Nitrogen-induced suppression of an indium-gallium interdiffusion in $In_xGa_{1-x}As_{1-y}N_y$/GaAs multiple-quantum wells

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In this letter, we present x-ray diffraction (XRD) measurements on as-grown and annealed (In,Ga)As/GaAs and (In,Ga)(As,N)/GaAs multiple-quantum wells grown on GaAs (001) substrates. Concerning the (In,Ga)As material system, we observe a shift of the envelope in the XRD curves of the annealed samples. This shift can be explained by an indium–gallium interdiffusion across the (In,Ga)As/GaAs interfaces. A diffusion model is employed to simulate the envelope shift which yields an activation energy of 0.8 eV. Regarding the XRD curves of the (In,Ga)(As,N) samples, no annealing-induced shift of the envelope is observed. Hence, we conclude that the incorporation of nitrogen suppresses the indium–gallium interdiffusion. Several models are discussed to explain this observation. © *2005 American Institute of Physics*.
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Extensive studies on Ga(As,N) and (In,Ga)(As,N) films are being performed by virtue of their unique properties. The incorporation of small amounts of nitrogen into GaAs and (In,Ga)As leads to a substantial band-gap reduction, allowing to control the band-gap between 1.4 and 0.8 eV.[1] Thus, (In,Ga)(As,N) is a promising candidate to realize laser diodes in the vital telecommunication wavelength range of 1.3–1.55 μm.[2] However, there are severe problems to harness this material system for light-emitting devices. For example, point defects, generated by the nitrogen rf plasma source—may deteriorate the optical properties in these material systems.[3] A post-growth thermal treatment is usually accomplished to heal out these defects in order to improve the optical properties. Concomitantly, the thermal treatment causes structural changes in these material systems.

Even though numerous authors have discussed annealing-induced structural changes in (In,Ga)(As,N)/GaAs quantum well (QW) structures, this issue is still under debate. Several authors claim that a thermal treatment causes an indium-gallium interdiffusion across the interfaces, whereas the nitrogen atom distribution remains unaffected.[4,5] In contrast, other investigations show an annealing-induced nitrogen-arsenic interdiffusion, whereas the indium atom distribution is not altered during the annealing procedure.[6] Moreover, some authors state a combined indium-gallium and nitrogen-arsenic interdiffusion that is induced by the thermal treatment,[7,8] while other studies show neither an indium-gallium nor a nitrogen-arsenic interdiffusion.[9,10] Apart from diffusion processes, the thermal treatment causes a change in the bond configuration in the (In,Ga)(As,N) material system, promoting the formation of indium-nitrogen bonds.[11,12]

In this letter, we investigate annealing-induced structural changes of (In,Ga)As/GaAs and (In,Ga)(As,N)/GaAs multiple-quantum wells (MQWs) by means of x-ray diffraction measurements. Four samples have been investigated. Samples 1 and 2 refer to 10-period (6/12)nm(In,Ga)As/GaAs MQWs, comprising 24% and 36% indium. Samples 3 and 4 denote 10-period (6/12)nm(In,Ga)(As,N)/GaAs MQWs containing 36% indium and 1.5% or 2.8% nitrogen. All samples were grown on GaAs (001) substrates. A low substrate temperature of 450 °C was chosen for the active layers that were grown at growth rates between 0.27 and 0.3 MLs per second. The samples were thermally treated in a rapid thermal annealing (RTA) furnace at various temperatures for 60 s in a nitrogen ambient. XRD measurements were made around the (004) reflection. To simulate the XRD curves, a computer program, based on the dynamical theory and developed at PDI[13] has been employed.

Figure 1 depicts XRD curves of the as-grown and at 800 °C for 60 s annealed (In,Ga)As samples comprising 24% and 36% indium (samples 1 and 2). There is unambiguously a broadening of the satellite peaks and a shift of the envelope —denoted by the arrows —in case of the annealed samples. Both observations can be explained by an indium–gallium interdiffusion across the (In,Ga)As/GaAs interfaces. The broadening can be understood in terms of a diminished QW periodicity, as an indium–gallium interdiffusion results in slightly different indium concentration profiles of each individual (In,Ga)As QW. The shift of the envelope can also be

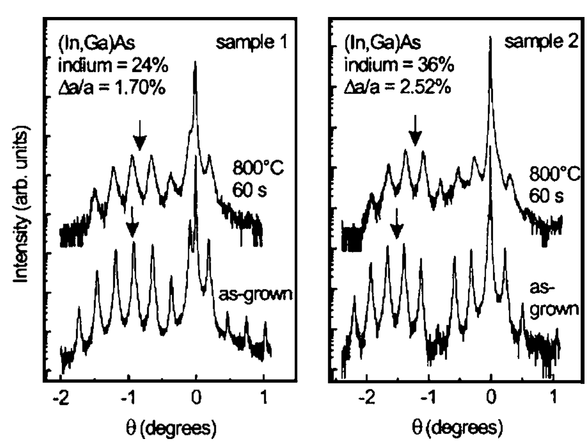

FIG. 1. XRD curves around the (004) reflection of the (In,Ga)As samples comprising 24% and 36% indium (samples 1 and 2). The maxima of the envelope are denoted by the arrows.

