ATOMIC STRUCTURE AND NON-ELECTRONIC PROPERTIES OF SEMICONDUCTORS

Indium layers in low-temperature gallium arsenide: structure and how it changes under annealing in the temperature range 500–700 °C

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Transmission electron microscopy is used to study the microstructure of indium δ layers in GaAs(001) grown by molecular beam epitaxy at low temperature (200 °C). This material, referred to as LT-GaAs, contains a high concentration ($\approx 10^{20}$ cm^{-3}) of point defects. It is established that when the material is δ-doped with indium to levels equivalent to 0.5 or 1 monolayer (ML), the roughness of the growth surface leads to the formation of InAs islands with characteristic lateral dimensions <10 nm, which are distributed primarily within four adjacent atomic layers, i.e., the thickness of the indium-containing layer is 1.12 nm. Subsequent annealing, even at relatively low temperatures, leads to significant broadening of the indium-containing layers due to the interdiffusion of In and Ga, which is enhanced by the presence of a high concentration of point defects, particularly V_{Ga}, in LT-GaAs. By measuring the thickness of indium-containing layers annealed at various temperatures, the interdiffusion coefficient is determined to be $D_{\mathrm{In-Ga}} = 5.1\times 10^{-12}\exp(-1.08\ \mathrm{eV}/kT)$ cm^2/s, which is more than an order of magnitude larger than $D_{\mathrm{In-Ga}}$ for stoichiometric GaAs at 700 °C. © *1998 American Institute of Physics.* [S1063-7826(98)00107-0]

INTRODUCTION

Gallium arsenide grown by molecular beam epitaxy (MBE) at low (about 200 °C) temperatures (so-called LT-GaAs) has aroused great interest since it was first described in papers at the end of the 1980's.[1–3] This interest is due to two unique properties of LT-GaAs: high resistivity and very short carrier lifetimes (about 100 fs). As shown in Refs. 2 and 3, these properties are caused by the presence of excess arsenic (of order 1 at. %) in the LT-GaAs host. The excess arsenic forms clusters that incorporate into the GaAs host with practically no defects when the material is annealed at temperatures above 500 °C. The concentration, size, and spatial distribution of these arsenic clusters play a key role in shaping the properties of the material. Usually the concentration and size of the arsenic precipitates are controlled by varying the growth conditions and the annealing temperature of the material. It has been shown[4–6] that the spatial distribution of the clusters can be controlled by introducing thin layers of InGaAs into the LT-GaAs or by isovalently δ doping the latter with indium during low-temperature MBE. During subsequent annealing, the indium-containing layers act as regions which accumulate excess arsenic. This makes it possible to obtain two-dimensional layers of arsenic clusters and to form As/GaAs heterostructures.

It is obvious that annealing not only gives rise to the diffusion and precipitation of excess arsenic, but also to the interdiffusion of indium and gallium, which leads to broadening and spreading of the indium-containing layers and can thus influence how effectively they accumulate arsenic clusters. In addition, on a more global scale, this concentration disordering alters the electronic and optical properties of the material. For this reason, the self-diffusion processes in semiconductor III–V compounds and their solid solutions are a subject of intense investigation (see, for example, the review in Ref. 7). The few papers on diffusion in LT-GaAs have revealed that the huge concentration of point defects in the material, particularly gallium vacancies,[8,9] leads to a decrease in the activation energy for the diffusion of Al[10–12] and to an increase in the diffusion coefficient by one to two orders of magnitude.[9] Unfortunately, there are practically no data on the diffusion of indium in low-temperature GaAs. However, it has been observed[13] in ordinary gallium arsenide near a layer of LT-GaAs, which serves as a source of V_{Ga}, that the activation energy for In-Ga interdiffusion is greatly decreased and that the effective diffusion coefficient in the temperature range $T=700-1000$ °C exceeds that of Al-Ga by one to two orders of magnitude. For this reason, investigation of the behavior of thin layers of InAs in a LT-GaAs host during annealing is a subject of considerable current interest.

This paper describes an investigation of the structure of indium δ layers in LT-GaAs and how it changes during annealing in the temperature range 500–700 °C. This research was performed using transmission electron microscopy (TEM), which has proven to be an effective tool[14,15] for studying interdiffusion at the atomic level.

