

**Resonant Raman scattering spectroscopy of GaP<sub>1-x</sub>N<sub>x</sub> and GaAs<sub>1-x</sub>N<sub>x</sub> in the ultraviolet range**

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We report resonant Raman scattering studies of GaP<sub>1-x</sub>N<sub>x</sub> and GaAs<sub>1-x</sub>N<sub>x</sub> in the ultraviolet (UV) spectral range. For both materials, strong intensity resonances and their rapid degradation near the respective  $E_1$  transition energies exhibited for the zone-center longitudinal optical phonons provide direct evidence that the  $L$ -point conduction-band edges of GaP<sub>1-x</sub>N<sub>x</sub> and GaAs<sub>1-x</sub>N<sub>x</sub> are strongly perturbed by nitrogen impurities. We also show that UV resonant Raman scattering is a powerful means to study higher lying conduction-band electronic states of semiconductor alloys.

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**I. INTRODUCTION**

There have been numerous theoretical and experimental studies which aim to explain the mechanism of the so-called giant band-gap bowing in GaAsN and GaPN, which are both technologically and physically important material systems.<sup>1</sup> As pointed out by Zhang *et al.*,<sup>2</sup> it might be difficult to apply one “unified” theory for both materials GaAsN and GaPN, yet several attempts have been made to explain the peculiar physics of both of these systems using a single mechanism. For example, Shan *et al.* proposed a simple two-band model based on level repulsion between the isolated nitrogen impurity level  $N_X$  and the conduction-band minimum (CBM) at  $\Gamma$  to explain the large band-gap lowering in GaAsN,<sup>3</sup> as well as in GaPN.<sup>4</sup> In this model,  $N_X$  and the CBM at  $\Gamma$  interact and evolve into two new states  $E_+$  and  $E_-$  where the lower energy state  $E_-$  forms the new CBM. This would imply that in GaPN the rapidly decreasing new CBM evolves from  $N_X$ . However, it has been reported that the  $A$ -line, which refers to the photoluminescence transitions from the  $N_X$  level, while being severely broadened, hardly moves with increased nitrogen doping, raising doubts about the validity of the two band repulsion model.<sup>5</sup>

On the other hand, Kent and Zunger, emphasizing intracduction band mixing, proposed that the band-gap reduction for both alloys is caused by the downward moving nitrogen-perturbed conduction-band edge overtaking the localized nitrogen states.<sup>6,7</sup> Thus, studying the evolution of conduction-band states including, e.g., the  $\Gamma$ ,  $X$ , and  $L$  critical points with respect to nitrogen concentration, would help clarify Kent and Zunger’s model. Another model for GaPN asserts that with increasing nitrogen concentration, the nitrogen impurities broaden to form an impurity band that lowers the band gap of the materials.<sup>5</sup> For GaPN, we recently showed that the absorption edge is comprised of nitrogen pairs and cluster states, hinting that the heavy nitrogen doping might be forming an impurity band in this material.<sup>8</sup>

In this study, we first present room-temperature resonant Raman scattering (RRS) results for GaPN in the visible to ultraviolet (UV) spectral range (2.41–4.51 eV). We monitored the conduction-band edge states near the  $L$  critical

point by examining the resonance behavior of a Raman active zone-center phonon. Our results directly indicate that although strongly perturbed, the host conduction-band electronic states near the  $L$  critical point did not plunge down with increasing nitrogen concentration in GaPN. The previous RRS measurement in the visible spectral range showed that the host conduction-band electronic states near the  $X$  critical point remained stationary with increasing nitrogen doping,<sup>8</sup> whereas states near the  $\Gamma$  and  $L$  points were shown to be moving up in energy with increased nitrogen doping by measuring the  $E_0$  and the  $E_1$  transitions using a spectroscopic ellipsometry technique.<sup>9</sup> Thus all these results indicate that the host conduction-band electronic states did not plunge down with increasing nitrogen concentration in GaPN, unlike some suggestions.<sup>6,7</sup> We next present the 80 K RRS results for GaAsN in the spectral range of 2.54–3.71 eV. Here again, the influence of nitrogen on the conduction-band electronic states was clearly observed through the change in the resonance behavior of a Raman active zone-center phonon with respect to the nitrogen concentration. Our results indicate that the conduction-band electronic states near the  $L$  critical point play an important role in the physics of GaAsN, as proposed by some authors.<sup>7,10,11</sup>

