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Global changes of the band structure and the crystal lattice of Ga(N,As) due to hydrogenation

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The effect of hydrogenation on five GaN_xAs_{1-x} epitaxial layers $(0.00043 \leqslant x \leqslant 0.019)$ grown by metal-organic vapor-phase epitaxy was investigated. Photomodulated reflectance (PR) and photoluminescence spectroscopy were used to study the electronic band structure, and x-ray diffraction (XRD) and Raman spectroscopy to probe, respectively, the static and dynamic properties of crystal lattice before and after hydrogenation. Hydrogen almost completely neutralizes the effect of N on the band structure of the GaAs host. The direct band gap E_- and the spin-orbit split-off band $E_- + \Delta_0$ blueshift toward the corresponding energies in GaAs and the E_+ band disappears after hydrogenation. The PR spectra of hydrogenated GaN_xAs_{1-x} resemble broad GaAs-like spectra. The XRD traces reveal that hydrogenation removes the tensile strain in GaN_xAs_{1-x} layers and even induces compressive strain. After hydrogenation the GaAs-like features in the Raman spectra persist whereas the local vibrational mode due to N disappears. Three H-related modes can be distinguished in the Raman spectra.

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GaN_xAs_{1-x} belongs to a class of semiconductor alloys where the conduction band structure is tuned by incorporating a few percent x of the N isoelectronic impurity into the host crystal.[1,2] The band structure changes due to N incorporation are dramatic. Examples are the strong redshift of the conduction band edge with increasing x or, at $x \approx 0.002$, the evolution of an N-induced band, the so-called E_+ band, which blueshifts with increasing x.[3–6] It is established by now that, due to the electronegativity and size mismatch, N causes a strong local perturbation of the crystal lattice which in turn modifies the band structure globally.[7–10] Recently, some of us reported that the photoluminescence properties of Ga(N,As) and (Ga,In)(N,As) heterostructures after hydrogenation resemble those of the host structures without N, e.g., exciton recombination lines in N-related complexes are quenched and the band gap shifts toward that of the N-free semiconductor.[11,12] This neutralization of the effects of N on the luminescence properties due to the presence of hydrogen, in particular for the band-gap-related emission band, was surprising and triggered a series of intensive theoretical studies.[13–16] The results are as follows: (1) N-H complexes are more likely to be formed than the interstitial H_2-molecule complex [which is known to be a stable complex in N-free GaAs (Ref. 17)]. (2) At low H doses monohydrogen complexes N-H are formed in p-type material, predominantly a complex where the H atom is bonded to N and situated in a bond-centered position between Ga and N atoms, the so-called N-H_{BC} configuration. This complex is not expected to lead to a reversal of the N-induced band structure changes. (3) At higher H doses, dihydrogen complexes N-H_2^* should be formed. Particularly in n-type material, the N-H_2^* complex should become dominant. It consists of H in a bond-centered position between Ga and N atoms and a second H bonded to that N atom on the antibonding site, so-called N-H_2^* $(BC\text{-}AB_N)$. It is predicted that this complex leads to an almost full neutralization of the N-induced band structure changes in Ga(N,As). Here, we present a comprehensive study of the electronic and lattice properties of GaN_xAs_{1-x} epitaxial layers before and after hydrogenation.

Five GaN_xAs_{1-x} epitaxial layers with $x = 0.00043$, 0.00095, 0.0021, 0.005, and 0.019 and a thickness of 0.5 μm were grown on (100) GaAs substrates by metal-organic vapor-phase epitaxy. The samples are unintentionally doped n type with about $2 \times 10^{16}\ \mathrm{cm}^{-3}$ at 300 K. Pieces of all samples were hydrogenated by ion-beam irradiation from a Kaufman source with the sample temperature held at 300 °C. Low ion energies (100 eV) and current densities (≈ 10 $\mu A/cm^2$) were used. To achieve full hydrogenation of the specimens high impinging hydrogen doses of typically 10^{18}–10^{19} ions/cm^2 were required. Before and after hydrogenation, the strain state of the samples was determined by double-crystal x-ray diffraction (XRD). Photomodulated reflectance (PR) and photoluminescence (PL) experiments were performed to study the band and impurity states. Raman experiments were carried out for studying the vibrational modes.

Figure 1 shows PL spectra of a GaN_xAs_{1-x} epitaxial layer with $x = 0.00095$ before and after hydrogenation, together with a GaAs reference spectrum. Two major effects occur after hydrogenation: (1) the E_- band is strongly blueshifted and the PL spectrum looks like that of GaAs with a band-gap-related feature at 1.515 eV and a C-acceptor-related band at about 1.493 eV (similar results have been obtained for a sample with $x = 0.000\,43$). This means that the perturbation of the host states due to the N-incorporation is effectively removed after hydrogenation. (2) The sharp PL features due to the N-cluster states disappear indicating that these are modified by the H incorporation, i.e., N-H complexes are formed.

