Optical Properties of GaAs Quantum Dots Fabricated by Filling of Self-Assembled Nanoholes

Ch. Heyn · A. Stemmann · T. Köppen · Ch. Strelow · T. Kipp · M. Grave · S. Mendach · W. Hansen

Abstract Experimental results of the local droplet etching technique for the self-assembled formation of nanoholes and quantum rings on semiconductor surfaces are discussed. Dependent on the sample design and the process parameters, filling of nanoholes in AlGaAs generates strain-free GaAs quantum dots with either broadband optical emission or sharp photoluminescence (PL) lines. Broadband emission is found for samples with completely filled flat holes, which have a very broad depth distribution. On the other hand, partly filling of deep holes yield highly uniform quantum dots with very sharp PL lines.

Keywords Quantum dots · Molecular beam epitaxy · Droplet etching · Photoluminescence · Atomic force microscopy

Introduction

Crystalline semiconductor quantum dots (QDs) can be regarded as artificial atomic-like entities, which intrigue from a fundamental point of view [1]. But semiconductor QDs are also very attractive for device applications where QDs turned out to be superior to bulk material. This has been demonstrated for instance by the first QD-based laser that exhibits a lower threshold current density compared to usual MBE growth conditions. After Ga droplet formation, an As pressure is applied in order to crystallize the droplets and transform them into GaAs QDs. Interestingly, deposition of Ga droplets on GaAs at significantly higher temperatures $T = 450–620^\circ$ results in the formation of deep nanoholes in the substrate surface. This effect was first observed by Wang et al. [18] in 2007 and represents a local removal of material from semiconductor surfaces without the need of any lithographic steps. As an important advantage compared to conventional lithography processes, this local droplet etching (LDE) is fully compatible with usual MBE equipment and can be easily integrated into the MBE growth of heterostructure devices. LDE was demonstrated in addition on AlGaAs [19, 20] and AlAs [21] surfaces proposed, such as qubits in quantum computing [3] or single-photon sources in quantum cryptography [4, 5].

Quantum dot fabrication techniques that are based on self-assembling mechanisms during epitaxial growth allow the integration of QD layers into semiconductor heterostructures. In this field, a very prominent example is strain-induced InAs QDs grown on GaAs in the Strainski–Krastanov mode [6–9]. A further interesting method for self-assembled QD generation is the droplet epitaxy in Volmer–Weber mode. The method was first demonstrated by Koguchi and Ishige [10] in 1993. In comparison with the Strainski–Krastanov technique, droplet epitaxy is more flexible regarding the choice of the QD material. For instance, the fabrication of strain-free GaAs QDs [11–13], InGaAs QDs with controlled In content [14, 15], and InAs QDs [16] has been demonstrated.

During droplet epitaxial QD fabrication [17], first liquid metallic droplets are generated on semiconductor surfaces, e.g., by Ga deposition without As flux. The growth temperature $T = 100–350^\circ$ typically is kept very low compared to usual MBE growth conditions. After Ga droplet formation, an As pressure is applied in order to crystallize the droplets and transform them into GaAs QDs. Interestingly, deposition of Ga droplets on GaAs at significantly higher temperatures $T = 450–620^\circ$ results in the formation of deep nanoholes in the substrate surface. This effect was first observed by Wang et al. [18] in 2007 and represents a local removal of material from semiconductor surfaces without the need of any lithographic steps. As an important advantage compared to conventional lithography processes, this local droplet etching (LDE) is fully compatible with usual MBE equipment and can be easily integrated into the MBE growth of heterostructure devices. LDE was demonstrated in addition on AlGaAs [19, 20] and AlAs [21] surfaces.
as well as etching with InGa [19, 22–24] and Al [21]
droplets.

After droplet etching, the nanohole openings are sur-
rounded by walls that are crystallized from droplet material
and may act as quantum rings [19, 22–25]. The crystalli-
zation of the walls [26] and the time evolution of the
transformation from the initial droplets into nanoholes with
wall [27] were studied in previous publications. A first
functionalization of the nanoholes, the fabrication of a
novel type of very uniform, strain-free GaAs QDs by filling
of LDE nanoholes in AlGaAs with GaAs, has been dem-
onstrated [21]. In the present paper we describe the influ-
ence of the LDE process and sample design on the optical
properties of such GaAs QDs.

