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H irradiation effects on the GaAs-like Raman modes in $GaAs_{1-x}N_x/GaAs_{1-x}N_x$:H planar heterostructures

E. Giulotto,[1,a)] M. Geddo,[1] M. Patrini,[1] G. Guizzetti,[1] M. Felici,[2] M. Capizzi,[2] A. Polimeni,[2]
F. Martelli,[3,4] and S. Rubini[3]
[1]*Dipartimento di Fisica, Università degli studi di Pavia, Via Bassi 6, I-27100 Pavia, Italy*
[2]*Dipartimento di Fisica, Sapienza Università di Roma, Piazzale A. Moro 2, I-00185 Roma, Italy*
[3]*Laboratorio Nazionale TASC-IOM-CNR, Area Science Park, S.S. 14, Km. 163.5, 34149 Trieste, Italy*
[4]*Istituto per la Microelettronica e i Microsistemi, CNR, Via del fosso del cavaliere 100, 00133 Roma, Italy*

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The GaAs-like longitudinal optical phonon frequency in two hydrogenated $GaAs_{1-x}N_x/GaAs_{1-x}N_x$:H microwire heterostructures—with similar N concentration, but different H dose and implantation conditions—has been investigated by micro-Raman mapping. In the case of $GaAs_{0.991}N_{0.009}$ wires embedded in barriers where GaAs-like properties are recovered through H irradiation, the phonon frequency in the barriers undergoes a blue shift with respect to the wires. In $GaAs_{0.992}N_{0.008}$ wires embedded in less hydrogenated barriers, the phonon frequency exhibits an opposite behavior (red shift). Strain, disorder, phonon localization effects induced by H-irradiation on the GaAs-like phonon frequency are discussed and related to different types of N-H complexes formed in the hydrogenated barriers. It is shown that the red (blue) character of the frequency shift is related to the dominant N-2H (N-3H) type of complexes. Moreover, for specific experimental conditions, an all-optical determination of the uniaxial strain field is obtained. This may improve the design of recently presented devices that exploit the correlation between uniaxial stress and the degree of polarization of photoluminescence.
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I. INTRODUCTION

It is well known that substitution of small percentages of arsenic atoms with nitrogen atoms strongly affects the structural and electronic properties of GaAs. Those properties can be partially or fully restored by post-growth irradiation with hydrogen ions, which form N-H complexes that quench the electronic activity of N.[1–5] Raman spectroscopy nicely monitors the plastic deformations that doping, implantation, annealing may induce in semiconductors.[6] Recently, the strain pattern in heterostructures of $GaAs_{0.991}N_{0.009}$ wires separated by hydrogenated $GaAs_{0.991}N_{0.009}$ barriers (H dose, $d_H = 3.0 \times 10^{18}$ ions/cm^2) has been investigated by Raman scattering.[7] Therein, the GaAs-like longitudinal optical (LO) phonon frequency and the Ga-N local-vibrational-mode (LVM) intensity have been measured along line scans perpendicular to the wire-barrier interfaces. The results well matched to the analysis of electronic transition energies derived from photoreflectance (PR) spectra. The strain pattern thus found was consistent with finite elements strain-simulations, which predict a sharp dependence of the local uniaxial strain at the interfaces of these heterostructures.[8]

From the earliest observations by Klar and coworkers,[4] experimental evidence indicated that hydrogenation of GaAsN produces a blue shift of GaAs-like LO-phonon frequency of about 1 cm^{-1} or more. The blue shift[4,7] was accounted for by the expansion of the host lattice caused by the formation of nitrogen-hydrogen complexes, that may even turn the native GaAsN tensile strain into a compressive one.[9,10] More precisely, with the hypothesis that in dilute nitrides the stiffness constants and the characteristic GaAs-like LO-phonon frequency of the untreated material do not change significantly with hydrogenation, its frequency depends linearly on strain.[11] Consequently, a frequency increase is expected to follow the enhancement of the compressive character of the in-plane strain. On the other hand, since hydrogen diffusion profiles and the formation of the different types of N-*n*H complexes strongly depend on hydrogenation conditions,[12] it is reasonable to believe that they influence the optical response of the material even when the same full nitrogen passivation is achieved.

