Electronic Raman scattering as an ultra-sensitive probe of strain effects in semiconductors

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Semiconductor strain engineering has become a critical feature of high-performance electronics because of the significant device performance enhancements that it enables. These improvements, which emerge from strain-induced modifications to the electronic band structure, necessitate new ultra-sensitive tools to probe the strain in semiconductors. Here, we demonstrate that minute amounts of strain in thin semiconductor epilayers can be measured using electronic Raman scattering. We applied this strain measurement technique to two different semiconductor alloy systems using coherently strained epitaxial thin films specifically designed to produce lattice-mismatch strains as small as $10^{-4}$. Comparing our strain sensitivity and signal strength in AlₓGa₁₋ₓAs with those obtained using the industry-standard technique of phonon Raman scattering, we found that there was a sensitivity improvement of 200-fold and a signal enhancement of $4 \times 10^3$, thus obviating key constraints in semiconductor strain metrology.
Tensile strain in the highly mismatched alloy GaAs$_{1-x}$N$_x$

Light-scattering strain measurements are not limited to the Al$_x$Ga$_{1-x}$As system. GaAs$_{1-x}$N$_x$ is a highly size-mismatched mixed-anion alloy in which minute concentrations of N cause notably strong changes, such as a giant bandgap bowing, in the alloy’s electronic properties. Despite these key differences between the GaAs$_{1-x}$N$_x$ and Al$_x$Ga$_{1-x}$As systems, the electronic Raman scattering technique can directly measure the inverted
valence-band splitting induced by N concentrations as low as \( x = 5 \times 10^{-4} \), as shown in Fig. 4. As in the case of \( \text{Al}_{x}\text{Ga}_{1-x}\text{As} \), the \( \text{GaAs}_{1-x}\text{N}_x \) electronic mode’s frequency increases with increasing strain, as plotted in Fig. 4a. The strong resonance also enables detailed observation of the polarization independence in Fig. 4c and the anti-Stokes scattering component in Fig. 4b. The latter is observed in the small peak at negative frequency shift. This shift corresponds to an increase of the photon energy, that is, the inverse of the process shown in Fig. 1a. This energy increase is fuelled by the thermal occupation of holes in the lower valence band and occurs at temperatures \( \geq 5 \) K. At higher

Figure 1 | Raman spectrum overview. (a) Schematic of the intrinsic intervalence-band electronic Raman scattering: the \( \text{Al}_{x}\text{Ga}_{1-x}\text{As} \) electronic bands that participate in the three-band Raman scattering process are shown. Wavy lines denote the incoming (\( \omega \)) and outgoing (\( \omega' \)) photons. The thin solid lines denote the scattering of a hole from the heavy-hole band to the light-hole band via the generation of an electron in the conduction band intermediate state. The Raman shift of the observed low-frequency mode results from the biaxial compressive strain-induced splitting energy \( D_{lh-hh} \). (b) The Raman scattering spectrum from the \( \text{AlGaAs} \) epilayer with 12% Al content grown on a GaAs substrate is separately shown for the low-frequency (electronic Raman scattering) and high-frequency (phonon Raman scattering) regions. The low-frequency spectral window, which was recorded using laser excitation at 1.668 eV and 12 mW of power in the depolarized scattering geometry, shows a low-energy electronic Raman scattering feature near the elastically scattered laser line. The high-frequency region, which was recorded using laser excitation at 1.745 eV and 2 mW of power in the polarized scattering geometry, shows the GaAs-like phonon at 291 cm\(^{-1}\) and the AlAs-like phonon at 370 cm\(^{-1}\).

Figure 2 | Energy of the low-frequency mode versus the theoretically predicted strain-induced valence-band splitting. The solid line displays the splitting between the light-hole and heavy-hole valence bands (see Fig. 1a) resulting from the lattice mismatch between the \( \text{AlGaAs} \) epilayer on the GaAs substrate, which was calculated using elastic moduli values at 0 K. The symbols show the energy of the low-frequency mode averaged over the dispersion for the resonance profile (see Fig. 3).

Figure 3 | Resonance Raman profile and frequency dispersion of the low-frequency mode. (a) Resonance Raman profile of the low-frequency mode for 12% \( \text{Al}_{x}\text{Ga}_{1-x}\text{As} \). (b) Frequency dispersion of the resonance Raman peaks that were measured in a. (c,d) Frequency dispersion and excitation profile of the low-frequency mode in GaAs. Error bars are the uncertainty in subtracting the underlying photoluminescence similar to that shown in Fig. 1b. The solid lines are smooth fits to the data. The arrows denote the maximum of the PLE peak that corresponds to the band edge of the epilayer.
laser excitation is at 1.470 eV, which is below the GaAs
GaAs substrate, were measured at various lattice temperatures. The 16-
energy. (x = p polarized, and excitation and collection polarizations as either left or right circularly
polarized, respectively.) Various N concentrations. The frequency was determined from spectra
similar to those shown in Fig. 3b, and the much lower required power (0.1–0.28 mW) was also measured
using molecular beam epitaxy on GaAs substrates. Because all excitation thickness values were
much lower than the critical thickness for the grown films, the films were assumed to be perfectly pseudomorphically strained to the substrate. The film compositions reported here were determined using PLE in the case of AlGaAs or X-ray diffraction in the case of GaAs/N.