In contrast to our previous measurements, the present RRS studies were conducted in the UV energy range for both GaPN and GaAsN. Due to the sharpness of resonance in the phonon intensity, RRS is known to be a very useful technique to locate critical points in the joint density of states of semiconductor materials. Additionally, by monitoring the behavior of RRS with a change in doping, one can get direct evidence of impurity-induced perturbation at certain points in the electronic band structure of the material.

**II. EXPERIMENTAL APPROACH**

The samples used in our study were a GaP substrate and 1- $\mu\text{m}$ -thick GaP<sub>1-x</sub>N<sub>x</sub> epilayers ( $x=0.25, 0.5, 1.0, 1.5,$  and  $2.0\%$ ), which were lifted off from the (001) GaP substrates. The nitrogen concentration  $x$  is estimated either by x-ray diffraction or secondary ion-mass spectroscopy (SIMS) mea-

measurements on these samples. Regarding the growth and preparation of the samples, refer to Ref. 8. We also measured 0.4- to 1.5- $\mu\text{m}$ -thick  $\text{GaAs}_{1-x}\text{N}_x$  epilayers ( $x=0, 0.41, 0.78, 1.02$ , and  $1.25\%$ ), which were grown by low-pressure metal-organic chemical-vapor deposition.<sup>10,12</sup> The room-temperature resonant Raman spectra for GaPN were measured in a pseudobackscattering geometry using a custom-made triple spectrometer (McPherson) equipped with a UV-sensitive nitrogen-cooled charge-coupled device (CCD) array detector and with a reflecting objective in a Cassegrain design featuring as its primary mirror an on-axis parabola with a numerical aperture of 0.5.<sup>13</sup> The 80-K resonant Raman spectra for GaAsN were measured in the same spectrometer system, using a continuous flow He cryostat. The samples were excited with 20 mW of either an  $\text{Ar}^+$  ion laser or a  $\text{Kr}^+$  ion laser (2.41–4.51 eV), focused to  $\sim 25\ \mu\text{m}$ . The spectra were obtained in the  $z(\text{YY})\bar{z}$  scattering geometry, where  $z$  and  $Y$  are the  $[001]$  and  $[110]$  crystal directions, respectively. In this scattering configuration, the  $\text{LO}_\Gamma$  phonon was Raman active, but the  $\text{TO}_\Gamma$  phonon was not Raman active for the  $T_d$  space group of zincblende structure crystals. Each spectrum was corrected for spectrometer response<sup>13</sup> and optical penetration depth, which was measured by spectroscopic ellipsometry (Sentech instruments).

### III. RESULTS AND DISCUSSIONS

#### A. GaPN

Figure 1(a) illustrates the room-temperature Raman spectra of a GaP substrate and a  $\text{GaP}_{0.985}\text{N}_{0.015}$  film measured at an excitation energy of 3.532 eV. For comparison, the Raman spectrum of  $\text{GaP}_{0.99}\text{N}_{0.01}$  measured with an excitation energy of 4.104 eV is shown in Fig. 1(b). Note that the  $\text{TO}_\Gamma$  and the  $\text{LO}_X$  phonons are barely observable in the Raman spectrum of the GaP substrate, indicating that the symmetrically forbidden  $\text{TO}_\Gamma$  and the non-zone-center  $\text{LO}_X$  (Ref. 14) phonons observed for the film are nitrogen-induced features. The activation of the  $\text{TO}_\Gamma$  phonon can be explained by the relaxation of the symmetry selection rules due to the nitrogen impurities which alter the local lattice structure, thus lowering the symmetry of GaP. The non-zone-center  $\text{LO}_X$  phonon is activated due to the relaxation of the momentum-conservation rules by an alloy disorder.