In this work, the GaAs-like LO frequency pattern recorded in two hydrogenated GaAsN/GaAsN:H heterostructures—with similar N concentration, but different H doses and implantation conditions—has been investigated by micro-Raman mapping. Their striking differences are discussed in terms of strain, disorder, phonon localization induced by H-irradiation on the GaAs-like LO frequency and related to different types of N-*n*H complexes formed in the hydrogenated barriers.[13] With regard to these complexes, indeed, it has been shown[9,14] that the formation of N-2H complexes results in a near-perfect lattice match between the hydrogenated alloy and the GaAs substrate, whereas the N-3H species is associated with a ~40% "overshooting" of the lattice parameter of the material—and, therefore, with the emergence of a significant compressive strain in the H-irradiated epilayer. The process of H diffusion in the presence of H-opaque masks on the surface of the material—at the basis of the spatially selective hydrogenation method used to fabricate the GaAsN wires investigated in this

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[a)] Author to whom correspondence should be addressed. Electronic mail: enricovirgilio.giulotto@unipv.it.

work[15,16]—can be successfully modelled by combining the system of *diffusion-reaction* equations defined in Ref. 12 with Finite-Elements Analysis. Moreover, for specific experimental conditions, a method is developed which allows the separation of the components of the built-in strain field arising from the isotropic stress in the epitaxial film from those due to uniaxial stress at wire-barrier interfaces. The uniaxial stress is determined in an all-optical way, a procedure of interest for application in optical devices where the correlation between the pattern of uniaxial strain and the photoluminescence degree of polarization in GaAsN wires has been well established.[8]

II. EXPERIMENTAL DETAILS

Two 200-nm thick layers of GaAsN were pseudomorphically grown at 500 °C by molecular beam epitaxy on top of GaAs buffers deposited on (001) GaAs substrates. Layer thickness and nitrogen concentration were characterized by X-ray diffraction. A 50 nm-thick titanium film, opaque to H, was deposited then on the GaAsN surface and patterned by electron beam lithography.

Table I summarizes the analyzed samples. The first sample (hereafter named HHD, [N] = 0.009) was hydrogenated at 300 °C (100 eV ion-beam energy, 42 μA/cm^2 ion current, 11340 s hydrogenation time) through the Ti mask, which has been then removed by chemical etching. The H dose ($d_H = 3.0 \times 10^{18}$ ions/cm^2) guarantees full passivation of the unpatterned parts of the GaAsN layer. GaAsN wires of different widths (0.5, 1.0, 2.0, 5, and 10 mm), directed along $\langle 110 \rangle$, and separated by 10-20 mm GaAsN hydrogenated barriers were thus obtained. The second sample (named LHD, [N] = 0.008) was exposed to a lower H dose ($d_H = 1.4 \times 10^{18}$ ions/cm^2, 22.8 mA/cm^2 ion current, 9780 s hydrogenation time), while hydrogenation temperature and H beam energy were the same as for HHD sample. Sequences of 5 mm GaAsN wires separated by 5 mm hydrogenated GaAsN barriers were obtained, with wires oriented along $\langle 110 \rangle$. A bare GaAs epitaxial layer was used as a reference sample for optical measurements. Moreover, homogeneous and pseudomorphic layers, i.e., an untreated GaAsN epitaxial layer and a H implanted GaAsN layer, were also analyzed.

In Raman scattering experiments, the incident beam was directed along z axis, normal to the growth plane, incident light polarization direction y was parallel to wire axis, whereas scans were done along x direction, normal to wire axis. A Jobin-Yvon Labram micro-spectrometer was used, equipped with a 100× objective, a 1800 lines/mm grating, and a cooled Si CCD detector. The exciting He-Ne laser beam ($\lambda = 632.8$ nm, spot diameter ~ 0.7 μm) was attenuated to about 1 mW to avoid dissociation of N-H complexes.[17]

PR measurements were performed at near-normal incidence in the 1.1–1.9 eV range, with a spectral resolution of 1 meV. A standard experimental apparatus was operated with a 100 W halogen lamp as probe source. The excitation source was provided by a 20 mW Coherent HeNe laser ($\lambda = 632.8$ nm; 1-mm spot diameter) chopped at 220 Hz. Further details on the PR apparatus can be found elsewhere.[18]

Topographic images of the sample surface were acquired through Atomic Force Microscopy with an Auto Probe CP Research Thermomicroscopes scanning system operated in tapping mode (Silicon NSG03 probe from NT-MDT) and analyzed by Image Processing 2.1 software.

