Improved synthesis of (In,Ga)N/GaN multiple quantum wells by plasma-assisted molecular-beam epitaxy

Oliver Brandt,[a] Yue Jun Sun, Hans-Peter Schönherr, and Klaus H. Ploog
Paul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5-7, D-10117 Berlin, Germany

Patrick Waltereit, Sung-Hwan Lim, and James S. Speck
Materials Department, University of California Santa Barbara, California 93106

(Received 4 March 2003; accepted 5 May 2003)

We present a simple strategy that minimizes the impact of surface segregation of In during the growth of (In,Ga)N/GaN multiple quantum wells by plasma-assisted molecular-beam epitaxy and simultaneously results in abrupt interfaces. The two ingredients of this strategy are (i) the use of a higher substrate temperature than commonly employed, that is, well above the In desorption point and (ii) the use of a modulated stoichiometry, that is, N-rich during growth of the well and Ga-stable during growth of the barrier. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1590428]

The growth of (In,Ga)N films by both molecular-beam epitaxy (MBE) and metalorganic vapor phase epitaxy (MOVPE) has been the subject of numerous investigations. Most of these studies were focused on the fact that (In,Ga)N exhibits a miscibility gap and is thus, from a thermodynamical point of view, subject to spinodal decomposition into InN and GaN.[1] In fact, even in the kinetically restricted environments of MBE[2] and MOVPE,[3] evidence of bulk segregation of In has been reported. The resulting compositional fluctuations within the layer have been demonstrated to have profound consequences for the optical properties of the material.[4]

However, a potentially even more significant phenomenon has been scarcely paid attention to; namely, In surface segregation.[5,6] Recent work of some of the present authors has shown In surface segregation to be unexpectedly strong for the desired metal-stable growth conditions and to severely distort the intended compositional profile of, for example, (In,Ga)N/GaN quantum wells (QWs).[6] This distortion may lead to a strong blueshift (several 100 meV) of the spontaneous emission from the QW as well as to a rather dramatic reduction of the overlap integral. Furthermore, In surface segregation has been found to proceed via a zeroth-order mechanism and thus to limit the In content of the layer to about 15% at a substrate temperature of 580 °C. N-rich conditions suppress In surface segregation to some extent, but inevitably result in a roughening of the growth front, particularly for multilayer structures such as multiple quantum wells (MQWs).

Furthermore, it is intuitively plausible that In surface segregation may not be entirely reproducible from well to well, and may lead thus to fluctuating well widths in a MQW. Indeed, depth-resolved cathodoluminescence measurements have demonstrated a fluctuation in emission energies from well to well, and the linewidth of our MQWs grown under standard conditions is, consequently, larger than that of our corresponding single quantum wells (SQWs) by as much as 20–40 meV.[7] It is noteworthy in this respect that MOVPE-grown (In,Ga)N/GaN MQWs so far exhibited significantly narrower emission linewidths than their MBE counterparts,[8] despite the fact that they are grown at higher temperatures, which are expected to facilitate bulk segregation and thus stronger compositional nonuniformity.

In this letter, we present a simple growth recipe that resolves these conflicts. First, instead of attempting to kinetically counteract In surface segregation by employing a low-growth temperature, we rather encourage it by using a high-growth temperature, well above the In desorption point. This strategy is essentially a different flavor of the *flash off* procedure established for (In,Ga)As/GaAs structures.[9] Second, we employ a modulated stoichiometry (N-rich during growth of the well, Ga-stable during growth of the barrier) to ensure that the individual interfaces are kept abrupt throughout the growth of the multilayer structure. These two remedies combined are implemented here by two groups (PDI and UCSB), using different MBE systems and substrates. The success of our method, and its independence of MBE system and substrate, is demonstrated by high-resolution x-ray diffraction (XRD), cross-sectional transmission electron microscopy (XTEM), and photoluminescence (PL) spectroscopy.

The (In,Ga)N/GaN structures investigated here were grown by plasma-assisted MBE (PAMBE) on either 6H-SiC(0001) substrates (PDI) or on 2-μm GaN/Al_2O_3 templates grown by MOVPE (UCSB). The substrate temperatures given in the following were calibrated by both groups via the visual observation of the melting point of Al (660 °C) attached to the respective substrate.

The PAMBE system employed at the PDI was assembled by VTS-CreaTec, and is equipped with solid-source effusion cells for Ga and In, and an SVT plasma source operating at 300 W. The N_2 flux is controlled by a digital flowmeter, and was set to 1 and 2 sccm for barrier and well growth, corresponding to N-limited growth rates of 500 and 900-nm/h, respectively. The In/Ga flux ratio was approximately 2. A growth interruption of 5 s after each layer is sufficient to stabilize the flux. The growth temperature for the 1-μm GaN buffer was set to 800 °C, and for the MQW to 680 °C.

