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Photoluminescence sensitivity to methanol vapours of surface InP quantum dot: Effect of dot size and coverage

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ABSTRACT

We investigate the effect of morphology and coverage of self-assembled epitaxial InP quantum dot on the photoluminescence sensitivity to methanol vapour. The photoluminescence of quantum dots is in the near infrared (750–900 nm) for quantum dot height and lateral size of 2–3 nm and 20–30 nm, respectively. Photoluminescence intensity undergoes an enhancement when the samples were exposed to methanol vapours. The dimension, density and effective surface of quantum dots have been estimated by statistical analysis of the dot morphology based on atomic force micrographs. We observed that it is possible to increase the magnitude of the intensity change due to methanol vapour by tailoring quantum dot size and density to increase the sample coverage. We observe a linear dependence on the coverage of the luminescence intensity changes induced by exposition to methanol vapours.

1. Introduction

Luminescent semiconductor quantum dots (QDs) are promising building blocks for optical chemical sensor devices and lab-on-chip [1–5]. An attractive property of nanostructure, and key for chemical sensing, is the high surface to volume ratio [6]. Broad absorption band, size dependent spectral emission, higher photostability, and enhanced dipole moment of QDs during contact with polar solvents [7] make QDs better suited for the development of vapour sensors than commonly used dyes as sensitive media in luminescence based devices. The vapour sensitivity of colloidal QDs embedded into polymeric [8–12], sol–gel [13] and porous oxide matrix [14] have been investigated by different research groups. We show here a complementary approach. Our research is focused on InP QDs synthesized by molecular beam epitaxy on $In_{0.48}Ga_{0.52}P$ buffer layer lattice matched to GaAs substrate [15–20]. Epitaxial QD are usually embedded into a semiconductor matrix to ensure the confinement of charge carriers into a defined potential well and the full passivation of their surface states; in the present system, the InP QDs would normally be capped with $In_{0.48}Ga_{0.52}P$. We recently reported room temperature near-infrared luminescence from surface InP QDs [21]. For such QDs, the peak position of the emission depends as usual on the quantum dot dimensions and takes place in our samples in the near-infrared (NIR) range (750–900 nm). The electronic and optical properties of surface InP QDs grown on InGaP on GaAs substrate have been accurately characterized and compared with the capped InP QDs [21]. Surface QDs are in direct contact with the surrounding gaseous environment and thus their photoluminescence can be influenced by its chemical composition as recently shown [22]. Consequently they are promising for miniaturized optical chemical sensor and hybrid inorganic–organic devices [21]. Moreover the epitaxial synthesis technique, the use of semiconductor substrates and the NIR emission range (compatible with fibre optic communication in the range 800–900 nm) are attractive properties for on-chip integration [23,24]. It is desirable to improve the performance of the material in terms of enhancement of the intensity change, selectivity (similar polar solvents gives analogous results) and limit of detection, which is still far too high for a practical application. A systematic investigation of the detection mechanisms is of potential interest. In the present study we performed a detailed investigation of the impact of QD morphology on the PL intensity enhancement due to the presence of methanol solvent vapour. In order to correlate the QD morphology with their response, we synthesized a number of samples, which present a different dot coverage (the average lateral dot area times the dot density). In the following, we describe correlation between morphological parameters and their methanol response.

2. Synthesis and morphological characterization

QDs composed of InP on $In_{0.48}Ga_{0.52}P$ buffer layer were grown using gas-source molecular beam epitaxy (GSMBE) in a RIBER 21T

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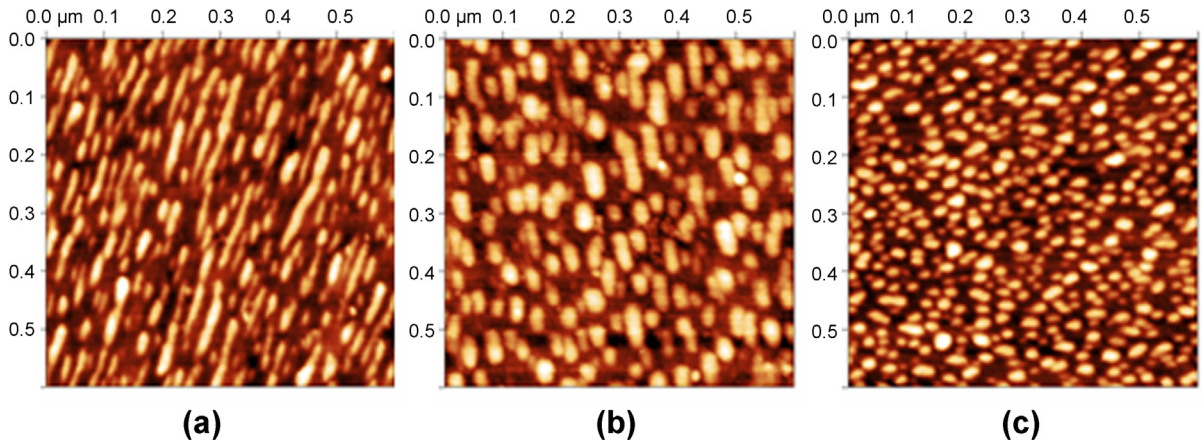