The zone-center phonons ( $\text{LO}_\Gamma$  and  $\text{TO}_\Gamma$ ), on the other hand, exhibit intensity resonances near 3.7 eV as shown in Fig. 2(a), where on- and off-resonance room-temperature Raman spectra are plotted for  $\text{GaP}_{0.985}\text{N}_{0.015}$ . It is clear that the scattering from these phonons gets enhanced by several orders of magnitude at resonance. Note that unlike the previous RRS measurements in the visible range,<sup>8</sup> we do *not* observe an anomaly in the  $\text{LO}_\Gamma$  phonon linewidth near resonance. In Fig. 2(b), we show the  $\text{LO}_\Gamma$  phonon-scattering intensity-resonance profile for  $x=0, 1.0$ , and  $2.0\%$  in the  $\text{GaP}_{1-x}\text{N}_x$  samples. The data from other samples ( $x=0.25, 0.5$ , and  $1.5\%$ ) show the same behavior. Notably, at resonance, the  $\text{LO}_\Gamma$  phonon scattering intensity decreases dramatically with increasing nitrogen concentration. This observation suggests that the intermediate, or resonating state shows GaP host statelike character. Indeed, the resonance near 3.7 eV is very

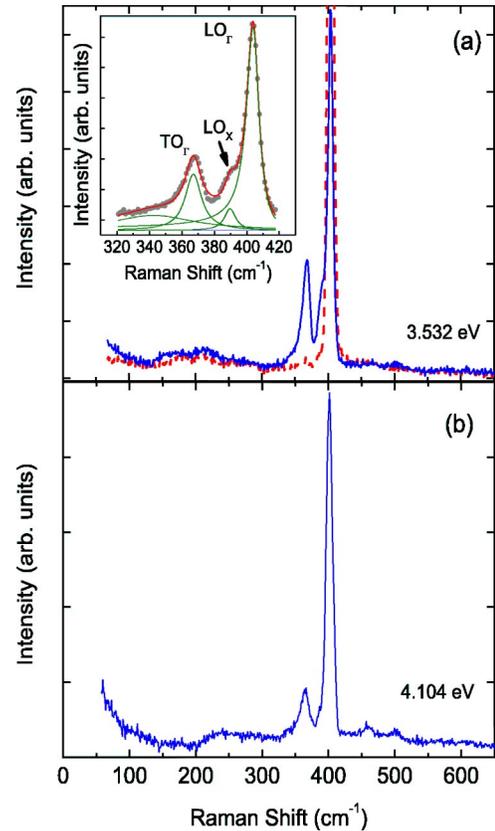


FIG. 1. (Color online) (a) Raman spectra of  $\text{GaP}_{0.985}\text{N}_{0.015}$  (solid line) and GaP substrate (dashed line) in  $z(\text{YY})\bar{z}$  scattering geometry at room temperature with an excitation energy of 3.532 eV. Three phonon modes are seen in the region shown in the inset, the  $\text{TO}_\Gamma$  phonon near  $367\ \text{cm}^{-1}$ , the  $\text{LO}_X$  phonon near  $388\ \text{cm}^{-1}$ , and the  $\text{LO}_\Gamma$  phonon near  $403\ \text{cm}^{-1}$ , in the order of increasing energy. Inset: Fitting the result of the phonons using Lorentzian (symmetric— $\text{TO}_\Gamma$  and  $\text{LO}_X$  phonon) and Fano (Ref. 15) (asymmetric— $\text{LO}_\Gamma$  phonon) functions, respectively, for  $\text{GaP}_{0.985}\text{N}_{0.015}$  with an excitation energy of 3.532 eV. The experimental data are circles. (b) The Raman spectra of  $\text{GaP}_{0.99}\text{N}_{0.01}$  in the same configuration, with an excitation energy of 4.104 eV.

