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1998 Jpn. J. Appl. Phys. 37 L319

(http://iopscience.iop.org/1347-4065/37/3B/L319)

Jpn. J. Appl. Phys. Vol. 37 (1998) pp. L 319–L 321
Part 2, No. 3B, 15 March 1998

Arsenic Precipitate Accumulation in Alternately Si/Be Delta-Doped GaAs Grown by Low-Temperature Molecular Beam Epitaxy

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(Received November 25, 1997; accepted for publication January 26, 1998)

The precipitation of arsenic in alternately [Si]=1.0 × 10^{13} cm^{-2} and [Be]=1.0 × 10^{14} cm^{-2} delta-doped GaAs grown at low temperature by molecular beam epitaxy has been studied using transmission electron microscopy. Following annealing at 600, 700 and 800°C, As precipitates were found to form preferentially not only on planes of Si but also on planes of Be. The as-grown and annealed samples were also characterized using secondary ion mass spectroscopy, and the results revealed that the interdiffusion of Si and Be dopants due to annealing was discernible. This is the first observation of As precipitate accumulation on Be delta-doped planes in low-temperature-grown GaAs.

KEYWORDS: As precipitate, low-temperature-grown GaAs, molecular beam epitaxy, transmission electron microscopy

GaAs and related compounds grown at low temperatures (LT) by molecular beam epitaxy (MBE) have been intensively studied because of their useful properties.[1–6] When grown at 200–300°C, the LT epilayers are highly strained and nonstoichiometric, containing an excess of ~1 at% As which causes a dilated lattice detectable by X-ray diffraction.[1] Upon post-growth annealing at 600–900°C, the excess As forms precipitates and the resulting layer exhibits an extremely high resistivity (>10^6 Ω-cm).[7] This semi-insulating property offers benefits in terms of excellent device isolation in GaAs field-effect transistor circuits,[1,8] and high gate-to-drain breakdown voltage in InAlAs/InGaAs modulation-doped transistors.[9]

The distribution of As precipitates in annealed LT materials can be controlled either by heterostructures or by impurity doping effects. Regarding the former, As precipitates were found to form preferentially inside GaAs regions for AlGaAs/GaAs heterostructures[10] and inside InGaAs regions for InGaAs/GaAs heterostructures.[11] Regarding the latter, As precipitates preferentially accumulate on the Si or In delta-doped planes,[12,13] while As precipitates are depleted from the regions delta-doped with Be or Al.[12,14] For all cases, with an appropriate design of structures and annealing, two-dimensional precipitate arrays can be formed, thus opening up new possibilities for both electronic and optical devices applications. In this letter, we report a different phenomenon of the As precipitation process with respect to the Be doping effect. It was found that with alternate delta doping of Be and Si in LT-GaAs, the As precipitates are accumulated not only on the planes of Si but also on the planes of Be, contrary to the prior reports.[12,14]

The layer structure studied was grown by molecular beam epitaxy on ⟨001⟩-oriented, nominally undoped GaAs substrates and is shown schematically in Fig. 1. All layers were grown under an arsenic-rich condition with an As_4/Ga beam equivalent pressure ratio of 30. First, a 0.3 μm GaAs buffer layer and a 0.23 μm $Al_{0.28}Ga_{0.72}As$ marker layer were successively grown at 600°C to smooth the surface. The growth was then interrupted and the substrate temperature was lowered to 270°C while maintaining the As_4 flux. The LT structure consists of three Si and two Be alternately delta-doped layers which were separated by 20-, 30-, 40-, 50-nm-thick LT-GaAs, and a cap layer of 0.23 μm LT-$Al_{0.28}Ga_{0.72}As$. The growth rates of GaAs and $Al_{0.28}Ga_{0.72}As$ were 1.0 and 1.4 μm/h, respectively. The sheet densities for Si and Be delta-doped layers were 1.0 and 10.0 × 10^{13} cm^{-2}, respectively. After growth, the wafer was cleaved into pieces and annealed for 30 s at 450–800°C by rapid thermal annealing, in forming gas, with a GaAs proximity cap.

