Physico-chemical mechanism for the vapors sensitivity of photoluminescent InP quantum dots

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Abstract. InP/InGaP surface quantum dots are interesting materials for optical chemical sensors since they present an intense emission at room temperature, whose intensity changes rapidly and reversibly depending on the composition of the environmental atmosphere. We present here their emission properties by time resolved photoluminescence spectroscopy investigation and we discuss the physico-chemical mechanism behind their sensitivity to the surrounding atmosphere. Photoluminescence transients in inert atmosphere (N\textsubscript{2}) and in solvent vapours of methanol, chlorophorm, acetone and water were measured. The presence of vapors of chlorophorm, acetone and water showed a very weak effect on the transient times, while an increase of up to 15\% of the decay time was observed for methanol vapour exposure. On the basis of the vapor molecule nature (polarity, proticity, steric hindrance, etc.) and of the interaction of the vapor molecules with the quantum dots surface a sensing mechanism involving quantum dots non-radiative surface states is proposed.

1. Introduction

The optical properties of many semiconductor quantum dots (QDs) such as broad absorption band and size-dependent spectral emission, together with a high effective surface area available for interaction with target chemicals are attractive for applications as chem-/bio-sensors and lab-on-chips\textsuperscript{1-3}. So far, most of the reports of optical chemical sensing with QDs are based on colloidal quantum dots, however recently a new approach has been introduced which is based on uncapped Surface QDs (SQDs) grown by epitaxy on solid substrates\textsuperscript{4,5}. In these cases it is possible to achieve sufficient quantum confinement and radiative emission in QDs even without a capping layer\textsuperscript{6,7}. In this case a direct contact with the external environment takes place and the short-range interaction between dots and environment allows their exploration as sensor (e.g. for organic molecules). A strong sensitivity to the surface environment has been reported for SQDs made of InAs\textsuperscript{8}, InGaAs\textsuperscript{4} and InP\textsuperscript{5}. These QDs are very attractive for chem-/bio-sensor and lab-on-chip design since they can be grown on a conventional wafer. On this regard, InP SQDs have some key advantages. Their emission

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intensity is only 2-5 times lower than buried ones, which is quite outstanding compared to analogous systems where the intensity for uncapped QDs is usually orders of magnitude lower than for capped QDs. Moreover, their near infrared emission, matching fibre optics and biological tissue transparency windows, make them suitable for a wide range of applications.

Recently, we characterized the methanol sensitivity of InP SQDs by continuous wave photoluminescence (CW-PL) spectroscopy. We observed a rapid and reversible increase in the PL intensity, proportional to the methanol concentration. However, a model of the sensing mechanism is still lacking and would be beneficial in order to fine tuning the property of the dots and the whole semiconductor heterostructure to achieve methanol sensing with resolution suitable for practical application.

In this work, we report on the sensing mechanism investigated by time resolved photoluminescence (TR-PL) spectroscopy. We compare the response of the InP SQDs in nitrogen atmosphere to that in vapor of methanol, water, acetone and chloroform solvents. We found that the decay transients of the PL in nitrogen environment can be well fitted by a three exponential decay function having characteristic times of 0.5, 2.0 and 7.0 ns. When the gas environment is changed introducing fixed amount of solvent vapour an increase of the fast and intermediate times was observed. Such an effect is particularly evident for methanol where a 15% enhancement of the fast decay time has been measured. We discuss here a physico-chemical model based on the saturation effect of the QD non-radiative surface states by the vapor organic molecules which is fully compatible with the observed experimental behaviour.

2. Experimental

Self-assembled epitaxial InP/In$_{0.48}$Ga$_{0.52}$P SQDs were grown by gas source molecular beam epitaxy on (100) GaAs substrate. The sample synthesis is described in detail elsewhere. Structural characterization was accomplished with atomic force microscopy. TR-PL spectra were recorded using a Ti:Sapphire laser Chameleon ULTRA-II (Coherent) equipped with an optical parametric oscillator tuned at 488 nm. The emitted light was analyzed with a Time-Correlated Single Photon Counting technique for the lifetimes measurements and with a spectrograph equipped with a CCD for the fluorescence surface images. Measurements were performed at 760 Torr and 25 °C in a sealed flow cell with an optical window where the atmosphere can be changed from pure N$_2$ to a mixture of solvent vapor and N$_2$. Such mixtures were produced by bubbling the solvent in a Drechsel bottle to obtain the saturated vapor of the solvent with N$_2$ in a controlled amount. The solvent concentration was estimated with an accuracy of 5%. The gas mixture was injected into the cell and the TR-PL measurements were taken in static atmosphere. The initial condition was restored flowing pure N$_2$ for 5 min. The liquid solvents used to produce the vapors were Sigma-Aldrich analytical reagent grade methanol (MeOH) 99.8%, chloroform (CF) 99.8% and acetone (Ac) 99.5% used without further purification.

3. Results and discussion

Figure 1 shows an AFM micrograph of the sample. The investigated SQDs have lens shaped with a lateral size of about 20 - 30 nm and a height in the range of 2 - 6 nm. The dot density is $9 \times 10^{10}$ dots/cm$^2$ and by a statistical analysis of the size and the shape of about 30 individual dots measured from a 600 × 600 nm$^2$ AFM micrograph we observed a bimodal Gaussian distribution for the QD heights, with peak positions of 2.8 and 4.3 nm.

