in the InAs/GaAs QD structures, for which we use as main experimental tools the transmission electron microscopy (TEM) to deduce the composition profiles and photorelectance spectroscopy to study the absorptionlike spectra. In particular, we would like to address the following issues: (i) Why do the WL optical transition energies seem to be constant independent of the structure history? (ii) Why do the WL experimental transition energies agree very well with the calculated ones for the rectangular QW shape, nominal WL thickness, and WL content, in spite of the fact that the intermixing processes should change the WL drastically? (iii) How does the capping layer content affect the energy structure in the WL? In order to answer these questions, we exploit a single band model in effective mass approximation for calculating the WL QW energy states, extended onto the intermixed well case and including the content profiles taken from the TEM images.

II. EXPERIMENT

A series of samples comprising a QD bilayer, optimized for photoluminescence in the 1300–1500 nm wavelength range, was grown by the solid source molecular beam epitaxy on semi-insulating (001)-oriented GaAs substrates with 300 nm GaAs buffer layers. The samples contained two closely spaced layers of self-assembled dots (of a planar density determined by atomic force microscopy to be about 10\textsuperscript{10} cm\textsuperscript{-2}) formed after the deposition of the nominal amount of InAs material corresponding to 2.4 monolayer. The use of bottom layer of the dots (called further “the lower layer”), which plays a role of a seeding layer for the next QD layer, allows an independent optimization of the planar dots density and emission wavelength and thus the extension of PL emission up to 1500 nm, as suggested in Ref. 20. In the following experiments, the lower layer can be treated as a reference QD layer, while the optical properties of the upper one are investigated under the influence of the capping layer content. We have studied four structures which were differing in the In content of a 5 nm thick InGaAs layer capping the second (“upper”) layer of InAs/GaAs dots, starting from the pure GaAs cap up to nominally 23.6\% of indium. The two layers of dots were separated by 11 nm of GaAs (annealed at 580 °C under As overpressure after the layer growth and before the deposition of the second layer of InAs QDs). The entire structure was capped with 100 nm of undoped GaAs. The two InAs layers varied in the growth conditions: the lower (reference) layer was deposited at 530 °C with a growth rate of 0.165 μm/h, whereas the upper one was deposited at 480 °C and with about ten times smaller growth rate (0.016 μm/h). These growth conditions are similar to those described in Ref. 20. The intentional difference in the growth conditions plus the very well-known effect of a slightly increased size of the upper layer in the stacked structure are the reasons for different properties of both layers, even in the structure where they are capped with GaAs. It has allowed us to follow independently the optical transitions related to both QD layers and to distinguish between those which remain unaffected after the In\textsubscript{x}Ga\textsubscript{1−x}As cap introduction (lower dots layer) and those whose properties are definitely altered (upper dots layer). The layer structure of the investigated samples is schematically shown in Fig. 1.

In order to determine the composition profiles, the cross-sectional transmission electron microscopy has been performed using 002 dark field image conditions for structures with no InGaAs cap and with the cap of the highest In content. Further details of the TEM experiment and derivation of the layer composition have been described elsewhere.\textsuperscript{7,8}

The spectroscopic measurements were performed in the setup based on a 0.55 m focal length monochromator with an InGaAs p-i-n thermoelectrically cooled photodiode as a detector. The 532 nm line of a frequency doubled Nd:YAG (yttrium aluminum garnet) laser was used as an excitation source in photoluminescence (PL) and a pump beam in photorelectance (PR) measurements. A 150 W tungsten halogen lamp served as a probe beam source for PR. All the spectra were recorded using a lock-in technique with a low frequency reference modulation of about 280 Hz.

III. RESULTS AND DISCUSSION

Figure 2 shows room temperature photorelectance and high excitation photoluminescence spectra for the series of structures with different contents of the In\textsubscript{x}Ga\textsubscript{1−x}As layer capping the top layer of dots. In general, all the PR spectra can be divided into three main parts: a strong intensity feature at about 1.42 eV related to the bulklike GaAs band gap transition, a set of relatively sharp and intensive lines on the low energy side, which are attributed to the existence of the wetting layer, i.e., quantum wells formed of this and InGaAs cap, and finally a group of transitions on the lowest energy side of the spectra with a quite high inhomogeneous broadening and low intensity, typical of self-assembled quantum dots (the dots cover only a small fraction of the whole illuminated surface and have low intrinsic absorption coefficient per dot: hence the optical response intensity in the absorptionlike experiment is expected to be weak). We do not ana-
lyze the GaAs feature which is a superposition of signals from different parts of the structure because it is of no interest to the present work.