close to the  $E_1$  transition energy of GaP at room temperature.<sup>16</sup> The  $E_1$  transition in GaP refers to the interband transition that occurs along the  $\Lambda$  direction of the Brillouin zone close to the  $L$  point. Thus, the dramatic decrease of the  $\text{LO}_\Gamma$  phonon's maximum intensity with increasing nitrogen concentration is a result of the perturbation of the conduction-band edge near the  $L$  point by nitrogen impurities. Note that the  $\text{LO}_\Gamma$  phonon intensities again show a rising trend toward the higher-energy portion of the plot ( $>4.51\ \text{eV}$ ) in Fig. 2(b). At 4.51 eV, it is clearly seen that the phonon intensity decreases with increasing nitrogen concentration, suggesting that this high-energy feature in the resonance profile is also related to a pure GaP host electronic-statelike character. Indeed, there is a critical point  $E'_0$  in GaP, which is located at the zone center near  $\sim 4.8\ \text{eV}$  from the valence-band maximum at room temperature.<sup>9,16</sup> Since our interest in this study is to examine the behavior of the lowest conduction-band critical points, we did not use excitations higher than 4.51 eV. We also analyzed the room-

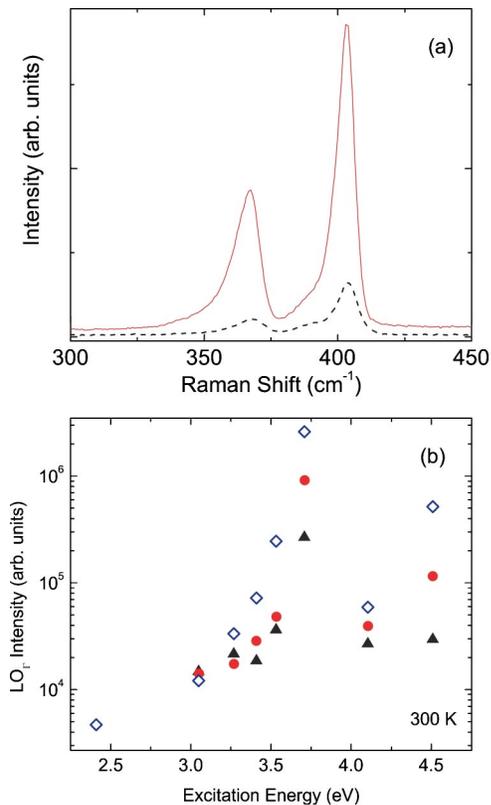


FIG. 2. (Color online) (a) Raman spectra of  $\text{GaP}_{0.985}\text{N}_{0.015}$  at room temperature with excitation energies of 3.532 eV (dashed line) and 3.708 eV (solid line), respectively. (b) The excitation energy dependence (resonance profile) of the  $\text{LO}_1$  phonon intensity for the GaP substrate (empty diamonds),  $\text{GaP}_{0.09}\text{N}_{0.01}$  (filled circles), and  $\text{GaP}_{0.98}\text{N}_{0.02}$  (filled triangles). The data from other samples are not shown for clarity.

temperature spectroscopic ellipsometry data to independently measure the  $E_1$  transition in the same samples, as shown in Fig. 3. In the low-electric-field limit or  $|\Delta R/R| \leq 10^{-3}$ , where  $R$  is the reflectance and  $\Delta R$  is the field-induced change in the reflectance, the third derivative of the dielectric function with respect to the energy  $E$   $[(1/E^2)(d^3/dE^3)(E^2\epsilon_2)]$  corresponds to the modulation spectrum.<sup>17</sup> From the modulation spectrum, we can get the critical-point energy and the width of the transition that occurs at the critical point by fitting the spectrum to a line-shape function which models that critical point (M1-type for our case). It is clearly seen that the critical point results from the RRS, and the spectroscopic ellipsometry measurements are reasonably close to each other, which confirms that the resonance maximum from the RRS measurements indeed originates from the  $E_1$  transition (see Fig. 4). It is also seen from Fig. 3(b) that the  $E_1$  transition linewidth gets broadened with increasing nitrogen concentration, which is a result of the nitrogen-induced perturbation to the  $L$ -point conduction-band edge of GaP.