The distributions of As precipitates in samples annealed at 600, 700, and 800°C were examined using a high-resolution JEOL JEM-4000EX electron microscope. Cross-sectional samples parallel to {110} planes were prepared by mechanical thinning and Ar-ion milling. Figure 2(a) shows the transmission electron microscopy (TEM) image of the 800°C-annealed sample. Five distinct lines with various densities and sizes of As precipitates are clearly observed in the image, and the rest of the areas are nearly free of As precipitates. Owing to the different contrasts between GaAs and AlGaAs (i.e., the AlGaAs layers appear as bright regions), the locations of

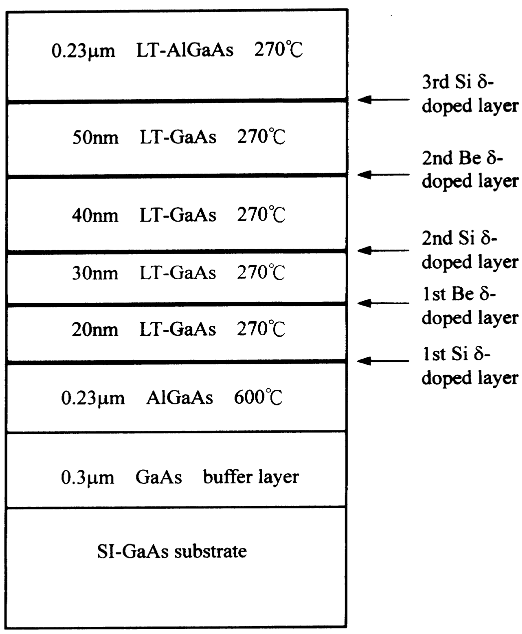
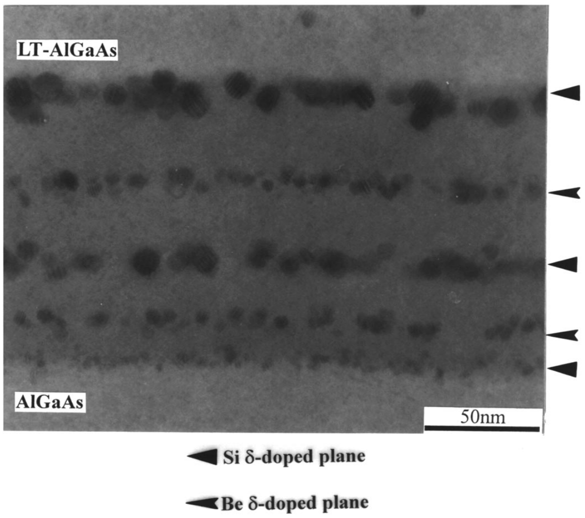
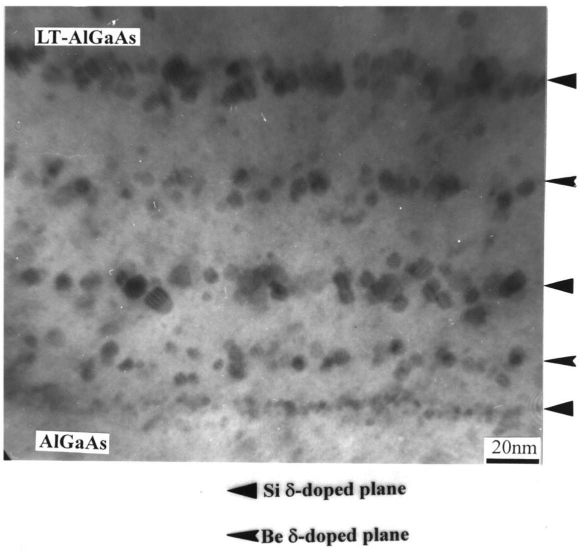


Fig. 1. Schematic structure of alternately Si and Be delta-doped LT GaAs.



