Electron beam prepatternning for site control of self-assembled quantum dots

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A site-control technique for individual InAs quantum dots (QDs), formed by self-assembling, has been developed, using scanning-electron-microscope assisted nanodeposition and metalorganic vapor phase epitaxy. We find that the nanoscale deposits, created at the focal point of the electron beam on a semiconductor surface, act as “nanogrowth masks”. Growth of a thin epitaxial layer produces nanoholes extending down to the deposits. The carbon deposits can be removed by oxygen plasma etching. When a compressively strained layer is deposited on this surface, QDs are self-organized at the hole sites, while no dots are observed in the flat surface region. © 2001 American Institute of Physics.

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The fabrication of semiconductor quantum dots (QDs) has recently been focused on regarding spontaneous three-dimensional islanding approaches in lattice-mismatched material systems. The high crystalline quality found in QDs formed by these processes enables incorporation of the dots in optical and electronic devices. However, in such self-organizing approaches the QDs are, in general, randomly distributed over the surface. By controlling nucleation sites for QDs, one can expect that the density and size of the dots can be manipulated independently and that laterally as well as vertically coupled QDs can be realized. Several groups have studied the possibility of controlling nucleation sites for QDs by using patterned substrates, where formation of QDs on mesa stripes, trenches, or in etched holes was reported. These techniques, however, need several processing steps of lithography and etching. A more elegant way is to produce growth masks directly on the semiconductor surface. Kohmoto et al., for instance, reported the successful use of scanning tunneling microscope tip induced deposits for this purpose. We present in this letter another approach: a site-control technique for self-assembled quantum dots using electron-beam produced carbon deposits as a growth mask. After partial epitaxial overgrowth (by, e.g., GaAs or InP), these carbon deposits are easily removed by oxygen plasma treatment. We demonstrate that the remaining holes at the surface offer highly selective nucleation sites for self-assembled QDs. This approach is intended to be used for the realization of a single electron-tunneling device. By the proper materials combination, with thin tunneling barriers embedding the holes and a sufficiently thick potential barrier surrounding the hole, one can expect to realize quantum devices with a vertical current flow restricted through one active QD only.

Figure 1 presents the site-control technique and its fabrication steps. The carbon growth masks were deposited on the epiready substrates by using an ordinary electron beam lithography system (JEOL) at an acceleration voltage of 35 kV, a probe current of 20 pA, and a pressure in the scanning electron microscope (SEM) of about 5 × 10⁻² Pa. The carbon was deposited on the surface for 200 or 100 ms per dot, forming a pattern of typically 50 × 50 nanogrowth masks. The deposition rate as well as the etching rate of the carbon was characterized by means of atomic force microscope (AFM) and SEM inspection. Prior to epitaxial overgrowth, the samples were treated with O plasma for 12 s at 10 mbar, in order to remove the thin carbon-containing surface layer around the carbon deposit, which forms due to electron backscattering (proximity effect). The samples were then treated with diluted sulphuric acid (for InP) or with diluted hydrochloric acid (for GaAs) and finally rinsed in deionized water.

For epitaxial growth we used low pressure (50 mbar) metalorganic vapor phase epitaxy (MOVPE), with phosphine, arsine (AsH₃), trimethyl–indium, and trimethyl–gallium as precursors, and hydrogen as the carrier gas. The process was controlled by a flow and pressure balanced ventilation/run system. The molar fractions were 5 × 10⁻⁴ for arsine and 1.5 × 10⁻² for phosphine. The total gas flow in the reactor cell was about 6000 cm³/min. We used Sn-doped (n⁺) InP (001) or Si-doped (n⁺) GaAs “epiready” wafers with a 0.2° misorientation towards the nearest (011) direction for our experiments. The surface with the pattern of carbon

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deposits was then epitaxially overgrown with various amounts of material, ranging from 10 to 50 nm, followed by a second oxygen plasma treatment for 2 min at 5 mbar to remove the partially overgrown carbon deposits completely. After the proper diluted acid treatment and rinsing in deionized water, the second MOVPE growth step followed, in order to deposit the dots site selectively at the positions where the carbon deposits were before removal. The samples were annealed under the proper hydride flow for 7 min at 630 °C, before cooling down to 500 °C during a 5 min period. The temperature was stabilized for 1 min before switching the precursors for deposition of 0.9, 0.6, 0.3, or 0 ML InAs on InP, or 1.8 and 1.2 ML InAs on GaAs. Subsequently, the samples were cooled down under arsine. Surfaces were studied with conventional contact mode AFM or SEM.

Figure 2 shows some details of the carbon mask deposition. In Fig. 2(a) an AFM image together with the height profile, Fig. 2(c), of carbon corresponding to 200 ms of deposition is shown. The carbon deposit in this case is 20 nm high and approximately 50 nm wide. The deposition rate of carbon shows a nonlinear dependence versus electron beam lithography exposure time, as is visualized in Fig. 2(b). Possible explanations are (i) the carbon is an insulating material and will therefore be charged by the electron beam, Coulomb forces repel the electron beam and hence deposition is suppressed, or (ii) as the carbon pillar is growing longer, we move out of focus of the electron beam. The deposition rate will vary with the background pressure in the SEM and therefore change from system to system. The principle will, however, be the same.