All the relevant transition energies as a function of nitrogen concentration are shown in Fig. 4 and its inset. It is apparent that  $E_1$  and therefore the conduction-band edge near the  $L$  point ( $L_{1C}$ ) is slowly increasing with nitrogen concentration, which is consistent with the result obtained by Leibiger *et al.*<sup>9</sup>  $E_0$ , which is the direct interband transition at

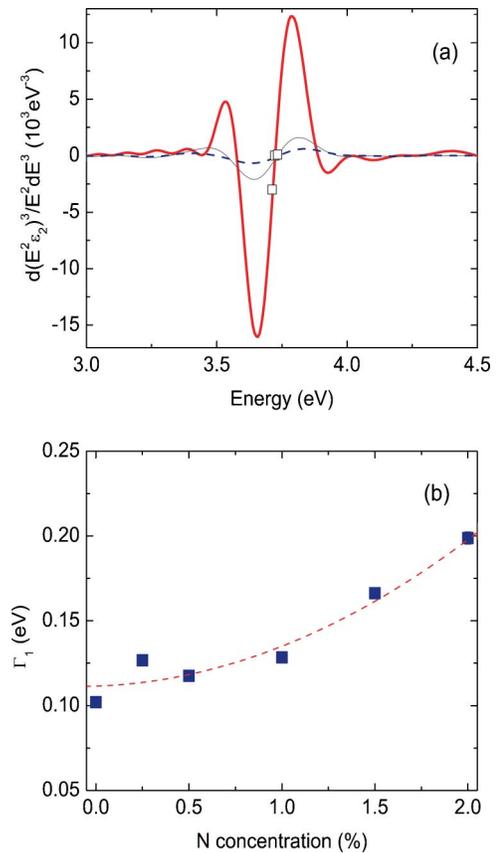


FIG. 3. (Color online) (a) The third numerical derivative of the imaginary part of the dielectric function ( $\epsilon_2$ ), of  $\text{GaP}_{0.9975}\text{N}_{0.0025}$  (thick solid line),  $\text{GaP}_{0.985}\text{N}_{0.015}$  (thin solid line), and  $\text{GaP}_{0.98}\text{N}_{0.02}$  (dashed line). The empty squares represent fitted  $E_1$  values. (b) The  $E_1$  transition linewidth  $\Gamma_1$  as a function of nitrogen concentration. The line is a guide to the eye.

the Brillouin zone center, was also reported to be increasing with nitrogen doping by the same authors.<sup>9</sup> From the previous RRS measurements,<sup>8</sup> we showed that the conduction band near the  $X$  critical point ( $X_{1C}$ ) remains stationary up to 2% of nitrogen concentration (circles in Fig. 4). Thus, even though it is apparent that conduction-band electronic states are perturbed by nitrogen impurities, we did not find evidence for any of the conduction-band states plunging down to form the lowest conduction-band edge state in the GaPN system as Kent and Zunger proposed.<sup>6,7</sup> Note that Leibiger *et al.*<sup>9</sup> concluded that their observation could be explained by Kent and Zunger's model,<sup>6,7</sup> even though the behavior near the  $L$ -point conduction-band edge that they observed is totally consistent with our current result. This contradiction can be explained as follows. Since Leibiger *et al.* did not probe the  $X$ -point conduction band, they assumed in their paper it was that the  $X$ -point conduction-band edge that would come down, satisfying the prediction of Kent and Zunger. We previously had already observed, however, that the  $X$ -point conduction band is stationary.<sup>8</sup> Using that information, we now can conclude that none of the conduction-band states plunge down with increasing nitrogen concentration. Rather, we previously showed that the band edge or absorption edge of GaPN is comprised of nitrogen-nitrogen