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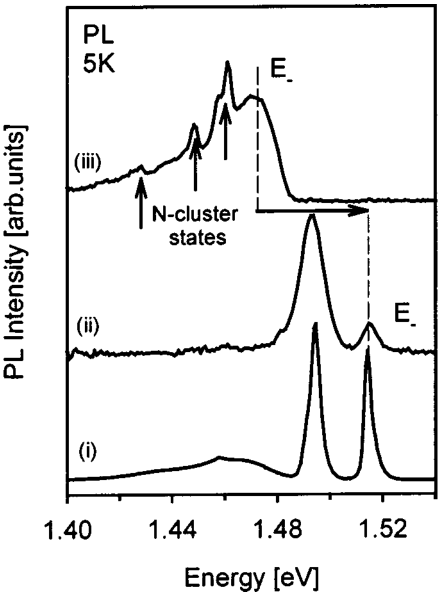

FIG. 1. Photoluminescence spectra taken at $T=5$ K of a (i) GaAs reference sample; a GaN_xAs_{1-x} sample with $x=0.00095$ (ii) after hydrogenation and (iii) as grown.

Further confirmation is given by Raman spectroscopy. The Ga-N local vibrational mode (LVM) at 475 cm^{-1} (which is observed for the as grown GaN_xAs_{1-x} samples with $x=0.005$ and 0.019) disappears after hydrogenation as shown in Fig. 2(a). This is also found by infrared-absorption measurements for *p*-type hydrogenated Ga(N,As).[18] In the spectral range from 1000 to 4000 cm^{-1} shown in Fig. 2(c) we detect three H-related signals at 1041, 3111, and 3912 cm^{-1} for hydrogenated $GaN_{0.019}As_{0.981}$. The modes at 1041 and 3111 cm^{-1} observed in our *n*-type samples after hydrogenation have not been observed simultaneously in any of the previous work to our knowledge.[19–21] Therefore, we believe that these modes are the N-H bond bending and bond stretching modes, respectively, of a hitherto unknown NH complex. Whether this NH complex is only observable in *n*-type material, and whether it is a monohydrogen NH or dihydrogen NH_2 complex, requires, further detailed studies. However, it confirms the predictions[13–16] that various different NH-related complexes can be formed in Ga(N,As) depending on doping, H doses, etc. The third H-related mode in Fig. 2(c) agrees with that of interstitial H_2 molecules in N-free GaAs.[17] This H_2 molecule mode and the disappearance of the Ga-N LVM in the Raman spectra indicate that the samples are fully hydrogenated at least close to the surface. The GaAs-like modes are only weakly affected by hydrogenation. It is worth noting, however, that the LO-phonon energy of the $GaN_{0.019}As_{0.981}$ layer [Fig. 2(b)] is shifted by about 0.8 cm^{-1} to higher wave numbers, indicating a significant reduction of the tensile strain after hydrogenation.

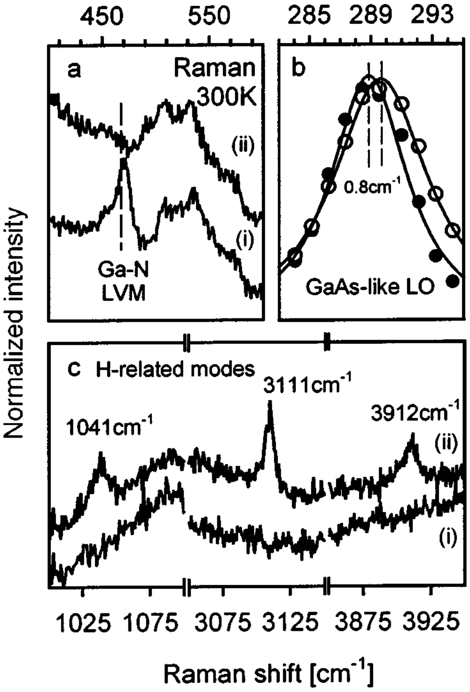

FIG. 2. Phonon Raman spectra of $GaN_{0.019}As_{0.981}$ excited with 514.5 nm (2.41 eV) at $T=300$ K (a) in the vicinity of the local vibrational *N* mode (LVM) of (i) as grown and (ii) after hydrogenation [scattering geometry $x(y',y')\text{-}x$], (b) of the GaAs-like LO-phonon of the as-grown sample (full circles) and after hydrogenation (open circles); the solid lines are Lorentzian fits [scattering geometry $x(y,z)\text{-}x$], and (c) in the spectral range of H-related modes of (i) as-grown and (ii) after hydrogenation (unpolarized in back scattering geometry).

