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Two-dimensional arsenic-precipitate structures in GaAs

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A technique is demonstrated to control the incorporation of excess arsenic and subsequent positioning of As clusters with coarsening anneals in AlGaAs/GaAs heterostructures. By growing at low substrate temperatures using molecular beam epitaxy, excess As can be incorporated in GaAs and AlGaAs epilayers. By switching the growth mode at these low substrate temperatures to migration enhanced epitaxy, close to stoichiometric epilayers can be obtained when the As flux is As_4. Upon anneal, the As precipitates form preferentially in the GaAs regions, even if the as-grown GaAs regions were highly-stoichiometric and the as-grown AlGaAs regions contained an excess of As. However, the excess As can be contained in the AlGaAs regions, where it will form clusters with anneal, if thin AlAs As-diffusion barriers clad the AlGaAs regions.

When GaAs or AlGaAs epilayers are grown by molecular beam epitaxy (MBE) at low substrate temperatures, a large excess of As can be incorporated into the structure [1]. This excess As is in the form of As antisites and interstitials that cause an increase in lattice constant of about 0.1% [1,2]. Upon annealing at temperatures of 600°C or above, this excess arsenic will form into clusters [3]. The total energy of these two-phase systems is reduced by an increase in size and hence decrease in density of the clusters, due to the reduction in total precipitate to matrix interfacial area. Such a coarsening process was first described by Ostwald and is referred to as Ostwald ripening [4]. This coarsening of the As clusters is observed with an increase in time or temperature of anneal for GaAs epilayers that contain an excess of As [5].

The As cluster to GaAs matrix interfacial energy is lower than the As cluster to AlGaAs matrix interfacial energy. This difference in interfacial energies influences the As cluster positioning in epilayers containing AlGaAs/GaAs heterojunctions. In AlGaAs/GaAs superlattices the clusters form preferentially in the GaAs well regions [5,6]. (Unless the GaAs well widths are so small that this would result in a higher density of smaller precipitates and higher total interfacial energy than if there were fewer larger precipitates that extend into the AlGaAs barriers.) It would be highly desirable to be able to control the placement of the As clusters such that one could position them in the AlGaAs barriers with the GaAs wells being free of As clusters. Such a structure should exhibit well-defined excitonic features from the GaAs wells, with a large density of charge storage sites available close by on the As clusters in the AlGaAs barriers. A device application of such a multiple quantum well (MQW) structure would be for photorefractive applications [7]. Current MQW structures used for photorefractive device applications have to be proton implanted to provide charge storage sites. This proton implantation results in charge trapping sites in both the GaAs wells and the AlGaAs barriers. A film structure with As clusters in the AlGaAs barriers and highly-stoichiometric GaAs wells results in a separation of the charge storage regions from the exciton regions, thereby allowing one to optimize the charge storage while retaining a large electro-optic effect. In this paper we describe a technique, using a combination of low-temperature MBE and migration enhanced epitaxy (MEE), to obtain such control of the positioning of the As clusters.

Several film structures were grown for this study in a Varian GEN II MBE system. The epilayers were grown on two-inch diameter semi-insulating (100) GaAs substrates. Epilayers were grown using both the dimer As_2 and the tetramer As_4 as the arsenic flux. The As_2 (As_4) to Ga beam equivalent pressure used was 20 (18). Initially a GaAs buffer layer was grown at a normal substrate temperature of 600°C and a growth rate of 1 μm/h. While continuing to grow GaAs, the substrate temperature was lowered to 260°C. This took about 15 min resulting in a 0.25 μm GaAs temperature transition region. This was followed by the growth of quantum well structures. The GaAs wells were grown by MEE. MEE consists of separately supplying the group III and group V atoms to the growing III–V surface [8]. The enhanced migration of the group III atoms on the group-III stabilized surface allows for growth of high quality, and hence highly stoichiometric, GaAs at substrate temperatures down to 200°C. The shutter sequence used for growing the MEE-GaAs well was 1 s of Ga exposure, a 1 s pause, a 1 s As_4 (or As_2) exposure, and a 1 s pause. The $Al_{0.2}Ga_{0.8}As$ barriers were grown at a rate of 1.2 μm/h by MBE and hence have a large excess of As. To keep the excess As in the AlGaAs barriers, they were clad by AlAs layers that were also grown by MEE so as not to contain excess As. (The effectiveness of AlAs as an As diffusion barrier was demonstrated by Yin et al. [9] who used a 20 nm AlAs layer between the n-GaAs channel of a transistor and a 50 nm top GaAs epilayer with excess As. The purpose of the top 50 nm GaAs epilayer with excess As was to