(a)



(b)

Fig. 2. TEM images of alternately Si and Be delta-doped LT GaAs annealed at (a) 800°C and (b) 700°C for 30 s.

these As precipitate accumulation lines can be easily identified and are found to coincide with the as-grown positions of the five Si and Be delta-doped planes. The uppermost accumulation line, which is adjacent to LT-AlGaAs and is seen on the third Si delta-doped layer, has the largest size of As precipitates, 10–15 nm in diameter. Two sources of As clusters may contribute to the formation of this line. One is from the top LT-AlGaAs layer and the other is from the LT-GaAs layer just below it due to the preference of excess As coarsening inside GaAs[10] and on Si-doped planes,[12,13] respectively. The center accumulation line of As precipitates, with diameters of 6–11 nm, is located around the second Si delta-doped layer. The formation of As precipitates on this line is attributed to the diffusion of As clusters from the two surrounding LT-GaAs layers toward the second Si delta-doped plane. Since these two LT-GaAs layers have fewer excess As incorporated during growth than the LT-GaAs and LT-AlGaAs layers which surround the uppermost Si delta-doped layer, the As precipitates on the center As accumulation line are smaller and less dense, compared to the topmost line. The bottom accumulation line, which is adjacent to the 600°C-grown AlGaAs layer, consists of the smallest and least distinct of the As precipitates. Although some of the As precipitates on this line are probably due to the residual impurities (possibly C) incorporated during the growth interruption,[15] most As precipitates result from the diffusion of excess As in the overlying LT-GaAs layer toward this line during annealing. In addition to the As accumulation lines on the three Si delta-doped planes, two lines with uniform distribution of As precipitates of 5–7 nm diameter, located on the two Be delta-doped planes, are also observed. As compared to the uppermost and center accumulation lines, these two lines have a lower degree of accumulation and smaller precipitates.

The redistribution of As precipitates in samples annealed at 600 and 700°C also shows the same tendency of accumulation toward Si and Be delta-doped planes. Figure 2(b) shows the TEM image of the sample annealed at 700°C, in which the precipitation of As clusters around the Si and Be doped planes can be clearly seen. However, due to the insufficient forming energy at a low annealing temperature, As precipitates in Fig. 2(b) are smaller and less confined on the Si and Be doped planes, and there exit a few As precipitates between doped planes, as compared to Fig. 2(a). For an even lower annealing temperature of 600°C, As precipitates with an average diameter of 4 nm (TEM image is not shown) distribute uniformly across the whole LT structure, but still exhibit accumulation zones around the Si and Be doped planes. The phenomenon of As precipitate accumulation on the Be delta-doped planes is opposite to previous observations made by Melloch *et al.*[12] and Cheng *et al.*,[14] who found that As precipitates were depleted from the planes doped with Be. The diffusion of a notable amount of Si dopants into the Be-doped planes during annealing was first suspected to be responsible for this observation. To ascertain what dopants actually exist in the Be delta-doped regions after annealing, the samples were examined using secondary ion mass spectroscopy (SIMS). Figure 3 shows the SIMS profiles of Si, Be and As in the sample annealed at the 800°C, in which the As profile was normalized to the value obtained from the GaAs buffer layer. The abnormal intensity enhancement of the As profile within the two AlGaAs layers is due to the much higher ionization rate of As in AlGaAs than in GaAs. Profiles almost identical to those in Fig. 3, within the detection limit, were also obtained for the as-grown sample and for samples annealed at 450, 600, and 700°C. This implies that the diffusion of dopants (both Si and Be) during annealing can be neglected. In fact, as seen in Fig. 3, the relative peak positions of both Si and Be profiles are consistent with our growth parameters. Broadening of the profiles is believed to be caused by the knockout effect during measurement and the background dopants incorporated during growth. However, since the minimum intensities of the Si profile in the LT-GaAs regions appear close to or at the peak positions of the Be profile, it is reasonable to neglect the Si residues and therefore their effects on the As precipitation process in the Be-doped planes. The zones almost completely depleted of precipitates between the doped planes observed in the TEM images (Figs. 2(a) and 2(b)) also support this assumption.