Under the excitation conditions which we have used in PL measurements (excitation power density of about 15 W/cm²), we could observe up to four QD-related lines for each sample and we were not able to reach the emission via the WL states at room temperature. However, besides the QD transitions corresponding to the ones seen in PL we could observe some higher order excited state QD transitions and several WL QW transitions in the PR absorptionlike spectra. The QD-related features can be easily divided into two groups: the two low energy ones shift significantly to the red with the increasing indium content of the upper QD layer cap, whereas the two higher energy ones remain constant. Therefore, we attribute the former to the dots in the upper layer ground and first excited state transitions in one population of dots in that layer observed due to the state filling effect and the latter to the lower layer of dots, i.e., ground and first excited state transitions again. Such an InGaAs cap-induced redshift has been already observed previously in similar structures, and the details of its origin will not be discussed here. However, we would like to focus on the properties of the WL QW related part of the spectra. The energies of the WL QW transitions as a function of the nominal InGaAs cap content are plotted in Fig. 3. First of all, as can also be seen directly from the spectra, we have observed two lines at approximately constant energies of 1.337 and 1.388 eV. Some additional ones appear on the low energy side after the introduction of the InGaAs cap and they shift to the red with the increase in the In content (one transition could also be resolved for the highest cap content structure between those two at 1.337 and 1.388 eV, and its origin will be explained further in the text). The energies of about 1.34 and 1.385 eV correspond well to the typically reported values for the heavy hole ground state and light hole ground state wetting layer transitions in the InAs/GaAs self-assembled dot system, therefore, we attribute them to the WL of the lower layer of dots capped by GaAs. We have calculated the energies of the transitions for a thin InAs/GaAs QW imitating the wetting layer, assuming an ideal rectangular shape of the potential and treating its thickness and the InAs/GaAs unstrained band offset as semifree parameters. We have employed the single band effective mass approximation to calculate the WL QW energy levels and wave functions by solving numerically the one-dimensional Schrödinger equation with the use of the transfer matrix method and by including strains. The material parameters have been taken from Ref. 25. The results of the calculation are shown in Fig. 4. The best agreement between the experiment and calculation has been obtained for the WL thickness of about 1.6 monolayer and the band offset in the conduction band taken for the unstrained materials, i.e., the so-called chemical band offset which corresponds to about 65% of the band offset in the real strained structure, which are reasonable values when compared to those cited in the literature.

In the real case, one would expect some intermixing of the WL QW due to the possible In–Ga atom exchange during growth or some interdiffusion. In general, these processes should modify the confinement potential significantly and also shift the optical transition energies. In order to simulate such process, we have calculated the energy levels for an intermixed InAs/GaAs quantum well applying a well-known diffusion model, where the distribution of the In and Ga atoms has been described by the error function.
changes the profile of the well from the square one with abrupt interfaces to the graded one. It can be seen in the insets of Fig. 5, which show the change in the In content profile and conduction band potential well for two diffusion lengths of 0.35 and 0.5 nm. It corresponds to the relatively strong intermixing and causes a decrease in the maximum In content in the well from 100% for the ideal squarelike case down to about 40% and 30%, respectively, and simultaneously increases the average QW width more than twice. Surprisingly, the calculated heavy and light hole related transition energies change very weakly as a function of the diffusion length even for its large value of 0.5 nm. The strongest transition energy change for that diffusion length range does not exceed 10 meV. It explains both the independence of the WL QW transition energies of the growth conditions in the two InAs layers of our structure and their almost constant values over a very broad range of different InAs/GaAs QD structures reported in the literature. In Fig. 6, we have summarized how the room temperature data are scattered in the published papers. It shows indeed that in spite of different growth conditions used in different laboratories, which influence the dot properties (e.g., the data concerning the QD ground state transition energy differ significantly in these reports), the WL transition energy remains almost constant within a very narrow range. It might be fully explained, thanks to the calculations we made assuming the QW interface intermixing (see Fig. 5).

