Surface passivation and oxide encapsulation to improve optical properties of a single GaAs quantum dot close to the surface

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ABSTRACT

Epitaxial GaAs quantum dots grown by droplet etching have recently shown excellent properties as sources of single photons as well as entangled photon pairs. Integration in some nanophotonic structures requires surface-to-dot distances of less than 100 nm. This demands a surface passivation scheme, which could be useful to lower the density of surface states. To address this issue, sulphur passivation with dielectric overlayer as an encapsulation is used for surface to QD distances of ≤40 nm, which results in the partial recovery of emission linewidths to bulk values as well as in the increase of the photoluminescence intensity.

1. Introduction

Single photon emitters are regarded as key elements in quantum optical networks for transferring qubits between network nodes. Solid state semiconductor quantum dots (mainly GaAs- and InP-based) are arguably the most promising sources for the integration into a practical and scalable networks [1–7]. However, in comparison with single atoms and ions in traps, quantum dots (QDs) are subject to more pronounced decoherence and spectral diffusion [8–10]. Out of those, the spectral diffusion, which determines random changes in the QD optical emission frequencies, becomes a big issue whenever a QD sits close to the surface (≤100 nm for GaAs-based QDs) [9,11,12]. This is due to the presence of a large density of surface states (e.g. \(12.5 ± 10.0\) \(\times 10^{13}\) eV\(^{-1}\)cm\(^{-2}\) at 300 K for GaAs [13]) at GaAs surface. A systematic decrease of emission linewidth with increasing QD-surface distance has been consistently observed by several groups [11,12,14]. Also, other quantum optical properties such as single photon emission probability and Hong-Ou-Mandel visibility are expected to benefit from a large separation between QD and surface. For many applications it is necessary to embed the QDs in nanophotonic structures like planar antenna [15,16], nanopillar [17], nanocone [18], and Bragg grating structure [19–21] etc., where QD to surface distance of <100 nm is really essential to out-couple the dot emission efficiently from a high refractive index material like GaAs. Therefore, a reduction of the surface state density is important to reduce charge fluctuations and hence spectral diffusion. To significantly reduce the surface state density proper surface passivation technique could be implemented. A specific example of photonic structure which would benefit from passivation is a planar Yagi-Uda antenna [16] where, for GaAs QDs operating at wavelengths around 780 nm and/or InGaAs QDs around 900 nm, it is necessary to have the dot to surface distance ≤40 nm for efficient outcoupling. Many works have been performed over several decades in order to get a proper passivation of III-V compound semiconductor surfaces mostly for electronics devices [22–28]. Such methods have been recently employed also for improving the performance of optical devices [11,22,29–32].

The aim of this work is to assess the effect of surface passivation with a dielectric over-layer on the emission linewidth and intensity of GaAs QDs located a few tens of nm (≤40 nm) away from the exposed surface.

2. Material and methods

2.1. Growth and processing

In this work, GaAs QDs embedded within an Al\(_x\)Ga\(_{1-x}\)As matrix (in this case \(x = 0.2\) or 0.4) were epitaxially grown using the droplet etching method [33,34] on a GaAs (001) substrate. It is already known that this method allows creating close-to-symmetrical dots with very low excitonic fine structure splitting (FSS) [35], which is critical for polarization entangled photon generations with near-unity entanglement fidelity [36]. Here we concentrate on the linewidth of the excitonic emission of single QDs. We studied two kinds of structures (see Fig. 1): (i) Str-1: In the ‘As-grown’ structure, the distance between the QD layer and the 1st GaAs cap layer is 36 nm and that to the very top surface is 126 nm; we then selectively etched the top GaAs cap layer
and the underlying Al_{0.75}Ga_{0.25}As sacrificial layer (the result is indicated with ‘Only etched’ in Fig. 1); finally we applied the surface passivation steps, which include sulphur passivation and Al_{2}O_{3} deposition, to obtain a ‘Passivated’ sample; (ii) Str-2: in the ‘As-grown’ structure, the QD-to-surface distance is 72 nm; for ‘Only Etched’, the GaAs cap is etched and also some portion of the Al_{0.7}Ga_{0.3}As matrix, so that the QD to surface distance is 40 nm without any GaAs cap; for ‘Passivated’, the sulphur passivation scheme is followed by Al_{2}O_{3} deposition on the bare Al_{0.7}Ga_{0.3}As surface.

