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Mechanism and applications of local droplet etching

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ABSTRACT

We give an overview on the fabrication and applications of deep nanoholes in semiconductor surfaces generated by self-assembled drilling with liquid metal droplets as etchant. The method is fully compatible with conventional molecular beam epitaxy equipment. We discuss the mechanism of nanohole formation and two applications: the creation of GaAs quantum rings and of GaAs quantum dots by nanohole filling.

1. Introduction

This paper gives an overview on the present state of the recently developed local droplet etching (LDE) technique which provides self-assembled nanoholes on semiconductor surfaces by a local removal of material without the need of any lithographic steps. As an important advantage compared to conventional lithography processes, LDE is fully compatible with usual MBE equipment, can be easily integrated into the MBE growth of heterostructure devices, and, thus, provides a new degree of freedom for the geometry and composition of novel semiconductor nanostructures. The method was introduced by Wang et al. [1] for etching of GaAs surfaces with Ga droplets. We have expanded the range of materials and demonstrated etching with Ga [2–5], Al [6–8], GaAl, In [2], and InGa [9] droplets on GaAs, AlAs [6–8], and AlGaAs [2–5] substrates. The nanohole openings are surrounded by distinct walls that are crystallized from the initial droplet material [2,3]. This allows, for instance, the fabrication of GaAs quantum rings using Ga droplets on AlGaAs [2,9], or the generation of isolating AlAs walls with Al droplets [6–8].

The nanohole formation is related to the droplet epitaxy [10–19], but takes place at higher temperatures which is favorable in view of undesired background impurities and crystal defects. In this paper, we discuss the present understanding of the mechanism behind LDE and applications such as the creation of GaAs quantum rings [2,9] and of GaAs quantum dots (QDs) by nanohole filling [6–8].

2. Mechanism of local droplet etching

Similar to the droplet epitaxy, the LDE process starts with the generation of metallic droplets in Volmer–Weber growth mode on the surface. In contrast to droplet epitaxy, the post-growth annealing step takes place without As flux. This in combination with the significantly higher temperatures used for LDE results in the transformation of the initial metallic droplets into nanoholes during post-growth annealing [5]. A sketch and corresponding atomic force microscopy (AFM) images of the different stages during LDE are shown in Fig. 1.

The nanohole openings are surrounded by distinct walls that are crystallized from droplet material and may act as quantum rings [2,3,9]. This establishes that the same droplet during LDE performs two opposite operations: first, the removal of material from the substrate which results in nanohole formation and, second, the deposition of material on the substrate which forms the wall around the nanohole openings. This interesting behaviour strongly suggests a substantial inhomogeneity of the droplets.

To explain these experimental findings, we propose the following mechanism for the local droplet etching. The central process for the removal of substrate material below the droplet is diffusion of arsenic from the substrate into the liquid [1,3]. But the solubility of As is limited for instance to a maximum value of about 7×10^{-4} in liquid Ga at a usual LDE temperature of 570 °C [20]. This would stop etching and an additional process reducing the As concentration inside the droplet material is required in order to keep etching running. We assume that the wall crystallization represents this process. In particular, the removal of the liquid droplet material by either desorption or by migration onto the substrate surface causes a local As enrichment at the droplet surface which leads to precipitation of GaAs. This excess GaAs might form a GaAs shell surrounding the liquid droplet core and will finally crystallize into the wall. Recently, the existence of a core-shell configuration has been observed for the very similar system of In droplets on GaAs [21] and a model of the LDE process basing on the above picture is discussed in Ref. [22].

Furthermore, the AFM measurements show that the hole density is slightly reduced compared to the initial droplet density [5]. This finding establishes the relevance of droplet coarsening by

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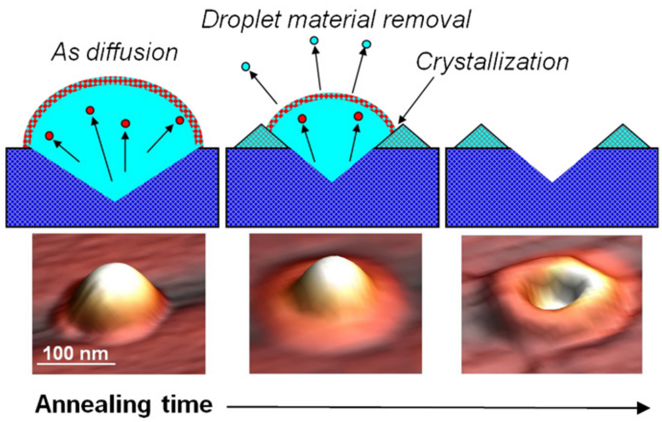

Fig. 1. Evolution from droplets to nanoholes during post-growth annealing. Top: sketch of the relevant processes. The wall surrounding the hole consists of recrystallized droplet material. Bottom: corresponding AFM micrographs.

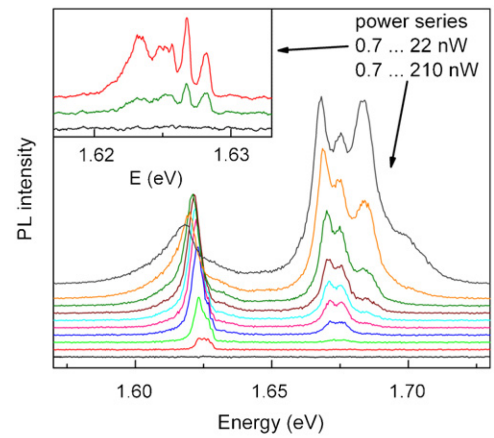

Fig. 2. Low-temperature PL measurements of a single GaAs quantum ring in $Al_{0.35}Ga_{0.65}As$. The excitation power was varied from 0.7 up to 210 nW. The inset shows a magnification of the peaks at 1.625 eV at an excitation power varied from 0.7 up to 22 nW.