The magnitude of the intermixing in the WL QWs of the structures investigated here can be seen in Fig. 7, where a cross-sectional TEM image for the sample with no InGaAs cap is shown. An evident gradually disappearing dark contrast may be observed above the bright line contrast of each WL. Further, we have derived the In content profile shown in Fig. 8 across the two InAs WLs using a method described in Refs. 7 and 8. It looks similar for both WLs, with maximum In content of about 35% depending slightly on the position on the sample which will surely contribute to the inhomogeneous broadening of the spectral lines and with some tendency to be higher in the upper layer by about 3%–4%, most probably due to its lower growth temperature and hence slightly weaker intermixing. Some WL composition fluctuation over the sample can be partly related to the fact that near a quantum dot (at a distance below 30–40 nm), the In content of the WL decreases substantially. The profiles of the composition have been established as far as possible from the QDs. However, the local density of the QDs is not perfectly uniform, which implies that in a small scale the WL content might differ depending on the distance to the nearest dot.

FIG. 4. InAs/GaAs WL QW transition energies calculated vs the value of the unstrained conduction band offset ratio for three different InAs QW layer thicknesses (solid lines). Dotted lines mark the experimental energy.

FIG. 5. InAs/GaAs WL QW transition energies calculated as a function of the In atoms diffusion length. Full squares mark the experimental energy. The insets show an In content profile for three diffusion length values of 0, 0.3, and 0.35 nm and the respective shapes of the conduction band well.

FIG. 6. Room temperature energies of optical transitions (full squares—heavy hole transition; open circles—light hole transition) related to InAs/GaAs WL QW taken after literature from emissionlike spectra (1—Ref. 9; 2—Ref. 10) and absorptionlike spectra (3—Ref. 11; 4—Ref. 12; 5—Ref. 13; 6—Ref. 14; 7 and 8—Ref. 15; and 9 and 10—Ref. 16). The dotted lines represent the mean values and are just guides to the eye.

FIG. 7. (Color online) Cross-sectional 002 dark field TEM image for the structure with two InAs/GaAs QD layers grown at different temperatures and different growth rates.
which gave first of all transition energies in agreement with the experimental ones determined for the lower wetting layer. Further, we have found that the content dispersion of about ±3% to 5% would give approximately 10–15 meV broadening in agreement with that which is seen in the experiment. It also means that the little difference in the peak In content of both WL layers will not be manifested in the spectra and will be covered by the layer inhomogeneity over the sample.

Now, we would like to draw attention to the structures with the InGaAs cap above the upper InAs layer. The capping procedure causes a number of changes in the structure, to both QDs and the WL QWs. The former will not be analyzed in this paper, and the main effects related to them have been discussed recently in the literature. As far as the WL QW is concerned, there are at least two major changes expected: modification of the confinement potential (into the steplike QW) and some influence on the intermixing degree of the WL. Figure 8(b) shows the In content profile across the WLs for the sample with the highest nominal In content (of about 23.6%). The main difference in comparison to Fig. 8(a) is a small broadening of the In content peak for the upper WL and the existence of the high In content shoulder due to the InGaAs cap. However, as it is seen in Fig. 8(b), the content is not exactly constant over the cap layer and its maximum value is significantly lower than the nominal one (less than 15% in Fig. 8(b) in contrast to 23.6% determined from the growth conditions), whereas the effective width is larger than the nominal 5 nm. The first reason can be the intermixing processes, similarly as for the WLs. However, a process known as “cap layer decomposition” cannot be excluded. We have performed the energy level calculations for such a QW consisting of a WL and InGaAs cap including the In content profile from Fig. 8(b). Figure 9 shows the calculation results (i.e., transition energies and corresponding overlap integrals) for the cases neglecting the tunneling between the two WL QWs and including it, and for rectangular QW shape approximation (the upper WL QW is a steplike one consisting of 1.6 InAs WL and 5 nm thick In0.236Ga0.764As) and real QW shape taken from the content profiles in Fig. 8(b). The calculated overlap integrals are shown in red and marked with letter “U” for the transitions occurring between the hole and electron states confined mostly in the upper WL QW, and in green and letter “L” for states confined mostly in the lower WL QW. Gray color has
been used to show transitions appearing only if the tunneling between the wells is taken into account, i.e., between the states almost equally extended over both QWs or between the states localized in two different layers (indirect in real space). For comparison, the experimentally obtained energies and transition intensities are shown in a form of moduli of the PR resonances seen in the spectra. Basing on this, the following conclusions can be drawn. First of all, there is no significant difference between the cases where a rectangular QW potential shape is assumed with and without tunneling, except for a change of the overlap integrals (oscillator strengths) of the transitions due to some leakage of the wave functions to the neighboring well. However, the energies of the high overlap integral (parity allowed) transitions correspond well to the four out of five experimentally observed lines, and explain their origin as respective heavy- and light-hole-related transitions occurring predominantly in the lower (L) or in the upper (U) WL QW (marked as h1-e1U and 11-e1U and h1-e1L and 11-e1L, respectively, in the language of single QW states, which correspond to h1-e1 and 11-e1 and h2-e2 and l2-e2 in the numeration of the double QW). The inclusion of the tunneling does not cause any significant changes besides the appearance of some additional transitions with low oscillator strength (occurring between the electrons localized mostly in one QW and holes in the other), which are not manifested in the spectra or are just superimposed with one of the strong transitions and could not be resolved within the inhomogeneous line broadening (which is of the order of 10–15 meV).

