Comment on "Experimental evidence for N-induced strong coupling of host conduction band states in GaN_xP_{1-x}: Insight into the dominant mechanism for giant band-gap bowing"

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A recently observed pinned peak in photoluminescence excitation spectroscopy studies (PLE) of GaN_xP_{1-x} epilayers, that remained stationary with nitrogen concentration, was attributed to a transition from the valence band edge to either the $t_2(X_3)$ or $t_2(L)$ conduction bands by Buyanova *et al.* [Phys. Rev. B **69**, 201303(R) (2004)]. Using absorption and PLE studies on carefully prepared samples, we show that this pinned peak is merely an artifact that arises from the GaP buffer layer and is not associated with the GaN_xP_{1-x} epilayers.

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In a recent Rapid Communication[1] the direct-gap conduction band minimum Γ_{1c} in GaN_xP_{1-x} was studied as a function of nitrogen doping using PLE. In addition to the excitonic peak that is derived from Γ_{1c} in GaP and that increases in energy with increasing nitrogen content, a second PLE peak was observed to emerge in the doped alloy, and to remain pinned at a constant energy of 2.87 eV. The authors identified this as a valence band to nitrogen-perturbed host conduction band transition, involving either the $t_2(X_3)$ or $t_2(L)$ conduction bands, that resulted from a splitting of the L_1 or X_3 conduction bands induced by the nitrogen impurity. Subsequently, an alternative explanation[2] based on a theoretical band structure calculation identified this pinned peak that remained stationary with nitrogen concentration, as arising from high energy nitrogen-localized states, despite the fact that the pinned peak in this theoretical calculation was above Γ_{1c} in GaP. In contrast to the above mentioned conclusions, our observations discussed below indicate that the pinned peak arises from the GaP buffer layer which is obviously independent of nitrogen content. This artifact arises for optically thin samples that remain on a GaP buffer or substrate. Our direct absorption measurements for GaN_xP_{1-x} at 1.6 K show that a 0.25-μm-thick epilayer with $x=0.1\%$, transmits 50% of the exciting laser at 2.87 eV. This light can photogenerate excitons in the underlying GaP buffer layer, which then transfer to nitrogen impurity sites in the epilayer, and contribute to the PLE intensity at 2.87 eV. Efficient transferred-excitation processes similar to this have been commonly observed, as in, e.g., the closely related system $GaAs_{1-x}N_x$.[3,4] To demonstrate this, we have measured 1.7 K PLE on the same samples used in Ref. 1 and also used earlier by us,[5] as well as on additional specially prepared samples, using a frequency-doubled Ti:sapphire laser, with spectral resolution of 1.3 meV and a pulse energy density of 5 nJ/cm^2. Identical results were obtained at $\times 10$ lower fluence. PLE was detected at the nitrogen cluster band at 2.101 eV, as in Ref. 1. Figure 1(a) illustrates the results for the same 0.12% sample used in Ref. 1 showing the 2.87 eV stationary peak and the direct-band edge exciton peak at 2.899 eV. The former is remarkably close to the expected energy for the direct gap exciton in the undoped GaP crystal, measured to be $E_{g\Gamma}(x=0)=2.8725\pm0.0005$ eV by optical absorption.[6] This is confirmed in Fig. 1(b) where we have directly measured the absorption peak in an undoped GaP epilayer to be 2.8718 ± 0.0005 eV. For this experiment, metal-organic chemical vapor deposition (MOCVD) was used to grow an epilayer 2 μm thick, permitting it to be lifted off from the substrate as in Ref. 7. As shown in Fig. 1(b), both the exciton peak energy and its linewidth are consistent with the 2.87 eV peak seen in Fig. 1(a). Note that the position of the peak related to the buffer may not appear at the exact energy of the bandgap of the buffer, due to absorption in the epilayer. Because PLE is a convoluted process of excitation and transfer, complications often occur when relating the PLE peak to the absorption peak.[8,9] We notice that the value of $E_{g\Gamma}(x=0)$ in Ref. 1 is significantly higher than that in Ref. 6 or in Fig. 1(b), by 4 meV, which exaggerates the actually small separation between $E_{g\Gamma}(x=0)$ and the pinned peak. This problem seems also to arise because of a deficiency of the PLE technique.