Local Droplet Etching and Nanohole Filling

We fabricate LDE nanoholes using solid-source molecular
beam epitaxy (MBE) on (001) GaAs wafers. Two different
sample designs will be discussed in the following, denoted
as type I and type II. After growth of a GaAs buffer layer, a
200-nm-thick Al0.36Ga0.64 As barrier layer was deposited.
For the samples of type II, an additional 5-nm-thick AlAs
layer was grown before LDE. Type I samples have no such
AlAs layer. Afterward, the As shutter and valve were
closed and droplet formation was initiated at a temperature
T1 by opening the Al shutter for a time t1 = 6 s. We used
Al droplets for etching in order to avoid an additional
carrier confinement by the wall. The temperatures were
T1 = 620°C for the type I samples and T1 = 650°C for the
type II samples with the additional AlAs layer. During this
stage, a strongly reduced arsenic flux is important [26]. The
As flux in our experiments was approximately hundred
times lower compared to typical GaAs growth conditions.
The Al flux F corresponded to a growth speed of 0.47
ML/s, and droplet material was deposited onto the surface
with coverage ϑ = F t1. After droplet deposition, the
temperature was set to a value T2, and a thermal annealing
step of time t2 was applied in order to remove liquid
etching residues. For the present samples, we have used
T2 = T1 and t2 = 180 s.

A sketch of the different stages during LDE is shown in
Fig. 1. The key process for nanohole creation is the dif-
fusion of As from the substrate into the droplet, which
causes the liquefaction of the substrate below the droplet.
From the measured hole volume, we have estimated a
value of 0.03 ± 0.01 for the average As concentration in
the droplet material [26]. The formation of the walls sur-
rounding the nanohole openings is explained by the
assumption that As diffuses to the droplet surface and
crystallizes during the annealing step with droplet material
at the interface to the substrate [19, 26]. Furthermore,
coarsening by Ostwald ripening [28] reduces the droplet
density before drilling and a delay of both, the hole drilling
process, as well as the removal of the liquid material after
etching was detected [27].

Figure 2a shows an atomic force microscopy (AFM)
image of an AlGaAs surface after local droplet etching
with Al and Fig. 2b the corresponding hole depth distri-
bution. Clearly visible is a bimodal depth distribution with
depth (Fig. 2d) and shallow (Fig. 2c) nanoholes in agree-
mement with previous results [20] for Ga LDE. Typical deep
holes have an average depth of dH = 14 nm, and slightly
elliptical openings with axis of 39 nm along [1–11] direc-
tion and 33 nm along [110]. The surface shown in
Fig. 2a is exemplary for type I samples and was used for
the fabrication of QDs with broadband light emission.
From earlier results, [20] we know that the formation of flat
nanoholes can be suppressed by performing the LDE

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**Fig. 1** Sketch of the different stages during LDE resulting in
nanohole and wall formation together with corresponding
AFM images.

**Droplet Growth (Tn, tn, F)**
Volmer-Weber-Mode

**Annealing (T2, t2)**
Coarsening, Drilling, Removal, Wall Formation

**As diffusion**

**Desorption**

**Crystallization**
process at higher temperatures. Due to decomposition of the surface, the maximum temperature for LDE on AlGaAs is about 630°C. Therefore, for high-temperature fabrication of uniform QDs, the LDE process was performed on more stable AlAs surfaces (type II samples). For AFM characterization, this has the disadvantage that the highly reactive AlAs surface oxidizes very fast under air. Therefore, measurements of the nanohole profile were not possible on pure AlAs surfaces. From the AFM images, we determine the nanohole density to be $4 \times 10^8 \text{cm}^{-2}$. Furthermore, the size of the hole openings indicates that LDE holes on AlAs are shaped like the deep nanoholes on AlGaAs and that no shallow holes have been formed.

For the LDE QD fabrication, the nanoholes were filled with GaAs at a substrate temperature of 600°C in a pulsed mode by applying several pulses with 0.5 s growth and 30 s pause, respectively. Finally, the QDs were capped by a 120-nm-thick AlGaAs barrier. A scheme of the resulting layer sequences for samples of type I and II is shown in Fig. 3. Figure 2d shows the AFM profile of a typical deep hole after filling with GaAs. The data demonstrate that pulsed-mode deposition of an only 0.45-nm-thin GaAs layer fills the nanohole to a height of about $h_{QD} = 7 \text{ nm}$. In Ref. [21], this experimental filling level was explained quantitatively with a model in which the part of the GaAs flux impinging on the area of the nanohole opening migrates downwards and fills up the hole starting from its bottom. Very importantly, deep holes are only partially filled with a filling level defined by the precise layer thickness control of the MBE technique. This results for samples of type II in very uniform GaAs QDs. These QDs are shaped like inverted cones with slightly elliptical base area (aspect ratio $1:1.2$) and height $h_{QD}$ being perfectly controlled by the thickness $d_f$ of the GaAs layer deposited for filling. On the other hand, flat holes in type I samples are completely filled and the height of these QDs reflect the very broad hole depth distribution.

