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In–Ga intermixing in low-temperature grown GaAs delta doped with In

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Low-temperature grown GaAs films with indium delta layers are studied by transmission electron microscopy. The delta layers in the as-grown film are found to be as thick as four monolayers (ML) independently of a nominal In deposit of 0.5 or 1 ML, a thickness which reflects the film surface roughness during the low-temperature growth. A pronounced In–Ga intermixing is observed in the films subjected to 500–700 °C isochronal anneals. The In–Ga interdiffusion diffusivity is evaluated. The effective activation energy for In–Ga interdiffusion is found to be 1.1 ± 0.3 eV which is significantly smaller than a value of 1.93 eV for a stoichiometric GaAs. The difference seems to result from a loss of the gallium vacancy supersaturation upon annealing, and is consistent with an annihilation enthalpy of 0.8 eV. [S0003-6951(99)00310-1]

Compositional intermixing in GaAs-based semiconductor heterostructures has been of great interest in the past few years.[1,2] This effect is undesirable for many devices based on the heterostructures where a smooth and abrupt interface is crucial for the device performance. On the other hand, because the interface intermixing alters the electronic and optical properties of the structure it is considered[3] to be a possible technological tool to tune some optoelectronic quantum-well device parameters such as emission wavelength, oscillator strength, and refraction index profile.

Interface intermixing may be enhanced by impurities or point defects. In particular, it should be noted that gallium vacancies are known to mediate diffusion on the group III zinc-blend sublattice. GaAs grown by molecular-beam epitaxy (MBE) at low (200 °C) substrate temperatures (LT-GaAs) is a unique material containing a huge number of intrinsic point defects of which the main are As antisites (up to $10^{20}\,\mathrm{cm}^{-3}$)[4] and Ga vacancies (up to $10^{18}\,\mathrm{cm}^{-3}$).[5] When annealed, the excess As conglomerates to form As precipitates randomly distributed over the film bulk. To produce a spatial ordering of As precipitates, indium-containing insertions were introduced in the growing film in the form of InGaAs wells[6] or In delta layers.[7] Upon subsequent annealing, In–Ga intermixing occurs along with As diffusion and precipitation. This intermixing slurs the interfaces and can influence the As cluster accumulation within the In-containing layers. Previous works[8–13] on the intermixing in low temperature grown AlAs/GaAs superlattices showed an intensive degradation of the interface abruptness and resulted in the Al diffusivity to orders of magnitude greater as compared with that in a similar stoichiometric structure. Little is known, however, on the In–Ga intermixing in LT-GaAs matrix. It has been shown only[14] that the LT-GaAs layer located close to InAs well or InAs/GaAs superlattice in stoichiometric GaAs matrix essentially enhances the In–Ga interdiffusion and decreases the effective activation energy from 1.9 down to 1.6 eV. In this letter, we present results of transmission electron microscopy (TEM) study on the In–Ga intermixing immediately in the LT-GaAs films delta doped with isovalent indium impurity.

The LT-GaAs films were grown in a dual-chamber ''Katun'' MBE system on undoped semi-insulating 2-in. GaAs(001) substrates which were prepared for the growth procedure in the conventional manner. A 85-nm-thick buffer layer of undoped GaAs was grown on the substrate at 580 °C, after which the substrate temperature was lowered down to 200 °C, and an LT-GaAs film was deposited at the growth rate of 1 μm/h under As pressure of 7×10^{-4} Pa. During the growth, indium delta layers were inserted in the film by interrupting the Ga beam and using the In beam instead for 4 or 8 s that produced approximately 0.5 or 1 monolayer (ML) of InAs, accordingly. The distance between the In delta layers was varied from 20 to 60 nm. The samples grown were cleaved into four pieces of which one remained as-grown, while three others were subjected to annealing in MBE chamber under As overpressure for 15 min at three different temperatures: 500, 600, or 700 °C. Plan-view TEM specimens were prepared by wet chemical etching. Cross-sectional samples were prepared by mechanical dimpling followed by Ar ion-beam milling. These TEM samples were studied using Philips EM 420 or JEOL JEM 4000 instruments.