To test our hypothesis that this undoped GaP exciton peak in Fig. 1(b) is the origin of the pinned peak at 2.87 eV in Ref. 1, we have grown two additional GaN_xP_{1-x} epilayers with $x=0.1\%$ using MOCVD on undoped substrates, with a 0.3 μm buffer and 0.25 μm epilayer thickness, thus emulating the sample in Ref. 1 which had 0.12% nitrogen doping. The two new samples differ only in the presence or absence of an AlP blocking layer. This 0.1 μm thick, nearly lattice-matched AlP layer was inserted above the buffer layer for one of the two samples to prevent excitation transfer from the buffer into the GaN_xP_{1-x} epilayer. To avoid a direct interaction between Al and N, which usually degrades the quality of the epilayer, we insert a very thin N free GaP layer (10 nm) between the AlP and the GaPN layer. The thin GaP layer would not cause any measurable effect on the PLE from the GaPN layer. This approach has worked remarkably well also for GaAsN where we were able to track the shifts of the band gap excitonic state and shallow N bound states simultaneously with as high an accuracy as has ever been achieved for the material.[10] Even though it is expected that the lift-off procedure would affect the surface quality of the sample to some degree, the actual effect is believed to be minimal, which is evidenced by the fact that the width of the excitonic absorption peak at the GaP Γ_{1c} point is found to be