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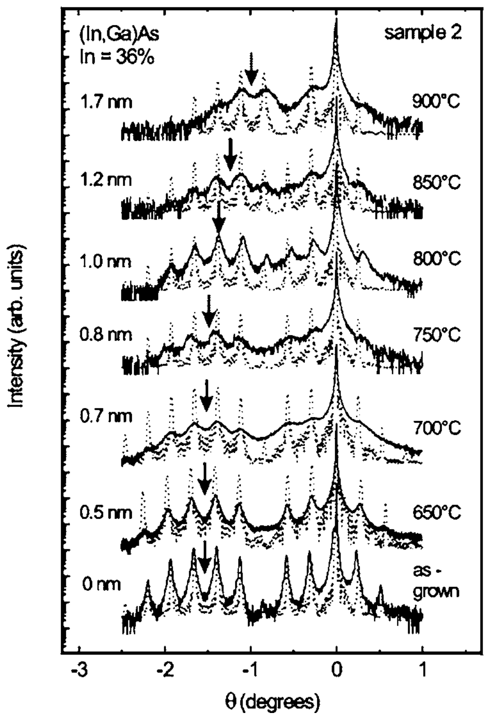

FIG. 2. XRD curves around the (004) reflection of the (In,Ga)As sample with 36% indium (sample 2) annealed at different temperatures for 60 s. The arrows denote the envelope maxima. The dotted lines refer to the computer simulation. The left-hand side number represents the diffusion lengths x_D employed for the simulations.

explained by an indium–gallium interdiffusion across the (In,Ga)As/GaAs interfaces, as the position of the envelope maximum is determined by the mean indium concentration within the (In,Ga)As QWs.[14] Therefore, an indium diffusion into the GaAs barriers and a gallium diffusion into the (In,Ga)As QWs results in a decrease of the mean indium concentration within the (In,Ga)As QWs.

Figure 2 illustrates the annealing-induced shift of the envelope concerning the (In,Ga)As sample with 36% indium (sample 2). Obviously, the shift of the envelope is larger for higher RTA temperatures, indicating a more pronounced indium–gallium interdiffusion. To quantitatively investigate this diffusion process, one has to solve Fick's equation. Assuming that prior to the thermal treatment, the indium concentration profile is rectangular with an indium concentration C_0 inside the QW, one can solve Fick's equation through:

$$C(x,t) = \frac{C_0}{2}\left[\operatorname{erf}\left(\frac{W+2x}{4x_D}\right) + \operatorname{erf}\left(\frac{W-2x}{4x_D}\right)\right], \quad (1)$$

where $C(x,t)$ is the indium concentration profile, $x_D=\sqrt{Dt}$ denotes the diffusion length, D stands for the diffusion coefficient, t is the annealing time, and W represents the width of the (In,Ga)As QW. The diffusion length x_D can be used as a parameter to describe the indium–gallium interdiffusion. An increase of the diffusion length results in a smearing out of the indium concentration profile. To simulate the shift of the XRD envelope, one can load the indium concentration profiles— derived from Eq. (1) into the XRD simulation program. By varying the diffusion length, one can find concordance concerning the envelope maxima of the experimental and simulated XRD curves. The dotted lines in Fig. 2 refer to these simulations. The left-hand side numbers stand for the diffusion lengths that have been employed for the pertinent

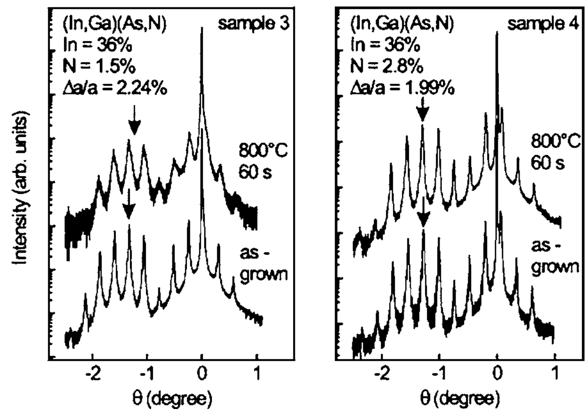

FIG. 3. XRD curves around the (004) reflection of the (In,Ga)(As,N) samples comprising 36% indium as well as 1.5% and 2.8% nitrogen (samples 3 and 4). The maxima of the envelope are denoted by the arrows.

simulated XRD curves. Indeed, higher RTA temperatures require larger diffusion lengths to fit the experimental XRD curves, evidencing an enhanced annealing-induced indium–gallium interdiffusion.