Finally, concentration maps of the N-2H and N-3H complexes in the samples were produced by Finite-Elements calculations of H diffusion in a masked GaAsN/GaAs epilayer.[12]

III. RESULTS AND DISCUSSION

The LO-phonon frequencies were determined by fitting a Lorentzian line-shape to the data, with an uncertainty of the order of ±0.1 cm^{-1} or less. The GaAs LO-phonon frequency is 292.8 cm^{-1}, as measured in the reference sample, while the GaAs-like LO-phonon frequency is equal to 291.2 cm^{-1} in the untreated GaAs$_{0.992}$N$_{0.008}$ and 290.9 cm^{-1} in the untreated GaAs$_{0.991}$N$_{0.009}$ epilayers. The negative frequency shifts result from contribution of both composition and strain effects, confirming that in-plane isotropic strain in the GaAsN thin films is tensile, in agreement with previous results.[19] However, in the present structures with wires and barriers, an anisotropic uniaxial strain is superimposed to the isotropic biaxial strain present in the as-grown and hydrogenated pseudomorphic films. In the following, phonon frequencies are assumed to depend linearly on the isotropic, biaxial in-plane strain, as commonly done to correlate LO-phonon frequencies and strain.[11] In addition, LO-phonon frequencies are assumed to depend linearly on local anisotropic strain components near the wire-barrier interfaces, hence on the diagonal stress component X_{xx}, acting orthogonally to the interfaces.[6,20]

Figure 1 shows the Raman mapping of the GaAs-like LO phonon frequency (~292 cm^{-1}) and the Ga-N local vibrational mode intensity profile (LVM frequency ~ 470 cm^{-1}) for a scan normal to a 10-micron wire axis in sample HHD. As the intensity of the LVM is proportional to the concentration of active nitrogen in GaAsN,[4] its spatial profile images each wire position and width, while its vanishing indicates complete N passivation in the hydrogenated barriers. In Figure 1, we applied a data reduction method in order to eliminate the contribution to the LO frequency from biaxial strain present in the overall pseudomorphic material. The LO

TABLE I. GaAs-like LO phonon frequencies as derived from the analysis of Raman scattering spectra in different sample structures.

		GaAsN ω_{LO} (cm^{-1})			GaAsN:H ω_{LO} (cm^{-1})	
Sample	N (%)	layer	wires	H dose (ions/cm^{-2})	layer	barriers
HHD	0.9	290.9	292.0	3×10^{18}	-	292.7
LHD	0.8	291.2	291.4	1.4×10^{18}	289.6	290.6
GaAs epitaxial	–			–	292.8	

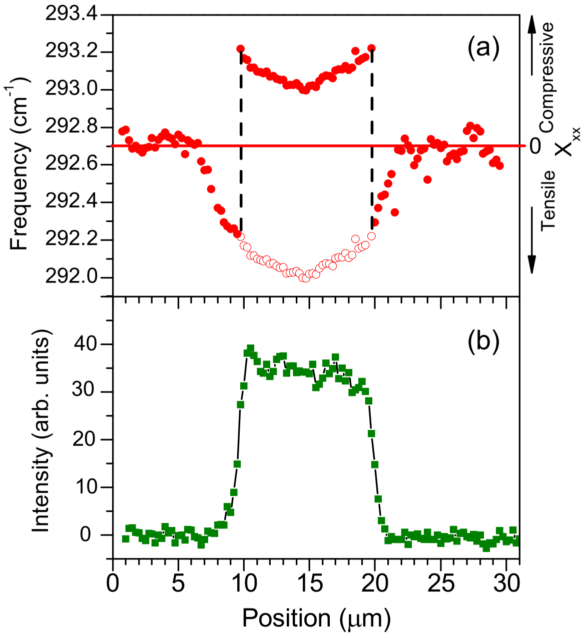

FIG. 1. Sample HHD. (a) Full dots: GaAs-like LO phonon frequency profile along a direction normal to a 10-mm wide wire, after data reduction as described in the text. Frequency differences with respect to that measured in barriers far from interfaces are proportional to uniaxial stress (right axis scale). Empty dots: GaAs-like LO phonon frequency profile in the wire before data reduction. Dashed vertical lines indicate wire-barrier interfaces, as derived from data in panel (b). (b) Corresponding profile of Ga-N local vibrational mode integrated intensity (arbitrary units) along the same scan.