EXPERIMENT

The experimental samples were grown by MBE in a two-chamber Katun' system on semi-insulating GaAs(001) substrates containing an 85 nm thick buffer layer of stoichiometric undoped gallium arsenide (grown at 600 °C) and a layer of LT-GaAs with a thickness of about 1 μm. The LT-GaAs was grown at a temperature of 200 °C at a rate of 1 μm/h under an As_4 vapor pressure $P=7\times10^{-4}$ Pa. Indium-containing δ layers were created in LT-GaAs by interrupting the Ga flux and depositing indium for 4 or 8 sec, which ensured nominal In layer thicknesses of 0.5 and 1 monolayer (ML), respectively. The distance between δ layers varied from 20 to 60 nm.

The samples grown were divided into four parts, one of which was not subjected to further procedures (the as-grown sample). The other three were annealed in the growth chamber under an arsenic vapor pressure for 15 min, each at a different temperature: 500, 600, or 700 °C.

For the TEM studies a series of samples was prepared in the form of (110) transverse sections using mechanical polishing and a final milling by Ar^+ ions with an energy of 4 keV at grazing angles on a Gatan Duo-Mill 600 machine. In order to minimize the radiation damage, the sample was cooled during the ion sputtering. In addition, a parallel series of samples was prepared in the form of (100) transverse section by cleaving.[16] Two transmission electron microscopes were used in these studies: a JEM4000EX microscope with an accelerating voltage of 400 kV, and an EM420 microscope operating with an accelerating voltage of 100 or 120 kV.

RESULTS AND DISCUSSION

Because strong contrast is needed in imaging epitaxial layers of semiconducting heterostructures with a sphalerite type of lattice, we chose a technique that is widely used for this type of image generation: dark-field electron microscopy using the (002) reflection, whose amplitude is proportional to the difference between the average atomic scattering factors of the A and B sublattices and is highly sensitive to the chemical composition of the material. Figure 1 shows the dark-field image in the (020) reflection of a (100) transverse section of an unannealed sample of LT-GaAs with indium δ layers having a nominal thickness of 0.5 ML.

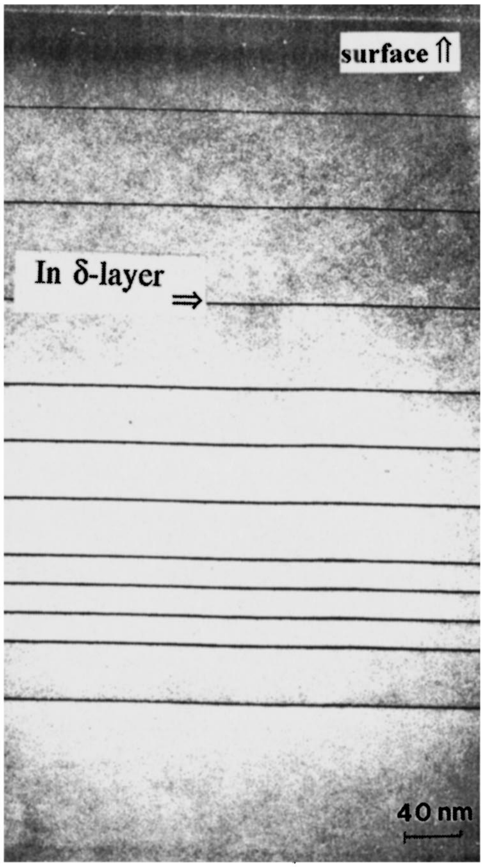

FIG. 1. Dark-field (020) TEM image of a transverse section of a (100) layer of LT-GaAs δ-doped with In to a nominal concentration of 0.5 ML.

Thin layers with dark contrast, whose spatial positions in the structure correspond to the positions of indium δ layers assigned by the growth regime, are clearly observed. The thickness of a δ layer in an unannealed sample measured from this image turns out to equal 1.2 ± 0.1 nm. In order to decrease the possibility of errors arising from the influence of the sample thickness on the contrast of the layer images, we also determined these thicknesses from dark-field images of cleaved samples using the (002) reflection with the sample tilted relative to the axis perpendicular to the growth direction to achieve conditions for two-beam diffraction. This situation is illustrated schematically in Fig. 2a. In this case, the observed thickness of the layer varies with the sample thickness. At thicknesses small compared to the extinction length, the contrast on the layer ceases to depend on thickness; therefore, a value for the layer thickness is obtained by extrapolating the dependence of the measured layer thickness on sample thickness to zero sample thickness (Fig. 2b). The thickness values obtained in this way for indium-containing layers in an unannealed sample equaled 1.1 ± 0.1 nm. Samples were also studied in a high-resolution regime. The thicknesses of indium-containing layers on transverse sec-

