

Si diffusion and segregation in low-temperature grown GaAs

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Heavily Si-doped ($5 \times 10^{19} \text{ cm}^{-3}$) low-temperature GaAs (LT-GaAs) sandwiched between undoped LT-GaAs layers has been grown by molecular beam epitaxy and annealed to 900 °C. Transmission electron microscopy showed that within the first few minutes of annealing an accumulation of As precipitates formed near each Si-doped/undoped LT-GaAs interface. With further annealing Si segregation to As precipitates was detected with secondary ion mass spectroscopy in the form of delta-like peaks at the As precipitate accumulations. The Si diffusion coefficient was initially concentration independent at a value of $2.5 \times 10^{-13} \text{ cm}^2/\text{s}$, comparable to diffusion under intrinsic conditions in As-rich GaAs grown at normal temperatures. After a 60 min anneal the Si concentration in the As precipitates reached $2.5 \times 10^{20} \text{ cm}^{-3}$.

GaAs or AlGaAs grown by molecular-beam epitaxy (MBE) at substrate temperatures of 200–250 °C contains a quenched-in quantity of As in excess of the bulk equilibrium concentration. This As is incorporated in the lattice as As antisites or interstitials¹ resulting in an expansion of the lattice detectable with x-ray diffraction.² If this low temperature (LT) grown material is subsequently heated above the growth temperature the excess As phase segregates, nucleating homogeneously to form a mixture of GaAs and As precipitates.³ The degree of nonstoichiometry and hence, the resulting precipitate volume, decreases with increasing substrate temperature.⁴

Annealed LT-GaAs and LT-AlGaAs are semi-insulating,⁴ a property that has been exploited to improve device isolation.⁵ The insulating properties can be explained as the result of overlapping depletion regions generated by the Schottky barrier at each precipitate/GaAs interface.⁶ This buried Schottky barrier model also explains the insulating properties of lightly *n*- or *p*-type doped annealed LT-GaAs and why the material becomes conducting when the precipitates coarsen through longer anneals.⁷

An intriguing question is whether very high electron densities might result from the combination of high Si doping and the metastable excess As concentration and subsequent large local As overpressures that might be present in the material. In this letter the results of such an investigation are described. High electrical activation was not obtained but large delta-like spikes in the Si concentration developed at doped/undoped LT-GaAs interfaces.

GaAs epitaxial layers were grown by MBE on semi-insulating GaAs(001) substrates with a growth rate of 1 $\mu\text{m}/\text{h}$ and a group V to group III ratio (beam equivalent pressure) of 22. The arsenic source used was the dimer As₂. The growth consisted of a buffer layer grown at 600 °C followed by 0.2 μm of growth during which the substrate temperature was decreased from 600 to 240 °C for growth of the LT-GaAs. The LT-GaAs structure consisted of a 0.5 μm undoped LT-GaAs layer followed by a 1.0 μm layer of heavily Si-doped LT-GaAs ($5 \times 10^{19} \text{ cm}^{-3}$) with finally a

top 1.0 μm layer of undoped LT-GaAs.

Samples were annealed in an arsine overpressure or in forming gas with a GaAs proximity wafer encapsulant. The material was characterized with Hall measurements, secondary ion mass spectroscopy (SIMS) using a Cs ion beam, and cross-sectional transmission electron microscopy (TEM) using a Philips CM30 at an accelerating voltage of 300 keV.

Figures 1(a) and 1(b) show the Si concentration profiles from SIMS data for a three layer LT-GaAs sample after anneals at 900 °C for 10, 30 (forming gas/GaAs wafer proximity), and 60 min (arsine). After 10 min, the Si diffuses apparently normally but by 30 min it has accumulated in delta-like peaks inside the original doped-undoped LT-GaAs interface. After 60 min the peak heights have saturated to about $5.5 \times 10^{19} \text{ cm}^{-3}$ as the Si continues to otherwise diffuse penetrating well into the undoped LT-GaAs and buffer layers. The Hall data from this sample showed that it had an average *n*-type carrier concentration of $2.0 \times 10^{18} \text{ cm}^{-3}$ at room temperature after the 60 min anneal.

