Arsenic cluster superlattice in gallium arsenide grown by low-temperature molecular-beam epitaxy

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(Submitted May 27, 1998; accepted for publication May 28, 1998)
Fiz. Tekh. Poluprovodn. **32**, 1161–1164 (October 1998)

Molecular-beam epitaxy at 200 °C is used to grow an InAs/GaAs superlattice containing 30 InAs delta-layers with a nominal thickness of 1 monolayer, separated by GaAs layers of thickness 30 nm. It is found that the excess arsenic concentration in such a superlattice is $0.9\times10^{20}\,\mathrm{cm}^{-3}$. Annealing the samples at 500 and 600 °C for 15 min leads to precipitation of the excess arsenic mainly into the InAs delta-layers. As a result, a superlattice of two-dimensional sheets of nanoscale arsenic clusters, which coincides with the superlattice of the InAs delta-layers in the GaAs matrix, is obtained. [S1063-7826(98)00310-X]

Gallium arsenide, grown by molecular-beam epitaxy (MBE) at low temperatures $T\sim200$ °C (LT-GaAs), has attracted significant attention because of its large electrical resistance, high breakdown voltage, and record-short lifetime of nonequilibrium charge carriers.[1–5] The primary peculiarity of LT-GaAs is an excess of arsenic As (up to 1.5 at. %), which is captured in the growing layer during low-temperature epitaxy. During annealing at a sufficiently high temperature $T\geqslant500$ °C the excess arsenic forms clusters built into the GaAs matrix. In ordinary LT-GaAs the clusters are randomly distributed over the entire volume of the epitaxial film. It has been shown, however, that the spatial distribution of the arsenic clusters can be controlled with the help of indium delta-doping.[6–8] In this case, heterogeneous creation of excess arsenic clusters on the InAs delta-layers leads to the formation of two-dimensional sheets of clusters.

Our aim was to construct a multiperiod superlattice of two-dimensional sheets of arsenic clusters separated by a GaAs matrix not containing any clusters. To create the two-dimensional sheets of clusters we used indium delta-doping.

An InAs/GaAs superlattice was grown by molecular-beam epitaxy at 200 °C in a two-chambered ''Katun'' MBE setup on a substrate of semi-insulating gallium arsenide of diameter 50 mm and orientation (100). The superlattice consisted of 30 periods. The nominal thickness of the InAs delta-layers was one monolayer (ML). The thickness of the GaAs layers was 30 nm. The structure was divided into three parts. One of those parts was not subjected to any processing. The other two were annealed at 500 and 600 °C, respectively, for 15 min on the MBE setup with excess arsenic pressure.

The average indium concentration in the structure was measured by x-ray structural micro-analysis (XSMA). This method was also used to estimate the excess arsenic concentration in the samples.[4] For a more accurate measurement of the excess arsenic we used measurements of optical absorption in the near-IR due to $\mathrm{As_{Ga}}$ antistructural defects.[9–11] The microstructure of the samples before and after annealing was investigated by transmission electron microscopy (TEM) of cross sections. To prepare the samples, we used the usual procedure of mechanical grinding and polishing with subsequent etching by Ar^+ ions.[4,12] The studies were performed in the diffraction regime and in the high-resolution regime with the help of Philips EM 420 and JEM 4000 electron microscopes.

Figure 1 shows a dark-field electron-microscope image of a cross section of a structure in which periodic contrast is observed in the form of thin dark lines. The positions of the dark contrast lines coincide with the expected positions of the InAs delta-layers in the superlattice. The period of the superlattice turned out to be equal to $T_{SL}=28\pm1$ nm. This value is in good agreement with the data of earlier studies utilizing the method of high-resolution x-ray diffraction ($T_{SL}=28\pm2$ nm).[13]

XSMA showed that the average indium concentration in the structure is 1.1 ± 0.1 mol.%. Allowing for the fact that the superlattice period $T_{SL}=28$ nm, the thickness of the InAs layers should be 0.3 nm, i.e., ~1 ML. However, electron-microscope studies in the high-resolution regime showed (Fig. 2) that the thickness of the indium-containing layers is 4 ML. The difference between the nominal layer thickness and the observed (using TEM) layer thickness is probably due to small-scale relief in the growth surface.[12]

According to the XSMA estimate, the excess arsenic concentration in the InAs/GaAs superlattice grown at 200 °C turned out to be on the order of 0.6 at. %. Figure 3 shows