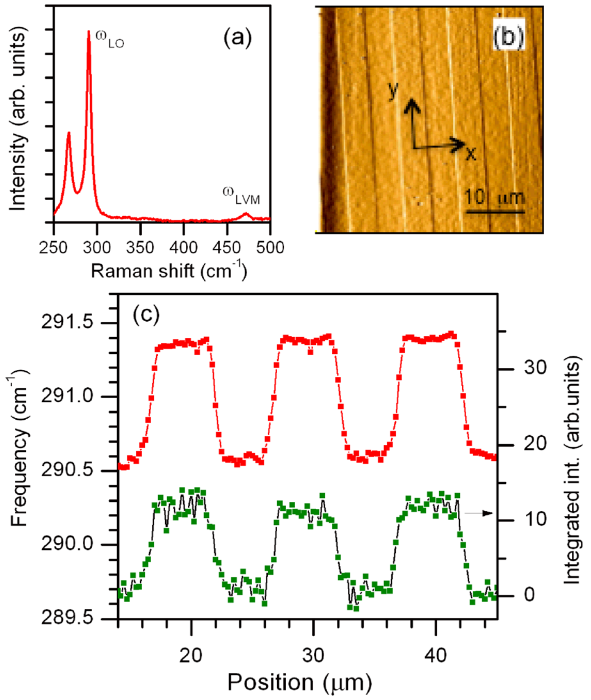

FIG. 2. Sample LHD: (a) typical Raman scattering spectrum in 5-mm wide wire area; (b) AFM topography image of sample surface; (c) GaAs-like LO frequency profile (circles) and LVM integrated intensity (squares) along a line scan perpendicular to the wire axis.

phonon frequency data corresponding to scan positions *inside the wire* have been shifted by $+1.0\,\mathrm{cm}^{-1}$—that is double the difference between the measured LO frequencies in the barrier far from the interface and at the interface. This is justified if, according to symmetry considerations, one assumes that local uniaxial stress X_{xx} at barrier-wire interfaces have the same intensity and opposite sign, and admits that elastic constants are equal in the untreated and hydrogenated material. The correctness of this procedure is confirmed by comparison with simulations of uniaxial strain in wires 5 μm wide or more.[8] The method allows us to evidence the different character of the anisotropic uniaxial strain component ε_{xx} (proportional to the diagonal stress component X_{xx}) for each position, as qualitatively indicated by the right scale in Figure 1. In fact, the results are in reasonable agreement with simulations of uniaxial strain pattern in the same heterostructure.[8] The present results, in particular, indicate that residual uniaxial stress is present even at wire axis, which is consistent with the absence of a frequency plateau inside the wire.

A typical Raman spectrum, as measured on a 5-mm wire and an AFM topography image of sample LHD are shown in Figures 2(a) and 2(b), respectively. A small step is measured at the interface between wires and barriers, most likely due to an excessively long etching in removing the Ti mask. The profile of the GaAs-like LO-phonon frequency, as derived from a Raman line scan, is shown in Figure 2(c). Strikingly, the LO-phonon frequency in the barriers is now *lower* than in the wires, the wire positions being identified by the intensity profile of the Ga-N LVM. Therefore, these results appear at variance with those found in the case of the more hydrogenated sample HHD.

Why? In order to elucidate this point, we discuss our results in terms of the three aforementioned effects, that is lattice strain, disorder and compositional effects due to N-*n*H complexes.

A. Lattice strain

We first performed a PR characterization of the strain nature in LHD sample. In Figure 3, the room temperature PR spectra for sample LHD (circles) and for the as-grown untreated sample (squares) are compared in the 1.1–1.9 eV energy range. In addition to the spectral structures near 1.42 eV (due to buffer/substrate GaAs band gap[21,22]), some interesting features can be observed in both spectra. For the untreated sample the E^{-U} feature at 1.270 eV marks the GaAsN band gap energy (E^{-} band). This spectral structure (red-shifted with respect to GaAs fundamental bandgap) is typical of dilute nitrides,[1,2] as well as the E^{+} band (near 1.80 eV) and the $E^{-} + \Delta_0$ band (near 1.60 eV). Their energy location mainly depends on the N concentration of GaAsN alloy;[23] moreover, for coherently grown layers, the native in-plane biaxial tensile strain is expected to produce a further (a few meV) red-shift of their transition energies,[24] and valence band splitting, as well. According to the deformation potential theory,[25] the split heavy-hole and light-hole character transitions both shift to higher energy for increasing compressive strain (or decreasing tensile strain). Due to broadening effects, the doublet is unresolved[7,10] in the present experimental conditions. So, a single Aspnes model function was used to derive the transition energy of the GaAsN band