**Optical Properties of LDE QDs**

Macro-photoluminescence (PL) measurements of QD ensembles were performed at $T = 3.5 \text{ K}$ and micro-PL measurements of single QDs at $T = 7 \text{ K}$. Using macro-PL, a reference sample without filling shows no optical signal (Fig. 4a) and, thus, demonstrates that there is no background emission from the AlGaAs layers. A second reference sample with $d_f = 0.65 \text{ nm}$ but without etching shows one strong PL peak at $E = 1.900 \text{ eV}$ (Fig. 4b) that is related to the GaAs quantum well. Interestingly, a quantum well–related peak is missing or very weak for the samples containing LDE QDs. Probably, the excitons from the GaAs quantum well migrate into the energetically favorable QDs and recombine there. PL measurements of samples that contain QDs fabricated in type I samples show a broadband optical emission without pronounced peaks. Furthermore, no clear dependence on the GaAs filling level is visible. We attribute the broad PL emission to the
nonuniform depth distribution of the completely filled shallow nanoholes.

Excitation power $I_e$ dependent micro-PL spectra of a single QD in a type I sample with $d_F = 0.57$ nm are shown in Fig. 5. The QD was selected by focusing the exciting laser beam. Clearly visible at low excitation power are sharp excitonic lines and the occurrence of multie excitonic features [29] at lower energy with increase of $I_e$ (Fig. 5b). Furthermore, also excited states (peaks P$_2$ and P$_3$ in Fig. 5a) arise at higher $I_e$. From a comparison of the ground-state energy (peak P$_1$ in Fig. 5a) of around 1.65 eV with data shown in Ref. [21], we estimate a QD height of about 6 nm. The excited-state peak P$_2$ has a quantization energy of 20 meV and peak P$_3$ of 42 meV. According to Ref. [21], the peak P$_2$ might represent recombinations of ground-state electrons with holes in the second excited state and peak P$_3$ recombinations between electrons and holes from the first excited states. The spectrum plotted in red color in Fig. 5a was measured at an excitation power of $I_e = 450$ W/cm$^2$, which is equal to the conditions applied in Fig. 4.

Figure 6 shows PL spectra from type II QDs fabricated at the higher temperature on AlAs surfaces. Importantly, at low $I_e$, ensembles of these QDs exhibit a very sharp PL line with minimum full width at half maximum as small as 9.7 meV. Here, only partially filled deep holes form highly uniform QDs. From the filling level $d_F = 0.57$ nm, we calculate a QD height of 7.6 nm according to Ref. [21]. Additional sharp peaks arise with increasing $I_e$ that are related to excited states. For an understanding of the PL, spectra we approximate the electron and hole energy quantization due to the anisotropic lateral confinement with
two parabolic potentials along \( x \) and \( y \) direction. Optical recombinations between electrons and holes from states with identical quantization numbers \( n_x, n_y \) are denoted in the form \( E_{n_xn_y} = E_{00} + n_x\hbar\omega_x + n_y\hbar\omega_y \), with the oscillator frequencies \( \omega_x \) and \( \omega_y \). In Fig. 6 a, the PL data are compared with energy levels calculated using \( E_{00} = 1.577 \) eV, and equidistant quantization energies \( \hbar\omega_x = 56 \) meV and \( \hbar\omega_y = 74 \) meV. Our approach of a parabolic potential with a slightly anisotropic QD base describes the data very well. Measurements of the dependence of the QD optical emission on QD height are discussed in Ref. [21] and theoretical results considering a similar type of QDs in Ref. [30].

Conclusions

The local droplet etching of nanoholes in semiconductor surfaces represents a powerful new degree of freedom for the design of novel semiconductor heterostructures and devices. This method allows to tune the structural properties over a wide range by adjusting the materials and the process parameters. Self-assembled quantum dots are created by filling of nanoholes in AlGaAs with GaAs. Dependent on the sample design and the LDE process parameters, these QDs show either broadband optical emission or discrete sharp lines. Broadband light sources are very attractive because of their wide range of applications, which include fiber-optic gyroscopes, fiber-optic sensors, optical coherence tomography, and wavelength-division multiplexing transmission [31]. On the other hand, self-assembly of strain-free quantum dots with very uniform size distribution may help to overcome some limitations of the widely used Stranski–Krastanov InAs QDs.

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