Interdiffusion of In and Ga in InGaN quantum wells

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Interdiffusion of In and Ga is observed in InGaN/GaN multiple quantum wells for annealing temperatures of 1300–1400 °C. Hydrostatic pressures of up to 15 kbar were applied to prevent surface decomposition. In as-grown material, x-ray diffraction spectra show InGaN diffraction peaks up to the fourth order. After annealing at 1400 °C for 15 min, only the zero-order peak is observed, as a result of compositional disordering of the quantum well superlattice. Transmission electron microscopy confirms that the superlattice is completely disordered after annealing at 1400 °C for 15 min. © *1998 American Institute of Physics.* [S0003-6951(98)04635-X]

The development of blue light-emitting diodes[1] and laser diodes[2] has focused a great deal of research activity on GaN-based III–V nitrides. The band gaps of $In_xGa_{1-x}N$ alloys cover a wide spectral range, from red (InN) to UV (GaN), making this alloy system ideal for optoelectronic applications.[3] Given the technological importance of $In_xGa_{1-x}N$ alloys, the diffusion characteristics of the host and impurity atoms are of considerable interest. Recently, the self-diffusion of N in GaN isotopic heterostructures was studied, and a self-diffusion enthalpy of 4.1 eV was derived.[4] In this letter, we present evidence of In–Ga interdiffusion in InGaN multiple quantum wells (MQWs).

Compositional disordering of superlattices within the InAlGaAs materials system has been extensively studied.[5,6] The interdiffusion of In and Ga in $In_xGa_{1-x}N$ alloys is complicated by the immiscibility of InN and GaN,[7] which can result in phase separation in thick InGaN layers.[8] It has also been reported that $In_{0.27}Ga_{0.73}N$/GaN MQWs form In-rich InGaN precipitates after annealing at 1100 °C.[9] In this study, we have investigated the diffusion of In and Ga in annealed $In_{0.18}Ga_{0.82}N$/GaN MQW structures. We observe quantum-well disordering, with no phase separation, for annealing temperatures of 1300–1400 °C. The lack of phase separation is consistent with theoretical calculations,[7] which indicate that InN and GaN are completely miscible for temperatures greater than 1250 °C.

The MQW structures were grown by metalorganic chemical vapor deposition. The structures consist of a 1 μm GaN:Mg layer, a 20 period superlattice of 16 Å $In_{0.18}Ga_{0.82}N$ well/64 Å GaN barrier, and a 4 μm GaN:Si layer on a sapphire substrate. The thickness of the well plus barrier was determined by the spacing between satellite peaks in the x-ray diffraction (XRD) spectrum. A barrier-to-well thickness ratio of approximately 4:1 was measured with transmission electron microscopy (TEM). The In concentration in the InGaN quantum wells was determined by Rutherford backscattering spectrometry (RBS) by assuming the absence of In within the GaN barriers.

The samples were annealed at temperatures ranging from 1200 to 1400 °C in a high-pressure furnace. Pressures of up to 15 kbar were applied, with purified N_2 as a pressure-transmitting medium, in order to prevent surface decomposition. Pieces of Mg were placed in the high-pressure furnace near the sample to provide a Mg overpressure during annealing. To ensure quasiequilibrium conditions for high-pressure annealing, GaN powder was placed in the crucible. The temperature was increased from room temperature, at a rate of 1800 °C/h, until it reached a point ~100 °C below the annealing temperature. At that point, the rate was reduced to 1000 °C/h until the annealing temperature was reached. After annealing for 15 min, the temperature was decreased at a rate of 3000 °C/h.

The XRD spectra for the as-grown and annealed material are shown in Fig. 1. In the as-grown spectrum, InGaN(0006) satellite diffraction peaks are observed up to the fourth order. The satellite peaks arise from the periodicity of the quantum-well superlattice. The XRD spectrum for material that was annealed at 1200 °C for 15 min (not shown) is identical to that of the as-grown spectrum. After annealing at a tempera-

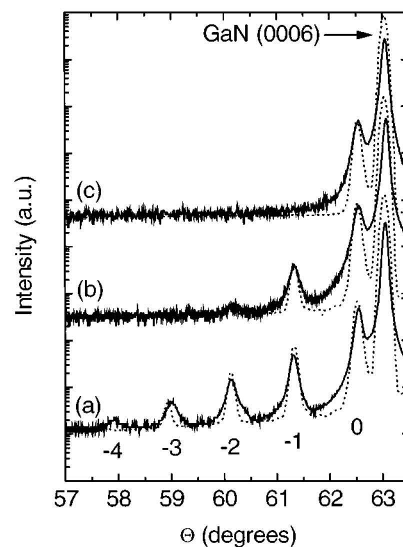

FIG. 1. Experimental (solid lines) and simulated (dotted lines) XRD spectra for the InGaN/GaN MQW structure: (a) as-grown, (b) annealed at 1300 °C for 15 min, and (c) annealed at 1400 °C for 15 min.