One problem with the proposed method is the electron backscattering towards the surface, which causes carbon-containing molecules to crack, forming a thin carbon film around the desired carbon pillar. This effect is visualized in Fig. 3, which is a SEM image, presenting 1 s of carbon deposits overgrown by 50 nm GaAs. Prior to overgrowth the surface was either unprocessed [Fig. 3(a)], or treated with 12 s O plasma at 5 mbar [Fig. 3(b)]. The effect is obvious: the lateral extension of the holes, surrounding the partially overgrown carbon deposits, reduces with oxygen plasma treatment. Therefore, the surfaces were generally treated with oxygen plasma for 12 s at 10 mbar to remove the thin carbon film. The etching rate of carbon under these conditions was about 1.5 nm/s vertically as well as laterally. The sizes of the holes, that develop when the carbon masks are overgrown, are related to the size of the carbon mask and the amount of deposited material. 25 nm deposition of InP on a prepatterned surface and subsequent removal of the carbon growth masks developed well defined holes with top diameters of about 500 nm for the 200 ms and 300 nm for the 100 ms deposit, as measured by AFM. The bottom diameters in the holes were about 110 and 100 nm, respectively, and the measured bottom surface was flat, i.e., no carbon residues were detected. The holes were elongated in ⟨110⟩, and measured facet angles were about 5° in ⟨110⟩, and 11° in ⟨10–10⟩. The observed bottom diameters are larger than the carbon pillar diameters at the base, which suggests that not all carbon deposits induced by electron backscattering was removed by the O-plasma treatment.

The holes at the surface are efficient sinks for epitaxial material: 25 nm deep InP holes were almost completely filled by 0.6 ML of InP deposition at an elevated temperature of 630 °C. Obviously, the mobile indium adatoms diffuse over the surface to be incorporated preferentially at the faster growing facets. Therefore, to maintain the holes for dot positioning, InAs had to be deposited directly on the patterned surface. Figure 4(a) shows an AFM image of the patterned area after 0.9 ML InAs deposition. Two features should be
The hole size effects the nucleation position of the critical nucleus is generally smaller in the groove than on the reasons and due to the fact that the formation energy of the ating between the facets due to surface energy minimization.

The number of dots decreases with decreasing InAs deposition between 0.9, 0.6, and 0.3 ML. However, it does not reach zero. For the extreme case, i.e., no deposition of InAs, only annealing of the surface under AsH3, we commonly find one dot per hole, see Fig. 4(b).

This indicates that the excess InAs caused by As/P exchange reactions10,11 is sufficient for the highly selective dot formation inside the holes. In this sample we used 200 ms carbon deposits, in a matrix with 3 μm in between the deposits. The prepatterned InP surface was annealed under arsine flow at 500 °C for 30 s. Note that no InAs dots were observed on the flat surface. One or no dot is observed inside the holes. The percentage of filled holes varies over the sample, from a very poor output to almost every hole filled.

We believe that even 100% of the holes could be successfully filled at optimized processing and annealing conditions. The one dot in the bottom nucleates at the intersection of the B-type facet and the (001) bottom plane. The InAs is nucleating between the facets due to surface energy minimization reasons and due to the fact that the formation energy of the critical nucleus is generally smaller in the groove than on the flat.12 The hole size effects the nucleation position of the dots, the smaller the hole, the more centered the dot. The dot densities in the pattern did not differ when annealing the samples for 12 or 30 s under arsine. It is difficult to evaluate the size homogeneity of dots formed inside the holes correctly due to tip convolution effects in our AFM measurements [see Fig. 4(b)] and we have no optical results. We were not able to measure dot luminescence due to the very low density of dots per surface area and thus low luminescence intensity. However, even when the dots only show low luminescence activity, they can be used as seeds for site-controlled vertical stacking experiments. For the InAs/GaAs system, two dots were often found in the holes after 1.2 ML InAs deposition, while noncoherent dots were observed inside the holes after 1.8 ML InAs deposition.

In summary, carbon deposition on a semiconductor surface, by means of electron beam irradiation, was successfully used as a nanogrowth mask. These deposits were removable by oxygen plasma etching, before and after epitaxial overgrowth. Extreme selectivity of InAs dot nucleation was observed within the holes at the surface after partial overgrowth and subsequent removal of the carbon deposits. For the InAs/InP system, structures with one InAs dot per hole but no dots outside the holes could be achieved reproducibly by using only the InAs produced by As/P exchange reactions. For the nonoptimized InAs/GaAs system, two dots were commonly found inside the holes after 1.2 ML InAs deposition. The described procedure opens a relatively simple way to overcome the randomness in self-assembling processes and to nucleate quantum dots in device applications desired positions.

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