Fig. 1. 600 nm × 600 nm AFM image of sample (a) A; (b) B; (c) C.

system on (100) GaAs substrates. The synthesis procedure has been described in detail in a previous paper [20]. The lattice mismatch of 3.8% between InP and $In_{0.48}Ga_{0.52}P$ (lattice matched to GaAs) drives the strain-induced formation of QDs *via* the Stranski-Krastanow mechanism. The areal density and the size of QDs were varied using the InP deposition rate and time [20]. For this study three samples showing differing dot morphology and coverage have been synthesized. The composition of the $In_{0.48}Ga_{0.52}P$ layers has been characterized using double-crystal x-ray diffractometry (DCXD). The results show lattice-matched $In_{0.48}Ga_{0.52}P$ to GaAs with good crystal quality [18]. The structural properties of the samples have been characterized using atomic force microscopy (AFM). Measurements were performed *ex situ* in air in the tapping mode to image the surfaces of the investigated samples. From 600 nm × 600 nm AFM images (showed in Fig. 1), a statistical analysis of the size and shape of about 100 dots for each sample has been preformed by using Gwyddyon™ software [25] to obtain dots height, lateral size, asymmetry of the base shape of the dots and surface area distributions. The asymmetry of the QD base dimensions has to be taken into account because InP QDs can display an ellipsoidal base shape depending on growth conditions [26]. The average values for these morphological parameters have been obtained from Gaussian fits of the data distributions. Also QD density and coverage (calculated as average surface area of a single QD times the density) have been estimated from the AFM images (see Table 1). The three samples, named A, B, C, are characterized by an increasing coverage.

3. Effect of methanol vapours on the photoluminescence

3.1. Experimental procedure

All photoluminescence data were measured using a 450 nm diode laser with power density of about 90 mW/cm^2 for excitation. Photoluminescence (PL) was collected and analyzed by a 25 cm monochromator (ARC SpectraPro-300i) and a photomultiplier (Hamamatsu R636-10) using lock-in detection. The sample was mounted in a sealed chamber in which the gaseous environment can be cycled between vacuum and a static atmosphere composed by a blend of solvent vapour and N_2. The saturated vapours were obtained by fluxing N_2 in a Drexel bottle, which allows the bubbling of the liquid solvent. Methanol (99.8%) solvent was purchased from Sigma–Aldrich; it was of analytical-reagent grade and of anhydrous type. Saturated vapour pressure was calculated according to the Antoine's law (equation parameters were taken from NIST database [27,28]). The mixed N_2/solvent vapour was injected into the chamber. The chamber was maintained at ambient pressure (monitored by a pressure gauge) and a temperature of 300 K (controlled by a thermocouple mounted on the sample stage). Gases and bubbler were stabilized at the same temperature. These precautions were required to discriminate the effect of PL changes due to temperature (an increase of temperature lowers QD PL intensity) from those induced by the vapour. The maximum error that can arise from a sample temperature fluctuation of ∼1 K near 300 K is ∼3% of the PL relative change. This is a source of error in the measurement because, although temperature is controlled by a thermocouple, local heating due to continuous illumination with laser light cannot be completely excluded. The thermal fluctuations of the bubbler (∼1 K) give rise to an error of about ∼5% on the determination of the vapour concentration.

4. Results and discussion

It is well known that the size and shape of QDs affect the energy peak positions and widths of their PL [29]. A fully reliable control of the sample morphology is still a challenging task for the investigated material but some issue like QD density and ordering have been successfully addressed [20]. Presently we investigate the role of morphology (obtained by AFM characterization) on the PL and on methanol sensitivity. The PL spectra of the investigated samples are showed in Fig. 2. Sample A–C presents emission maxima at 826, 834, and 848 nm with full width at half maximum (FWHM) of 58, 55, and 57 nm, respectively. The spectral positions show small difference as well as the values of dot height (see Table 1). Exposure of samples to methanol vapour results in an

Table 1
Morphological information from statistical analysis of AFM images. Average value obtained by Gaussian fit of the size distribution are reported in terms of $\mu \pm \sigma$.

Sample	Height (nm)	Lateral size (nm)	Asymmetry	QD surface area ($\times 10^{-16}$ m^2)	QD density (dots/cm^2)	Coverage
A	1.9 ± 0.5	22 ± 4	0.43 ± 0.04 0.22 ±0.06[a]	9 ± 4	3×10^{10}	0.27
B	3.0 ± 0.8	32 ± 7	0.6 ± 0.1	11 ± 8	3×10^{10}	0.33
C	3 ± 1	20 ± 5	0.7 ± 0.1	4 ± 3	9×10^{10}	0.36

[a] In this case the data showed a bi-modal distribution. Nearly 48% of the dots are under the first Gaussian peak.