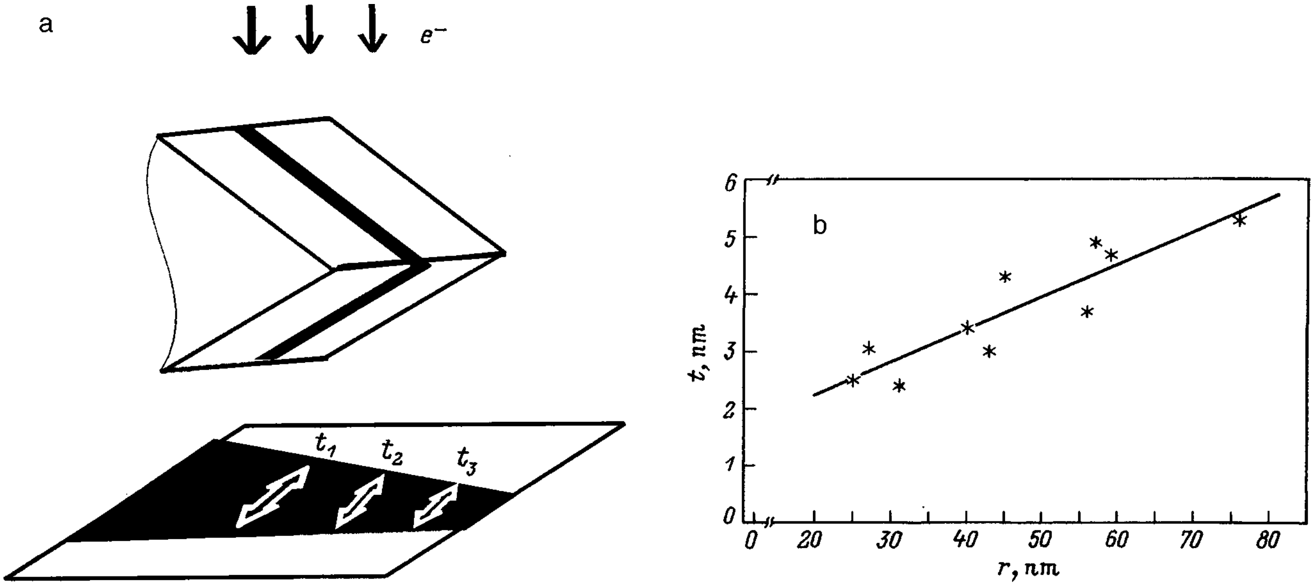

FIG. 2. Schematic representation of the formation of an image in projection along a [100] transverse section of a sample prepared by cleaving (a) and plot of the measured thickness of a layer with a nominal In concentration of 0.5 ML versus the distance to the edge of the sample (b), * — experimental values, straight line — least-squares averaging.

tions of *LT*-GaAs samples were determined from high-resolution [100] zone axis images. Under these conditions an image is formed by four (220) beams and four ''chemically sensitive'' (200) beams. This allowed us to change the relative contributions of the spatial frequencies by choosing the thickness of the portion of the sample being imaged and the degree of defocusing to thereby obtain markedly different images for layers of diverse chemical composition. Figure 3*a* shows a high-resolution image of an unannealed sample of *LT*-GaAs with indium δ layers having a nominal thickness of 0.5 ML and clearly demonstrates that most of the indium atoms are actually distributed in four adjacent (002) atomic planes, i.e., the observed thickness of the indium-containing layer is 4 ML or 1.12 nm.

Analogous studies of an unannealed sample with a nominally deposited amount of indium equivalent to 1 ML show that the real thickness of a δ layer is also 4 ML.

Thus, the deposition of indium during growth in amounts equivalent to 0.5 or 1 ML leads in both cases to the formation of indium-containing layers, whose thickness turns out to equal 4 ML. The spreading of thin layers and interfaces in heteroepitaxial structures observed in the electron microscope is difficult to interpret and is widely discussed in the literature. Even when additional processing of the images is used, as a rule it is not possible to determine unambiguously whether this spreading is a result of interdiffusion or is caused by interface morphologies whose characteristic lateral dimensions are smaller than the sample thickness in the direction of the electron beam, because high-resolution images are in reality projections of the atomic structure averaged over the sample thickness along the direction of the electron beam. Under our conditions, the epitaxial growth temperature is quite low (200 °C), the interdiffusion of Ga and In atoms is very improbable, and the observed broadening of