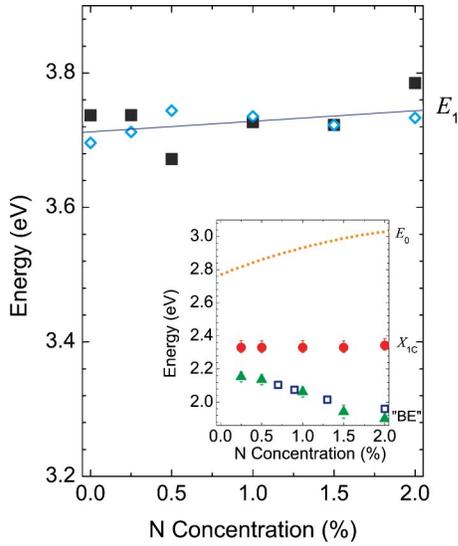


FIG. 4. (Color online) Evolution of electronic state with respect to nitrogen concentration. The filled squares are the  $LO_{\Gamma}$  phonon intensity-resonance maxima, and the  $E_1$  transition energy derived from the spectroscopic ellipsometry measurements (empty diamonds) is also shown for comparison. The line is a guide to the eye. Inset: Evolution of various electronic states with respect to nitrogen concentration. The filled circles and triangles are the  $LO_{\Gamma}$  phonon “linewidth” resonance maxima from previous RRS measurements in the visible range.<sup>8</sup> See the text for the explanation of each state. The dotted line ( $E_0$ ) is from the ellipsometry data of Ref. 9, and the empty squares are the photomodulated transmission data from Ref. 4. “BE” stands for the “band edge.”

pairs and cluster states (triangles in Fig. 4 of Ref. 8), which indicates that the nitrogen impurity pair and cluster states are responsible for the band-gap decrease in this material.

### B. GaAsN

Figure 5(a) illustrates on- and off-resonance Raman spectra of  $GaAs_{0.9959}N_{0.0041}$  measured at 80 K. Similar to the case of GaPN as shown in Fig. 2(a), the  $LO_{\Gamma}$  phonon near  $293\text{ cm}^{-1}$  exhibits an enhancement in intensity at resonance. The symmetrically forbidden  $TO_{\Gamma}$  phonon near  $270\text{ cm}^{-1}$  is observed due to changes in the local lattice structure induced by nitrogen impurities. Note that the  $LO_{\Gamma}$  phonon linewidth resonance in the UV energy range was not clearly observed, not as in the situation for the visible energy range.<sup>8,18</sup> The resonance profile for  $GaAs_{1-x}N_x$  ( $x=0, 0.41, 0.78, 1.02,$  and  $1.25\%$ ) is shown in Fig. 5(b). The suppression of resonance-scattering intensity with increasing nitrogen concentration is apparent in the figure, which suggests that the intermediate state for resonance exhibits GaAs host electronic-statelike character. Each resonance profile is composed of two peaks, whose positions are close to the  $E_1$  and  $E_1 + \Delta_1$  transitions of GaAs at 80 K, respectively. The abrupt decrease in the  $LO_{\Gamma}$  phonon intensity with increasing nitrogen concentration indicates a nitrogen-induced perturbation to the conduction-band edge near the  $L$  point of GaAs, as in the case of GaPN.

Interestingly, when plotted after subtracting 1.2 eV from the resonance energy, which is the energy difference between