Etching of GaAs or Al_{0.7}Ga_{0.3}As was performed with a mixture of citric acid and H_{2}O_{2} with a ratio of 25:1, with roughly the same etching rate of ~2.5 nm/sec [37]. The Al_{0.75}Ga_{0.25}As sacrificial layer for Str-1 is etched selectively using a buffered oxide etch (BOE) HF with an etching rate of ~2 nm/sec [38]. After immediate etching of the sacrificial layer, HCl treatment is done to remove native oxide by dipping in HCl:H_{2}O (1:1) solution for 1 min followed by deionized water rinsing and N_{2} drying. Afterwards, (NH_{4})_{2}S treatment is accomplished by soaking the sample in (NH_{4})_{2}S for 10 min at room temperature followed by N_{2} drying [39]. For some samples (with Str-1), we carried out an alternative treatment involving NH_{4}OH instead of (NH_{4})_{2}S [39]. It was done by soaking the samples in 20% NH_{4}OH solution for 3 min followed by rinsing in flowing deionized (DI) water and N_{2} drying. After these surface pretreatments, the samples were immediately loaded inside an atomic layer deposition (ALD) chamber to deposit Al_{2}O_{3} layer by using alternating pulses of trimethyl aluminum (TMA) and water (H_{2}O) precursors at a substrate temperature of 200 °C. Two different Al_{2}O_{3} layer thicknesses of 6 and 12 nm were used for both sample structures.

2.2. Optical measurements

The optical measurements were carried out using a micro-photoluminescence (µ-PL) setup. A continuous flow helium cryostat was used to cool down the samples to 5 K. A continuous wave (cw) laser at 514 nm was used to excite the GaAs QDs. An objective lens with a numerical aperture of 0.65 (spot size of ~1 µm in diameter) was used to focus the laser onto the samples and also to collect the PL of the QDs with a typical integration time of 1 sec. The PL signal was sent through a monochromator and detected with a liquid-nitrogen-cooled CCD. The resolution of our monochromator is approximately 40 µeV in the QD emission wavelength range (around 780 nm).

3. Results and discussion

3.1. Role of passivation/oxide encapsulation

We now discuss the function of the sulphur passivation and oxide encapsulation. Unlike native SiO_{2} on Si, native oxides of GaAs possess built-up charges at the surface/interface [13]. (NH_{4})_{2}S is employed to remove the native oxides of GaAs, if any, followed by the etch-down of GaAs by a few Å and incorporation of S-atoms to saturate the GaAs surface dangling bonds [40]. Henceforth, a lower probability holds for GaAs surface to get oxidized. In spite of that, the laser illumination during photoluminescence measurements can make it possible to change Ga-S, As-S bonds to Ga-O and As-O and so also to increase again surface state density [41]. For this reason we protect the S-passivated GaAs surface with an Al_{2}O_{3} capping layer obtained by ALD. This method is a slow monolayer-by-monolayer deposition technique based on surface chemical reactions, which can provide high-quality, thermodynamically stable oxides on III-V semiconductors like GaAs [39]. In addition to that, ALD growth for Al_{2}O_{3} works as a self-cleaning reaction process for an extra removal of native oxides after (NH_{4})_{2}S treatment [40]. Here, the dielectric Al_{2}O_{3} layer acts as a diffusion barrier to prevent re-oxidation of the semiconductor region.