Ostwald ripening during the annealing step. As an interesting method to control the nanohole density and size, we have etched GaAs and AlGaAs surfaces with In_xGa_{1-x} [9]. With increasing x, we find a decrease of the hole density and an increase of the hole depth. The influence of the indium content on the hole density was quantitatively reproduced by a model that considers different surface diffusion activation energies for Ga and In [9]. By etching with pure In, holes with densities as low as $5\times10^6\,cm^{-2}$ and depths of 40 nm have been achieved.

3. Applications of local droplet etching

To study the optical properties of the quantum-ring-like walls around the nanohole openings, we have performed low-temperature photoluminescence (PL) measurements [2,9]. For the selection of single rings, a micro-PL setup was used with a focussed laser beam. Fig. 2 shows a PL power series of a single GaAs quantum ring embedded in AlGaAs. For low excitation power, we find a set of PL peaks at about 1.625 eV. The inset of Fig. 2 shows a magnification of these peaks. We attribute the sharp lines to excitons and the broader ones at lower energy to multiexcitonic transitions. With increasing excitation power, additional peaks occur at higher energies (about 1.67 eV). These we attribute to quantum-ring excited-states.

Recently, we have demonstrated the creation of a novel type of strain-free GaAs QDs by filling of LDE nanoholes [6–8]. For these experiments, etching was performed using Al droplets in order to avoid an additional confinement induced by the wall. Fig. 3a shows an AFM image of an AlGaAs surface after Al LDE at $T=620\,^{\circ}C$. Clearly visible on this surface is the coexistence of shallow holes (up to 7 nm depth) and deep holes (deeper than 7 nm). We have already observed this effect earlier for Ga LDE on AlGaAs at low temperatures [4]. On the other hand, PL-spectra indicate that LDE on AlAs surfaces at $T=650\,^{\circ}C$ yields no such bimodal depth distribution and the resulting surfaces show only deep holes [6,7]. Since the AlAs surfaces oxidate very fast and, thus, are not accessible to AFM measurements under air, for illustration we provide a sample where Ga LDE has been performed on AlGaAs at $T=620\,^{\circ}C$. The corresponding surface (Fig. 3b) shows only deep holes, similar to the samples etched in AlAs. These surfaces are now used as a template for QD formation. For this, the nanoholes are filled with a GaAs layer with thickness d_f in a pulsed mode with 0.5 s deposition and 30 s pause.

Importantly, two different types of QDs are distinguished dependent on the type of the initial nanoholes. Shallow holes

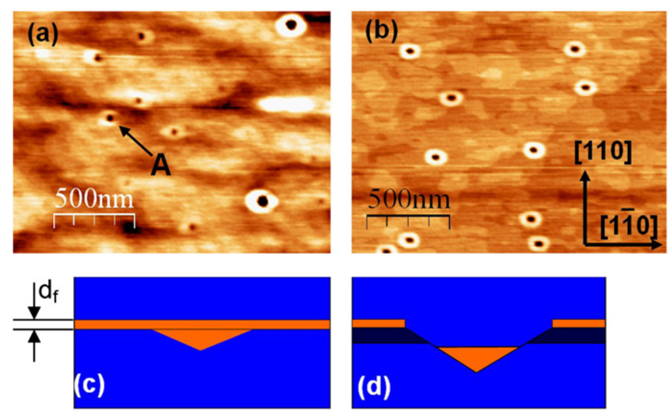

Fig. 3. AFM images of AlGaAs surfaces after (a) LDE with Al droplets at $T=620\,^{\circ}C$ and (b) LDE at $T=620\,^{\circ}C$ with Ga droplets. Arrow "A" in (a) marks a shallow hole. (c) Schematic cross-section of a completely filled shallow-hole QD. (d) Schematic cross-section of a partially filled deep-hole QD.

are completely filled (Fig. 3c) which yields highly nonuniform QDs due to the broad hole depth distribution [4]. Furthermore, shallow-hole QDs are in contact with the GaAs quantum well induced by filling. On the other hand, deep holes are only partially filled and the size of deep-hole QD is very uniform and perfectly controlled by the amount of Ga d_f deposited for filling (Fig. 3d). Due to the spatial separation, we assume an only negligible interaction between the deep-hole QDs and the GaAs quantum well.

Corresponding PL measurements are shown in Fig. 4 [7]. Starting with the samples with shallow holes, a reference sample without filling shows no optical signal (Fig. 4a). This demonstrates that there is no background emission from the AlGaAs layers. A second reference sample with filling but without etching shows one strong PL peak (Fig. 4b) that is related to the $d_f=0.65$ nm thick GaAs quantum well. PL measurements of samples that contain shallow-hole QDs show a broadband optical emission without pronounced peaks (Fig. 4c and d). Furthermore, no clear dependence on d_f is visible. These results are consistent with the picture of a very broad QD size distribution caused by complete filling of the nonuniform shallow holes. 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 [23].