AIP Applied Physics Letters

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Citation: Applied Physics Letters **104**, 142101 (2014); doi: 10.1063/1.4870529
View online: http://dx.doi.org/10.1063/1.4870529
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APPLIED PHYSICS LETTERS 104, 142101 (2014)

High-pressure Raman scattering in InGaN heteroepitaxial layers: Effect of the substrate on the phonon pressure coefficients

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(Received 7 March 2014; accepted 25 March 2014; published online 7 April 2014)

We perform high-pressure Raman-scattering measurements on different $In_xGa_{1-x}N$/Si(111) epilayers ($0.19 < x < 0.45$). We find that the experimental pressure coefficient of the A_1(LO) mode measured in these samples is larger than that expected from the linear interpolation between the corresponding values of GaN and InN. Similar measurements in InGaN epilayers grown on GaN/sapphire templates yield much lower values, below the linearly interpolated pressure coefficients. We conclude that the phonon pressure coefficients measured in InGaN are mainly determined by the different compressibility of the substrate and epilayer material. Neglecting substrate effects may yield highly inaccurate phonon pressure coefficients and mode Grüneisen parameters. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4870529]

Group-III nitrides and their alloys are already being used as the active material of a variety of commercial electronic and optoelectronic devices. The bandgap energy of InGaN can be tuned to cover the entire visible spectral range, from the ultraviolet (UV) down to the near-infrared, and this could be exploited to design and fabricate high-efficiency multijunction solar cells, infrared detectors, or white-light emitting devices.[1] InGaN alloys are also being studied as a promising candidate to fabricate photoelectrochemical cells for hydrogen generation by solar water splitting.[2] Thus, a great deal of research work is currently being devoted to improve the crystal quality of InGaN layers, which are most usually grown on sapphire substrates. The growth of InGaN on Si offers a potential alternative for low-cost production of device applications based on this alloy system. In the particular case of multijunction solar cells, the bandgap of Si at 1.1 eV makes it ideally suited for the bottom junction of the stucture.[3]

Raman spectroscopy is widely employed to characterize the strain, composition, and crystal quality of semiconductor materials and structures. Raman-scattering experiments performed under high hydrostatic pressures also allow one to determine important thermodynamic properties of crystalline compounds such as the mode Grüneisen parameters. In addition, the high-pressure Raman measurements provide a highly useful benchmark to test existing models for the calculation of the lattice-dynamical properties of semiconductors. The measurement of phonon pressure coefficients from heterostructured material, however, may be strongly affected by the particular substrate employed for the growth. This might be particularly relevant for the case of III-nitrides, which are grown on a variety of different substrates.

Several works have been devoted to carry out high-pressure Raman-scattering measurements on GaN[4–6] and InN.[7–11] Pressure coefficients and mode Grüneisen parameters for the non-polar E_2 modes and the polar A_1 and E_1 modes of these two compounds have been measured. Also, the softening of the E_{2l} mode in both GaN and InN has been observed and the pressure dependence of the TO-LO splitting has been investigated and analyzed. The wurtzite-to-rocksalt transition has been found to occur at 42–49 GPa in GaN[5] and at 12–14 GPa in InN,[8,11] and the pressure behavior of the Raman modes of the rocksalt phases has been monitored. The rocksalt-to-wurtzite backtransition has also been observed in InN in the downstroke cycle at pressure values as low as 3.6 GPa.[11] No substrate effects on the experimental phonon pressure coefficients of these two compounds have been observed so far.[11]

The compositional dependence of several structural and vibrational properties of the InGaN alloy has been found to display important deviations from the linear behavior. For instance, the ambient-pressure E_{2h} frequencies seem to exhibit a sizable bowing in relation to the linear dependence predicted by the modified random-element isodisplacement (MREI) model.[12] Similarly, the surface acoustic wave velocity of InGaN has been recently found to exhibit a sublinear dependence on alloy composition.[13] This observation supports the predictions of *ab initio* calculations of the elastic constants of wurtzite InGaN.[14] According to these calculations, the elastic constants of InGaN may significantly deviate from the linearly interpolated values between GaN and InN. The bulk modulus of InGaN, however, seems to follow an almost compositional linear behavior between the pure binary compounds.[14] With regard to the compositional behavior of the phonon pressure coefficients and mode Grüneisen parameters of InGaN, no data are available so far.

In the present work, we report high-pressure Raman-scattering measurements on $In_xGa_{1-x}N$/Si(111) epilayers with $0.19 < x < 0.45$. The aim of this work is to experimentally determine the pressure coefficient and mode Grüneisen parameters of the A_1(LO) phonons of InGaN as a function of

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composition. We find that the experimental pressure coefficient of this mode measured in InGaN/Si(111) is larger than the values obtained by linear interpolation between GaN and InN. Additional experiments with different excitation wavelengths and on InGaN epilayers grown on GaN/sapphire suggest that the experimental phonon pressure coefficients are mainly determined by the differential compressibility between InGaN and the substrate material.