The measurements from 200 DF image have revealed the delta layer in the as-grown sample to be as thick as 1.1 ± 0.1 nm. This value has been evidenced by imaging the sample in high-resolution mode along [010] zone axis. The high resolution electron microscope (HREM) micrograph taken from the as-grown sample with the In deposit equivalent to 0.5 ML in each delta layer is represented by Fig. 1(a)

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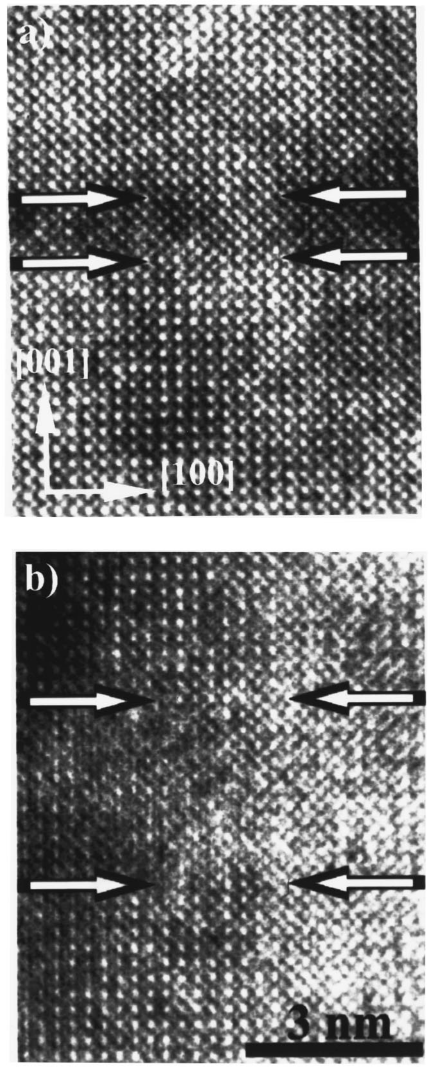

FIG. 1. High-resolution TEM images along [010] direction of as-grown (a) and annealed at 600 °C (b) samples. The boundaries of In-containing layers are arrowed.

and shows the indium-containing layer to occupy 4 ML (1.13 nm). The same thickness of indium-containing layer has been observed when increasing the nominal In content in each delta layer to 1 ML.

Because the depth distribution of the In-rich region is not altered by the In dose, and the film is deposited at low temperature, we attribute the width of the In-containing delta layer to the roughness of the growth surface prior to In deposition. We consider then the In-containing layer to consist mainly of islands dispersed within 4 ML. The lateral size of the In-containing islands can be estimated to be less than 10 nm proceeding from the TEM specimen thickness. This is consistent with the results of recent study of LT-GaAs growth surface by scanning tunneling microscopy.[15]

200 DF TEM and HREM observations of the samples annealed at 500 °C revealed indium containing within 6 ML (i.e., 1.70 nm) for the samples delta doped with In to 0.5 ML. 1 ML of the nominal In deposit resulted in an observed In-containing layer thickness of 8 ML (2.26 nm). The annealing at 600 °C resulted in further thickening of the In-containing layers. Figure 1(b) demonstrates HREM image of the sample with 0.5 ML nominal In deposit after annealing at 600 °C. As

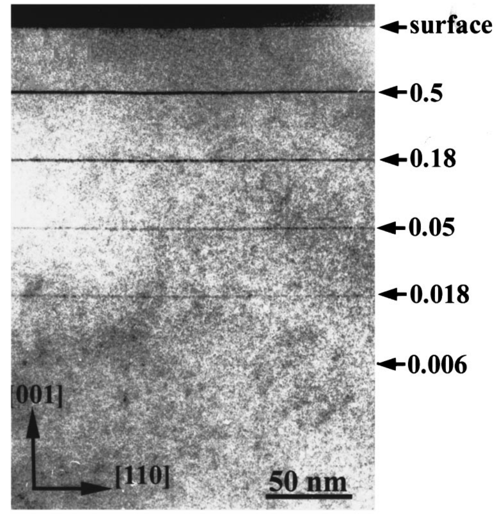

FIG. 2. Cross-sectional TEM micrograph taken in 002 reflection from LT-GaAs sample with various In content in delta layers. Arrows at the right side show the positions of the In delta layers, and the numbers give the nominal In deposit in ML.

can be seen, indium is detected over 12 ML, i.e. 3.39 nm. With increasing nominal In deposit up to 1 ML the In-containing layer begins to occupy 15 ML (4.24 nm).

When the annealing temperature is as high as 700 °C the local indium concentration in the thickening delta layer becomes too low to be detectable in the HREM imaging mode. In addition, the growing As clusters obscure the contrast of the delta layer in the 200 DF image. In this case, the estimated thickness of the In-containing layer for 0.5 ML indium deposit is 6 nm as extracted from the 200 DF image.