3.2. Role of band bending and dot optical properties

In Fig. 2 we show the schematic band bending and different dot positions with respect to the surface for a p-type semiconductor for different surface conditions. Since the background doping in our samples is p-type, the band bending is similar like Fig. 2. However, the band bending could be in the opposite direction from the one shown in that figure in case of an n-type semiconductor [13,26]. In an ideal case of no surface states band bending does not occur in the bulk or near the surface (Fig. 2(a)). But, with the formation of surface states, a negative space charge region layer (depletion mode) will be induced in the GaAs cap–Al_{0.7}Ga_{0.3}As layer near the surface by the occupation of the surface.
states by holes, resulting in the bending of band edges downwards near the surface (Fig. 2(b),(c)). A small density of surface states results in a small band bending (Fig. 2(c)), whereas in the case of a high density of surface states (Fig. 2(b)) (more than one surface state per hundred surface atoms [42]), the surface states are filled to a level close to the surface Fermi level and the band bending is significant and Fermi level pinning is likely. In our case, 'Only etched' samples without any kind of passivation exhibit similar nature like Fig. 2(b), whereas after
passivation it is like Fig. 2(c). It is noteworthy that the electric field, arisen out of the band bending driven potential gradient, drops linearly when moving away from the surface to the end of the space charge region and this electric field is of fluctuating character because of trapping/detrapping of charge carriers on the surface. Therefore, a QD located within the depletion region and close to the surface will feel more fluctuating environment compared to the position near the end of the depletion region or beyond it. As a result, the exciton emission energy will be influenced depending on the position of the QDs. Since the dependence of the DC Stark energy shift ($dE$) on electric field ($F$) is quadratic ($dE \propto F^2$), the magnitude of the change in energy shift ($\Delta dE$) and so also the linewidth, owing to a fluctuating field ($dF$), will depend on the average field as well as the fluctuating field ($\langle \Delta dE \rangle \propto \langle F^2 \rangle$). Another possible scenario is that the electric field present in the depletion region polarizes the exciton inducing an electric dipole, which then interacts with fluctuations in the electric field or nearby charges more strongly than an unpolarized exciton. Consequently, QDs far away from surface, with a smaller average field, should possess narrower diffusion-induced linewidths than the one close to the surface. Hence the sulphur passivation scheme along with the encapsulation is helpful to reduce the density of surface states (by more than one order of magnitude [43]), leading to the reduction in the band bending, and so also the line broadening. It is noteworthy that the surface passivation can only decrease the surface states density but cannot change anything in the bulk region. A local electric field created by charge carrier trapping/detrapping near a QD might also contribute to the spectral diffusion or PL intensity dropping [9,44,45].

3.3. Optical measurements

In Fig. 3 we present low temperature (~5 K) PL spectra for arbitrarily selected single QDs in the different structures illustrated in Fig. 1. Neutral excitons along with different charge complexes are typical in the spectra. Among all the spectra, ‘Only etched’ case for Str-2 show the undulated background over all the powers ranging from the start of QD emission to its saturation. This might be attributed to the sulphur passivation is helpful to reduce the density of surface states (by more than one order of magnitude [39]), leading to the reduction in the band bending, and so also the line broadening. It is noteworthy that the surface passivation can only decrease the surface states density but cannot change anything in the bulk region. A local electric field created by charge carrier trapping/detrapping near a QD might also contribute to the spectral diffusion or PL intensity dropping [9,44,45]. However, no improvement in PL linewidth decrement can be observed (inset of Fig. 5) by this treatment, although improvement in electrical properties have been shown before [39]. This might be due to the laser illumination which rapidly degrades the surface and increases density of surface states [41].

Along with the line broadening, a slight decrement of integrated PL intensity takes place for the ‘Only etched’ cases compared to the ‘As-grown’ or ‘Passivated’ ones, as shown in the Fig. 6. This comparative PL intensity study is performed by saturating the neutral exciton emission intensity. In this case, the decrement in intensity is not large (< 1.5), as shown before, for a surface to dot distance of ~40 nm [12]. Furthermore, it was shown in [12] that a distance of < 15 nm can cause a substantial reduction in PL intensity by more than 50%. In the case of Str-2, a 12 nm thick Al$_2$O$_3$ is found to be more functional than 6 nm Al$_2$O$_3$ capping to recover the intensity, and it might be due to the absence of the GaAs cap layer and detrimental surface etching. Since a QD inside the space charge region is strongly influenced by the electric field, the polarization of exciton can take place, which can lead to the decrease in the electron-hole overlap and so also the PL intensity. Another effect can stem from the fact that the excitation energy is larger than the bandgap of the barrier. Tunneling of captured carriers from quantum dot to the surface as well as carrier diffusion to the surface from the barrier region can take place. Both will lead to the decrease of PL intensity. Consequently, PL intensity will increase with increasing tunnel barrier thickness as well as increasing the barrier height. One could also use excitation energy much lower than the barrier bandgap to avoid the carrier diffusion [14].

3.4. Analysis of random Gaussian fluctuation

In this section we estimate the strength of the random fluctuating environment, a characteristic figure responsible for the amount of spectral diffusion, which in turn is dependent on the density of surface states. Considering a system coupled to a fluctuating reservoir, we can extract the fluctuation strength or amplitude by employing Kubo-Anderson’s stochastic theory [47–49]. In our case the origin of this random fluctuation process is nothing but the trapping/detrapping of charge carriers in presence of laser excitation at the surface. Assuming a Gaussian fluctuation of Markovian character, the lineshape function $I(\omega)$ takes the form [47]:

$$I(\omega) = \frac{2}{\pi} \text{Re} \int_0^\infty \text{exp}\left\{-\frac{\Delta^2}{\gamma^2}(\cos(\omega t - \gamma) - 1 + \gamma t)\right\} \exp(-\text{i}\omega t) dt$$