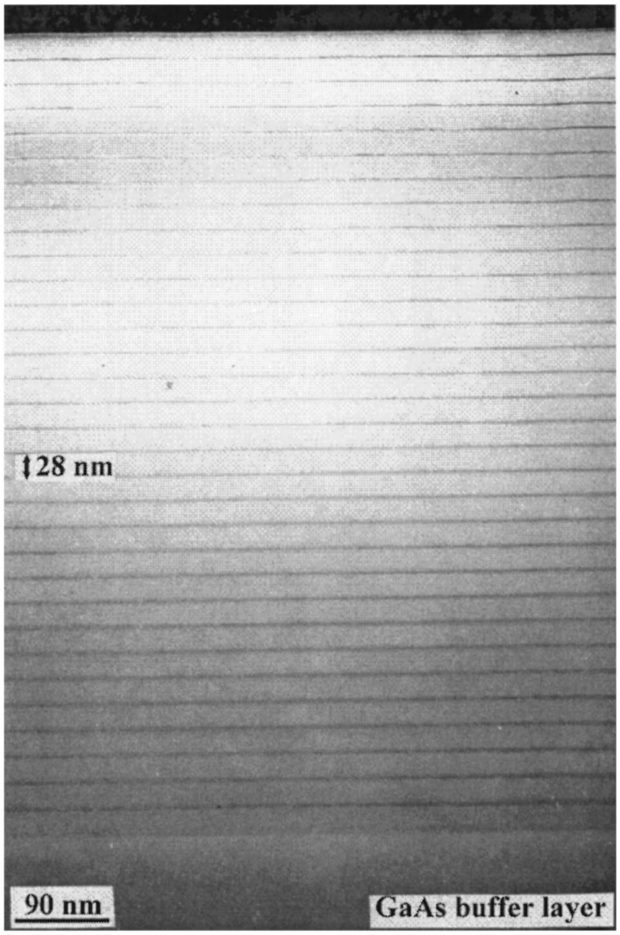

FIG. 1. Dark-field electron-microscope image of a cross section of an InAs/GaAs superlattice grown at low temperature; (200) reflection. The dark contrast corresponds to delta-layers of InAs. The sample was not annealed.

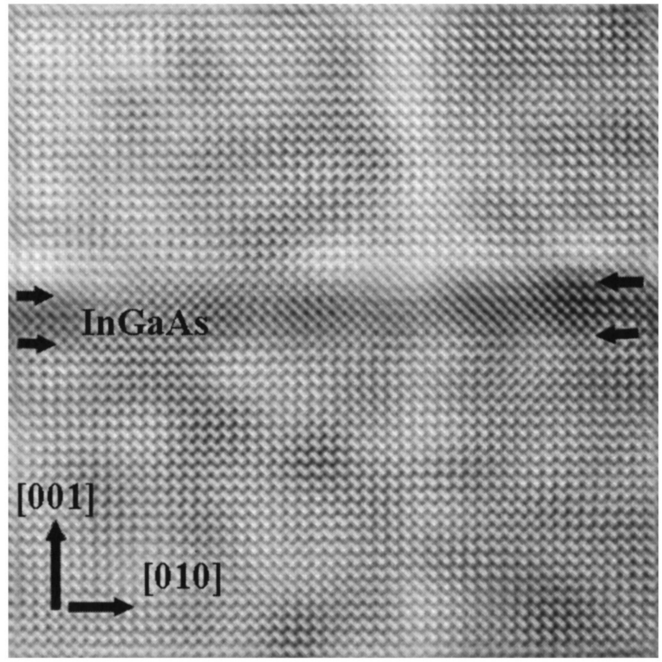

FIG. 2. High-resolution electron-microscope image of an InAs delta-layer in a GaAs matrix grown at low temperature. The nominal indium content in the layer is one monolayer. The sample was not annealed.

optical absorption spectra in the wavelength range $0.9 - 1.2\ \mu$m, measured at 300 K, for an InAs/GaAs superlattice before and after annealing. It can be seen that the absorption coefficient in the unannealed sample at 1 μm wavelength is equal to $1.2\times10^4\ \text{cm}^{-1}$, which corresponds according to Martin's calibration[14] to a concentration of antistructural arsenic defects of $0.9\times10^{20}\ \text{cm}^{-3}$ and an excess arsenic concentration of 0.8 at. %. This latter value is in satisfactory agreement with data on the relaxation of the lattice parameter of the structure upon annealing,[13] from which it follows that the arsenic excess is equal to 0.7 at. %.