$In_xGa_{1-x}N$ layers were grown by metal-organic chemical vapor deposition on 10-nm-thick $In_yAl_{1-y}N$ buffer layers deposited on Si(111) substrates. The indium content (thickness) of the different $In_xGa_{1-x}N$/Si(111) epilayers was $x = 19\%$ (300 nm), 30% (360 nm), 37% (463 nm), 43% (541 nm), and 45% (446 nm). Two of these samples ($x = 43\%$ and 45%) were chemically etched with nitric acid to remove metallic In clusters from the surface. As-grown and etched samples were both included in this study. Three additional $In_xGa_{1-x}N$ layers ($x = 33\%$, 34%, and 42%) grown by molecular beam epitaxy on GaN/sapphire templates were also used in this work. Details about these samples can be found elsewhere.[12]

Small flakes ($\approx$30 μm thick) of the samples were loaded in a gasketed membrane-type diamond anvil cell (DAC). A mixture of methanol-ethanol-water (16:3:1) was used as pressure transmission medium, and the applied pressure was determined by the ruby fluorescence method. Confocal micro-Raman measurements were performed at room temperature with a Jobin-Yvon T-64000 spectrometer equipped with a LN_2-cooled CCD detector. The 514.5-nm line of an Ar^+ laser was used as excitation source. To investigate the role of excitation wavelength on the measured pressure coefficients, additional experiments were performed with 457.9-nm radiation. A 50$\times$ objective was used to focus the laser beam and to collect the backscattered radiation. The applied pressure was kept below the diamond-to-metallic β-Sn phase transition of Si at $\sim$12 GPa.

Figure 1 shows selected room-temperature Raman spectra excited with 514.5-nm radiation at different hydrostatic pressures (upstroke cycle) for the case of the $In_{0.45}Ga_{0.55}N$ /Si(111) epilayer. Similar results are found for the rest of InGaN/Si(111) samples investigated in this work. In Fig. 1, the intensity of the different curves has been normalized for scaling reasons, and a strong photoluminescence background signal has been removed from the spectra. As can be seen in the figure, the spectra are dominated by a broad band arising from the A_1(LO) mode of InGaN, which displays the expected blueshift with increasing pressure. In the spectra excited with 514.5-nm radiation, and given the In content of the samples studied in this work ($0.19 < x < 0.45$), the A_1(LO) phonons in all the samples are resonantly or near-resonantly excited via the Fröhlich interaction mechanisms. Below the A_1(LO) band, a broad shoulder related to alloy disorder is also observed. Besides, a weak feature corresponding to the first-order optical phonon of Si shows up in the spectra. The pressure coefficient that we obtain for this mode is $4.6 \pm 0.3\ cm^{-1}\ GPa^{-1}$ in all the InGaN/Si(111) samples, in agreement with the $\sim 4.5\ cm^{-1}\ GPa^{-1}$ value reported in the literature for bulk Si.[15]

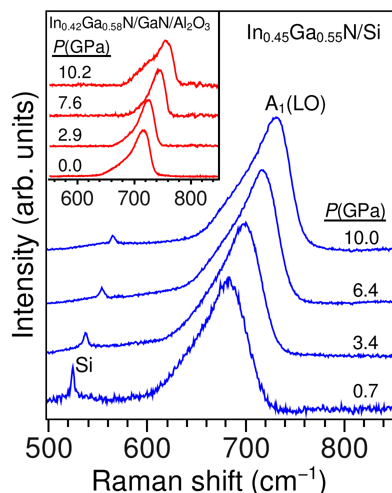

FIG. 1. Raman spectra acquired at different hydrostatic pressures up to 10 GPa from an $In_xGa_{1-x}N$ epilayer ($x = 0.45$) grown on Si(111). Inset: High-pressure Raman spectra of $In_xGa_{1-x}N$ /GaN/sapphire ($x = 0.42$).

Figure 2 shows the frequency of the A_1(LO) mode (ω_{LO}) as a function of applied pressure for three of the as-grown InGaN/Si(111) samples. In all cases, the A_1(LO) frequency is found to display a linear pressure dependence. From a linear fit to the experimental data, linear pressure coefficients $(d\omega_{LO}/dp)_{p=0}$ in the 4.2–5.3 $cm^{-1}\ GPa^{-1}$ range are obtained. The figure clearly shows the expected reduction of the zero-pressure A_1(LO) frequency with increasing In content.