From the XRD simulation, one can now determine an activation energy that describes the indium–gallium interdiffusion. The relation between E_a and D is given by $D = D_0 \exp(-E_a/k_BT)$, whereas D_0 is a constant and k_BT denotes the thermal energy. As the annealing time is constant for all thermal treatments, the diffusion length is proportional to the square root of the diffusion coefficient: $x_D \propto \sqrt{D}$. Hence, from an Arrhenius plot of $\ln(x_D^2)$ with respect to $1/k_BT$, we obtained an activation energy of 0.8 eV (plot is not shown here). This activation energy is lower than the reported literature value of 1.93 eV—determined from photoluminescence studies of (In,Ga)As/GaAs MQWs.[15] However, in the same report the authors state a reduction of the activation energy to 1.63 eV in the presence of gallium vacancies, which mediate the indium–gallium interdiffusion.[16] Hence, one may exemplify the low activation energy obtained in this study by a high gallium vacancy concentration, which may be attributed to the low growth temperature. In fact, indium–gallium interdiffusion studies on low-temperature (In,Ga)As/GaAs MQWs—determined by means of transmission electron microscopy—yielded an activation energy of 1.1 eV,[17] which lies in the same range as the value reported here.

Concerning the (In,Ga)(As,N) material system, Fig. 3 depicts XRD curves of as-grown and at 800 °C for 60 s annealed (In,Ga)(As,N) samples comprising 36% indium and 1.5% or 2.8% nitrogen. Evidently, the shift of the envelope and the broadening of the satellite peaks is less pronounced for the (In,Ga)(As,N) sample with 36% indium and 1.5% nitrogen (sample 3) with respect to the (In,Ga)As sample comprising 36% indium (sample 2). Regarding the (In,Ga)(As,N) sample with 36% indium and 2.8% nitrogen (sample 4), no change between the XRD curves of the as-grown and annealed samples is ascertained. Hence, the incorporation of nitrogen into (In,Ga)As suppresses the annealing-induced indium–gallium interdiffusion.

One may explain the indium-gallium interdiffusion suppression by a strain reduction induced by the incorporation of nitrogen. However, by comparing the XRD curves of the (In,Ga)As sample with 24% (sample 1, $\Delta a/a = 1.70\%$) with the (In,Ga)(As,N) sample comprising 36% indium and 2.8%

nitrogen (sample 4, $\Delta a/a = 1.99\%$), one ascertains that in the less strained (In,Ga)As sample an interdiffusion occurs, whereas in the highly strained (In,Ga)(As,N) sample the interdiffusion is suppressed. Hence, one can rule out the assumption that the nitrogen-induced suppression of the indium-gallium interdiffusion originates from a strain reduction. On the other hand, it is known that nitrogen incorporates into gallium vacancies.[18] Hence, as gallium vacancies mediate the indium–gallium interdiffusion, one may assume that the interdiffusion suppression is caused by the incorporation of nitrogen into gallium vacancies. Another sound conclusion is that the annealing promotes the formation of In–N bonds.[11,12] As the In–N bond energy is much higher with respect to the In–As bond energy (In–N bond $= 1.93$ eV In–As bond $= 1.55$ eV[12]), one may assume that the indium–gallium interdiffusion suppression is a result of an annealing-induced change of the bond configuration. Hence, instead of diffusing out of the QWs, the indium atoms become strongly bonded to nitrogen atoms during the annealing procedure, which consequently leads to an indium-gallium interdiffusion suppression.

To summarize, we have shown that there is an annealing-induced indium–gallium interdiffusion in (In,Ga)As/GaAs MQWs that is more pronounced for higher indium concentrations. We have derived an activation energy of 0.8 eV to describe the indium–gallium interdiffusion. In contrast, we have demonstrated that the incorporation of nitrogen into (In,Ga)As suppresses the annealing-induced indium-gallium interdiffusion. This observation cannot be explained by a strain reduction, but is possibly related to a filling of gallium vacancies by nitrogen or the formation of In–N bonds during the annealing process.

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