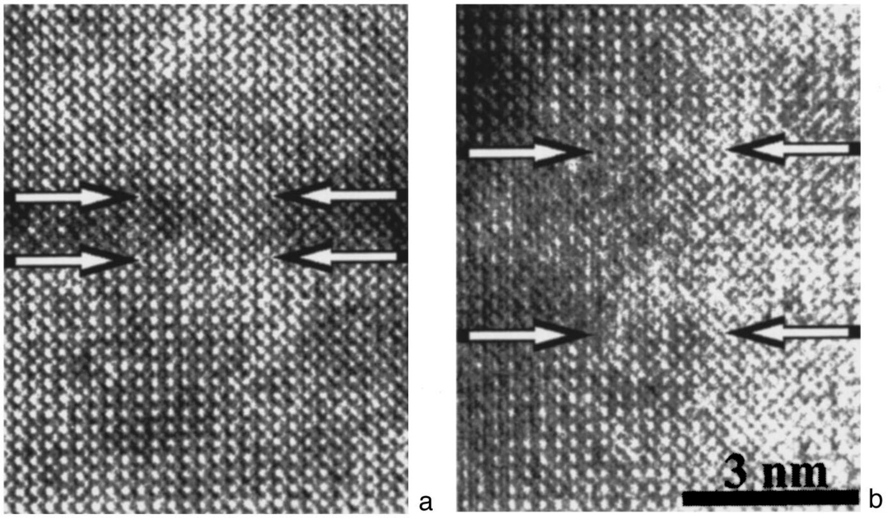

FIG. 3. High-resolution electron photomicrographs of *LT*-GaAs layers along [100] exhibiting layers with a nominal In concentration of 0.5 ML in the following samples: a — unannealed, b — annealed at 600 °C for 15 min. The arrows show the boundaries of the In-containing layer.

the layers must be related to the morphology of the growth front. Additional confirmation of the small role played by interdiffusion in the broadening of the δ layers is provided by the fact that their thicknesses in the two unannealed samples are the same, despite the considerable, twofold, difference between the nominal indium concentrations (1 and 0.5 ML). Step-like interface morphologies with an amplitude of several atomic layers and a characteristic lateral dimension of 1–5 nm along [010] have been observed previously in electron-microscopic studies of transverse sections of GaAlAs/GaAs,[17] GaInAs/AlInAs,[14] and CdHgTe/CdTe[18] heterostructures using the high-resolution technique in projections along [100]. The structures investigated in Refs. 14,17, and 18 were grown by MBE at ordinary temperatures (600–680 °C) on substrates oriented precisely along (001); nevertheless, even under these conditions the growth front can have bumps with heights as large as 4–5 ML, which are not smoothed by interdiffusion, despite the fact that the samples studied in Ref. 14 were additionally annealed at 700–900 °C. Decreasing the epitaxial growth temperature to 200 °C, as we have done in this work, significantly suppresses the migration of deposited atoms over the growth surface, and thus the formation of steps or bumps with a height of several atomic layers at the growth surface is far more natural. From this we conclude that the δ layers probably consist of InAs islands in GaAs, which are distributed primarily within four adjacent atomic layers.

An investigation of the samples annealed for 15 min at 500 °C reveals a considerable increase in the thickness of the δ layers beyond the initial 4 ML. After annealing samples with a nominal indium content of 0.5 and 1 ML, indium is observed in layers 6 ML thick, i.e., 1.7 nm, and 8 ML thick, i.e., 2.24 nm, respectively.

Annealing at 600 °C has the consequence of further increasing the thickness of the indium-containing layers. In Fig. 3b we show a photomicrograph obtained using the high-resolution technique of a sample with a nominal indium content of 0.5 ML. The indium-containing layer occupies 12 ML (3.4 nm). In a sample with a nominal indium content of 1 ML, the experimental thickness comes to 15 ML (4.2 nm).

When the anneal temperature is increased to 700 °C and the δ layers spread further, their visualization in the high-resolution regime turns out to be impossible due to the strong decrease in the indium concentration. The thickness of the δ layers in samples with a nominal indium content of 0.5 ML determined from dark-field (002) images is estimated to be 6 nm. The results of measuring the thickness of the δ layers in samples with nominal indium contents of 0.5 and 1 ML for various anneal temperatures are listed in Table I.

TABLE I. Measured values of the thickness of an indium-containing layer and diffusion constants.

