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Quantum confined Stark effect due to built-in internal polarization fields in (Al,Ga)N/GaN quantum wells

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(Al,Ga)N/GaN quantum wells have been studied by temperature-dependent luminescence and reflectivity. The samples were grown by molecular beam epitaxy on (0001) sapphire substrates, and well widths were varied from 3 to 15 monolayers (ML's) with a 2-ML increment, thus providing a reliable data set for the study of the well width dependence of transition energies. The latter shows a strong quantum confined Stark effect for wide wells, and an internal electric-field strength of 450 kV/cm is deduced. X-ray diffraction performed on the same samples shows that the GaN layers are nearly unstrained, whereas the (Al,Ga)N barriers are pseudomorphically strained on GaN. We conclude that the origin of the electric field is predominently due to spontaneous polarization effects rather than a piezoelectric effect in the well material.

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The progress in the growth and electronic quality of group-III nitrides has been very rapid in the last few years, as illustrated by the realization of bright blue and green light-emitting diodes and near-UV laser diodes.[1,2] The active region of these devices consists of (Ga,In)N quantum wells (QW's). There is also an increasing interest for (Al,Ga)N/GaN QW's, in view of extending the domain of application of this group-III nitride family towards the UV range. (Al,Ga)N/GaN QW's can be grown either by metalorganic vapor phase epitaxy[3,4] (MOVPE) or by molecular beam epitaxy[5,6] (MBE). A striking feature is that whatever the growth method, the photoluminescence (PL) energy of sufficiently thick (Al,Ga)N/GaN QW's (typically >4 nm) is lower than that of the A free exciton of GaN.[3,4,6,7] This was attributed by Im *et al.*[7] to a strong piezoelectric field present in biaxially compressed GaN QW's. In this paper, we discuss the optical properties of thin $Al_{0.1}Ga_{0.9}N$/GaN quantum wells, whose widths have been varied by a small increment of 2 molecular monolayers (ML's), 1 ML corresponding to 2.59 Å. We show that excitons are localized at low temperature, with a localization energy of 20 meV on the average. The study of the well width dependence of the QW energies provides evidence for a quantum confined Stark effect due to an internal electric field of about 450 kV/cm. In the light of x-ray diffraction (XRD) study of the samples, we conclude that spontaneous polarization effects are highly important in the determination of this field.

The samples were grown on (0001) sapphire substrates by molecular beam epitaxy using NH_3 as the nitrogen precursor. Details of the MBE growth of the GaN template on which heterostructures are grown can be found in Ref. 8. The parameters of the heterostructures (i.e., well width and barrier composition) are determined *in situ* by using reflection high-energy electron diffraction (RHEED) intensity oscillations.[9] Three samples are discussed. The first two contain single $Al_{0.11}Ga_{0.89}N$ (50 Å)/GaN QW's of width 5, 9, and 13 ML's in sample A, and 3, 7, 11, and 15 ML's in sample B. Sample C is a 17-ML-wide QW embedded in $Al_{0.09}Ga_{0.91}N$ barriers. PL was excited with the 325-nm line of an HeCd laser, and reflectivity was recorded by shining white light from a halogen lamp onto the sample. XRD mapping was performed using a high-resolution diffractometer using narrow slits in front of the detector.

Figure 1 displays the photoluminescence spectra at 9 K of samples A and B. The first point to be noted is that PL energies of the 5-, 9-, and 13-ML-wide wells are well intercalated with those of the 3-, 7-, 11-, and 15-ML-wide ones. This is a clear demonstration of the monolayer control of thicknesses achievable in the MBE growth of nitrides. The PL linewidths in Fig. 1 are 20–30 meV. As also shown in Fig. 1, the samples exhibit well resolved reflectivity structures, due to each individual quantum well, providing a reliable data set for the study of the well width dependence of QW transition energies. The free exciton energies are obtained by assigning a Drude-Lorentz oscillator to each transition, and the dotted line in Fig. 1 shows such a calculated reflectivity spectrum. Figure 1 indicates that the luminescence at 9 K originates from localized excitons, with binding energy of the order of 20 meV for wide wells, increasing to 46 meV for the 5-ML-wide well. Another way of estimating localization energies is to study temperature-dependent PL. As shown in Fig. 2, when the temperature increases, the QW PL energy first increases for $T<100$ K and decreases for higher temperatures. This is assigned to a thermal delocalization of QW excitons. The solid lines through the data, including the GaN buffer luminescence, correspond to the temperature dependence of the A excitonic gap of GaN, which we determined previously from typical GaN/Al_2O_3 samples of similar thickness:

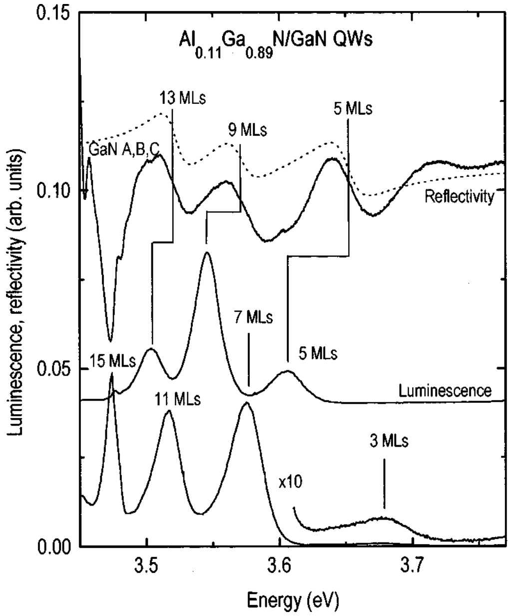

FIG. 1. Luminescence spectra at 9 K of two $Al_{0.11}Ga_{0.89}N$/GaN quantum well samples (samples A and B). The well widths are given in ML units ($1\ \text{ML}=2.59$ Å). Also shown is the reflectivity spectrum of sample A with a calculated spectrum (dotted line).

$$E(T)=E(0)-8.87\times10^{-4}T^2/(T+874) \qquad (1)$$

(this expression is in very good agreement with that given in Ref. 10). The difference between the extrapolated low-temperature free exciton energy and the PL energy gives an independent estimation of the excitonic localization energy. The squares in Fig. 2 correspond to transition energies obtained from reflectivity. We find a rather good agreement between the two determinations of localization energy, when both are available, for well widths larger than 5 ML's (see also Fig. 3 below). For narrower wells, the discrepancy between the two determinations of the free exciton energies could be due to incomplete thermal detrapping of these deeply localized excitons.

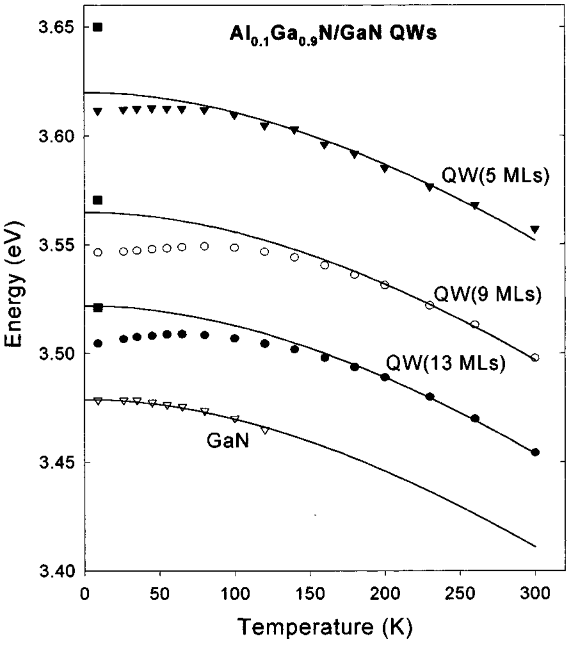

FIG. 2. Temperature dependence of the PL energies of sample A. The closed squares are free exciton energies deduced from reflectivity.

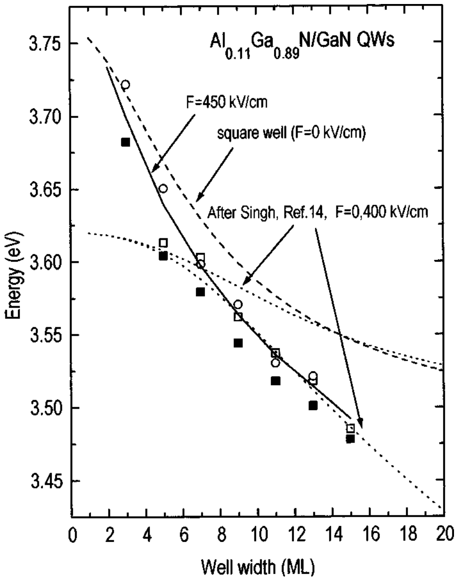

FIG. 3. Well width dependence of $Al_{0.11}Ga_{0.89}N$/GaN quantum well energies (samples A, B, and C). Closed squares are luminescence energies, open circles and open squares are free exciton energies deduced from reflectivity or temperature-dependent PL, respectively.