We have plotted in Fig. 3 the linear pressure coefficient of the A_1(LO) mode obtained for all the as-grown (triangle symbols) and the etched (crosses) InGaN/Si(111) epilayers studied in this work. This figure shows that, within the experimental error associated to DAC experiments, the measured pressure coefficients tend to be larger in the samples with higher In contents. In contrast, no significant differences are found between as-grown and etched samples, which suggests that the presence of In clusters at the surface does not affect the pressure behavior of the InGaN/Si(111) epilayers. The dashed line in Fig. 3 corresponds to linearly interpolated pressure coefficients obtained from the values measured in InN and GaN. Note that there is a relatively large dispersion of reported pressure-coefficient values in the literature for these two compounds. For instance, in the case of the A_1(LO) mode of w-InN, pressure coefficients ranging from $4.73\ cm^{-1}\ GPa^{-1}$ (Ref. 9) up to $5.96\ cm^{-1}\ GPa^{-1}$ (Ref. 8) have been reported. The pressure coefficient values used to plot the linear composition dependence in Fig. 3 (3.8 and

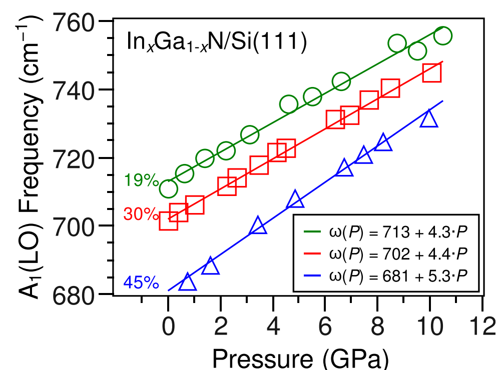

FIG. 2. Pressure dependence of the A_1(LO) phonon frequency of InGaN as measured in three different $In_xGa_{1-x}N$/Si(111) epilayers with $x = 0.19$, 0.3, and 0.45. The solid lines are linear fits to the experimental data.

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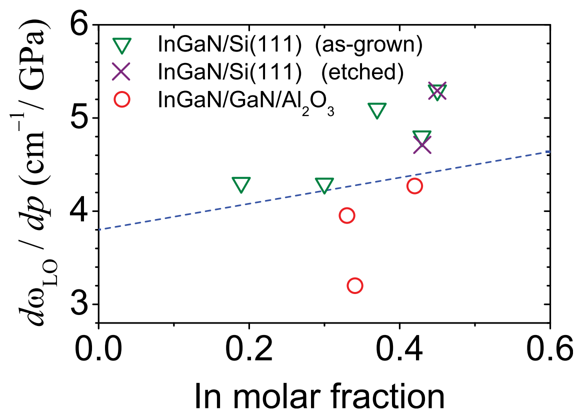

FIG. 3. Pressure coefficient of the A_1(LO) phonon mode as a function of In content as obtained by high-pressure Raman-scattering measurements on all the InGaN/Si(111) and InGaN/GaN/sapphire epilayers studied in this work. The dashed line shows the pressure coefficient values expected from a linear interpolation between the GaN and InN end members.

5.2 cm^{-1} GPa^{-1} for GaN and InN, respectively) were taken by averaging the data available in the literature (Refs. 4–6 for GaN and Refs. 8, 9, and 11 for InN). In the particular case of InN, recent measurements on several high-quality InN/Al_2O_3 epilayers of different thicknesses[11] suggest that the A_1(LO) pressure coefficient for InN is not larger than 5.2 cm^{-1} GPa^{-1}, not far from the value measured in strain-free InN nanowires (4.73 cm^{-1} GPa^{-1}).[9]

As can be seen in Fig. 3, for intermediate In compositions, the experimental pressure coefficients measured on InGaN/Si(111) tend to be larger, up to 0.8 cm^{-1} GPa^{-1}, than those expected from the linear interpolation between the corresponding values of GaN and InN. Although the observed deviation is relatively low, it is consistently observed in the etched and non-etched samples with intermediate compositions ($x \sim 0.4$). This result could be attributed to a compositional bowing of the pressure coefficients that would also affect to the resulting mode Grüneisen parameters. However, two additional effects may be invoked to explain the present results: (i) variations of the measured pressure coefficients induced by compositional fluctuation in the InGaN layers; (ii) a strain-related substrate effect.

