Enhanced precipitation of excess As on antimony delta layers in low-temperature-grown GaAs

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Delta doping with antimony isovalent impurity has been employed as a precursor for two-dimensional precipitation of excess arsenic in GaAs grown by molecular-beam epitaxy at low substrate temperature (LT-GaAs), and subsequently annealed. LT-GaAs films delta doped with indium isovalent impurity showed previously to provide two-dimensional As cluster sheets were studied for comparison. Small clusters observed by transmission electron microscopy at the Sb delta layers had an unusual lens shape and, probably, nonrhombohedral microstructure. These clusters induced strong local strains in the surrounding GaAs matrix. After annealing under the same conditions, the clusters at the Sb delta layers were found to be bigger than those at the In delta layers. Additionally, nucleation of the arsenic clusters at the Sb delta layers occurs at a relatively low annealing temperature. The observed precipitation features indicate that delta doping with Sb is more effective for two-dimensional precipitation of the excess As in LT-GaAs as compared with In delta doping. © *1999 American Institute of Physics.* [S0003-6951(99)02511-5]

Gallium arsenide grown by molecular-beam epitaxy (MBE) at low temperature (LT-GaAs) has attracted much attention during the past few years due to a number of interesting properties, such as ultrashort carrier lifetime and extremely high electrical resistivity.[1–5] These properties of LT-GaAs arise from a high arsenic excess captured into the films during the low-temperature MBE. Upon postgrowth anneal the excess arsenic precipitates in nanoscale clusters built in the GaAs matrix. These clusters are electrically active and can play an important role in the electronic properties of the material.[6]

The spatial distribution of As clusters in conventional LT-GaAs is as a rule random. However, it has been shown that delta doping of LT-GaAs with a Si donor or isovalent In impurities results in formation of two-dimensional cluster sheets.[7–11] An important advantage of In delta doping is that two-dimensional precipitation can be realized even when the LT-GaAs matrix should be independently doped with Si donors or Be acceptors for use in a device structure.[11] In spite of the fact that In delta doping was successfully employed to produce As cluster sheets separated by almost cluster-free GaAs spacers,[9–11] there is an important limitation for engineering of such structures. The limitation is caused by a difference in the coarsening kinetics in two- and three-dimensional cluster systems upon annealing.[12] This difference leads to transformation of the As cluster system to a random rather than to an artificially ordered one, when the LT-GaAs spacers between the In delta layers are too thick. This limitation can be diminished by enhancement of two-dimensional precipitation.

In this letter we propose delta doping with isovalent Sb impurity as an effective precursor for two-dimensional precipitation of excess arsenic in LT-GaAs films.

The LT-GaAs films were grown at 200 °C on semi-insulating 2 in. GaAs(001) substrates in a dual-chamber MBE ''Katun'' system. The films were periodically delta doped with antimony. The As and Sb sources were kept cold, respectively, during the growth of the Sb delta layers and GaAs spacers. The nominal thickness of each Sb delta layer was approximately 1 monolayer (ML). The thickness of the LT-GaAs spacers was varied from 20 to 80 ML. In addition to the samples delta doped with Sb, similar LT-GaAs samples delta doped with In were grown under the same growth conditions. The indium delta layers were produced by interrupting the Ga beam and using an In beam. The nominal thickness of the In delta layers was 1 ML. All the samples were cut into several parts, of which one was kept as grown and the others were annealed under arsenic overpressure at 400, 500, 600, or 700 °C in either the MBE machine or closed ampoules. The annealing duration was varied from 10 to 60 min.

The arsenic excess in the samples was deduced from the near-infrared optical absorption related to arsenic antisite defects.[13] Martin's calibration[14] was used in the evaluation. The concentration of the excess arsenic in all the samples was found to be as high as ~0.5 at. %.