In previous studies, we found that the composition of the surrounding gaseous environment strongly affects the PL intensity of InP SQDs. In particular, we observed that the exposure of samples to methanol vapor results in an enhancement of the PL intensity while spectral shape and position remain unchanged, as shown in the inset of figure 2. Such findings pointed out the need of a model of the sensing mechanism that at present is still lacking. On this regard we performed TR-PL measurement with and without vapors. Figure 2 shows the PL transients measured at 1.47 eV (the peak of the emission spectrum) in N$_2$ and methanol, and its initial response function (IRF). Taking into account
the IRF, the transients can be well fitted with a 3-exponential decay law with an initial fast ($\tau_F$), an intermediate ($\tau_I$) and a slower ($\tau_L$) decay time of about 0.5 ns, 2 ns and 7 ns, respectively.

**Figure 1.** AFM image of InP SQDs.

**Figure 2.** PL transients, red curves are related to methanol vapor while black ones are in inert atmosphere of nitrogen. Blue dashed line is the IRF. Inset shows the InP SQDs CW emission.

The fast and intermediate times are due to the emission of confined states in QDs. For InP SQDs with large lateral size the main parameter responsible for the emission energy and radiative lifetime is the dot height. Likely, the presence of two different radiative lifetimes is a direct consequence of the bimodal height distribution in this particular sample. The longest component can be attributed to QDs coupling. A recent theoretical investigation showed the relevance of InP SQDs lateral coupling in determining emission energy and optical spectra. According to this study, the appearance of molecular terms in the optical spectra are likely to occur in our samples. When the sample is exposed to methanol vapor the initial and middle components of the PL transient lengthen while for the long component we did not observe any significant change. To test the sensitivity and selectivity of the InP SQDs we performed a series of experiments with other common solvents, namely chloroform, acetone and water with fixed concentration of $2\times10^4$ ppm. The results are summarized in table I.

| Environment | Pure N$_2$ | MeOH | CF | Ac | H$_2$O |
|-------------|------------|------|----|----|-------|
| $\tau_F$ (ns) | 0.53 | 0.61 | 0.56 | 0.56 | 0.56 |
| $\tau_I$ (ns) | 1.83 | 2.03 | 1.93 | 1.94 | 1.91 |
| $\tau_L$ (ns) | 7.41 | 7.40 | 7.44 | 7.65 | 7.54 |

We evaluated the lifetime relative change induced by the presence of the vapor solvents as $\Delta \tau / \tau \% = (\tau_{\text{solvent}} - \tau_{N_2}) / \tau_{N_2} \%$, where i=F,I,L indicates the fast, intermediate and long decay times, respectively. $\tau_{\text{solvent}}$ represents the decay time when the sample is exposed to solvent vapor and $\tau_{N_2}$ is the decay time in pure N$_2$. Methanol presents a consistent stretching of the decay times with values of 15% and 11% for $\tau_F$ and $\tau_I$, respectively. The other solvents produce only a slight increase of both $\tau_F$ and $\tau_I$ of approximately few percents irrespective of the solvent type.

The time resolved photoluminescence results strongly support the sensing mechanism model we previously hypothesized. The target molecules present in the gas environment, passivating the non-radiative decay channels related to the QDs surface states, produce at the same time an enhancement
of the PL signal in the steady state and an increase in the luminescence decay time. In our case the surface states are mostly represented by the dangling bonds that could be both positive In+ and negative P ions. In particular, we believe that the involved defect type are in prevalence negatively charged (donor). Indeed, the molecules employed for the experiments present differences regarding the polarity, charge distribution and steric hindrance. Chloroform is a solvent with a weak polarity, its interaction with defects may occur by weak London dispersion force and therefore its effectiveness in the passivation of the radiative pathway is limited. Acetone is a polar aprotic species having a positive charge distribution rather spread on the carbon moiety with respect to the negative one (around oxygen) so it preferentially interacts with positive defects. Since it has a very limited effect on our system we suggest that the involved defects are not positively charged. Moreover, its low response can be ascribed both to its low polarity and its large steric hindrance. Methanol produces the most noticeable effect and it is a polar and protic solvent. In this case the positive charge is rather localized on the hydrogen of the OH group which tends to interact with negatively charged species on the surface. On the other side, using water which is a very polar and protic molecule the effect we measured is very low. To explain such apparent inconsistency, a more complex representation has to be taken into account where the solvent-solvent intermolecular interactions play an important role. Water molecules tend to interact strongly with each other forming a complex network of hydrogen bonds that interacts with the QD surface in a less effective way with respect to methanol that instead tends to be adsorbed on the surface as a monolayer. This could explain its higher effectiveness in luminescence intensity enhancing.

4. Conclusion
We studied the chemical sensitivity of InP SQDs by TR-PL spectroscopy. PL transients with and without vapors were fitted with a 3-exponential decay law. A very weak effect was found for acetone, chloroform and water while a consistent increment of the decay times was measured for methanol. This result suggests a sensing mechanism based on the ability of the organic molecules to saturate non-radiative QDs surface states. The model we propose can satisfactorily account for both the observed experimental effects since by hindering the non-radiative channels a more intense CW-luminescence signal and a longer lifetime have been found.

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