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Wavelength tuning of InAs/InP quantum dots: Control of As/P surface exchange reaction

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Wavelength tuning of single and vertically stacked InAs quantum dot (QD) layers embedded in InGaAsP/InP (100) grown by metal organic vapor-phase epitaxy is achieved by controlling the As/P surface exchange reaction during InAs deposition. The As/P exchange reaction is suppressed for decreased QD growth temperature and group V-III flow ratio, reducing the QD size and photoluminescence (PL) emission wavelength. The As/P exchange reaction and QD PL wavelength are then reproducibly controlled by the thickness of an ultrathin (0–2 ML) GaAs interlayer underneath the QDs. Submonolayer GaAs coverages result in a shape transition from QDs to quantum dashes at low group V-III flow ratio. Temperature dependent PL measurements reveal excellent optical properties of the QDs up to room temperature with PL peak wavelengths in the technologically important 1.55 μm region for telecom applications. Widely stacked QD layers are reproduced with identical PL emission to increase the active volume, while closely stacked QD layers reveal a systematic PL redshift and linewidth reduction due to vertical electronic coupling which is proven by the linear polarization of the cleaved-side PL changing from in plane to isotropic. © 2006 American Vacuum Society. [DOI: 10.1116/1.2216719]

I. INTRODUCTION

Control of the As/P surface exchange reaction during growth of InAs/InP (100) quantum dots (QDs) by chemical beam epitaxy^{1,2} (CBE) and metal organic vapor-phase epitaxy³ (MOVPE) is achieved by inserting ultrathin GaAs (Refs. 1 and 3) or GaP (Ref. 2) interlayers underneath the QDs. Suppression of As/P exchange is revealed by a continuous reduction of the QD height as a function of the GaAs and GaP interlayer thickness to allow wavelength tuning of the QDs in the technologically important 1.55 μm region for telecom applications.

Self-assembled InAs QDs grown on InP substrates have great potential for QD lasers and semiconductor optical amplifiers (SOAs) operating in the 1.55 μm wavelength region for fiber optical telecommunication systems. However, InAs/InP QDs usually emit at wavelengths longer than 1.6 μm at room temperature (RT) due to the small lattice mismatch of 3.2% and the presence of As/P exchange during InAs growth, resulting in relatively large QDs. Though shorter wavelengths have been realized for QDs by double capping on InP (311)B,⁴ reduction of group V-III ratio and InAs supply,⁵ InGaAs growth,⁶ and postgrowth annealing,⁷

or in the case of quantum dashes,⁸ the reproducible, continuous wavelength control in the 1.55 μm region, is still a major challenge.

We have solved this problem for the case of CBE-grown InAs/InP QDs by inserting ultrathin (0–2 ML) GaAs or GaP interlayers between the InAs QDs and the underlying lattice-matched InGaAsP layer with a band gap at 1.3 μm (Q1.3 InGaAsP), which is a standard waveguide core material for InP based photonic devices. As/P exchange is effectively suppressed as a function of the GaAs or GaP interlayer thickness, which is directly reflected in a continuous reduction of the QD height. The photoluminescence (PL) emission wavelength of the InAs QDs, when embedded in Q1.3 InGaAsP, is, hence, continuously tuned from above 1.6 to below 1.5 μm at RT by solely increasing the GaAs or GaP interlayer thickness in the (sub-) ML range.

The suppression of As/P exchange is understood by the relation of the binary compound bond strengths: The Ga–P bond strength (54.9 kcal/mol) is larger than the Ga–As bond strength (50.1 kcal/mol), while the smaller In–P bond strength (47.3 kcal/mol) is even smaller than the In–As bond strength (48.0 kcal/mol). Hence, both GaAs and GaP surface terminations prevent the substitution of P bound to In by As. For GaAs interlayers on InGaAsP, however, As/P exchange takes place at the initial stage of growth. Therefore, GaP interlayers with the largest binary compound bond strength are most effective in suppressing the As/P exchange and,

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hence, in tuning the InAs QD emission wavelength at RT over the 1.55 μm region for submonolayer coverages.

