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Droplet etching: Application to Quantum Dots and Nanopillars for Thermoelectrics

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1. Introduction

We give a brief overview on the mechanism and first applications of the self-organized patterning of semiconductor surfaces by the local droplet etching (LDE) technique. LDE is fully compatible with the molecular beam epitaxy (MBE) fabrication of semiconductor heterostructures with its precise control of the composition profile inside the device combined with a high crystalline perfection. During LDE, metallic droplets drill nanoholes into a semiconductor surface with structural parameters adjustable over a wide range by the process conditions. Two recent applications of the LDE method, the fabrication of GaAs quantum dots (QDs) by nanohole filling and the creation of nanopillars for thermoelectrics are discussed.

2. Local Droplet Etching

The self-organized drilling of nanoholes into GaAs surfaces by using Ga droplets as etchant was first demonstrated by Wang et al. in 2007 [1]. Later, we have expanded the range of droplet as well as of substrate materials and demonstrated etching of GaAs, AlGaAs, and AlAs surfaces with Ga, Al, and In droplets [2-6]. The insets of Fig. 1 show typical atomic force microscopy (AFM) images of AlGaAs surfaces with nanoholes. The walls surrounding the hole openings are composed of droplet material and As from the substrate [2,5]. That means, etching of AlGaAs with Ga droplets yields GaAs quantum rings [2,3], whereas Al droplets result in optically inactive AlAs walls.

Deposition of a few monolayers (ML) of Al, Ga, or In leads to the formation of droplets on the substrate surface in Volmer-Weber growth mode. The transformation of these droplets into nanoholes takes place during a post-growth annealing step [4]. Here, diffusion of As from the substrate into the droplet driven by the concentration gradient together with desorption of the droplet material represent the central processes for hole etching [5]. A simulation model of the time evolution during etching quantitatively reproduces the surface morphology as well as the influence of the process temperature on the hole depth [5].

In the so-called standard regime, hole densities for etching of AlGaAs and AlAs with Al or Ga droplets are in the range of $1\text{-}5{\cdot}10^{8}$ cm^{-2}, dependent on the process temperature [2,4,5]. Ultra-low density (ULD) holes with densities of $1\text{-}7{\cdot}10^{6}$ cm^{-2} have been achieved very recently by an optimization of the As background pressure. Higher hole densities are possible by multiple etching. An overview on the three regimes is given in Fig. 1.

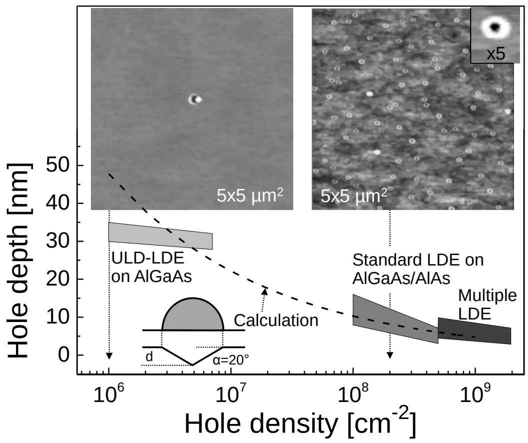

Fig. 1 Relation between the depth and the density of nanoholes created by local droplet etching (LDE) in different process regimes: ultra-low density (ULD), standard, and multiple-etching regime. The dashed line is calculated assuming that the diameter of the hole openings is equal to that of the semispherically shaped initial droplets. The insets show AFM micrographs from AlGaAs surfaces after LDE in ULD (left) and standard (right) regime.