Figure 3 displays the QW transition energies at 9 K of GaN QW's with an Al barrier composition of 0.11, for widths ranging from 3 (8 Å) up to 15 ML's (39 Å). Dark squares are PL energies, circles and open squares are free exciton energies obtained from reflectivity and temperature-dependent PL, respectively. A first remark regards localization energies (Stokes shift) in our samples. As Fig. 3 shows, it is nearly constant with a value of 22 ± 5 meV for widths larger than 5 ML, and higher for narrower wells. If excitons are localized due to QW thickness fluctuations, for a given corrugation, the Stokes shift is expected to be proportional to the slope of the energy versus width curve.[11] This is what we observe, with a nearly constant Stokes shift in a well width range where the transition energy varies linearly with width due to the Stark effect discussed below. Such a localization scheme is in good agreement with the results of the time resolved PL study of $Al_{0.07}Ga_{0.93}N$/GaN QW's by Lefebvre *et al.*[12]

As shown in Figs. 1 and 3, a 15-ML-wide well emits at an energy slightly lower than the excitonic energy of the GaN buffer. As mentioned in the Introduction, this has already been reported[3,4,6,7] for wide GaN QW's. Figure 4 emphasizes this effect, by displaying the PL spectrum of a 17-ML-wide $Al_{0.09}Ga_{0.91}N$/GaN quantum well. The luminescence energy is indeed 85 meV lower than that of GaN. This is the signature of the quantum confined Stark effect, the physical origin of which is now discussed.

In Fig. 3 are given the results of different calculations. A difficulty arises from the fact that, as Fig. 1 shows, no signal from the barrier has been observed either in PL or in reflectivity in our samples with $Al_{0.11}Ga_{0.89}N$ barriers. This testifies to a very efficient capture of carriers by the wells. By

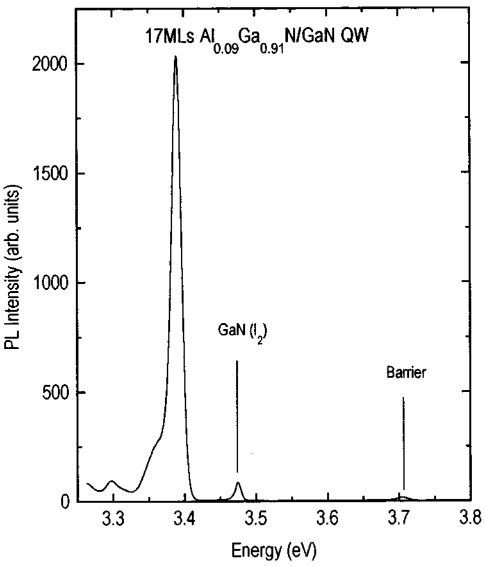

FIG. 4. Luminescence spectrum at 9 K of a 17-ML-wide $Al_{0.09}Ga_{0.91}N$/GaN quantum well (sample C).