Nominal In content, ML	Thickness of In-containing layer, nm			
	as-grown	500 °C	600 °C	700 °C
0.5	1.1	1.7	3.4	6
1	1.1	2.2	4.2	⋯
Nominal In content, ML	Diffusion coefficient $D_{\mathrm{In-Ga}}$, cm^2/s			
0.5	⋯	3.6×10^{-19}	2.6×10^{-18}	1.2×10^{-17}
1	⋯	6.2×10^{-19}	3.5×10^{-18}	⋯

Thus, in the temperature range 500–700 °C we investigated, LT-GaAs exhibits significant interdiffusion of indium and gallium, which leads to an increase in the thickness of the δ layers and, evidently, spreads the InAs islands into a $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ solid solution. Starting from measured values of the thickness of the indium-containing layers for various anneal temperatures, we can determine the In-Ga interdiffusion coefficient in LT-GaAs. We represent the initial profile of the indium concentration in an unannealed sample as follows:

$$c_{\mathrm{In}}(z)=\frac{c_0}{\sqrt{2\pi}\sigma_0}\exp\left(-\frac{z^2}{2\sigma_0^2}\right), \tag{1}$$

where c_0 is the nominal indium concentration, σ_0 is the standard deviation, and z is the coordinate in the growth direction. In this case the solution to the diffusion equation

$$\frac{\partial}{\partial t}c_{\mathrm{In}}(z,t)=D_{\mathrm{In-Ga}}\frac{\partial^2}{\partial z^2}c_{\mathrm{In}}(z,t) \tag{2}$$

will be a Gaussian, whose standard deviation σ is related to the diffusion coefficient $D_{\mathrm{In-Ga}}$ by

$$2D_{\mathrm{In-Ga}}t=\sigma^2-\sigma_0^2. \tag{3}$$

When experimental values of the layer thickness are used to determine the diffusion coefficient, it is necessary to establish the indium concentration level at which the layer boundary is observed. In order to determine this level we investigated samples of LT-GaAs containing δ layers with various indium concentrations from 0.5 down to 0.006 ML. The (002) dark-field image of such a sample is shown in Fig. 4, from which it is clear that the smallest nominal concentration of InAs in a δ layer that can be reliably measured is 1.8 mole %. Taking into account that the thickness of the δ layer in an unannealed sample is at least 4 ML, the lowest indium concentration that can be detected in a (002) dark-field image is estimated to be 0.5 mole %. Solving Eq. (2) numerically with allowance for the fact that the thickness of an indium-containing layer deduced from electron-microscopic images corresponds to a width of the Gaussian distribution at an absolute level of 0.5 mole % In, we obtain the values of the effective diffusion coefficients for the anneal temperatures used. The effective diffusion coefficients determined in this way for indium in LT-GaAs at 500, 600, and 700 °C are listed in Table I. A plot of the temperature dependence of the effective diffusion coefficient in log ($D_{\mathrm{In-Ga}}$) versus $1/T$ coordinates is shown in Fig. 5. Because the diffusion coefficient depends exponentially on temperature, i.e.,

$$D_{\mathrm{In-Ga}}=D_0\ \exp(-Q/kT), \tag{4}$$

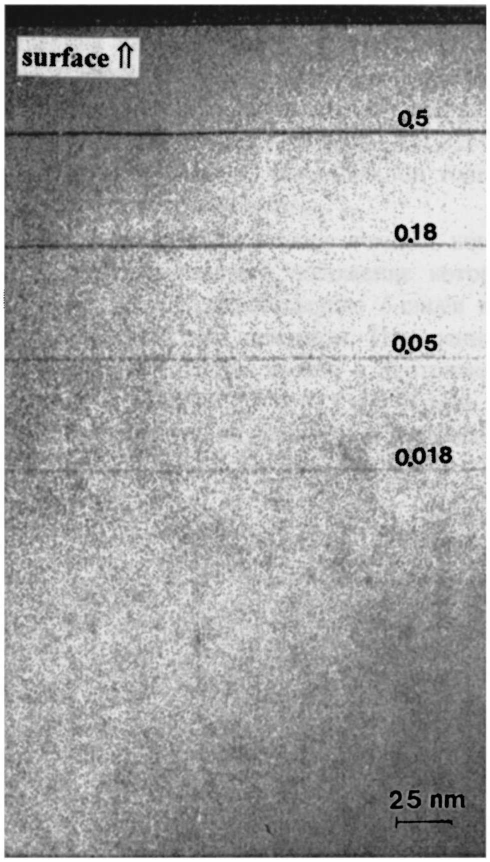

FIG. 4. Dark-field (002) image of a (110) transverse section of a LT-GaAs layer containing In δ layers with various indium contents.

we can use an Arrhenius plot to find the pre-exponential factor D_0 and the effective activation energy for diffusion Q. They turn out to equal 5.1×10^{-12} cm^2/s and 1.1 ± 0.3 eV, respectively.