Regarding the growth technique, realization of wavelength tunable InAs/InP QDs by MOVPE is highly desirable, which is the most common growth technique for InP based photonic devices. As/P exchange, however, is enhanced in MOVPE due to higher growth temperature, larger group V-III flow ratio, high reactor pressure, long gas-phase diffusion lengths, and complex gas switching and gas exchange processes, making the wavelength control of InAs/InP QDs more critical. Once, however, these parameters are optimized, insertion of an ultrathin GaAs interlayer is as effective for controlling As/P exchange as in CBE, tuning the QD size and QD emission wavelength over the 1.55 μm region, producing wavelength controlled QDs with excellent optical quality at RT.³

Moreover, we have vertically stacked the QD layers.⁹ For widely stacked layers, the wavelength tuning of the QDs is reproduced with identical PL emission to increase the active volume. For closely stacked layers, linear polarization control is achieved due to electronic coupling, rendering the PL emission from the cleaved side unpolarized. These results are of particular importance for realizing polarization independent SOAs required for fiber optical telecommunication systems.

II. EXPERIMENT

Here we concentrate on the samples grown by MOVPE. Trimethyl indium (TMI), trimethyl gallium (TMG), tertiarybutyl arsine (TBA), and tertiarybutyl phosphine (TBP) are used as gas sources. The InP (100) substrates are misoriented by 2° toward (110). The sample structure commenced with 100 nm InP followed by single or stacked InAs QD plus GaAs interlayers underneath which are placed in the center of a lattice-matched InGaAsP (Q1.3) layer with a total thickness of 200–500 nm grown at 500 °C. The GaAs interlayer thickness is 0–2 ML, the nominal amount of InAs for QD growth is 3 and 3.5 ML, and the InGaAsP separation layer thicknesses between the stacked QD layers are 40 and 4 nm. On the sample surface the InAs QDs plus GaAs interlayer are repeated for atomic force microscopy (AFM) measurement. Buried InAs QDs are studied by (002) dark-field cross-sectional transmission electron microscopy (TEM). PL measurements are performed using a Nd:YAG (yttrium aluminum garnet) laser (532 nm) as an excitation source with the samples mounted in a He-flow cryostat. The PL is dispersed by a 1 m single monochromator and recorded by a cooled InGaAs charge-coupled device. For linear polarization dependent measurements the PL is excited on the cleaved side and the TE- and TM-polarized signals from the cleaved side are collected by setting the polarizer along the in-plane and growth directions, respectively.

III. QD WAVELENGTH TUNING BY AS/P EXCHANGE REACTION CONTROL

Figure 1 summarizes the PL spectra at 4.8 K of the 3 ML InAs single QD layers without and with GaAs interlayer and

Fig. 1. Normalized PL spectra taken at 4.8 K of the 3 ML InAs single QD layers grown (a) without and (b) with 2 ML GaAs interlayer at TBA flow rate of 6.1 SCCM. [(c)–(e)] PL spectra of the QDs with 2 ML GaAs interlayer and 45 s TMG flushing grown at TBA flow rates of (c) 6.1, (d) 2.0, and (e) 1.0 SCCM. The shaded area is above the detection limit at 1.6 μm . A scheme of the InAs QD structure with GaAs interlayer on InGaAsP is shown in the inset.

an additional flushing step grown under various TBA flows. A scheme of the InAs QD structure with GaAs interlayer is shown in the inset. The growth temperature is reduced from 585 to 500 °C to reduce the QD size. The QD morphology without GaAs interlayer is similar to that obtained by CBE. The PL peak wavelength of the QDs, however, is beyond 1600 nm both at RT and 4.8 K [Fig. 1(a)]. In order to shift the PL peak wavelength to shorter values, 2 ML GaAs are inserted on the InGaAsP layer underneath the QDs. The 2 ML GaAs interlayer thickness is the upper limit for defect-free QD structures.

The average QD height in the presence of the GaAs interlayer is reduced from 6.0 to 3.1 nm, and the PL peak wavelength is blueshifted to 1580 nm [Fig. 1(b)]. The GaAs interlayer effectively suppresses As/P exchange and consumes surface segregated In adatoms, leading to a distinct reduction of the average QD height and PL peak wavelength. The shoulder observed on the short-wavelength side of the PL spectrum in Fig. 1(b) is attributed to Ga incorporation into the QD layer, caused by incomplete gas exchange after GaAs interlayer growth. A flushing step of TMG for 45 s under TBA flow before QD growth ensures pure TMI as group-III source for QD formation. This results in a smaller QD size due to increased lattice mismatch and an additional PL blueshift to 1558 nm. No shoulder is observed in the corresponding PL spectra of the QDs in Fig. 1(c).