At UCSB, a Varian GenII™ system is used, which is equipped with twin solid-source effusion cells for Ga and an

[a]Electronic mail: brandt@pdi-berlin.de

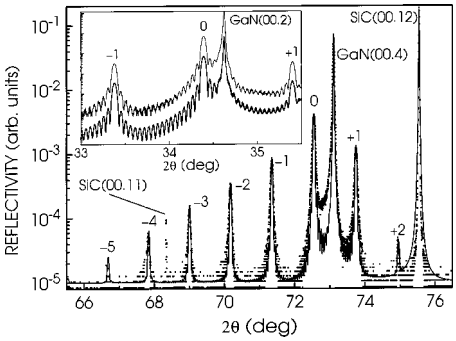

FIG. 1. Experimental (■) and simulated (—) triple-crystal XRD profiles across the symmetric (00.4) reflection for a 20-period (In,Ga)N/GaN MQW on 6H-SiC(0001). The simulation utilizes the kinematically obtained parameters. The inset shows the interference fringes around the zeroth-order satellite for the (00.2) reflection. The thin and thick solid lines represent the experimental and simulated profile, respectively.

EPI Unibulb™ plasma source operating at 150 W and a constant N_2 flux of 0.4 sccm. The In/Ga flux ratio was approximately 1. The Ga flux was switched for barrier and well growth by utilizing the twin Ga cell, yielding growth rates of 140 and 80-nm/h, respectively. The growth temperature for the 50-nm GaN buffer was set to 750 °C, and for the MQW to 620 °C.

Symmetric XRD ω–2θ scans were taken with a Philips X'Pert PRO™ triple-axis diffractometer equipped with a $Cu\,K_{\alpha 1}$ source in the focus of a multilayer x-ray mirror, a four-bounce Ge(022) monochromator in dispersive configuration, and a two-bounce Ge(022) analyzer. The x-ray profiles were analyzed by a modified dynamical diffraction model valid for arbitrary strain. XTEM was carried out in a JEOL2010 microscope operating at 200 kV. PL was excited with the 325-nm line of a He-Cd laser with an excitation density of 1 W/cm^2.

The benefit of a modulated stoichiometry even at comparatively low temperature (580 °C) can be most clearly seen in Ref. 10. The atomic force micrograph of an (In,Ga)N/GaN MQW shown there exhibits clearly resolved atomic steps and a peak-to-valley roughness of 7-nm, similar to state-of-the-art GaN layers grown by PAMBE. The modulated stoichiometry is thus quite effective in maintaining a smooth growth front, resulting in structurally abrupt interfaces. The higher temperature used in the present work furthermore minimizes the impact of In surface segregation, as will be shown subsequently.

Figure 1 displays the experimental and simulated[11] triple-crystal XRD profiles for a 20-period (In,Ga)N/GaN MQW grown on 6H-SiC(0001) under the conditions specified in the experimental section. The (0004) reflection is more sensitive to deviations from the intended compositional profile,[12] whereas the (0002) reflection, shown in the inset, can be measured with the highest angular resolution by our setup. Evidently, the interface quality of this MQW is high:[13] superlattice satellites up to the fifth order as well as pronounced interference fringes (cf. inset) are observed. Moreover, the kinematically obtained parameters[11] (1.86-nm $In_{0.211}Ga_{0.789}N$ wells separated by 7.31-nm GaN barriers) yield an excellent fit of the experimental data, as shown in Fig. 1 for both the (0002) and (0004) reflections. Any deviation from these values degrades the fit. In particular, a simulation with our previous maximum value[6] for the In content of 15% and a resulting well width of 2.61-nm results in higher-order satellites that are systematically *lower* in reflectivity than the experimental ones, which is physically impossible. This finding shows that the synthesis of (In,Ga)N/GaN wells without having to pay attention to In surface segregation is indeed feasible.

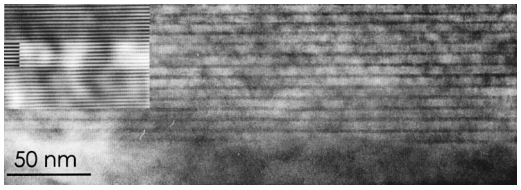

FIG. 2. Bright-field XTEM micrograph of a 20-period (In,Ga)N/GaN MQW on GaN/Al_2O_3. The scale is indicated. The inset shows a Fourier-filtered high-resolution micrograph of one of the wells. The (0001) lattice planes belonging to the well are highlighted.