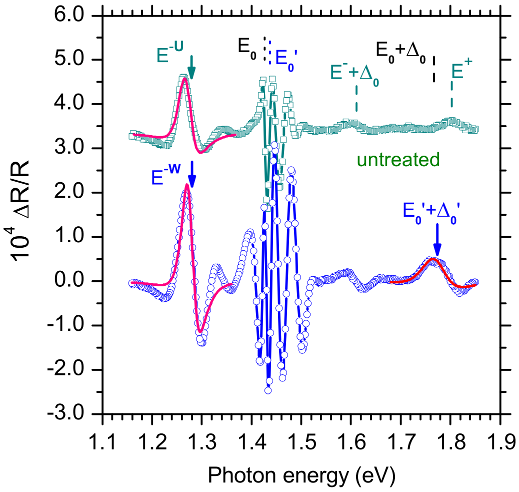

FIG. 3. Room-temperature PR spectra of LHD sample (circles) and of the untreated sample (open squares, vertically shifted for clarity). In both spectra, the PR features near 1.27 eV (E^{-w} and E^{-u}) are related to the red-shifted GaAsN fundamental gap (E^- band). In the first spectrum, note how the GaAsN:H SO band $E_0' + \Delta_0'$ (due to PR signal coming from the hydrogenated sections) obscures the E^+ band (due to PR signal coming from GaAsN wires). Arrows mark the transition energy, as obtained from the best fit (thick lines) of the experimental line-shape. Dashed bars indicate the transition energies of the main GaAs (E_0 and $E_0 + \Delta_0$) and GaAsN spectral features, as taken from the literature, and of the GaAsN:H fundamental gap E_0' (simulation results).

gap. Anyway, the "center of mass" of the band gap structures is expected to move towards higher energy as the tensile character of the strain field is reduced.

Just a look to the spectrum of the LHD wire sample highlights the blue shift undergone by the transition energy of the GaAsN band gap (labeled E^{-W}). This feature is due to PR signal coming from the GaAsN wire sections. We obtained a (7 ± 2) meV blue shift with respect to E^{-U}, as determined performing the best fit (solid lines in Figure 3) of the corresponding spectral features to the appropriate Aspnes line-shape model.[21] This result indicates that the in-plane average strain in GaAsN wires is less tensile (or it has a more compressive character[7,8]) with respect to the as-grown sample value. Comparison with the similar situation of sample HHD[7] suggests that the origin of the increased compressive character of the GaAsN wire strain can be found in the hydrogenated sections of the sample, and specifically in the compressive stress acting along ⟨1-10⟩ direction. Obviously, this occurs as a consequence of the compressive strain in the hydrogenated barriers.

An estimate of the average in-plane strain value in the barriers can be obtained by analyzing the contribution of the hydrogenated sections to the PR spectrum of sample LHD. The latter is evidenced by the structures of the fundamental gap (E_0') and of the split-off (SO) band ($E_0' + \Delta_0'$) of the GaAsN:H. These features appear broadened and more intense with respect to the corresponding features, E_0 and $E_0 + \Delta_0$, reported in the literature for N free GaAs, as previously observed.[10,24] For this reason, the SO band of GaAsN:H (barriers) obscures the GaAsN E^+ band (wires). From the best fit of the barrier SO band, a blue shift of 5 ± 2 meV has been measured with respect to the corresponding SO one in GaAs. This suggests that the hydrogenated sections of the LHD sample in the growth plane are under an average compressive strain.[25] By applying an analytical procedure thoroughly described elsewhere,[20] an average compressive in-plane strain value $\varepsilon_{//}$ roughly equal to -0.5×10^{-3} is estimated.