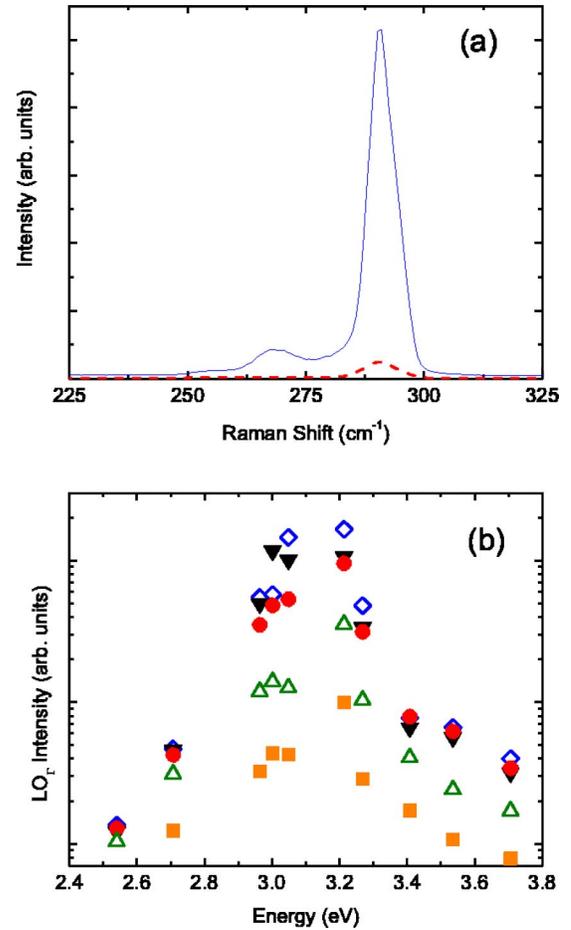


FIG. 5. (Color online) (a) Raman spectra of  $GaAs_{0.9959}N_{0.0041}$  at 80 K with excitation energies of 3.001 eV (solid line) and 3.535 eV (dashed line), respectively. (b) The excitation energy dependence (resonance profile) of the  $LO_{\Gamma}$  phonon intensity for the undoped GaAs epilayer (empty diamonds),  $GaAs_{0.9959}N_{0.0041}$  (filled triangles),  $GaAs_{0.9922}N_{0.0078}$  (filled circles),  $GaAs_{0.9898}N_{0.0102}$  (empty triangles), and  $GaAs_{0.9875}N_{0.0125}$  (filled squares). The data from other samples are not shown for clarity.

the valence-band maximum at the Brillouin zone center ( $\Gamma_{15v}$ ) and the valence-band extremum at the  $L$  point ( $L_{3v}$ ), the resonance maximum near the  $E_1$  transition closely follows the previously observed  $E_W$  level, as shown in Fig. 6.  $E_W$  and  $E'_W$ , shown in the inset of Fig. 6, represent energy positions, measured from previous resonant Raman scattering measurements,<sup>10</sup> at which the  $LO_{\Gamma}$  phonon linewidth exhibits double resonance behavior. This result directly corroborates the conclusion that the  $E_W$  level is closely related to electronic states near the  $L$ -point conduction band, as we have previously suggested<sup>10</sup> and it supports the proposal that conduction-band electronic states near the  $L$  critical point, which are perturbed by nitrogen doping, indeed play an important role in the physics of GaAsN.<sup>7,10,11</sup>

### IV. SUMMARY

In conclusion, using UV excitation to study the high-energy conduction-band states near the  $L$  critical point pro-

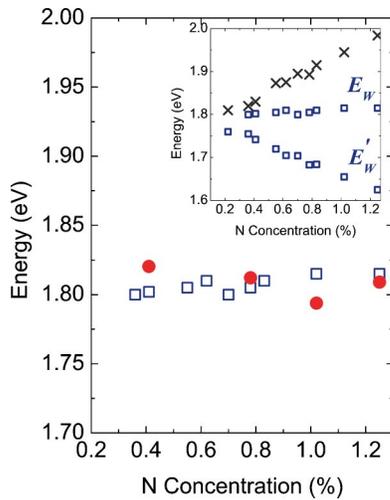


FIG. 6. (Color online) Evolution of the electronic state with respect to nitrogen concentration. The filled circles are the  $LO_{\Gamma}$  phonon intensity-resonance maxima shifted by  $-1.2$  eV. Shown for comparison are the  $LO_{\Gamma}$  phonon linewidth resonance maximum  $E_W$  (empty squares). Inset: The  $LO_{\Gamma}$  phonon scattering intensity-resonance maxima (crosses) and the  $LO_{\Gamma}$  phonon linewidth resonance maxima  $E_W$  and  $E'_W$  (empty squares) in the visible range, which are reproduced from Fig. 2 of Ref. 10. See text.

vides additional crucial evidence for the fact that the conduction-band electronic states of  $GaP_{1-x}N_x$  and  $GaAs_{1-x}N_x$  are perturbed by nitrogen impurities. For  $GaP_{1-x}N_x$ , they do not come plunging down to become the conduction-band edge. Thus, together with the evidence of the broadening of  $N_x$  (Ref. 5) and the evolution of nitrogen pairs and cluster states into the absorption edge,<sup>8</sup> we believe that  $GaP_{1-x}N_x$  can be best described as an impurity band system. For  $GaAs_{1-x}N_x$ , conduction-band electronic states other than those at the Brilluoin zone center have to be taken into account in order to properly address the giant band-gap lowering observed.

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