To study the effect of the group V-III flow ratio on QD formation on the 2 ML GaAs interlayer, the TBA flow rate is reduced from 6.1 [Fig. 1(c)] to 2.0 [Fig. 1(d)] and 1.0 SCCM [Fig. 1(e)], while the TMI flow rate is kept constant (SCCM denotes cubic centimeter per minute at STP). For 6.1 SCCM TBA flow rate, the PL peak wavelength is 1558 nm at 4.8 K and beyond 1600 nm at RT despite of the small QD sizes. With reduction of the TBA flow rate, the PL peak continuously shifts to shorter wavelengths, reaching 1355 nm for the TBA flow rate of 1.0 SCCM [Fig. 1(e)]. Simultaneously, the PL linewidth becomes smaller, pointing toward reduced

FIG. 2. PL peak wavelength at RT as a function of GaAs interlayer thickness of the single and vertically stacked QD layers formed by various InAs amounts [InAs (monolayers)], InGaAsP separation layer thicknesses (sep. l), and numbers of stacked QD layers (stack No.).

As/P exchange under low TBA flow, reducing size fluctuations of the QDs caused by nonuniform As/P exchange.^{1,3} However, the QDs are wider due to the larger In adatom migration length at low TBA flow.

After establishing the growth conditions such as growth temperature, gas switching sequence, and group V-III flow ratio, the QDs emit at 1480 nm at RT in the presence of a 2 ML GaAs interlayer. The QD emission is then tuned over the 1.55 μm wavelength region by reducing the GaAs interlayer thickness. When the GaAs interlayer thickness is decreased from 2 to 1.2 ML, the PL peak wavelength continuously shifts to larger values reaching 1560 nm for 1.2 ML GaAs, covering the 1.55 μm wavelength region [open squares in Fig. 2(a)]. Simultaneously, the PL efficiency improves, which is attributed to the reduction of tensile strain for thinner GaAs interlayer, improving the structural quality. The average QD height increases from 4.5 nm for 2 ML to 5.6 nm for 1.2 ML GaAs [Figs. 3(a) and 3(b)]. This confirms the continuous reduction of As/P exchange and consumption of surface segregated In with GaAs interlayer thickness to continuously reduce the QD height and, hence, the PL peak wavelength.

Surprisingly, the PL peak wavelength shortens for GaAs interlayer thicknesses smaller than 1 ML. This is understood by the gradual shape transition from QDs to quantum dashes elongated along [0–11] depicted in Figs. 3(c) and 3(d) for 0.4 and 0 ML GaAs. Obviously the low TBA flow rate changes the properties of the InGaAsP surface, most probably related to P enrichment, to cause anisotropic surface diffusion leading to dash formation. Moreover, the low TBA flow rate favors P incorporation into the quantum dashes causing the PL blueshift, which cannot be explained by the geometrical features. The minimum of the PL peak wavelength for a GaAs interlayer thickness around 0.4 ML is attributed to the interplay between shape transition, shortening the PL peak wavelength, and As/P exchange, increasing the quantum dash height and PL peak wavelength. Only the combination of low growth temperature and low TBA flow rate with the insertion of GaAs interlayers above 1 ML thickness allows continuous tuning of the PL emission wavelength over the

FIG. 3. AFM images of the 3 ML InAs surface QDs with GaAs interlayer thicknesses of (a) 2.0, (b) 1.2, (c) 0.4, and (d) 0 ML. The height contrast is 10 nm.

1.55 μm region without formation of dashes. Experiments with GaP interlayers were not successful. The RT PL efficiency was very weak, most probably due to a higher sensitivity of MOVPE compared to CBE to the high tensile strain in GaP introducing defects in the QDs.

The excellent optical properties of the InAs QDs with GaAs interlayers are confirmed by detailed temperature dependent PL measurements.³ The integrated PL intensity of the InAs QDs is almost constant up to 140 K and decreases exponentially at higher temperatures. The activation energy describing the quenching of the PL intensity closely compares to the difference of the InGaAsP band gap energy and the InAs QD emission energy. This is consistent with thermionic emission of carriers from the InAs QDs to the InGaAsP barriers, revealing QDs which are free of nonradiative recombination centers.