The Si concentration profile after the 10 min anneal can be fitted relatively well with two error functions of the following form:

$$C_{\text{Si}}(x,t) = 2.45 \times 10^{19} \{ \text{erf}[(0.94-x)/2\sqrt{D_1 t}] + \text{erf}[(x-2)/2\sqrt{D_2 t}] \} \text{ cm}^{-3},$$

where D_1 and D_2 are the diffusion coefficients near the top and bottom interfaces, equal to 2.5 and $4.5 \times 10^{-13} \text{ cm}^2/\text{s}$, respectively, and x is depth in units of microns.⁸ The solid line overlaying the 10 min anneal data in Fig. 1(a) is a plot of this expression. Note that the fit is better for the top interface compared to the lower interface closer to the normal GaAs. The use of constant diffusion coefficients means that in the beginning, at least, the Si diffusion coefficient in LT-GaAs is independent of Si doping concentration in the range 2×10^{17} – $5 \times 10^{19} \text{ cm}^{-3}$. The diffusion coefficients obtained are smaller than those reported for Si diffusion in heavily Si-doped regions of bulk GaAs under As-rich conditions ($10^{-12} \text{ cm}^2/\text{s}$) but interestingly comparable to dif-

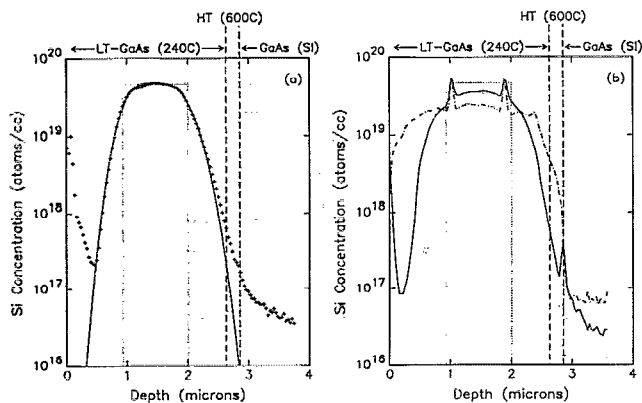


FIG. 1. Si concentration profiles from secondary ion mass spectroscopy data for a three layer low-temperature GaAs sample as a function of anneal time at 900 °C (a) crosses 10 min, (b) solid line 30 min and dot-dashed line 60 min. In both cases the dotted line is the as-grown Si doping profile.

fusion reported for intrinsic conditions ($3 \times 10^{-13} \text{ cm}^2/\text{s}$) at the same anneal temperature.⁹ With increasing anneal time the diffusion profiles adopt a significant concentration dependence as evidenced by the steeper concentration gradient of the 30 and 60 min anneals.^{9,10} Segregation of Si to the precipitates further complicates the analysis.

Figure 2 shows the TEM results from cross sections of the same three layer structure after the 10 and 60 min

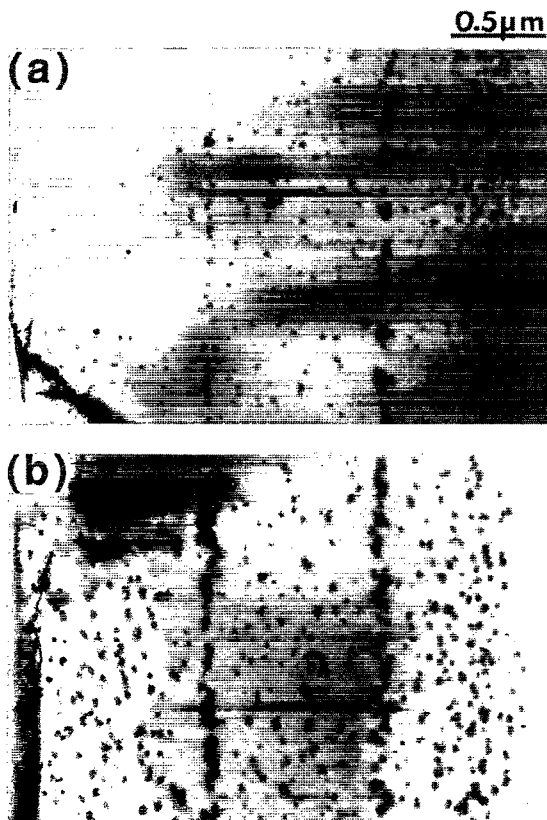


FIG. 2. Transmission electron microscopy in [110] cross section of a three layer low-temperature GaAs sample annealed at 900 °C for (a) 10 min and (b) 60 min. The sample surfaces are on the left side of each micrograph.

anneals. The thickness of the thinned cross sections are not uniform particularly in the case of the 10 min annealed sample, however, it is clearly evident that there is an accumulation of As precipitates near each of the original undoped/doped LT-GaAs interfaces. A comparison with the SIMS profiles shows that the position of the As precipitate accumulation is essentially identical to the position of the Si peaks. However, the As precipitate accumulation from this data certainly occurs within the first 10 min of annealing and probably within the first 30 s long before the Si peaks are detected and significant Si has diffused.