using the bowing parameter for (Al,Ga)N proposed by Amano *et al.*,[13] we estimate the barrier excitonic gap to be 3.75 eV. On the other hand, reflectivity performed on sample C places the excitonic gap of $Al_{0.09}Ga_{0.91}N$ at 3.731 eV, a linear interpolation leading then to an excitonic gap of 3.788 eV for $Al_{0.11}Ga_{0.89}N$. A value of 3.76 eV has been used in the following calculation. The valence-band offset is assumed to vary linearly with the Al barrier composition, a value of about 800 meV for the AlN/GaN heterostructure has been used.[14,15] First, the dashed line in Fig. 3 shows that the linear decrease with well width of the QW energies for widths higher than 5 ML's cannot be explained by assuming square QW potential profiles. In order to include the electric-field effect, we first use the approximate band to band, but analytical, model of Singh.[16] This model is known to fail for very narrow wells (as Fig. 3 shows), but is valid for wide ones. The results of this model for electric fields F of 0 and 400 kV/cm are shown as dotted lines in Fig. 3. In the case of $F=0$, this model reproduces the previous square well calculation only for wide wells, as expected. Now, it can be seen that an electric field of 400 kV/cm is necessary to reproduce the linear decrease of QW energies with well width. Finally, the solid line in Fig. 3 gives the results of a self-consistent envelope function calculation, including excitonic effects and the modification of the band lineups produced by the presence of the excitonic dipole.[17] A good agreement with the experiment is obtained for the whole range of well widths investigated, assuming a field strength of 450 kV/cm, 50 kV/cm higher than the value obtained with a less sophisticated calculation. It is important to note that this value compares well also with that determined by Im *et al.*,[7] who determined a piezoelectric field of 420 kV/cm for MOVPE-grown $Al_{0.15}Ga_{0.85}N$/GaN QW's, and with the value of 450 kV/cm used by Honda *et al.*[18] for $Al_{0.1}Ga_{0.9}N$/GaN QW's.

We now discuss the possible origins of this field. The piezoelectric field magnitude for (0001) biaxial strain is given by[13,15,19,20]

$$\begin{aligned} F_{pz} &= -P_{pz}/\varepsilon\varepsilon_0 = -(2e_{31}\in_{xx}+e_{33}\in_{zz})/\varepsilon\varepsilon_0 \\ &= -(2e_{31}-2c_{13}e_{33}/c_{33})\in_{xx}/\varepsilon\varepsilon_0, \end{aligned} \tag{2}$$

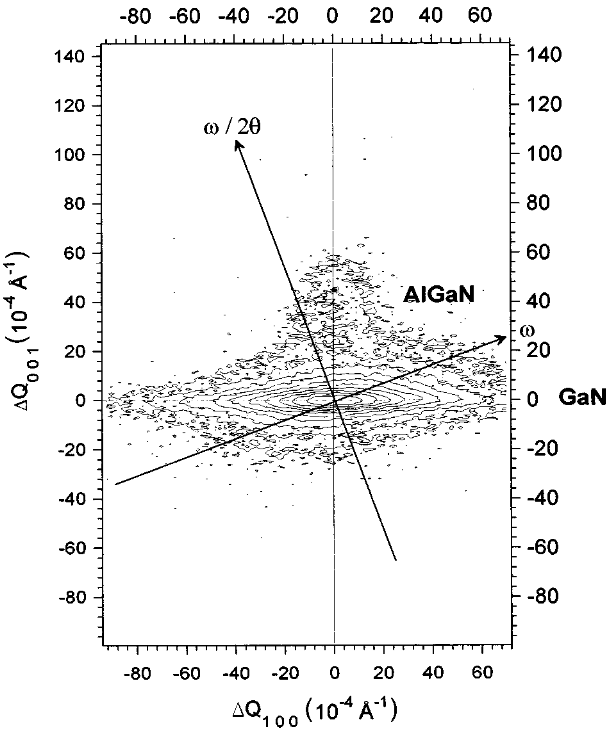

FIG. 5. X-ray map of sample A around the -105 reciprocal lattice point. The abscissa leads to the in-plane a lattice parameter and the ordinate to the on-axis c one.