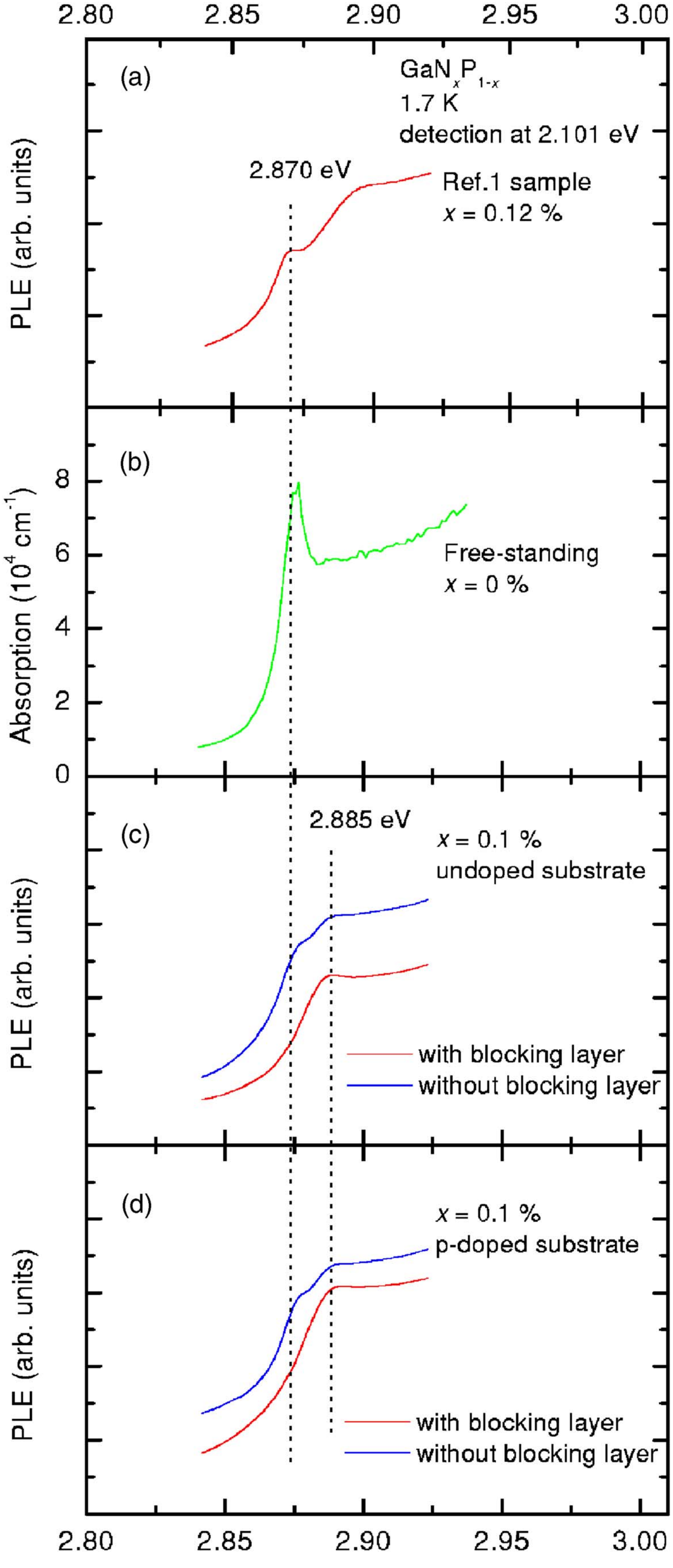

FIG. 1. (Color online) Low temperature spectroscopy of GaN_xP_{1-x} near the direct band edge at Γ_{1c}. (a) PLE of the $x=0.12\%$ sample used in Ref. 1, showing the stationary peak at 2.87 eV and the nitrogen concentration-dependent peak at higher energy corresponding to the shifted bandedge. (b) Optical absorption of a free-standing 2-μm-thick undoped GaP buffer layer showing the intrinsic exciton at 2.872 eV. (c) PLE comparing two $x=0.10\%$ samples designed to emulate the sample in (a). The upper curve is from the sample similar to that in Ref. 1, whereas the lower curve is from the sample with the additional AlP blocking layer inserted between the buffer layer and the GaN_xP_{1-x} epilayer. (d) Data is similar to (c), except that here the samples were grown on Zn (p) doped substrates. Curves are displaced vertically for clarity.

5.4 meV in our measurement, as compared to ~5 meV obtained using single crystal GaP by Dean *et al.*[8] In our MOCVD samples, either in PL or absorption, the NN pair peaks remain as sharp as those shown in Fig. 2 of the commented paper. In fact, in our absorption spectra, even the weak phonon replicas of the NN states are observable.[11]

Figure 1(c) shows PLE of the samples with and without the blocking layer. Both samples show the nitrogen concentration-dependent peak at 2.885 eV, consistent with the concentration dependence found in Refs. 1 and 12. However, the stationary peak is present only in the sample without a blocking layer, and it is completely absent in the sample where carrier transfer from the buffer is prevented. The same experiment was repeated for samples grown on *p*-type substrates. The similarity of the spectra in Fig. 1(c) and Fig. 1(d) reveals that the results are qualitatively independent of any possible surface depletion from the substrate doping.

To conclude, the results in Fig. 1 demonstrate that the recently observed pinned peak in PLE studies of GaN_xP_{1-x} epilayers is merely an artifact that arises from the GaP buffer layer and is not associated with the GaN_xP_{1-x} epilayers.

Note added in proofs. Recently, Felici *et al.*[13] also reported the observation of the same "pinned" peak in PLE spectra (though at slightly different energy of 2.89 eV). The authors attributed this peak to "an excitonic level introduced near the Γ_{1c} CB minimum by the isolated nitrogen atom", as predicted by Dudiy *et al.*[2] In addition to our PLE data reported in this Comment, we have since published another paper where direct absorption measurements on free-standing GaPN films were used to provide further proof that the pinned peak is indeed an experimental artifact that does not exist in the free-standing epilayers.[14]

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