The energy of the ground state heavy hole transition of the upper layer calculated for the nominal parameters (23.6% of the In content in cap) is redshifted in comparison with the experimental value (by approximately 15 meV), which could be a signature of the cap layer decomposition (and the over-estimation of the effective In content in the cap layer); i.e., some of the In atoms of the cap layer join the dots during the cap deposition\(^{21,30,31}\) (a process which is typically reflected in the increase in the dots height or In content and will be a subject of an independent paper). In other words, one would need to decrease the In content of the cap to get an agreement with the experimental value of the ground state transitions. In our case, the content profile regarding the cap layer [Fig. 8(b)] shows some intermixing. Both these effects cause a decrease of a peak In content and are rather impossible to distinguish. However, using this profile, a better understanding of the experimental spectra (revealing several higher order transitions as well) can be obtained. For the more realistic confinement potential derived after Fig. 8(b) the four main transitions appear to have also high intensity (overlap integral). There are, however, qualitatively two main differences observed for this case, in comparison to Figs. 9(a) and 9(b). First, the transition energies shift slightly (the ground state heavy hole shifts to blue and falls well into the experimental one). Second, several new transitions appear (absent for the rectangular QWs), and one of them at the energy of about 1.37 eV [h2-e2 in Fig. 9(c) and h2-e3 in Fig. 9(d)] has a very significant overlap integral (allowed from the point of view of the selection rules) and corresponds to the fifth transition observed in the PR spectrum and is shown also in Fig. 3. Again, as in the case of the rectangular shape wells, the effects related to the tunneling seem to be still of secondary importance (in spite of the shallower effective confining potential and deeper carrier wave function penetration into the barriers). It appears that the line splittings or shifts due to the coupling are still below 10 meV (independent of the assumptions on the equal or not exactly equal QW content profiles); i.e., they will be hidden within the inhomogeneous broadening as well, and they cause only some quantitative changes in the optical transitions (e.g., modifications of the overlap integrals), which are rather difficult to observe in the PR spectra.

IV. CONCLUSIONS

In summary, we have first of all shown that the transition energies observed in the optical spectra and related to the thin wetting layer of the InAs/GaAs QD system are almost independent of the structure history, and based on the diffusion QW interfaces model, we have proven that they should always have energies close to 1.34 and 1.385 eV for the heavy hole and light hole transitions, respectively, with variations of about ±10 meV. Using transmission electron microscopy and composition profiles, we have also shown that the wetting layer is significantly intermixed, but the effect on the optical transitions is unobservable in the spectral response in the case of such thin layers. The observed QW transitions connected with the existence of the two wetting layers in the investigated bilayer InAs/GaAs QD system can indeed be theoretically explained on the basis of a simple thin rectangular well model. For the WL QW, including the InGaAs cap layer, the simplified approach will work only in a rough approximation. The experimental spectra are in fact a superposition of several transitions, and the appearance of some of these can only be explained by taking into account the real compositional profile, including the effect of an intermixing and a layer content decomposition.

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