

Formation of arsenic precipitates in GaAs buffer layers grown by molecular beam epitaxy at low substrate temperatures

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We have grown film structures by molecular beam epitaxy which include GaAs buffer layers grown at low substrate temperatures (250 °C). The film structures have been examined using transmission electron microscopy. The layers grown at normal temperatures (600 °C) were free of defects or clusters. In contrast, the layer which was grown at low substrate temperatures contained precipitates which have been identified as hexagonal arsenic. The density of the arsenic precipitates is found to be very sensitive to the substrate temperature during growth.

The growth of GaAs by molecular beam epitaxy (MBE) at low substrate temperatures has recently attracted much attention.¹⁻⁵ These low-temperature buffer layers (LTBLs) are highly resistive and have been shown to virtually eliminate side gating in GaAs integrated circuits.^{1,2} LTBLs have been found to contain an excess of arsenic.⁵ We have used transmission electron microscopy (TEM) to examine film structures grown by MBE which include an LTBL. The layers grown at normal substrate temperatures (600 °C) were found to be free of defects. In contrast the layer grown at low substrate temperatures (250 °C) was found to contain precipitates which have been identified as hexagonal arsenic. The formation of the arsenic precipitates is very sensitive to the growth conditions and post-growth "thermo-history" of the sample. This point is clearly evident from previous lack of observation of arsenic precipitates in as-grown LTBLs and LTBLs which were annealed at 600 °C.⁵ However, several groups have recently reported the observation of arsenic precipitates in LTBLs following growth of a layer at normal substrate temperatures on top of the LTBL or after an anneal following the growth of the LTBL.⁶⁻⁸ In this letter we present the details of the MBE of our LTBLs and TEM analysis of our films.

The film used in this work was grown in a Varian GEN II MBE system on a 2-in.-diam liquid-encapsulated Czochralski GaAs substrate. Some of the details of the film growth have been reported previously.³ However, the thermo-history of the sample plays a key role in the formation of the arsenic precipitates. Therefore, a more detailed description of the film growth will be presented so that the TEM results at various levels of the film structure can be correlated with the growth conditions.

The substrate was degreased, etched in a 60 °C solution of 5:1:1 of H₂SO₄:H₂O₂:H₂O for 1 min and placed in a nonbonded substrate mount. The substrate was outgassed for 2 h at 200 °C in the entry chamber of the MBE, moved to the buffer chamber where it was outgassed for 1 h at

300 °C, and then loaded into the growth chamber. In the growth chamber, the sample was heated to 615 °C for 2 min (the surface oxides desorbed at 580 °C) and then lowered to the initial growth temperature of 600 °C.

The growth rates for all layers were 1 μm/h with a group V to group III beam equivalent pressure of 16. (The arsenic source was the tetramer As₄.) Initially, 0.8 μm of undoped GaAs was grown. Then the substrate temperature was lowered from 600 to 250 °C during the growth of the next 0.25 μm of GaAs. The evolution of the reflection high-energy electron diffraction (RHEED) pattern during this lowering of the substrate temperature has been reported previously.³ After reaching a substrate temperature of 250 °C, 1 μm of undoped GaAs was grown. The substrate temperature was then ramped back to 600 °C during the growth of the next 0.15 μm of GaAs. After attaining the normal growth temperature of 600 °C, an additional 0.85 μm of undoped GaAs was grown. This was followed by the growth of a modulation-doped heterojunction which consisted of a 200 Å Al_{0.3}Ga_{0.7}As spacer layer, an *n*-type 600 Å Al_{0.3}Ga_{0.7}As region, and a 50 Å *n*⁺ GaAs cap. The gallium furnace temperature was lowered during the growth of the last 2000 Å of the GaAs before initiating growth of the Al_{0.3}Ga_{0.7}As spacer layer so that the Al_{0.3}Ga_{0.7}As growth rate would be 1 μm/h. The Al_{0.3}Ga_{0.7}As regions were grown at a substrate temperature of 615 °C.

There was no interruption of the growth process except in the early stages of the GaAs layer grown at a substrate temperature of 600 °C following the growth of the LTBL. The purpose of the growth interruptions (which were of ~15 s in duration) was to see if RHEED oscillations could be observed shortly after completion of the growth of the LTBL. RHEED oscillations were clearly visible indicating a layer-by-layer growth with up to 40 periods being observed after growing as little as 300 Å of GaAs at normal substrate temperatures.