Conventional transmission electron microscope (TEM) and high-resolution electron microscope (HREM) electron microscopies were applied to study the microstructure of the as-grown samples and As precipitation upon annealing. Philips EM 420 and JEOL JEM 4000EX microscopes were exploited. The TEM specimens were prepared by a conven-

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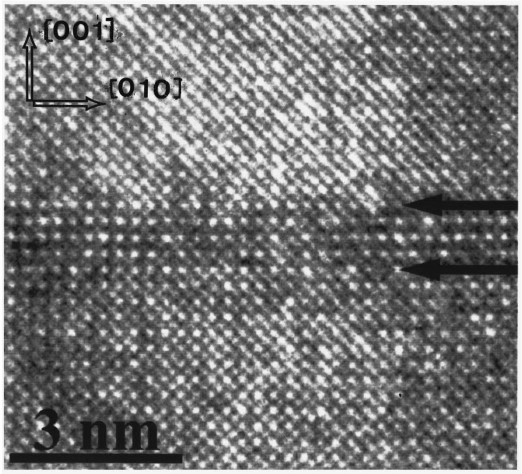

FIG. 1. HREM image along the [100] zone axes of a Sb delta layer in the as-grown LT-GaAs film. The nominal Sb deposit corresponds to approximately 1 ML. The interfaces between the GaAs matrix and Sb-containing layer are arrowed. The Sb-containing layer is seen to occupy 4 ML.

tional Ar^+-ion-milling procedure or by cleaving technique for cross-sectional observations and by wet etching for plan view.

The TEM study of the as-grown LT-GaAs films delta doped with Sb showed a perfect microstructure with no extended defects in spite of the GaSb insertions and high arsenic excess. The Sb delta layers were observed as thin lines of a white contrast in the 002 dark-field (DF) mode. Figure 1 represents a cross-sectional high-resolution electron microscope image of a Sb delta layer in the as-grown film. One can distinguish 4 ML which contain antimony while ~1 ML of Sb was deposited. A similar phenomenon was observed for In delta layers in the LT-GaAs films and was previously attributed[15,16] to the growth surface roughness with nanoscale lateral dimensions.

The postgrowth annealings caused precipitation of the excess As at the isovalent impurity delta layers and in between. Small clusters were revealed at the Sb delta layers after annealing at 400 °C. No clusters were detected at the In delta layers and in the LT-GaAs spacers under the same annealing conditions. When the annealing temperature was elevated to 500 °C, the clusters were observed at both Sb and In delta layers as well as in between. Figure 2 demonstrates

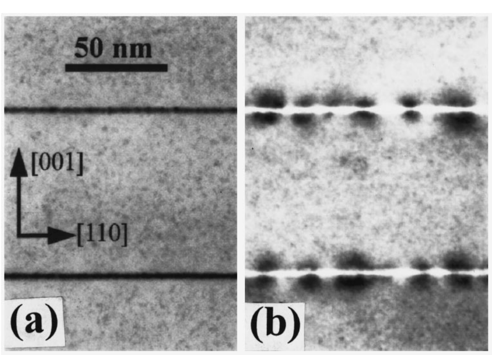

FIG. 2. Cross-sectional 002 DF micrographs taken from the samples delta doped with In (a) or Sb (b) after annealing at 500 °C for 10 min. The In-containing layers exhibit a dark contrast while the Sb delta layers are seen to be white. Note the pronounced strain-induced contrast appeared around the clusters located at the Sb delta layers.

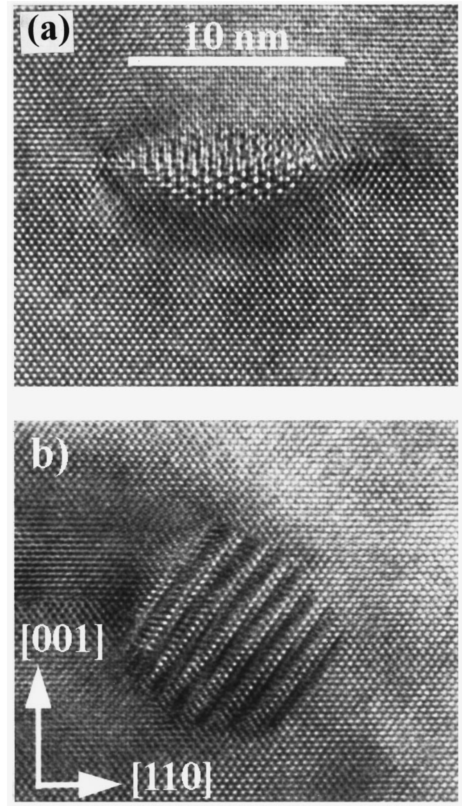

FIG. 3. HREM images of the clusters attached to the Sb delta layers: the lens-shaped cluster at the early formation stage (a) and the cluster with a developed rhombohedral structure exhibiting moiré fringes (b).