During annealing the concentration of antistructural defects decreases substantially (Fig. 3) and the excess arsenic forms clusters. Figure 4 shows an electron-microscope image of a cross section of the sample after annealing at 500 °C. It can be seen that most of the clusters are accumulated into two-dimensional sheets, whose positions coincide with the positions of the InAs delta-layers. The actual thickness of the two-dimensional layers of clusters is 5–6 nm. Note that a considerable fraction of the clusters are located between the two-dimensional sheets and form a disordered system. It is important that the mean size (diameter) of the clusters in the two-dimensional sheets ($\sim$3 nm) is larger than the mean size of the clusters between sheets ($\sim$2.5 nm). This difference should lead to the result that during Ostwald ripening, upon increasing the duration or temperature of the anneal, the clusters located between the two-dimensional sheets will tend to dissolve.[8,15,16]

Figure 5 shows an electron-microscope image of a cross section of a structure annealed at 600 °C. It can be seen that the mean size of the clusters has increased to $\sim$6 nm, but in the electron-microscope images of the clusters one observes the characteristic moiré pattern, which reflects the difference between their atomic structure and the structure of the GaAs matrix.[17,18] The cluster concentration after annealing at 600 °C is significantly lower than after annealing at 500 °C, and is equal to $\sim2\times10^{11}\ \text{cm}^{-2}$ in each two-dimensional

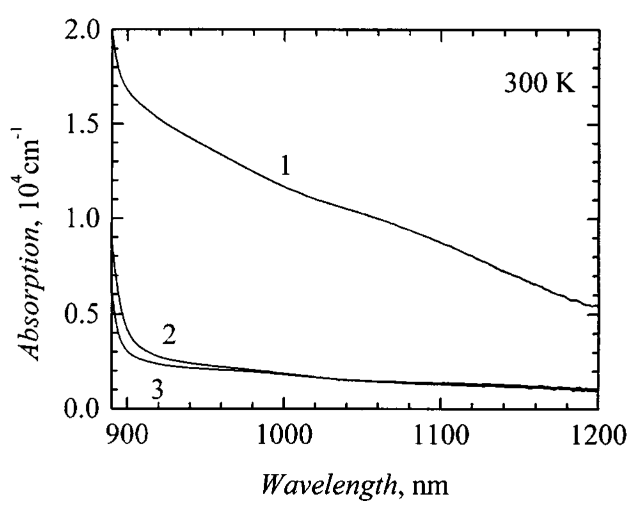

FIG. 3. Optical absorption spectra of an InAs/GaAs superlattice grown at low temperature, before annealing (*1*) and after annealing at 500 (*2*) and 600 °C (*3*) for 15 min.

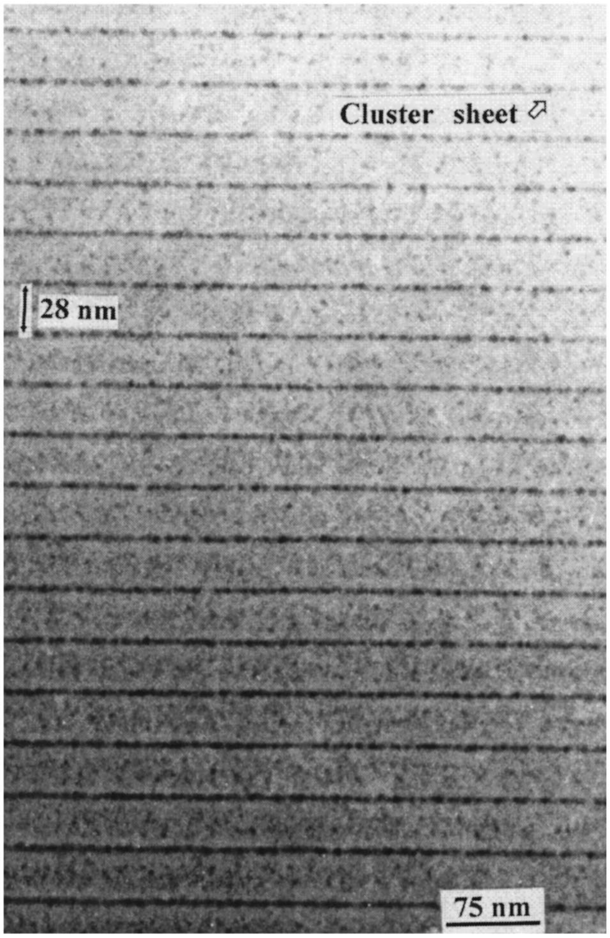

FIG. 4. Light-field electron-microscope image of a cross section of an InAs/GaAs superlattice grown at low temperature and annealed at 500 °C. The positions of the two-dimensional sheets of clusters correspond to the positions of the InAs delta-layers.