where ε and ε_0 are the dielectric constant of GaN and the permittivity of free space, c_{ij} are the material elastic constants,[21] and $\in$ are the strain components. We use the piezoelectric constants e_{ij} of Bernardini, Fiorentini, and Vanderbilt,[20] linearly interpolating for the alloy between the values of GaN and AlN. The in-plane lattice constants of GaN and AlN are about 3.189_1 and 3.11_2 Å, respectively. It can be verified that if one assumes that the GaN wells are strained by relaxed (Al,Ga)N barriers, a correct value for the piezoelectric field is obtained. However this does not correspond to the situation of our samples. Figure 5 shows an XRD reciprocal space map of sample A. It shows that (Al,Ga)N barriers are in-plane lattice matched to the GaN buffer layer. (This is in agreement with the work of Takeuchi *et al.*,[22] showing that up to 6000-Å $Al_{0.1}Ga_{0.9}N$ can be grown lattice matched to GaN.) The in-plane lattice parameter of the whole sample A structure is $a=3.189_2$ Å, i.e., the GaN is nearly relaxed (the buffer A exciton energy in this sample is 3.474 eV). This means that there is a negligible piezoelectric field in the wells. Note that the value of 3.189_1 Å for the in-plane lattice parameter of *relaxed* GaN (Refs. 23 and 24) can be questioned. Recently, Skromme *et al.*[25] suggested that this value could be as high as 3.191_2 Å (corresponding to an A exciton energy of 3.468 eV). However, even using this last value, a piezoelectric field of about 100 kV/cm is deduced, much lower than the field present in our QW's. (The inclusion of the additional 2.9×10^{-4} compressive strain[25] that occurs when cooling GaN on sapphire samples from 300–9 K increases this value to only 140 kV/cm.) We then attribute the quantum confined Stark effect that we observe to the difference in polarization (piezoelectric+spontaneous) between wells and barriers, following the works of Bernardini, Fiorentini, and Vanderbilt.[20,26] In their work, the electric field is due to interface charge accumulation due to the change in polarization between two materials. In a well with infinite barriers, this field is given by[26]

$$F_w=(P_b-P_w)/\varepsilon\varepsilon_0, \tag{3}$$

where P_b (P_w) is the total polarization in the barrier (well) material. For a superlattice, it is given by (assuming a same value of ε for well and barrier material)

$$F_w=l_b(P_b-P_w)/(l_b+l_w)\varepsilon\varepsilon_0, \tag{4}$$

where l_b (l_w) is the barrier (well) thickness. Using the values of spontaneous polarization computed in Ref. 20 and Eq. (3), we obtain a field of 1.1 MV/cm in the infinite barrier case, with the largest contribution coming from the difference in spontaneous polarization rather than from the piezoelectric field in the barrier (640 kV/cm and 440 kV/cm, respectively). On another hand, in our samples, the barriers are not infinite ($l_b=50$ Å), and noting that the quantum confined Stark effect is noticeable in Fig. 4 for wells of thickness 9–15 ML's ($l_w=23$–39 Å), the use of Eq. (4) gives fields in the 750–620 kV/cm range. This is larger, but of the order of magnitude of the value deduced from Fig. 4. The origin of the remaining discrepancy could be due to the fact that GaN on sapphire heterostructures are highly defective crystals, as shown in particular on the reciprocal space map in Fig. 5, where the GaN large peak width in the horizontal direction is due to diffraction by these defects.[27] These defects may influence the internal field value.

In conclusion, from the study of the quantum well energies as a function of well width with an increment of 2 ML's for a series of (Al,Ga)N/GaN QW's grown by MBE (a technique that allows a control of widths at the monolayer scale), a quantum confined Stark effect is revealed, and we deduced an internal electric-field strength of 450 kV/cm for $Al_{0.11}Ga_{0.89}N$/GaN QW's. On the other hand, reciprocal space maps show that in our structures the barriers are lattice matched to nearly strain-free GaN. As such, the origin of this field is not a piezoelectric effect in the well material, but rather the difference in polarization between well and barrier materials, while the piezoelectric effect is mainly present in the barriers.

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[1] S. Nakamura and G. Fasol, *The Blue Laser Diode* (Springer-Verlag, Berlin, 1997).

[2] For a more recent review, see, for instance, *Group III Nitride Semiconductor Compounds*, edited by Bernard Gil (Clarendon, Oxford, 1998).

[3] R. Niebuhr, K. H. Bachem, D. Behr, C. Hoffman, U. Kaufmann, Y. Lu, B. Santic, J. Wagner, M. Arlery, J. L. Rouvière, and H. Jürgensen, in *III-V Nitrides*, edited by F. A. Ponce, T.D. Moustakas, I. Akasaki, and B. A. Monemar, MRS Symposia Proceedings No. 449 (Materials Research Society, Pittsburgh, 1997), p. 769.

[4] J. S. Im, J. Off, A. Sohmer, F. Scholz, and A. Angleiter, in *Proceedings of the International Conference on Silicon Carbide, III-Nitrides and Related Materials, Stockholm, 1997*, edited by G. Pensl, H. Morkoç, B. Monemar, and E. Janzén (Trans. Tech., Zurich, Switzerland, 1998), p. 1299.