B. Lattice disorder

Since the hydrogenated barriers are under compressive strain, the strain itself cannot be the origin of the GaAs-like LO frequency red shift. Thus, we did not attempt a reduction on the LHD sample Raman data, along the same lines as for HHD sample. On the other hand, hydrogen implantation and complex formation usually increase lattice disorder. It is well known that in III-V alloys compositional disorder or whatever effect inducing phonon localization, e.g., the presence of defects induced by ion implantation, produces broadening and red shift in the Raman line shape of the GaAs-like LO mode. In $GaAs_{1-x}N_x$ the first order Raman scattering intensity can be expressed by:[26]

$$I(\omega) \propto \int_0^1 \exp\left[\frac{-q^2L^2}{4}\right] \times \frac{d^3q}{[\omega - \omega(q)]^2 + (\Gamma_0/2)^2}, \tag{1}$$

where q is expressed in units of $2\pi/a$, a is the lattice constant of GaAs, Γ_0 is line width of LO phonon in pure GaAs crystal, L is the correlation length in $GaAs_{1-x}N_x$, and the dispersion function $\omega(q)$ of LO mode based on the one-dimensional linear chain model is given by:[26,27]

$$\omega^2(q) = A + \{A^2 - B[1 - \cos(\pi q)]\}^{1/2}, \tag{2}$$

with $A = 4.6 \times 10^4\,\mathrm{cm}^{-2}$ and $B = 7.11 \times 10^8\,\mathrm{cm}^{-4}$.

We note that, in order to obtain the red shift experimentally observed (1–$1.5\,\mathrm{cm}^{-1}$) in sample LHD when going from wires to hydrogenated barriers, the correlation length L value has to be set between 5.5 and 6.5 nm, a range consistent with values reported for other III-V alloys[27] (between 3.5 and 11.0 nm in $GaAs_{1-x}N_x$ with x within 2.3% and 0%).

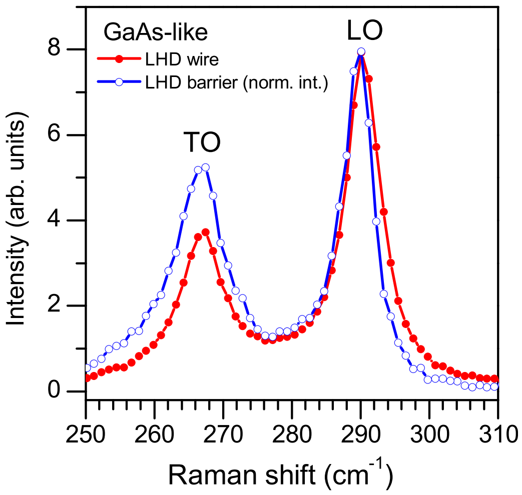

FIG. 4. Comparison of the Raman spectra of sample LHD, near the GaAs-like LO and TO phonon peaks, in the hydrogenated barriers (open circles) and in the wires (full circles).

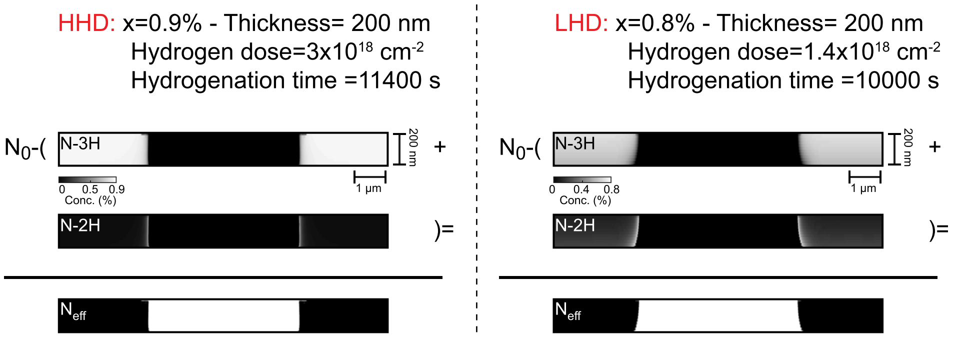

FIG. 5. Hydrogen diffusion maps, as obtained by Finite-Elements calculations of H diffusion in a masked GaAsN/GaAs epilayer (see text). Note the higher concentration of N-3H complexes in sample HHD and of N-2H ones in sample LHD.

Nevertheless, the experimentally observed red shift should be accompanied by an increase of the LO linewidth of 30% or more. On the contrary, as shown in Figure 4, the linewidth does not change significantly. In the same way, the intensity ratio of transverse optical (TO) to LO phonon lines I_{TO}/I_{LO} (very small in pure GaAs) which is known to increase in $GaAs_{1-x}N_x$ for increasing N concentration and lattice disorder, does not vary significantly. Consequently we may infer that in the present case neither strain nor disorder could produce the observed LO red shift.