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ture of 1300 °C for 15 min, the intensities of the first- and second-order peaks are reduced, and the third- and fourth-order peaks are not detected. The reduction in satellite peak intensity is consistent with interdiffusion of In and Ga in the MQW region, resulting in a broadening of the quantum-well profiles. After annealing at a temperature of 1400 °C for 15 min, only the zero-order peak is observed. The absence of higher-order peaks indicates that, to within the limits of detection, the MQW region is replaced by a uniformly disordered layer of InGaN.

Simulated XRD spectra are shown in Fig. 1 (dotted lines). The simulated spectra were obtained with dynamical diffraction theory, in which the x-ray reflectivity is calculated as a function of depth. The Takagi–Taupin equations[10] were numerically integrated in the MQW region, with initial conditions given by the infinite-crystal solution for GaN. Although the infinite-crystal assumption yields a GaN diffraction peak that is larger than the experiment, the fit to the experimental InGaN peaks is good (Fig. 1). In the as-grown material, the quantum-well profiles were assumed to have a Gaussian line shape:

$$x(z)=\sum_{i=1}^{N} x_0 \exp[-\pi(z-z_i)^2/w^2], \quad (1)$$

where x is the In concentration, z is the distance from the surface, $N=20$ is the number of periods, x_0 is the peak In concentration, and w is approximately the full width at half maximum of a single well. The well positions z_i are given by

$$z_i=L(i+1), \quad (2)$$

where $L=80$ Å is the superlattice period. For simplicity, the c lattice constants were determined by linear interpolation between InN and GaN (Vegard's law), with the assumption of relaxed layers.

A good fit to the XRD spectrum of the as-grown material is obtained with $x_0=0.22$ and $w=16$ Å. The discrepancy between $x_0=0.22$ and the value of $x=0.18$ determined by RBS measurement can be attributed to strain in the InGaN layers.[11] From Fick's law of diffusion, the widths of the quantum wells evolve according to

$$w=\sqrt{w_0^2+4\pi Dt}, \quad (3)$$

where D is the In–Ga interdiffusion coefficient and t is the annealing time. For the material annealed at 1300 °C for $t=15$ min, a fit to the experimental XRD spectrum is obtained with $w=34$ Å [Fig. 1(b)]. Solving Eq. (3) for D yields an In–Ga interdiffusion coefficient of $D=8\times10^{-18}$ cm^2/s. For the material annealed at 1400 °C, a fit to experiment is obtained with $w=80$ Å [Fig. 1(c)], yielding $D=5\times10^{-17}$ cm^2/s. However, since larger values of w yield identical XRD spectra, this value for D should be regarded as a lower bound. In addition, since the dependence of the In–Ga interdiffusion on annealing time has not been studied, the assumption of first-order kinetics [Eq. (3)] may not be valid.

TEM measurements were performed on samples that were first mechanically thinned, then ion milled to electron transparency with low-voltage (3.5 kV) Ar^+ ions on a liquid-nitrogen cold stage to minimize surface damage. Figures 2(a) and 2(b) are bright-field images taken near the [11$\bar{2}$0] zone with $g=(0002)$, in order to maximize the contrast between regions of different composition. The image of the as-grown sample [Fig. 2(a)] shows a contrast between the quantum wells and the barriers. After the sample was annealed at 1400 °C, no well/barrier contrast could be observed in the ''MQW region'' [Fig. 2(b)], consistent with quantum-well disordering. Energy dispersive x-ray chemical analysis in the TEM indicated that indium is present only in the MQW region.

