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. © 1999 American Institute of Physics. [S0003-6951(99)00310-1]

Compositional intermixing in GaAs-based semiconductor heterostructures has been of great interest in the past few years. 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 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 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 $10^{20}$ cm$^{-3}$) and Ga vacancies (up to $10^{18}$ cm$^{-3}$). 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 or In delta layers. 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 on the intermixing in low-temperature grown AIAs/GaAs superlattices showed an intensive degradation of the interface abruptness and resulted in the AI 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 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 “Katon” 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 $7 \times 10^{-4}$ 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).
and shows the indium-containing layer to occupy 4 ML ($\sim 1.13$ 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 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:

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

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

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

[x(z)–In mole fraction, $x_0$–its nominal value, $d_{002}$–monolayer thickness, i.e., 002 interplanar distance, $\sigma_0$–dispersion] the analytical solution of Eq. (1) is also Gaussian with the dispersion $\sigma$ that is connected with the interdiffusion coefficient as

$$2D_{\text{In-Ga}}(T)t = \sigma^2 - \sigma_0^2.$$
steady state, the obtained activation energy when the annealing duration is long enough to attain the linear diffusion with a time-dependent diffusion coefficient.

The enthalpy of gallium vacancy $H_m$ can be calculated numerically from the measured 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 $1.1 \pm 0.3$ eV, which is significantly less than the value of 1.9 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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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 deposition 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 $1.1 \pm 0.3$ eV, which is significantly less than the value of 1.9 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.

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

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