C. N-*n*H complexes

Let us now examine indirect effects of N-H complexes on the frequency of LO GaAs-like mode. Previous results[4,7] indicated that the GaAs-like LO phonon energy of $GaAs_{1-x}N_x$ layers shifts to higher frequencies after a hydrogenation process leading to full nitrogen passivation. As outlined in the introduction, this was explained by the lattice expansion caused by the formation of N-*n*H centers and the ensuing strain inversion. In more detail, N-2H complexes, responsible for N electronic passivation,[13,28] are known to modify the $GaAs_{1-x}N_x$ lattice parameter (reduced after N incorporation[29]) in a value roughly equal to the GaAs one. In contrast, N-*n*H ($n > 2$) centers that form when one or more H atoms get trapped near a strongly bound N-2H complex lead to an even larger lattice expansion.[9,13]

It is plausible that in the presence of high H doses and long hydrogenation times, as usually occurred in early experiments,[4,7,9] N-*n*H ($n > 2$) were the dominant centers. This is consistent with the large lattice expansion independently observed with different experimental techniques. On the other hand, our PR measurements performed on hydrogenated samples subjected to thermal treatment[24] ensure that after a few hours of annealing at 250 °C (that is the activation temperature of N-3H centers[14]) the host lattice (N-2H being now the dominant center) preserves the full N electronic passivation and resumes the GaAs lattice parameter, as evidenced by the vanishing of the characteristic blue shift[10] of the GaAsN:H SO energy.

In recent years, it has been shown that the same result of full N passivation can be obtained by using *soft* hydrogenation experimental conditions[30] with sizeable concentration of N-2H centers (and a less pronounced lattice expansion). In fact, this should be the case of sample LHD. Moreover, the higher slope of the LO frequency change between wire and barrier in sample LHD with respect to sample HHD is consistent with a compositional effect and not with a strain one. On the contrary, the slightly increased LO frequency at the wire/barrier interface with respect to the wire center is similar to that occurring in HHD sample and should be attributed to lattice strain, as confirmed by calculations.[8]

For a given set of hydrogenation conditions, Finite Element Analysis[31] allows for the determination of the individual concentrations of N-2H and N-3H complexes in any point of a patterned sample. In turn, the comparison of these results with the micro-Raman experiments reported in the present work clearly shows that the red (blue) character of the frequency shift is strictly related to the dominant N-2H (N-3H) type of complexes. The concentration maps of the N-2H and N-3H complexes as well as the effective N concentration (N_{eff}), are shown in Figure 5. We note that in sample HHD there is a higher concentration of N-3H complexes, as well as a lower concentration of N-2H ones, and wire sidewalls are steeper with respect to sample LHD. Moreover, overall differences in N_{eff} are negligible, especially close to the wire center and well within the hydrogenated barriers, where micro-photoluminescence measurements ensured full nitrogen passivation for both samples.

In conclusion, our experimental results suggest that strain and disorder effects are overcome by another effect, by an agent capable of changing the characteristic frequency of the LO GaAs-like mode in GaAsN. We suggest that soft hydrogenation favors the coexistence of N-2H center (where two H atoms are bound to one N atoms) with the complex α-$H_2(N)$[31] (theoretically predicted but never experimentally observed). This last, including N-H and Ga-H mono-hydride bonds, constitutes the minimum energy (e.g., the ground state) of complex modeling. This complex may reduce the strength of Ga-As bonds, affecting the energy of the GaAs-like mode, and in turn producing an intrinsic red shift of its characteristic frequency.

IV. SUMMARY

In this work, we applied an all-optical strain mapping procedure based on micro-Raman scattering to GaAsN/GaAsN:H wire heterostructures, which enlightens the differences between heavily and softly hydrogenated samples. The origin of the intriguing frequency red-shift of the LO GaAs-like phonon mode at lower H doses has been addressed and tentatively explained as related to N-2H centers concentration. Clear evidence is produced for the possibility of strain modulation in planar GaAsN-GaAsN:H wire heterostructures through the coexistence of different N-*n*H complexes (more or less lattice expanding), thus improving strain engineering facilities for the design of photoemitting GaAs-based devices, as well as their structural efficiency.

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