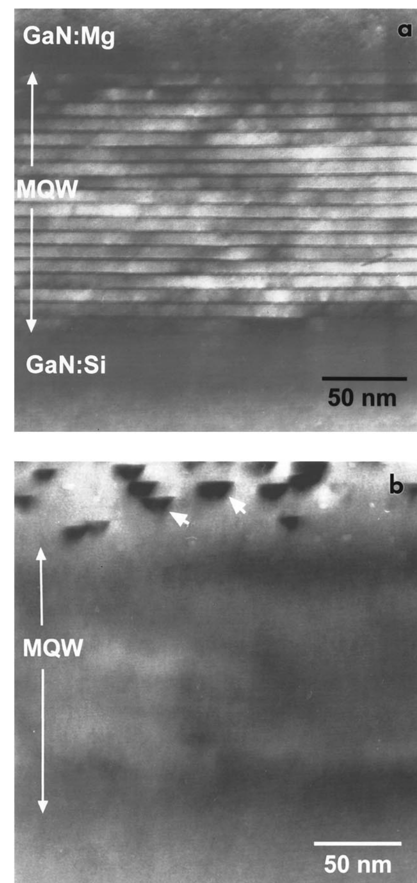

FIG. 2. TEM micrograph of InGaN/GaN MQWs (a) as-grown and (b) annealed at 1400 °C for 15 min. Pyramidal defects are indicated by arrows.

It is noteworthy that the annealed sample exhibited pyramidal defects in the upper GaN:Mg layer, indicated by arrows in Fig. 2(b). These defects were not present in the MQW region or the lower GaN:Si layer. Since similar structures have been observed in hydrogen-implanted GaN after annealing,[12] it is conceivable that hydrogen in the GaN:Mg layer plays a role in their formation.

The In and Mg concentrations were measured as a function of depth with secondary ion mass spectrometry (SIMS). The depth resolution was limited to ~500 Å, due to surface roughness, so that the individual quantum wells are not resolved. Before annealing, the Mg concentration is constant to a depth of 1 μm, after which point it sharply decreases to a level below the detection limit ($\sim10^{16}$ cm^{-3}). After annealing at 1400 °C for 15 min, the Mg diffuses approximately 1 μm (see Fig. 3). Compared to Mg, however, In does not show significant diffusion under these annealing conditions.

It is possible that the diffusion of Mg enhances the interdiffusion of In and Ga in InGaN/GaN MQW's. Silicon and oxygen, which were not measured by SIMS, may also

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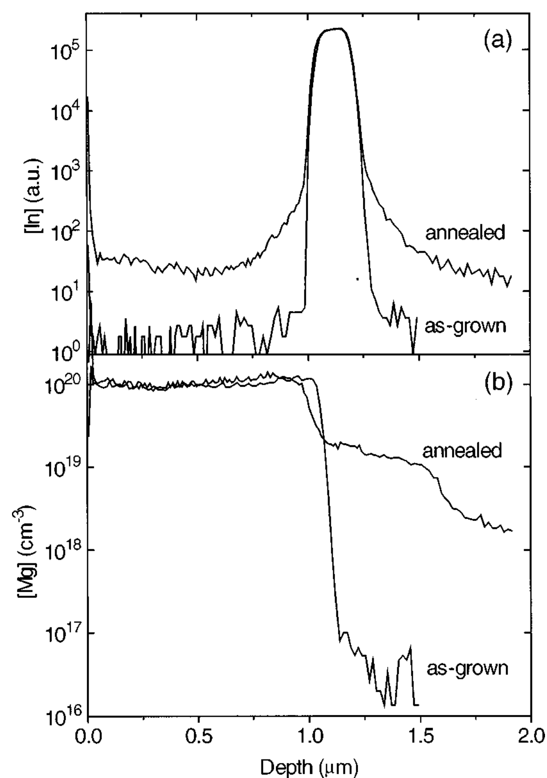

FIG. 3. SIMS profiles for (a) In and (b) Mg concentrations before and after annealing at 1400 °C for 15 min.

diffuse into the active region and affect compositional disordering. Impurity-induced disordering was first observed in Zn-diffused AlAs/GaAs superlattices.[13] In the case of $In_xGa_{1-x}As$/GaAs MQW's with $x=0.15$, significant interdiffusion has been observed at temperatures less than 700 °C.[14] The fact that no interdiffusion is observed in $In_xGa_{1-x}N$/GaN MQW's for temperatures below 1300 °C is a result of the comparatively low rates of diffusion in the III–V nitrides. Although our results are suggestive of impurity-induced disordering, further studies will be required to determine the effect of impurities on the interdiffusion of In and Ga in InGaN.

In conclusion, compositional disordering has been observed in $In_xGa_{1-x}N$/GaN MQW's with $x=0.18$. After annealing at 1400 °C for 15 min, the MQW region is replaced by a homogeneous InGaN layer, which results in a loss of the higher-order XRD diffraction peaks. As in the case of Zn diffusion in AlGaAs, it is conceivable that Mg diffusion enhances In–Ga interdiffusion in InGaN.

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