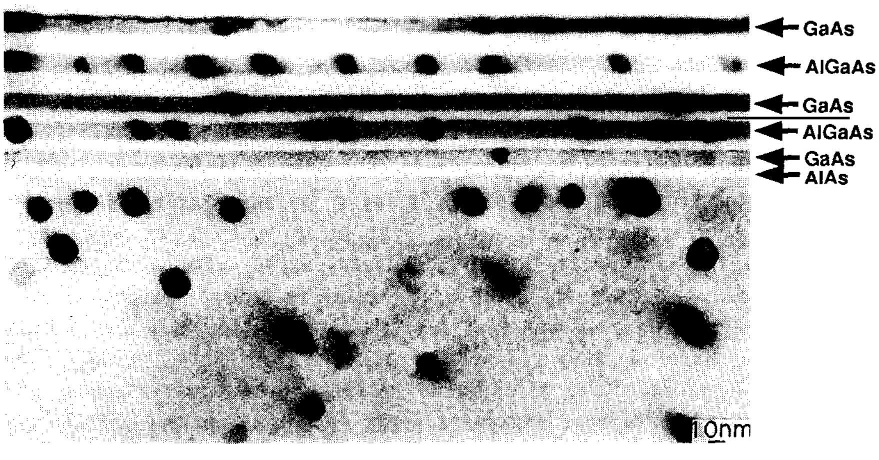

Fig. 1. TEM image of a film structure grown at 260°C using As_4. The bright lines are AlAs layers (the lowest one is marked) and were either 6 or 12 nm thick. The region below the marked AlAs layer is the GaAs temperature transition region. The three GaAs wells in the image are indicated with arrows. The AlAs layers and the GaAs regions between the AlAs layers were grown by MEE and as-grown are highly stoichiometric. The $Al_{0.2}Ga_{0.8}As$ layers were grown by MBE and therefore as-grown have a large excess of As. A 30 s 800°C anneal caused a precipitation of the excess As that remained in the AlGaAs regions due to the AlAs regions acting as As diffusion barriers.

improve the transistor breakdown voltage. In transistor structures without the AlAs As-diffusion barrier, Yin et al. [9] observed complete compensation of the transistors' n-GaAs channels due to diffusion of excess As from the top GaAs epilayer, while no compensation of the channel occurred in structures with the AlAs barrier.) After film growth, the wafers were cleaved and samples annealed for 30 s at temperatures ranging from 600 to 800°C to cause precipitation o the excess As and subsequent coarsening of the As clusters.

The samples were examined by cross-sectional transmission electron microscopy (TEM) using a JEM 2000 EX electron microscope. Shown in fig. 1 is a TEM image of a sample grown using As_4. The GaAs wells and $Al_{0.2}Ga_{0.8}As$ barriers were 10 nm thick with 6 nm (lower region) or 12 nm (upper region) AlAs diffusion barriers. These AlAs layers appear as bright lines in fig. 1. The fig. 1 sample was annealed for 30 s at 800°C. A large density of As clusters is observed in the $Al_{0.2}Ga_{0.8}As$ barriers, while very few are observed in the GaAs wells and no As clusters are observed in the AlAs layers. This is the reverse of what is observed in a GaAs/$Al_{0.2}Ga_{0.8}As$ superlattice grown at low-temperatures by MBE and then annealed as shown in fig. 2. In the fig. 2 image, the As clusters are all located in the GaAs wells with no clusters in the $Al_{0.2}Ga_{0.8}As$ barriers. Therefore, the fig. 1 image confirms that there is very little excess As in the GaAs well regions grown by MEE using As_4 and the 6 nm AlAs cladding layers are an effective As diffusion barrier. Another interesting observation in fig. 1 is that the As clusters in the GaAs temperature transition region are as large as 20 nm in diameter whereas the As clusters in the AlGaAs re-