Hall bridges were fabricated and complete electrical characterization of the two-dimensional electron gas (2-deg) has been reported previously.³ In brief, the 2-deg exhibited a carrier density of $5.5 \times 10^{11} \text{ cm}^{-2}$ and mobility of $7800 \text{ cm}^2/\text{V s}$ at a temperature of 300 K and a carrier density of $4 \times 10^{11} \text{ cm}^{-2}$ and mobility of $2.0 \times 10^6 \text{ cm}^2/\text{V s}$ at a temperature of 4.2 K. Only recently have there been reports of higher mobilities in a 2-deg,^{9,11} clearly indicating high quality MBE material can be grown on top of these LTBLs.

For the TEM observation, (011) cross-sectional samples were prepared by Ar ion thinning. A JEM 2000 EX electron microscope with an ultrahigh resolution objective lens pole piece was used. The spherical aberration coefficient of the pole piece is 0.7 mm which yields a point resolution of 2.0 Å. Bright field images of cross-sectional samples showed a large number of small particles in the area corresponding to the LTBL. Figure 1(a) is a bright field image taken from an area including the LTBL, boundaries of which are indicated by arrows. In the image, the small particles appear as dark circular spots with a nearly uniform distribution. Diameters of observed particles range from 20 to 100 Å, and their density is of the order of 10^{17} to 10^{18} cm^{-3} . Despite the existence of a large number of particles, no defects such as dislocation lines or dislocation loops were found in the sample, including the LTBL.

In selected area diffraction patterns taken from the LTBL, weak spots appear near the spots of GaAs as seen in Fig. 1(b). The small particles in the LTBL appear with bright contrast in a dark field image taken by using one of these weak spots. This observation suggests that the small particles have a different crystal structure from that of GaAs and have a certain orientation relationship with the surrounding GaAs crystal. By analyzing diffraction patterns and high-resolution electron microscope (HREM) images, these particles have been identified as elemental arsenic having a hexagonal structure with lattice parameters of $a = 3.760 \text{ Å}$ and $c = 10.548 \text{ Å}$.¹² Weak spots indicated by arrows in Fig. 1(b) correspond to the (102) and (003) planes of the hexagonal structure. In HREM images, clear lattice fringes are observed in the arsenic precipitates which exist in the thinner parts of the sample. Figure 2 is a HREM image showing one arsenic precipitate. The beam direction is in the [011] direction of the GaAs crystal, and the amount of defocusing is about 450 Å. Lattice fringes corresponding to (102) and (003) planes of the hexagonal structure are seen in the precipitates near the edge of the sample. As expected from diffraction patterns, these lattice fringes are nearly parallel to (111) type lattice planes of GaAs. A part of the area in this precipitate shows an amorphous-like image which is believed to be caused by destruction of the arsenic crystal during the ion thinning. In the precipitates existing in the thicker part of the observed area, no lattice fringes of the arsenic crystal are seen due to overlapping of the arsenic and GaAs crystals, which gives rise to Moiré fringes. These HREM images suggest that the shapes of the arsenic precipitates are spherical or ellipsoidal without having any well-defined boundary planes.