The activation energy for In-Ga interdiffusion in ordinary gallium arsenide found experimentally in Ref. 13 is 1.9 eV. In the same paper it was shown that the activation energy drops to 1.6 eV when there is an excess concentration of Ga vacancies supplied by a layer of LT-GaAs at a distance of 0.17 μm from the indium-containing layer.

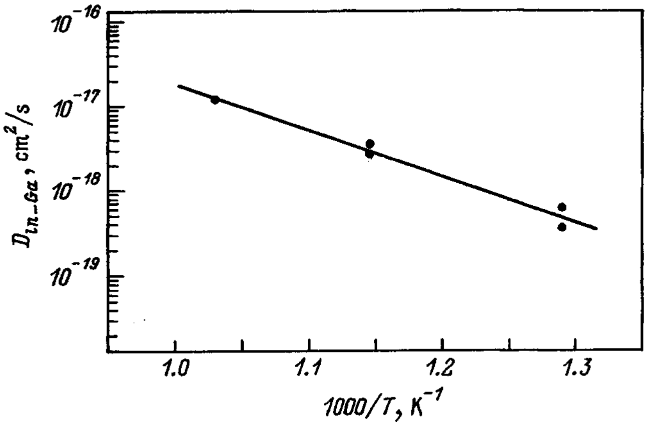

FIG. 5. Plot of the interdiffusion coefficient of In and Ga versus the reciprocal temperature.

The value of the effective activation energy that we obtain is considerably smaller than either of these values. In our view there are two fundamental reasons for this. First, Gebauer *et al.*[19] used experiments involving the annihilation of slow positrons to establish that LT-GaAs grown at 200 °C contains gallium vacancies with a density of $(1-2)\times10^{18}$ cm^{-3}, which exceeds their thermodynamic equilibrium concentration in ordinary GaAs at 600 °C by almost two orders of magnitude. The migration of V_{Ga} should be assumed to play a decisive role in the interdiffusion of In and Ga atoms in LT-GaAs, enhancing it considerably. Unlike Tsang *et al.*,[13] we studied interdiffusion directly in LT-GaAs, where the concentration of V_{Ga} is obviously higher than it is at some distance away. Second, in addition to V_{Ga}, LT-GaAs contains a huge number of other point defects, particularly $\mathrm{As_{Ga}}$, whose concentration reaches 10^{20} cm^{-3} in our samples.[6] The interaction of these defects with gallium vacancies and among themselves can turn out to have a strong influence on the interdiffusion processes. Thus, in Ref. 20 Feng *et al.* established that lowering the growth temperature of LT-GaAs from 400 to 270 °C with a resultant increase in the concentration of point defects in the latter leads to a decrease in the activation energy for the interdiffusion of Al and Ga from 4.15 to 0.39 eV. The samples we investigated were grown at 200 °C and obviously contain close to the maximum concentration of point defects for LT-GaAs, which can result in a low value of the effective activation energy.

CONCLUSION

Our electron-microscopic investigations of LT-GaAs layers grown at 200 °C and δ-doped by indium have revealed that the thickness of the indium-containing layers is 4 ML, i.e., 1.1 nm, regardless of whether the nominal indium content is 0.5 or 1 ML. Because the diffusion of indium from the surface into the bulk of a growing layer is highly improbable at 200 °C, this observation implies that during the MBE of LT-GaAs the growth front has a profile with an amplitude of 4 ML and characteristic lateral dimensions less than 10 nm, and the deposition of indium leads to the formation of InAs islands located in four adjacent atomic layers.

Annealing for 15 min at $T=500-700$ °C gives rise to a considerable broadening of the indium-containing layers from the original thickness due to In-Ga interdiffusion, which is enhanced by the presence of a high concentration of point defects, particularly V_{Ga}, in LT-GaAs. The temperature dependence of the In-Ga interdiffusion coefficient is faithfully described by the expression

$$D_{\mathrm{In-Ga}}=5.1\times10^{-12}\exp(-1.08\ \mathrm{eV}/kT)\ \mathrm{cm^2/s} \tag{5}$$

and turns out to be more than an order of magnitude higher than $D_{\mathrm{In-Ga}}$ for stoichiometric GaAs in the neighborhood of 700 °C.

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