The In concentration profile across an In delta layer after the intermixing can be deduced then from the conventional diffusion equation:

$$\frac{\partial}{\partial t} c_{\mathrm{In}}(z,t) = D_{\mathrm{In-Ga}}(T) \frac{\partial^2}{\partial z^2} c_{\mathrm{In}}(z,t), \tag{1}$$

where $c_{\mathrm{In}}(z,t)$ is the In concentration, and $D_{\mathrm{In-Ga}}(T)$ is the In–Ga interdiffusion diffusivity. If we accept that the In distribution in the as-grown sample is described by Gauss error function

$$x(z) = \frac{x_0 d_{002}}{\sqrt{2\pi}\sigma_0} \exp\left(- \frac{z^2}{2\sigma_0^2} \right) \tag{2}$$

[$x(z)$–In mole fraction, x_0–its nominal value, d_{002}–monolayer thickness, i.e., 002 interplanar distance, σ_0–dispersion] the analytical solution of Eq. (1) is also Gaussian with the dispersion σ that is connected with the interdiffusion coefficient as

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

To extract σ from the experimental delta-layer thickness one has to understand what minimum In content is distinguishable from the TEM image; that is at what level of the In concentration the delta-layer thickness has been measured. An as-grown LT-GaAs sample delta doped with In to various nominal content was studied for this purpose. Figure 2 exhibits 002 DF image of the as-grown LT-GaAs film where the nominal In content is reduced from 0.5 ML in the upper

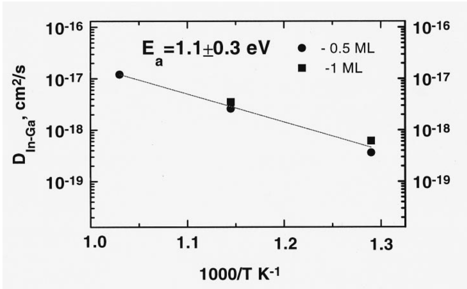

FIG. 3. Arrhenius plot of effective In–Ga interdiffusion diffusivity D_{In-Ga}. The vertical symbol size corresponds to error bar. The activation energy is 1.1 ± 0.3 eV.

delta layer down to 0.006 ML in the bottom one. The last delta layer confidently seen in the image has a nominal In content of 0.018 ML. Taking into account the fact that the delta-layer thickness in the as-grown sample is 4 ML, we estimate the threshold In mole fraction x_{th} to be 0.005. Then σ can be calculated numerically from the measured delta-layer thickness w using the equation

$$\frac{w^2}{8\sigma^2} = \ln\frac{x_0}{x_{th}} - \ln\frac{\sqrt{2\pi}\sigma}{d_{002}}. \tag{4}$$

We calculated the effective In–Ga interdiffusion diffusivity for the temperatures 500, 600, and 700 °C regarding the delta-layer thicknesses measured from 200 DF images as the full width of the In distribution at the level $x_{th} = 0.005$ In mole fraction. Figure 3 shows the Arrhenius plot of the effective interdiffusion diffusivity D_{In-Ga}. The least square fit (straight line in Fig. 3) yields the temperature dependence $D_{In-Ga} = f(T)$ as

$$D_{In-Ga} = 5.1 \times 10^{-12} \exp(-1.08 \ \text{eV/kT}) \ \text{cm}^2/\text{s}. \tag{5}$$

An activation energy of 1.1 ± 0.3 eV is obtained, with the accuracy being determined by the standard deviation of the least square fit taking into account both the dispersion of the experimental points in Fig. 3 and the random error in the delta-layer thickness measurements. For stoichiometric InAs/GaAs, the interdiffusion diffusivity in the temperature range 750–850 °C has an activation energy of 1.93 eV[14] which is close to the reported experimental migration enthalpy for gallium vacancies H_m.[16–18] In our approach we have regarded D_{In-Ga} as a time independent constant despite decreasing V_{Ga} concentration during annealing. In this case, when the annealing duration is long enough to attain the steady state, the obtained activation energy E_d is the difference between the migration enthalpy H_m and the annihilation enthalpy H_a. Accepting a value of 1.9 eV as the migration enthalpy of gallium vacancy H_m, we estimate the annihilation enthalpy for gallium vacancy H_a to be 0.8 eV. This value is similar to that obtained by Lahiri *et al.*,[10] assuming linear diffusion with a time-dependent diffusion coefficient (due to annihilation of V_{Ga} in LT AlAs/GaAs multiple quantum wells).

In conclusion, we have performed a TEM study of low-temperature grown GaAs films with indium delta layers. The delta layers in the as-grown film are found to be as thick as four monolayers independently of a nominal In deposit of 0.5 or 1 ML. The delta-layer width of the as-grown samples reflects the film surface roughness during the low-temperature growth. A pronounced In–Ga intermixing is observed in the films subjected to 500–700 °C isochronal anneals. To find the diffusivity we have defined experimentally the smallest indium content observable in 002 DF mode to be 0.005 mole fraction and regarded the measured In delta-layer thickness as the width of In concentration profile at this level. The In–Ga interdiffusion diffusivity is greater by almost two orders of magnitude than that of a stoichiometric material. The effective activation energy for In–Ga interdiffusion is found to be 1.1 ± 0.3 eV, which is significantly less than the value of 1.93 eV for stoichiometric GaAs. We consider this difference to be due to a loss of the gallium vacancy supersaturation upon annealing that is consistent with an annihilation enthalpy of 0.8 eV.

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