For structures with a shorter period, XRD is not sufficiently sensitive to detect deviations from the intended compositional profile.[12] In this case, XTEM is the only technique that will help in deciding if In surface segregation occurred, and distorted the nominal compositional profile. Figure 2 shows a micrograph of a 20-period (In,Ga)N/GaN MQW grown on $GaN/Al_2O_3(0001)$. Although the image suffers from preparation-induced inhomogeneities, it is clear that the (In,Ga)N wells are well defined and straight, even over a rather large area. Most important, however, is the high-resolution micrograph shown in the inset of Fig. 2, which demonstrates that the well thickness indeed corresponds to that obtained by a kinematical analysis of XRD profiles from this sample, namely, 1.85-nm $In_{0.175}Ga_{0.825}N$ wells separated by 4.6-nm GaN barriers [seven monolayer (ML), as counted for the well, correspond to 1.82-nm].

The consequences of our altered growth procedure also manifest themselves in the optical properties of the structures. Figure 3 shows the PL spectra of both the PDI and UCSB samples at 5 K. Both structures emit in the blue wavelength range, and the spectral width of this emission compares favorably to the best values reported in the literature for the same emission energy, regardless of the growth technique.[8,14] The emission from both structures is, in fact, narrower than that from our SWQs grown at lower temperature.[7] In this context, it is interesting to compare both the measured emission energies and the widths to those of theoretical predictions.

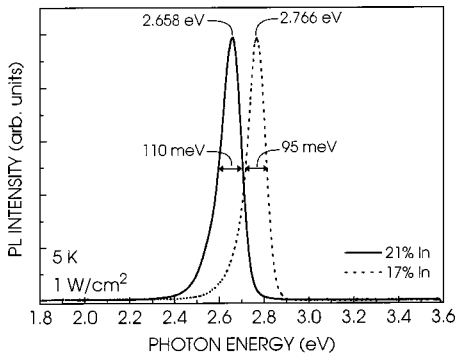

FIG. 3. PL spectra of the two 20-period (In,Ga)N/GaN MQWs on 6H-SiC(0001) and on $GaN/Al_2O_3(0001)$.

Concerning the emission energy, self-consistent Schrödinger–Poisson calculations[15] using the structural parameters deduced from XRD return interband transition energies of 2.729 eV (21% In) and 2.876 eV (17.5%), that is, about 70 and 110 meV *higher* than experimentally observed, respectively. This finding is expected (since the calculation neglects excitonic effects as well as localization) but is in striking contrast to our previous one, where the calculated transition energies were always substantially (100 meV and more) *lower* than the experimental ones.[6] This result thus further attests to the virtual absence of distortions of the intended compositional profiles by In surface segregation.

Concerning the width of the PL bands, Mayrock *et al.*[16] have calculated the variation of the center-of mass potential (which is an upper bound for the PL linewidth) of a 2-nm-thick $In_{0.2}Ga_{0.8}N$/GaN SQW, with the well being assumed to be a perfect random alloy and an interface roughness of ± 1 ML. According to this calculation, pure alloy broadening in field-free $In_{0.2}Ga_{0.8}N$ results in a potential variation of 90 meV. More recent work has arrived at values for the PL linewidth of perfect random alloys of 70 meV[17] and 80 meV[18] at an In content of 20%, demonstrating that alloy broadening in (In,Ga)N is indeed at least one order of magnitude stronger than in conventional III-V alloys. The linewidths obtained in a QW, however, depend additionally on the correlation length of the interface roughness as well as on the internal electrostatic field within the QW. Atomic force micrographs taken from our samples show terrace sizes on the order of 50–100-nm; that is, the correlation length is significantly larger than the exciton Bohr radius. The electrostatic fields are obtained from the self-consistent Schrödinger–Poisson calculations, yielding values of 2.1 and 3.0 M/cm in the samples with In contents of 17.5% and 21%, respectively. The theoretically predicted potential variations in these samples are 120 and 140 meV, respectively. The PL linewidths measured in the present work of 95 and 110 meV thus do evidence abrupt interfaces and an excellent well-to-well homogeneity, and also demonstrate that excessive clustering does not take place, despite the high-growth temperatures employed. Indeed, we believe that compositional inhomogeneities in (In,Ga)N are largely driven by In surface segregation, since the bulk diffusivity of In is too low to account for the commonly observed degree of clustering. Avoiding In surface segregation may thus also kinetically restrict the phase separation in (In,Ga)N.