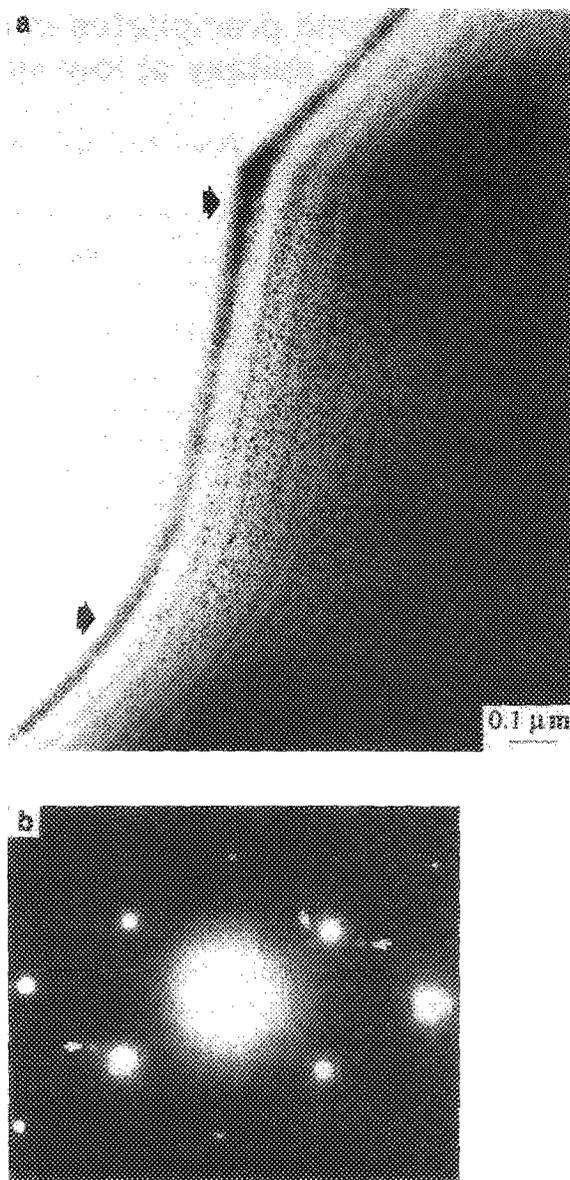


FIG. 1. (a) Bright field image of a cross-sectional sample which includes a LTBL. (b) Electron diffraction pattern taken from the LTBL. Weak spots of arsenic are indicated by arrows.

In earlier TEM studies, the existence of elemental arsenic precipitates were found in annealed arsenic-rich bulk GaAs crystals.^{13,14} Diffraction patterns and HREM images of those arsenic particles are very similar to the ones observed in the present study. There is, however, one important difference. In the annealed bulk GaAs crystals, arsenic precipitates are always observed along dislocation lines or inside dislocation loops, which is explained as a result of preferential nucleation of arsenic precipitates on these defects. In our LTBLs, no such defects are found around the arsenic precipitates. The arsenic precipitates in the LTBLs are surrounded by a perfect GaAs crystal and uniformly distributed.

One interesting feature regarding the distribution of the arsenic precipitates is found in the GaAs layer where the substrate temperature was gradually reduced from 600 to 250 °C over a thickness of 0.25 μm prior to the growth

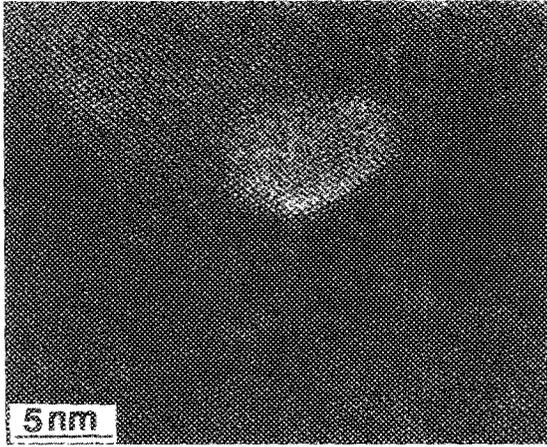


FIG. 2. High-resolution electron microscope image showing one arsenic precipitate in the LTBL.

of the LTBL. Figure 3 is a bright field image taken from this GaAs region. As seen in the image, the density of arsenic precipitates gradually increases towards the LTBL as the substrate temperature was lowered. This observation suggests that the formation of arsenic precipitates occurs even at temperatures considerably higher than the growth temperature of the LTBL (250 °C) and that the density and sizes of the precipitates have a direct correlation with the substrate temperature during the growth of the GaAs.

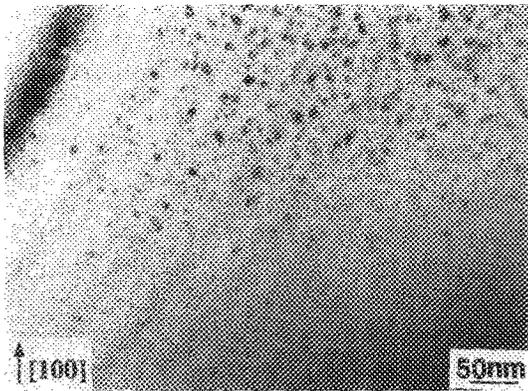


FIG. 3. Bright field image of the boundary region between the LTBL and the lower GaAs buffer layer. The direction of growth, [100], is indicated by an arrow.

The TEM images reported in this letter were of LTBLs which were grown using As_4 . We have recently grown LTBLs using As_2 . We have not investigated the LTBLs which were grown with As_2 by TEM, but indications from the optoelectronic response of the material indicate the presence of As precipitates.¹⁵

In summary, we have observed the formation of arsenic precipitates in GaAs regions which were grown by MBE at low substrate temperatures. For growth at a substrate temperature of 250 °C and an As_4 to Ga beam equivalent pressure of 16, the precipitates were found to range in size from 20 to 100 Å with a density of 10^{17} – 10^{18} cm.⁻³ In earlier TEM studies of LTBLs, arsenic precipitates were not observed.⁵ In order for the arsenic precipitates to condense, growth of a layer at normal substrate temperatures on top of the LTBL or an anneal sometime following the growth of the LTBL is required as has been observed recently by several groups.^{6–8}

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