It is well-known that, in resonant or near-resonant Raman-scattering by the A_1(LO) phonons in InGaN, lateral and in-depth compositional fluctuations give rise to the selective excitation of sample regions with a particular In content.[16,17] Due to this effect, sizable frequency shifts of the A_1(LO) bands are reported in the literature as a function of the excitation wavelength used to perform the Raman measurements.[12,17] Given that hydrostatic pressure modifies the band-gap energy of the material, the A_1(LO) pressure coefficient ($d\omega_{LO}/dp$) in inhomogeneous samples may be affected by the selective excitation process. For instance, in InGaN layers with a band-gap energy slightly below the exciting photon energy (2.41 eV for 514.5-nm wavelength), the Raman-scattering cross section of sample domains with high In contents should become larger with increasing pressure, since the band-gap energy of such domains progressively approaches the excitation energy. Given that the A_1(LO) frequency of InGaN decreases with increasing In content, this effect could yield reduced pressure coefficients. In contrast, given that the A_1(LO) pressure coefficient is larger in InN than in GaN, large compositional fluctuations in In-rich samples could yield increased $d\omega_{LO}/dp$ values relative to the homogeneous alloy (i.e., relative to the linear behavior plotted in Fig. 3). These two competing effects could counteract each other or, depending on their relative magnitudes, give rise to sizable variations of the measured pressure coefficients.

To evaluate the role of compositional fluctuations on the measured pressure coefficients in InGaN/Si(111), we have performed additional high-pressure Raman experiments on the sample with the largest In content ($x = 0.45$) using a much shorter wavelength (457.9-nm), i.e., with excitation photon energies far from the bandgap energy corresponding to the In concentration of this sample. The pressure coefficient thus obtained turns out to be virtually identical to that obtained with 514.5-nm radiation (5.3 ± 0.2 cm^{-1} GPa^{-1}). This result suggests that selective resonant excitation does not have any significant bearing on the measured pressure coefficients of this InGaN epilayer.

On the other hand, the large experimental $d\omega_{LO}/dp$ values of Fig. 3 could be attributed to the different compressibility of the epilayer and the substrate. Since the bulk modulus of InGaN (175 GPa for $x \sim 40\%$)[14] is sizably larger than that of Si (98 GPa),[18] the effective pressure that is applied to the epilayer may be significantly larger, as it tries to accommodate to the more compressed substrate. The pressure amplification effect arising from the larger substrate compressibility may be expected to occur in material that is totally or partially lattice-matched to the substrate, regardless of the sign of the strain built-in in the epilayer.

To assess the influence of the particular substrate on the $d\omega_{LO}/dp$ values measured in InGaN epilayers, we have carried out additional high-pressure Raman experiments on InGaN material grown on GaN/sapphire. Given that the GaN/sapphire templates are much less compressible than InGaN (the bulk modulus of sapphire is around 250 GPa),[19] an opposite effect would be expected in this case, i.e., lowered $d\omega_{LO}/dp$ values. We plot in the inset of Fig. 1 selected Raman spectra as a function of applied pressure for one of the $In_xGa_{1-x}N$/GaN/sapphire heterostructures studied in this work ($x = 0.42$). As can be seen in Fig. 3 (circles), our measurements yield sizably lower A_1(LO) pressure coefficients on the three InGaN/GaN/sapphire samples. The measured pressure coefficients lie below the linear interpolation between the GaN and InN values. This result confirms that in the InGaN/Si(111) samples, increased $d\omega_{LO}/dp$ values are measured as a consequence of the high compressibility of the Si substrate. In the case of the InGaN/GaN/sapphire epilayers, the opposite effect is observed because the compressibility of the GaN/sapphire template is significantly lower than that of InGaN.[18] It is thus concluded that the actual A_1(LO) pressure coefficients of InGaN are not far from the linearly interpolated values between the pure binary compounds, GaN and InN.

In conclusion, neglecting substrate effects for the measurement of the phonon pressure coefficients in InGaN epilayers may yield highly inaccurate results. We have performed high-pressure Raman measurements on InGaN epilayers grown on two different substrates (silicon and

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sapphire) and found that the experimental phonon pressure coefficients exhibit an important substrate effect. In InGaN layers grown on Si(111), the measured A_1(LO) pressure coefficients turn out to be above the linear compositional dependence between GaN and InN, while the opposite effect is observed in InGaN grown on GaN/sapphire templates. This observation may be attributed to the lower (larger) compressibility of InGaN relative to silicon (GaN/sapphire), giving rise to increased (decreased) effective applied pressures on the epilayer. Thus, we conclude that the A_1(LO) pressure coefficients and the corresponding mode Grüneisen parameters in the InGaN alloy are not far from the linear composition dependence. While further studies on free-standing material would be required to measure the actual phonon pressure coefficients of InGaN, our work also suggests that it might be necessary to reevaluate the pressure coefficient of the fundamental bandgap of InGaN, since the experimental values so far obtained[20,21] might also exhibit important substrate effects. These conclusions can be extrapolated to other heterostructures in which the bulk modulus of the substrate and the epilayer are markedly different. In such cases, free-standing material should be employed in order to obtain accurate pressure dependencies of the fundamental properties of the epilayer material.

The work was supported by the Spanish Ministry of Economy and Competitiveness (MINECO) under project MAT2010-16116.

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