We are indebted to Achim Trampert for his help with the high-resolution XTEM micrograph.

[1] M. Ferhat and F. Bechstedt, Phys. Rev. B **65**, 075213 (2002), and references therein.
[2] D. Doppalapudi, S. N. Basu, K. F. Ludwig, Jr., and T. D. Moustakas, J. Appl. Phys. **84**, 1389 (1998).
[3] N. A. El-Masry, E. L. Piner, S. X. Liu, and S. M. Bedair, Appl. Phys. Lett. **72**, 40 (1998).
[4] S. Chichibu, K. Wada, and S. Nakamura, Appl. Phys. Lett. **71**, 2346 (1997); Y. Narukawa, Y. Kawakami, S. Fujita, S. Fujita, and S. Nakamura, Phys. Rev. B **55**, R1938 (1997); P. Waltereit, O. Brandt, J. Ringling, and K. H. Ploog, *ibid.* **64**, 245305 (2001); S. Dhar, U. Jahn, O. Brandt, P. Waltereit, and K. H. Ploog, Appl. Phys. Lett. **81**, 673 (2002).
[5] O. Mayrock, H.-J. Wünsche, and F. Henneberger, Phys. Rev. B **62**, 16870 (2000).
[6] P. Waltereit, O. Brandt, K. H. Ploog, M. A. Tagliente, and L. Tapfer, Phys. Rev. B **66**, 165322 (2002).
[7] U. Jahn, O. Brandt, and K. H. Ploog (unpublished).
[8] H. Kollmer, J. S. Kim, S. Heppel, J. Off, F. Scholz, and A. Hangleiter, Appl. Phys. Lett. **74**, 82 (1999); E. Berkowicz, D. Gershoni, G. Bahir, E. Lakin, D. Shilo, E. Zolotoyabko, A. C. Abara, S. P. Denbaars, and L. A. Coldren, Phys. Rev. B **61**, 10994 (2000).
[9] O. Brandt, K. Ploog, L. Tapfer, M. Hohenstein, R. Bierwolf, and F. Phillipp, Phys. Rev. B **45**, 8443 (1992).
[10] P. Waltereit, M. D. Craven, S. P. DenBaars, and J. S. Speck, J. Appl. Phys. **92**, 456 (2002).
[11] O. Brandt, P. Waltereit, and K. Ploog, J. Phys. D **35**, 577 (2002).
[12] O. Brandt, P. Waltereit, S. Dhar, U. Jahn, Y. J. Sun, A. Trampert, K. H. Ploog, M. A. Tagliente, and L. Tapfer, J. Vac. Sci. Technol. B **20**, 1626 (2002).
[13] P. F. Fewster, N. L. Andrews, O. H. Hughes, C. Staddon, C. T. Foxon, A. Bell, T. S. Cheng, T. Wang, S. Sakai, K. Jacobs, and I. Moerman, J. Vac. Sci. Technol. B **18**, 2300 (2000).
[14] K. P. O'Donnell, H. Kalt, T. Breitkopf, W. Van der Stricht, I. Moerman, P. Demeester, and P. G. Middleton, Appl. Phys. Lett. **70**, 1843 (1997); B. Damilano, N. Grandjean, J. Massies, L. Siozade, and J. Leymarie, *ibid.* **77**, 1268 (2000); X. Q. Shen, T. Ide, M. Shimizu, and H. Okumura, J. Appl. Phys. **89**, 5731 (2001); H.-K. Yuh, E. Yoon, S. K. Shee, J. B. Lam, C. K. Choi, G. H. Gainer, G. H. Park, S. J. Hwang, and J. J. Song, *ibid.* **91**, 3483 (2002); S. Pereira, E. Pereira, E. Alves, N. P. Barradas, K. P. O'Donnell, C. Liu, C. J. Deatcher, and I. M. Watson, Appl. Phys. Lett. **81**, 2950 (2002).
[15] We used the same procedure and parameters as outlined in Refs. 5 and 6, except for taking into account the nonlinear polarization for (In,Ga)N, see F. Bernardini and V. Fiorentini, Phys. Rev. B **64**, 085207 (2001).
[16] O. Mayrock, H.-J. Wünsche, F. Henneberger, and O. Brandt, Phys. Status Solidi B **216**, 419 (1999).
[17] V. I. Litvinov, Appl. Phys. Lett. **77**, 2210 (2000).
[18] L.-W. Wang, Phys. Rev. B **63**, 245107 (2001).