The development of internal Si peaks has not been previously observed in LT-GaAs or GaAs. It can be explained simply as the result of Si segregation to liquid As precipitates. The Ga-As-Si ternary phase diagram at 900 °C shows a two phase equilibrium of liquid As:Si and GaAs:Si.^{9,11} Arsenic precipitate nucleation and growth occurs until the equilibrium As concentration in the GaAs:Si is reached. The final As concentration in the GaAs will be determined by the local Si concentration, and since the solubility of Si in liquid As is higher than in GaAs total equilibrium will be reached only after some Si redistributes to the precipitates. As long as the As precipitates are liquid the rate of this segregation will be determined solely by the Si diffusivity in GaAs. At anneal temperatures below the As melting temperature $< 810 \text{ °C}$ the segregation would also depend on the diffusivity of Si in solid As.

The anneal time after which SIMS would detect an accumulation of Si would depend on the magnitude of the equilibrium concentration difference between the Si in the GaAs and in the precipitates (unknown quantities) as well as on the Si diffusivity. The precipitate spacing in the bulk regions of the LT-GaAs is estimated from the TEM micrographs to be about 170 nm with an As volume fraction of about 3%. In the two planes where accumulation of precipitates has occurred the density is about five times higher corresponding to a spacing of about 110 nm and an As volume fraction of about 15%. Therefore, given the Si peak height of $5.5 \times 10^{19} \text{ cm}^{-3}$ and a background Si concentration of 3.0×10^{19} and $2.0 \times 10^{19} \text{ cm}^{-3}$ after the 30 and 60 min anneals, respectively, the Si concentration in the precipitates was about 2 and $2.5 \times 10^{20} \text{ cm}^{-3}$. The average diffusion length of the Si after 10 and 30 min $x = \sqrt{Dt}$ was about 130 and 230 nm, respectively. Based on these diffusion lengths and the precipitate spacings it is conceivable that 10 min was insufficient to segregate a detectable amount of Si whereas 30 min was adequate.

A second question concerns the initial accumulation of As precipitates near the undoped/doped LT-GaAs interface. This effect has not been previously observed although a preference for precipitation in *n*-type doped LT-GaAs as compared with *p*-type or undoped regions has been reported^{12,13} and similar accumulations of As precipitates have been reported at LT-GaAs/LT-AlGaAs interfaces.¹⁴ There have been two plausible explanations suggested. One explanation is that the accumulation is due to uphill diffusion of As in response to a gradient in its chemical potential.¹⁴ This assumes that the initial As concentration is

uniform, dependent primarily on surface growth kinetics. The second possibility is that the nucleation rate in LT-AlGaAs (undoped LT-GaAs) is lower than in LT-GaAs (*n*-type LT-GaAs).¹⁵ This may result from a difference in the precipitate/matrix interfacial energy. Then, normal diffusion at the interface would initially generate a greater supply of As on the side that nucleated fastest. From the data available it is not possible to determine the relative importance of the two effects.

We have grown thick layers of heavily Si-doped LT-GaAs ($5 \times 10^{19} \text{ cm}^{-3}$) sandwiched between undoped LT-GaAs and studied the diffusion of the Si after anneals at 900 °C. Si diffusion is initially independent of concentration with a diffusion coefficient, $2.5 \times 10^{-13} \text{ cm}^2/\text{s}$, comparable to the diffusivity in intrinsic material. An accumulation of As precipitates is observed at each undoped/heavily Si-doped LT-GaAs interface that form within the first few minutes of annealing. The effect is either due to the uphill diffusion of As point defects, perhaps interstitials, driven by a chemical potential gradient or to a difference in the nucleation rates in undoped and *n*-type material. The Si segregates to the As precipitates reaching concentrations of about $2.5 \times 10^{20} \text{ cm}^{-3}$ as evidenced by the development of delta-like Si peaks at the As precipitate accumulation.

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