[5] M. Smith, J. Y. Lin, H. X. Jiang, A. Khan, Q. Chen, A. Salvador, A. Botchkarev, and H. Morkoç, in *III-V Nitrides* (Ref. 3), p. 829.

[6] N. Grandjean and J. Massies, Appl. Phys. Lett. **73**, 31 (1998).

[7] J. M. Im, H. Kollmer, J. Off, A. Sohmer, F. Scholz, and A. Angleiter, in *Nitride Semiconductors*, edited by F. A. Ponce, S. P. DenBaars, B. K. Meyer, S. Nakamura, and S. Strite, MRS Symposia Proceedings No. 482 (Materials Research Society, Pittsburgh, 1998), p. 513.

[8] N. Grandjean, M. Leroux, M. Laügt, and J. Massies, Appl. Phys. Lett. **71**, 240 (1997).

[9] N. Grandjean and J. Massies, Appl. Phys. Lett. **71**, 1816 (1997).

[10] W. Shan, T. J. Schmidt, X. H. Yang, S. J. Hwang, J. J. Song, and B. Goldenberg, Appl. Phys. Lett. **66**, 985 (1995).

[11] R. Grousson, V. Voliotis, N. Grandjean, J. Massies, M. Leroux, and C. Deparis, Phys. Rev. B **55**, 5253 (1997).

[12] P. Lefebvre, J. Allègre, B. Gil, A. Kavokin, H. Mathieu, W. Kim, A. Salvador, A. Botchkarev, and H. Morkoç, Phys. Rev. B **57**, R9447 (1998).

[13] H. Amano, T. Takeuchi, S. Sota, and I. Akasaki, in *III-V Nitrides* (Ref. 3), p. 1143.

[14] S. H. Wei and A. Zunger, Appl. Phys. Lett. **72**, 2011 (1998).

[15] G. Martin, A. Botchkarev, A. Rockett, and H. Morkoç, Appl. Phys. Lett. **68**, 2541 (1996).

[16] J. Singh, Appl. Phys. Lett. **64**, 2694 (1994).

[17] B. Gil and P. Bigenwald, Solid State Commun. **94**, 883 (1995); P. Bigenwald and B. Gil, Phys. Rev. B **51**, 9780 (1995).

[18] T. Honda, T. Miyamoto, T. Sakaguchi, H. Kawanishi, F. Koyama, and K. Iga, in *Proceedings of the 2nd International Conference on Nitride Semiconductors, Tokushima, Japan, 1997* [J. Cryst. Growth (**189/190**, 644 (1988)].

[19] W. Liu, K. L. Teo, M. F. Li, S. J. Chua, K. Ushida, H. Tokunaga, N. Akutsu, and K. Matsumoto, in *Proceedings of the 2nd International Conference on Nitride Semiconductors*, Tokushima, Japan, 1997 [J. Cryst. Growth (**189/190**, 648 (1998)].

[20] F. Bernardini, V. Fiorentini, and D. Vanderbilt, Phys. Rev. B **56**, R10 024 (1997).

[21] A. Polian, M. Grimsditch, and I. Grzegory, J. Appl. Phys. **79**, 3343 (1996).

[22] T. Takeuchi, H. Takeuchi, S. Sota, H. Sakai, H. Amano, and I. Akasaki, Jpn. J. Appl. Phys., Part 2 **36**, L177 (1997).

[23] T. Detchprohm, K. Hiramatsu, K. Itoh, and I. Akasaki, Jpn. J. Appl. Phys., Part 2 **31**, L1454 (1992).

[24] W. G. Perry, T. Zheleva, M. D. Bremser, R. F. Davis, W. Shan, and J. J. Song, J. Electron. Mater. **26**, 224 (1997).

[25] B. J. Skromme, H. Zhao, D. Wang, H. S. Kong, M. T. Leonard, G. E. Bulman, and R. J. Molnar, Appl. Phys. Lett. **71**, 829 (1997).

[26] F. Bernardini and V. Fiorentini, Phys. Rev. B (to be published).

[27] B. Heying, X. H. Wu, S. Keller, Y. Li, D. Kapolnek, B. P. Keller, S. P. Denbaars, and J. S. Speck, Appl. Phys. Lett. **68**, 643 (1996).