IV. QD STACKING AND POLARIZATION CONTROL

For the stacked 3 and 3.5 ML InAs QDs separated by 40 nm InGaAsP in up to five layers, the linear dependence of the PL peak wavelength as a function of the GaAs interlayer thickness coincides with that of the single QD layers (open circles and open squares in Fig. 2). For the larger InAs amount the PL peak wavelengths are consistently shifted by about 20 nm to larger values due to larger average QD height (solid circles and open diamond in Fig. 2). The wavelength tuning with GaAs interlayer thickness remains unchanged, identifying the InAs amount together with the group V-III ratio as another parameters to adjust the QD emission wavelength in combination with the GaAs interlayer thickness. These results reveal the reproduction and wavelength tuning of widely stacked QDs in identical layers, where vertical strain and electronic coupling can be neglected, to increase the active volume. The TEM image of the three-fold widely-stacked QDs with 40 nm InGaAsP separation layers is shown in Fig. 4(a).

FIG. 4. Cross-sectional TEM image of the threefold stacked InAs QDs with (a) 40 and (b) 4 nm InGaAsP separation layers. The InAs amount is 3.5 ML and the GaAs interlayer thicknesses are (a) 1.5 and (b) 1.7 ML, chosen for similar structural properties. The white arrows mark the growth direction.

On the other hand, the PL peak wavelength of the threefold closely-stacked 3.5 ML InAs QDs with 4 nm InGaAsP separation layer thickness is redshifted by about 90 nm compared to that of the widely-stacked ones [solid squares in Fig. 2]. The PL linewidth at 4.8 K is reduced by more than 30 meV. Such PL redshift and linewidth reduction are well documented to originate from efficient strain- and electronic coupling resulting in vertically aligned QDs with strong overlap of the electron wavefunctions.¹⁰ Tuning of the PL peak wavelength with the GaAs interlayer thickness is unaltered for the coupled QDs. The TEM image of the threefold closely stacked QDs with 4 nm InGaAsP separation layers is shown in Fig. 4(b).

Vertical electronic coupling of the threefold closely stacked QDs with 4 nm InGaAsP separation layers is proven by the linear polarization of the cleaved-side PL taken at RT in comparison to that of the widely stacked QDs [Fig. 5(a) and 5(b)]. For the threefold widely stacked QDs [Fig. 5(a)], the PL is strongly TE polarized (in plane) with a degree of linear polarization $P = (I_{TE} - I_{TM}) / (I_{TE} + I_{TM})$ at the PL peak position of 0.7. In these compressively strained QD structures with valence band ground state of dominantly heavy-hole character, this anisotropy of the linear polarization is governed by the shape anisotropy of the QDs having an average height-to-diameter ratio of 0.1–0.2. In contrast, P for the threefold closely stacked QDs at the PL peak position is reduced to 0.1 and it crosses zero at the short-wavelength

FIG. 5. Linear polarized cleaved-side PL spectra at RT of the threefold stacked InAs QDs with (a) 40 and (b) 4 nm InGaAsP separation layers. The InAs amount is 3.5 ML and the GaAs interlayer thicknesses are (a) 1.5 and (b) 1.7 ML.

side of the PL spectrum around 1.5 μm [Fig. 5(b)]. Hence, the shape anisotropy of the closely stacked QDs is effectively reduced due to strong vertical electronic coupling. The PL efficiency of the threefold closely stacked QDs at RT is one order of magnitude larger than that of the single QD layers, confirming the high structural and optical quality of the QDs without introduction of defects upon stacking.

V. CONCLUSIONS

We have achieved wavelength tuning of MOVPE-grown single and vertically stacked InAs/InGaAsP/InP (100) QD layers by controlling the As/P surface exchange reaction during InAs deposition. The As/P exchange reaction is suppressed for decreased QD growth temperature and group V-III flow ratio, to values common for CBE growth, reducing the QD size and PL emission wavelength. The As/P exchange reaction and QD PL wavelength are then reproducibly controlled by the thickness of an ultrathin (0–2 ML) GaAs interlayer underneath the QDs. Submonolayer GaAs coverages result in a shape transition from QDs to quantum dashes at low group V-III flow ratio. Only the combination of reduced growth temperature and group V-III flow ratio with the insertion of GaAs interlayers above 1 ML thickness allows wavelength tuning of QDs at room temperature over the technologically important 1.55 μm region for telecom applications. Temperature dependent PL measurements reveal excellent optical properties of the QDs. Widely stacked QD layers are reproduced with identical PL emission to increase the active volume. Closely stacked QD layers reveal a sys-

tematic PL redshift and linewidth reduction due to vertical electronic coupling which is proven by the linear polarization of the cleaved-side PL changing from in plane to isotropic. We have also fabricated ridge-waveguide laser diodes with stacked QD layers as an active region which exhibit threshold currents at room temperature among the lowest ones achieved for MOVPE-grown InAs/InP QD lasers.¹¹

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