3. GaAs Quantum Dots by Nanohole Filling

For the self-assembled generation of strain-free GaAs QDs, LDE nanoholes in AlGaAs or AlAs surfaces are filled by deposition of GaAs with precisely defined filling level [6-11]. From the AFM topography of the holes we expect that the QDs are shaped like inverted cones. Controlled by the process conditions and the resulting dot-size distribution, QD ensembles show either very broad photoluminescence (PL) emission close to a white-light source [7] or very sharp PL lines with line width of less than 10 meV [6]. The QD size and with this the wavelength of the PL emission can be precisely adjusted by the filling level in the range between 700 and 800 nm [6]. The dot-size dependent quantization energies range from 30 to 90 meV [6]. Several layers with uniform LDE QDs can be stacked without PL peak broadening and the dots exhibit optical emission up to room temperature [10].

Single-dot spectroscopy of LDE GaAs QDs demonstrates sharp excitonic lines with line widths of less than 50 µeV for nonresonant excitation [8]. An example is shown in Fig. 2a. The lifetimes of the exciton and biexciton peaks are measured using a streak camera and we determine values of 390 and 426 ps, respectively [9]. The excitonic energy levels inside the QDs are analyzed by comparing experimental data with results of a simulation model [12] which is based on k·p theory and configuration interaction. Examples of the measured and simulated exciton ground-state energy E_x as well as of the splitting between exciton and biexciton E_{xx} peaks as function of the height of the QDs is shown in Figs. 2b and c.

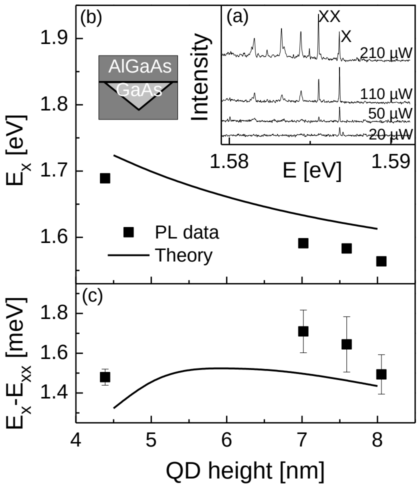

Fig. 2 a) Single-dot PL spectra at $T = 4$ K from a LDE GaAs QD at varied excitation power as indicated. Exiton X and biexciton XX peaks are marked. The spectra are vertically shifted for clarity. b) Exciton ground-state energy E_x as function of the QD height measured (symbols) and simulated (line) as is described in the text. The error bars are smaller than the size of the symbols. c) Measured and simulated splitting E_x - E_{xx} between exciton and biexciton peaks.

4. Nanopillars for Thermoelectrics

The self-assembled creation of crystalline nanopillars represents an additional recently realized application of the LDE technique. Here, nanoholes are etched in a thin AlAs layer which is grown on a GaAs substrate. Afterwards, the holes are completely filled and overgrown with GaAs. When the holes are deeper than the AlAs layer thickness, a subsequent removal of only the AlAs by material selective wet-chemical etching leads to so-called air-gap heterostructures (AGHs) [13]. Here, two epitaxial GaAs layers are separated only by GaAs nanopillars with length precisely controlled by the thickness of the initial AlAs layer. The separation of the epitaxial layers is proved by optical reflectivity measurements [13].

Measurements of the thermal conductance perpendicular to the substrate surface establish two major results [14]. First, the temperature dependence of the thermal conductance through an AGH is even qualitatively different to that of bulk material [14]. Second, the thermal conductance through an ensemble of nanopillars is several orders of magnitude reduced in comparison to thermal transport through the bulk before removal of the AlAs layer. A model that considers ballistic phonon transport through the nanopillars reproduces the experimental data quantitatively [14].

5. Conclusions

Local droplet etching is a versatile method, which greatly enhances the possibilities of conventional molecular beam epitaxy by allowing the inclusion of top-down procedures into the usual bottom-up fabrication of semiconductor heterostructures. GaAs quantum dots fabricated by filling of droplet etched nanoholes have substantial advantages in comparison to the established InAs QDs, since they are strain-free, highly uniform, precisely adjustable in size, and their composition is not affected by unintentional intermixing effects. Air-gap heterostructures with crystalline nanopillars open novel possibilities to study ballistic thermal transport and are promising building blocks for the design of nanostructured thermoelectric devices.

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