cross-sectional TEM images of the films delta doped with In or Sb and annealed at 500 °C for 10 min, both viewed along the [−110] axes with the 002 DF technique. The clusters at the delta layers and between them can be seen in Figs. 2(a) and 2(b). The clusters between the delta layers, i.e., in the LT-GaAs spacers, show a weak contrast due to their small size estimated as 2 nm for both In and Sb delta-doped samples. The clusters at the In delta layers in Fig. 2(a) exhibit a strong dark contrast superimposed on a dark contrast of the In-containing layers. A careful examination yields the mean cluster size to be 3 nm. The clusters at the Sb delta layers are essentially bigger (7 nm) and exhibit a strain-induced contrast [Fig. 2(b)] that does not appear for the clusters at the In delta layers [Fig. 2(a)].

A high-resolution image of a cluster at the Sb delta layer is exemplified by Fig. 3(a) for the sample annealed at 500 °C for 10 min. As seen in Fig. 3(a), the cluster has a lens shape, whereas in the LT-GaAs films, either undoped or delta doped with In, the cluster shape is always close to spherical.[17,18] The cluster microstructure also differs from the rhombohedral one previously observed[17,18] for As clusters in LT-GaAs when the cluster size was greater than 3 nm. The specific cluster microstructure seems to be the reason for the strong local strain in the surrounding matrix [Fig. 2(b)]. When the annealing temperature is elevated, the clusters grow in size. This growth is accompanied by transformation of the cluster shape and microstructure. The fairly big clusters at the Sb delta layers become spherical and rhombohedral, as illustrated by Fig. 3(b).

After annealing at 600 °C for 15 min under As overpressure in the MBE chamber, the average cluster diameter was evaluated as 6 nm for the As precipitates located at the In delta layers, while the clusters attached to the Sb delta layers were found to be as large as 18 nm. This difference in the average cluster diameter means that delta doping with Sb provides much more efficient accumulation of the excess As atoms in the precipitates attached to the delta layers than In delta doping.

The reason for the two-dimensional precipitation of the excess arsenic at indium delta layers is the lower barrier for heterogeneous nucleation than for the homogeneous one.[12] As a result, the clusters observed at the indium delta layers after the initial stage of precipitation are bigger than those in the GaAs spacers. In the case of antimony delta doping, small clusters were observed after annealing at 400 °C. No As clusters were found in between the Sb delta layers. No clusters were also revealed by TEM in the samples delta doped with indium and annealed under the same conditions at 400 °C. After annealing at 500 °C, the clusters at the Sb delta layers are always bigger than those at the In delta layers and much bigger than the clusters in the GaAs spacers. These facts evidence that antimony delta doping provides a lower barrier for nucleation of the arsenic clusters when compared to In delta doping. A reason for the reduced nucleation barrier may be the incorporation of Sb atoms in the nuclei. Another difference between Sb and In delta doping as precursors for two-dimensional precipitation of the excess arsenic is the higher growth rate of the clusters at the Ostwald ripening stage in the former case. While the arsenic clusters in the conventional LT-GaAs and in the LT-GaAs films delta doped with indium produce rather low local strains in the surrounding matrix,[17] the clusters at the Sb delta layers cause strong local strains. These strains should influence the migration of the native point defects (gallium vacancies, arsenic antisite defects, and interstitials) upon annealing and may enhance accumulation of the excess arsenic in the clusters.

In summary, we have employed delta doping with antimony isovalent impurity as a precursor for two-dimensional precipitation of the excess arsenic in GaAs grown by MBE at 200 °C and subsequently annealed at various temperatures. The TEM study of the as-grown samples showed the Sb delta layers to be as thin as 4 ML. No extended defects were observed at the interfaces. The postgrowth anneal caused two-dimensional precipitation of the excess arsenic at the Sb delta layers. Small clusters observed at the Sb delta layers had an unusual lens shape and, probably, a nonrhombohedral microstructure. These clusters induced strong local strains in the surrounding GaAs matrix. After annealing under the same conditions, the clusters at the Sb delta layers were found by TEM to be bigger than those at the In delta layers. Additionally, nucleation of the arsenic clusters at the Sb delta layers occurs at a relatively low annealing temperature. Thus, delta doping with Sb is a more effective precursor for two-dimensional precipitation of the excess As in LT-GaAs as compared with In delta doping.

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