Figures 3 and 4 demonstrate that the band structure changes are not restricted to the bottom of the conduction band only, but to the conduction band as a whole. Indeed, the spin-orbit split-off transition $E_- + \Delta_0$ and the E_+ transition (which both, as the E_- band, change dramatically by incorporating N into GaAs) are also strongly affected by the hydrogenation process. The PR spectrum of a GaN_xAs_{1-x} epitaxial layer with $x=0.005$ after hydrogenation shows, as already observed in PL, the shift of the E_- band gap toward that of GaAs. The corresponding $E_- + \Delta_0$ band exhibits a comparable blueshift. In addition, the E_+ feature (which can be distinguished in PR spectra of as-grown samples for $x > 0.002$) disappears after hydrogenation. This was also observed for the $GaN_{0.019}As_{0.981}$ sample. The E_- signal after hydrogenation shows a tail-like broadening on the low-energy side. It is an indication that the sample is not homogeneously hydrogenated. As the band gap of the lower-lying less-hydrogenated layers is smaller than that of the fully hydrogenated top layer, the former contribute strongly to the low energy side of the measured E_- signal, in particular, as none of the probe light in this energy range is absorbed by the top layer. Such broadening of the E_- signal also is observed for the $GaN_{0.019}As_{0.981}$ sample. In the case of the $E_- + \Delta_0$ signal, these broadening effects are less pronounced as the probe light mainly probes the top layer due to its strong absorption in this spectral range. Therefore, it is very clear that the E_+ signal disappears in the spectra of the hydrogenated GaN_xAs_{1-x} samples with $x=0.005$ and 0.019. The PR signals of all hydrogenated samples show line widths comparable to those of the as grown samples and much broader than GaAs. The relative strength of the $E_- + \Delta_0$ signal with respect to the E_- signal after hydrogenation is simi-

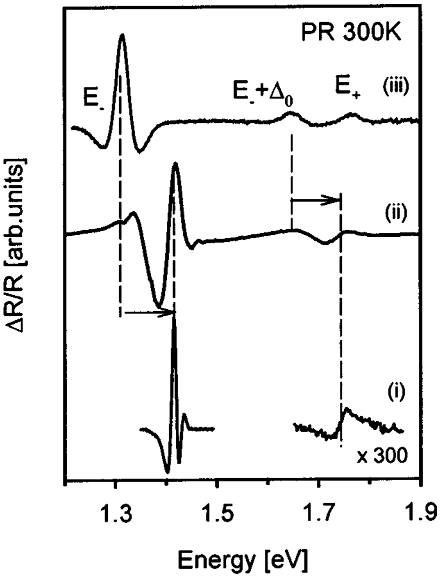

FIG. 3. Photomodulated reflectance spectra taken at $T = 300$ K of (i) GaAs, (ii) $GaN_{0.005}As_{0.995}$ after hydrogenation, and (iii) $GaN_{0.005}As_{0.995}$ as grown.

lar to that of the as-grown samples, therefore, remains significantly bigger than that in GaAs. The energy positions of the three signals before and after hydrogenation are summarized in Fig. 4. The solid lines are a fit of the level repulsion model to the experimental data.[5,6] The dashed horizontal lines indicate the position of E_- and $E_- + \Delta_0$ in GaAs.

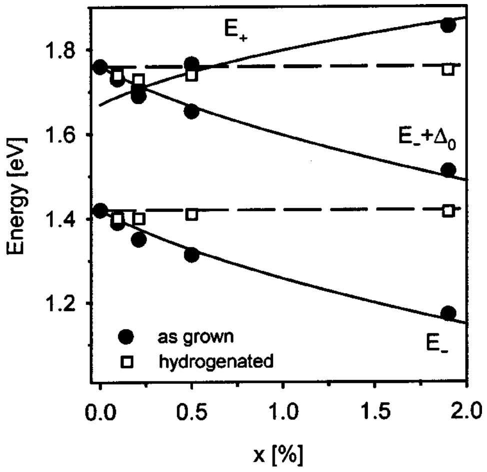

FIG. 4. Energy positions vs N concentration x of the direct band gap E_-, the spin-orbit split-off band $E_- + \Delta_0$ and the N-induced E_+ band of the as-grown GaN_xAs_{1-x} samples (full circles). The solid lines are a fit of the level repulsion model to the experimental data. Corresponding data for E_- and $E_- + \Delta_0$ of the hydrogenated samples (open squares); there is no E_+ signal after hydrogenation. The dashed horizontal lines indicate the position of E_- and $E_- + \Delta_0$ in GaAs. $T = 300$ K.