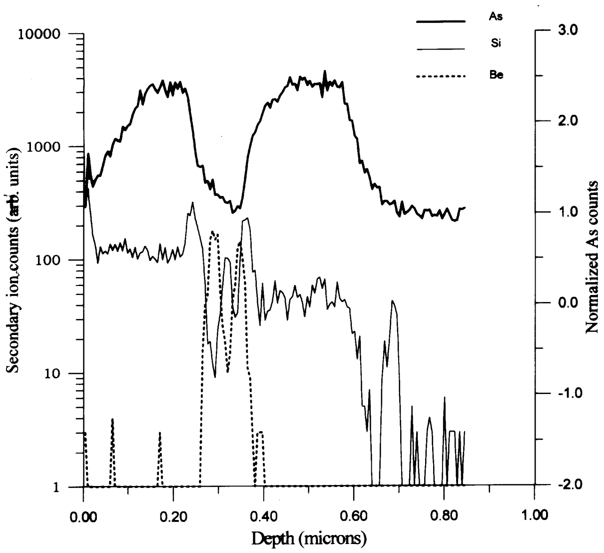


Fig. 3. SIMS profiles of alternately Si and Be delta-doped LT GaAs annealed at 800°C for 30 s.

Several factors have been proposed to explain the As precipitate accumulation or depletion effects in some LT structures. Mahalingam *et al.*[16] suggested that the difference in precipitate/matrix interfacial energies between GaAs and AlGaAs is responsible for the precipitate accumulation/depletion zones in GaAs/AlGaAs heterostructures. From the viewpoint of strain relaxation upon high-temperature annealing, Hsieh *et al.*[17] proposed a vacancy-assisted mechanism to account for the preferential segregation of As clusters in heterostructures and doped materials. The accumulation phenomenon of As precipitates on Be delta-doped planes observed in this work, however, cannot be fully explained by the aforementioned mechanisms. We speculate that the extremely high sheet concentration of Be ($\sim 1.0 \times 10^{14}\,\mathrm{cm}^{-2}$) may be responsible for this. To confirm this assumption, a similar LT structure as shown in Fig. 1, but with the same separation of 50-nm-thick GaAs between doped planes and lower sheet density of $5.0 \times 10^{13}\,\mathrm{cm}^{-2}$ for Be doping, was also grown under otherwise the same growth conditions. The TEM analysis of this sample shows that the accumulation phenomenon of As precipitates on Be doped planes only appears in the 700°C-annealed sample. This result rules out the possibility of a short-range attraction (due to the alternate Si/Be doping) that would allow As precipitates to form on the Be doped planes. It also implies that the ability of As precipitates to accumulate at Be doped planes decreases as the sheet concentration of Be decreases. Regardless of the effect of annealing on the As precipitation process in LT epilayers,[18] there must exist a transition region of Be concentration below which the Be doped planes would deplete As precipitates as expected. Further studies are needed to identify such a transition region of Be concentration and to clarify the underlying mechanism.

In summary, we have investigated the distribution of As precipitates in alternately Si and Be delta doped GaAs grown at low substrate temperatures by MBE. Following 800°C, annealing, two-dimensional As precipitates were found to form not only on the Si but also on the Be delta-doped planes. The accumulation of As precipitates on the Be delta-doped planes is contrary to the results in previous reports. This result shows that the effect of Be doping on the As precipitation process in annealed LT GaAs varies with the Be concentration. Much care is required in controlling the distribution of As precipitates with the use of Be.

This work has been supported by the National Science Council, Republic of China, under Contract No. NSC 87-2112-M-007-014.

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