$$= \frac{2}{\pi} \text{Re} \sum_{n=0}^{\infty} \frac{\Delta^{2n}}{(2^n n!)^2} (-\omega t)^n$$

where $\Delta$ is the amplitude or strength of the random modulation, $\gamma$ is the inverse of the correlation time or relaxation frequency and $C(t) = \exp\left\{-\frac{\Delta^2}{\gamma^2}(\cos(\omega t - \gamma) - 1 + \gamma t)\right\}$ is the correlation function. Depending on the strength of the random modulation of the system’s frequency, the lineshape could be Gaussian or Lorentzian or a mixture of those [47]. To explicitly achieve that we have performed the Fourier transform of the correlation function $C(t)$ without any approximation using Mathematica package directly for different values of $\alpha = \gamma/\Delta$. It comes out that if the amplitude of the random modulation is stronger than the relaxation frequency, the lineshape becomes dominated by the Gaussian nature, whereas reducing the amplitude with respect to the relaxation pushes it towards the Lorentzian nature. This implies to the validity of slow modulation or inhomogeneous limit for our case and the lineshape happens to be the direct reflection of the random distribution of the emission frequencies. Considering strong random modulation we have calculated and plotted the values of $\Delta$ (linewidth $\Delta = 2\sqrt{2}\ln 2$) for different samples and shown it in Fig. 7. It is clear from the Fig. 7 that the fluctuation strength increases for the ‘Only etched’ cases, as the broadening takes place for the excitonic line, and can be suppressed with the help of passivation via decreasing surface states. In case of ‘Only etched’ samples with Str-2, $\Delta$ is more dispersed compared to other cases. It is to be noted that the lineshape looks almost Gaussian for $\alpha < 0.3$ (checked with Mathematica) and so the
relaxation frequency follows \( \gamma < 0.3 \, \Delta \). Hence, we can extract the lower bound of the correlation time of charge trapping/detrapping as \( 400 \pm 72 \) ps for the ‘Only etched’ case for Str-2, and for other samples lower bound is comparatively higher.

3.5. Aging properties

Finally, we have checked the temporal stability of the passivation. We have repeated the measurements after two months of the first measurement and presented in the Fig. 8, which clearly shows that the sulphur passivation and \( \text{Al}_2\text{O}_3 \) encapsulation have a noticeable impact on the aging of the samples; for ‘Only etched’ samples, we observed a large change of the linewidth and the standard deviation after the above said period, whereas the linewidth increment and the degradation of the surface was relatively slower for ‘Passivated’ samples. We can also notice that the degradation corresponding to a thicker encapsulating oxide of 12 nm is slower than the 6 nm one.

4. Conclusions

In conclusion, we have shown that the sulphur passivation of the GaAs surface followed by a dielectric layer of \( \text{Al}_2\text{O}_3 \) of 6–12 nm results in the partial recovery of the linewidth of the excitonic emission for dot-to-surface distances of \( \leq 40 \) nm, which indicates a decrease of surface states density at passivated surface. The illustrated results are of importance because of the possible applications in the different nanostructures (pillar-like photonic cavities, metal-semiconductor-metal antenna, bull’s eye cavity, nanocone cavity etc.), where wet or dry etching is involved or the surface to dot distance is quite small without any etching involvement. The charge fluctuation strength, the main reason for spectral diffusion, can be lessened by the proposed passivation scheme. Furthermore, the described passivation process can recover the PL intensity for single GaAs QDs. Noticeably the surface passivation can only decrease the density of surface states and so also the strength of random charge fluctuation but cannot change anything in the bulk region. So, for the quantum dots well below the surface, the charge noise arising from only the bulk volume cannot be suppressed without optimizing the quality of the growth and/or applying external electric fields [50].

CRediT authorship contribution statement

Santanu Manna: Conceptualization, Investigation, Methodology, Software, Formal analysis, Data curation, Writing - original draft, Visualization, Validation, Supervision. Huiying Huang: Investigation, Methodology, Writing - review & editing, Visualization. Saimon Filipe Covre Silva: Investigation, Writing - review & editing. Christian Schimpf: Methodology, Writing - review & editing. Michele B. Rota:
Investigation, Writing - review & editing. Barbara Lehner: Software, Methodology. Marcus Reindl: Methodology, Writing - review & editing. Rinaldo Trotta: Conceptualization, Resources, Project administration, Funding acquisition, Writing - review & editing. Armando Rastelli: Conceptualization, Resources, Project administration, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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