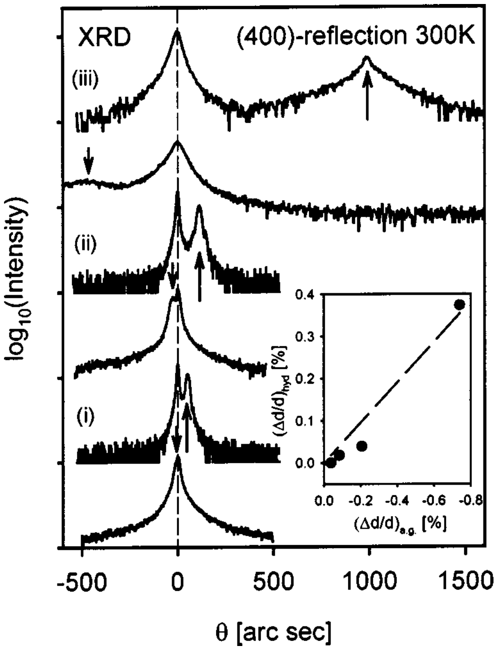

FIG. 5. Pairs of x-ray-diffraction traces of the (400)-reflection of three GaN_xAs_{1-x} samples before (top spectrum of each pair) and after hydrogenation (lower spectrum of each pair) for (i) $x = 0.00095$, (ii) $x = 0.0021$, and (iii) $x = 0.019$. The dashed line indicates the position of GaAs (400) reflex; the arrows pointing up and down indicate the positions of the (400) reflexes of the as-grown and hydrogenated GaN_xAs_{1-x} layers, respectively. $T = 300$ K. Inset: Plot of the relative change of the lattice constant in the growth direction after hydrogenation $(\Delta d/d)_{\mathrm{hyd.}}$ vs that before hydrogenation $(\Delta d/d)_{\mathrm{a.g.}}$ for the GaN_xAs_{1-x} layers with $x \geqslant 0.00095$.

Figure 5 depicts pairs of XRD traces of the (400)-reflection of three GaN_xAs_{1-x} samples before (top trace of each pair) and after hydrogenation (lower trace of each pair) for $x = 0.00095$, 0.0021, and 0.019. The dashed line indicates the position of GaAs (400) reflex which is used as reference point. The arrows pointing up and down indicate the positions of the (400)-reflexes of the strained as grown and hydrogenated GaN_xAs_{1-x} layers, respectively. The pseudomorphically grown samples before hydrogenation are under biaxial tensile strain. Assuming Vegard's law the tensile strain is proportional to the N concentration x of the GaN_xAs_{1-x} layers. Hydrogenation converts the biaxial tensile strain of the layers to a biaxial compressive strain. In the inset of Fig. 5, the relative change of the lattice constant in growth direction after hydrogenation $(\Delta d/d)_{\mathrm{hyd}}$ is plotted versus that before hydrogenation $(\Delta d/d)_{\mathrm{a.g.}}$ for the GaN_xAs_{1-x} layers with $x \geqslant 0.00095$. It shows that the compressive strain in the hydrogenated samples increases with x. This dependence is a further confirmation that N-H complexes are formed. The N-H complexes lead to a change of the local strain around the N atoms, i.e., widen the lattice. This change of the strain state $\Delta\varepsilon_{zz}$ explains the frequency shift of the LO-phonon shown in Fig. 2(b) for the $GaN_{0.019}As_{0.981}$ sample. An estimate using GaAs parameters given in Ref. 22 yields $\Delta\omega \approx 2\ \mathrm{cm}^{-1}$ for $\Delta\varepsilon_{zz} \approx 1.1\%$. Taking into account the uncertainties of the material parameters, this is in reasonable agreement with the observed shift of about 1 cm^{-1}.

In summary, hydrogenation leads to an effective removal of the N-related perturbation due to the formation of a NH-complex which seems to be different from those reported for *p*-type material. Hydrogenation literally reverses all the effects of N on the band structure of the GaAs host. In addition, it removes the tensile strain of pseudomorphically grown GaN_xAs_{1-x} layers and even introduces compressive strain as reflected by the static and dynamic properties of the crystal lattice. Our results are in good agreement with recent theoretical predictions and a further manifestation of the sensitivity of the global properties of these alloys on the local environment of the N site.

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