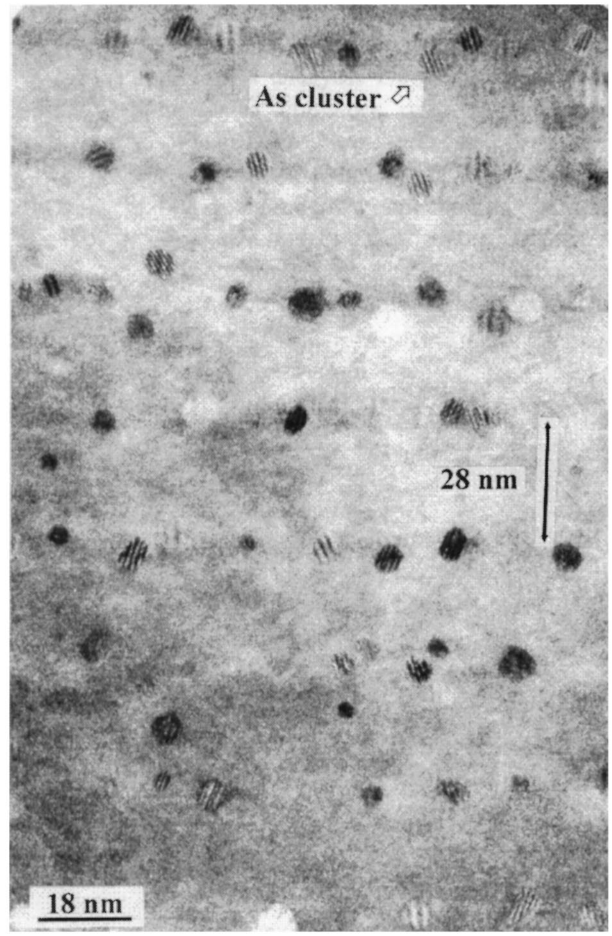

FIG. 5. Light-field electron-microscope image of a cross section of an InAs/GaAs superlattice grown at low temperature and annealed at 600 °C. The positions of the two-dimensional sheets of clusters correspond to the positions of the InAs delta-layers.

sheet. In this case the As clusters located between the two-dimensional sheets have mostly dissolved as a result of Oswald ripening, and the two-dimensional sheets contain more than 90% of the clusters. The remaining uncoalesced large-scale clusters have reached the size of the clusters in the two-dimensional sheets. This is a consequence of the difference in the kinetics of Ostwald ripening (coalescence) in two-dimensional and three-dimensional systems.[15] According to the Lifshitz–Slezov theory[16] and the results of experimental studies,[15] such large-scale clusters between the two-dimensional sheets cannot be eliminated by further increasing the temperature or the anneal times.

As was shown in Ref. 15, the actual thickness of the two-dimensional sheets of arsenic clusters is close to double the mean diameter of the clusters. The increase in the thickness of the sheets during Ostwald ripening (coalescence) is due to nonequilibrium growth of the clusters in different directions, depending on the local environment of each cluster, and to diffusion smearing of the InAs delta-layers, which is significantly enhanced due to the large concentration of intrinsic point defects.[12] After the anneal at 600 °C the thickness of the two-dimensional sheets of clusters reached ~12 nm. Further increases in the temperature or duration of the anneal should lead to further growth of the thickness of the sheets of clusters. As a result, when the thickness of the sheets of clusters reaches one period of the superlattice (28 nm), the ordered system of two-dimensional sheets of clusters should transition to a disordered system of clusters, described by the Lifshitz–Slezov theory.[16] Such a transition was observed for arsenic clusters in GaAs in Ref. 15.

In summary, we have used low-temperature molecular-beam epitaxy to grow an InAs/GaAs superlattice containing 30 periods of thickness 28 nm each. The superlattice contained 0.8 at. % excess arsenic. Annealing of such a superlattice led to the formation of a periodic structure of two-dimensional sheets of nanoscale arsenic clusters. As a result of annealing at 500 °C for 15 min, the thickness of the two-dimensional sheets of clusters was reduced to a thickness corresponding to much less than one period of the superlattice; however, a fraction of the clusters are now located between the two-dimensional sheets. Such clusters for the most part dissolve when the annealing temperature is raised to 600 °C. As a result, more than 90% of the clusters are now concentrated in the two-dimensional sheets. In this case, however, the thickness of the two-dimensional sheets of clusters is increased to ~12 nm.

This work was carried out with the support of the Russian Ministry of Science (within the programs ''Fullerenes and atomic clusters'' and ''Physics of solid-state nanostructures''), the Russian Fund for Fundamental Research, and the Deutsche Forschungsgesellschaft.

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Translated by Paul F. Schippnick