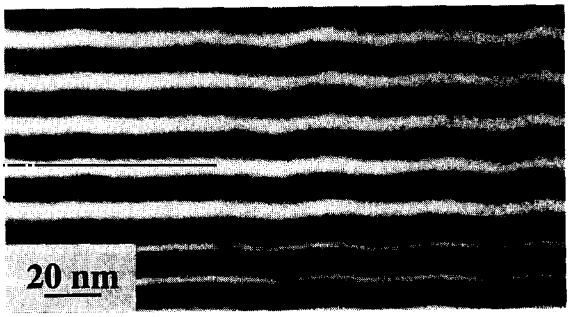

Fig. 2. TEM image of a GaAs/AlGaAs superlattice grown at 250°C by MBE and annealed to cause the excess As to precipitate. The AlGaAs regions appear as bright lines. The As clusters are all located in the GaAs regions due to the lower interfacial energy of an As cluster to GaAs matrix compared to an As cluster to AlGaAs matrix.

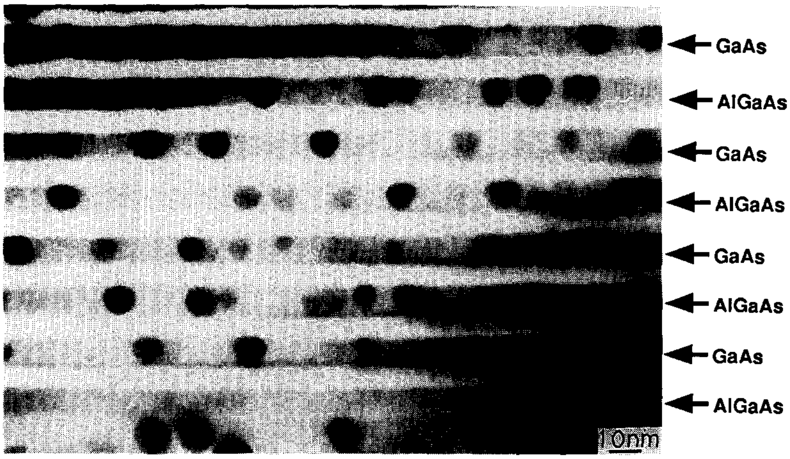

Fig. 3. TEM image of a film structure grown at 260°C using As_2. The bright lines are AlAs layers and were 6 nm thick. The AlAs layers and the GaAs regions between the AlAs layers were grown by MEE. The $Al_{0.2}Ga_{0.8}As$ layers were grown by MBE. A 30 s 700°C anneal was used to cause precipitation of the excess As. As clusters of about the same density are present in the GaAs and $Al_{0.2}Ga_{0.8}As$ layers. Since a 6 nm AlAs layer is an effective barrier to As diffusion, even the as-grown MEE regions contained an excess of As when grown using As_2.

gions are all about 10 nm in diameter. The AlAs layers cladding the $Al_{0.2}Ga_{0.8}As$ layers are constraining the As clusters to a diameter of the width of the $Al_{0.2}Ga_{0.8}As$ layer because a cluster extending into the AlAs cladding layers would result in a substantial increase in interfacial energy. When a structure similar to fig. 1 was grown but with 3 nm AlAs cladding layers, all the As clusters were found in the GaAs well regions with the $Al_{0.2}Ga_{0.8}As$ and AlAs regions free of precipitates. Apparently 3 nm AlAs regions are not sufficiently thick to provide a diffusion barrier to the excess As. A TEM image of a film structure similar to the fig. 1 film, but grown with As_2, is shown in fig. 3. The AlAs layers are all 12 nm thick and appear as bright lines in fig. 3. The AlGaAs and GaAs regions are 10 nm thick. In this film structure there are As clusters of approximately the same densities in both the GaAs and $Al_{0.2}Ga_{0.8}As$ regions. Since we have already seen that 6 nm AlAs layers are efficient As diffusion barriers, the only conclusion is that MEE of the GaAs well regions and AlAs cladding layers using As_2 resulted in substantial incorporation of excess As.

In summary we have shown that one can vary the incorporation of excess As in GaAs and AlGaAs epilayers by growing at low substrate temperatures using As_4 and switching between MBE and MEE modes of growth. Apparently MEE using As_2 results in substantial incorporation of excess As. Upon anneal, the excess As precipitates preferentially in the GaAs regions of AlGaAs/GaAs heterojunctions due to the lower interfacial energy of an As cluster to GaAs matrix than that of an As cluster to AlGaAs matrix. The excess As can be retained in the AlGaAs regions where it will precipitate with anneal if thin AlAs As-diffusion barriers are used to clad the AlGaAs regions.

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