**Methods**

**Growth.** The set of 0.4–0.5-μm-thick, undoped AlGaAs x As epilayers was grown using molecular beam epitaxy on commercial semi-insulating (001) GaAs substrates. GaAs x As epilayers with a thickness of 0.3 μm were also grown using molecular beam epitaxy on GaAs substrates. Because all epilayer thickness values were much lower than the critical thickness for the grown films, the films were assumed to be perfectly pseudomorphically strained to the substrate. The film compositions reported here were determined using PLE in the case of AlGaAs x As or X-ray diffraction in the case of GaAs x As.

**Strain estimate.** The accepted values for the lattice constants for GaAs (5.6525 Å) and AlAs (5.6605 Å) at 10 K were used to estimate the strain values in Fig. 2. The in-plane biaxial strain component is given by \( \varepsilon_{xx} = -(\varepsilon_{22} - \varepsilon_{11}) \) and the out-of-plane component is given by \( \varepsilon_{zz} = -(\varepsilon_{11} - \varepsilon_{22}) \), where \( \varepsilon_{11} = (1 - x) \varepsilon_{GaAs} \) and \( \varepsilon_{22} = x \varepsilon_{GaAs} \). The elastic constants \( c_{11}, c_{22}, \text{ and } c_{12} \) are taken as linear inter-
polations of those for GaAs and AlAs at 0 K. For GaAs, \( c_{11} = 11.26 \) and \( c_{22} = 5.71; \) for AlAs, \( c_{11} = 12.02 \) and \( c_{22} = 5.7 \) (ref. 26); all values have units of 10\(^11\) dyn cm\(^{-2}\). The energy levels of the heavy-hole and light-hole states can be expressed as follows according to the conventional perturbation treatment of the strain-induced valence-band splitting (\( \Delta \))

\[
E_{\text{HH}} = \frac{1}{2} \left[ q + E_{\text{SO}} + \sqrt{E_{\text{SO}}^2 - 4qE_{\text{SO}} + 9q^2} \right],
\]

where \( q = b(\varepsilon_{zz} - \varepsilon_{zz}) \) and \( E_{\text{SO}} = (1 - x)0.341 \) eV + 0.28 eV is the spin–orbit splitting in AlGaAs. The deformation potential \( b \) was taken to be \(-1.9 \) eV.

**Raman spectroscopy.** A DCM dye laser and a Ti:sapphire laser were used as the excitation light sources for the excitation wavelength range of 640–695 nm and 700–910 nm, respectively. The excitation spot size was 100 x 100 μm\(^2\) for AlGaAs x As and 25 μm in diameter for GaAs x N. Unless noted in the figures, all low-frequency spectra were collected in the ‘depolarized’ configuration, where the laser light was linearly polarized, and the polarizing and analysing elements for the incoming and scattered light were arranged perpendicular to each other. The phonon spectrum in Fig. 1b was collected in the ‘polarized’ configuration, where the polarizing and analysing elements for the incoming and scattered light were arranged in parallel. The Raman spectra were analysed using a charge-coupled device detector on a triple-stage Jobin Yvon T64000 spectrometer for the AlGaAs x As samples and on a single-stage spectrometer with a focal length of 0.27 m for the GaAs x N samples.

**Discussion**

A key limitation in high-spatial-resolution Raman spectroscopy is that, when the laser probe size is decreased, the required power density to maintain reasonable Raman scattering intensities becomes sufficiently high to cause local heating effects. In this regard, as the ratios of signal strengths to laser powers in Fig. 1b indicates, the much lower required power (≈ 4 x 10\(^3\) lower power) for electronic Raman scattering compared with photon Raman scattering can be significantly advantageous. In strongly resonant cases, as observed in Figs 1b and 4b, the signal can be concurrently measured with the laser, which negates the requirement for a Raman spectrometer or other laser filtering.

In addition, a comparative reference of unstrained material, which is required in other strain measurement techniques, is not necessary because the electronic Raman shift is a direct measure of strain. The measured strain at low temperatures can be mapped to the corresponding strain at room temperature using the temperature dependence of the lattice constants\(^25\), such low-temperature measurements are necessary in the case of small valence-band splittings.

The advent of silicon-based photonics\(^2\) and III–V-based nanoelectronics\(^1\) and the integration of photonics and electronics\(^27\) require new metrology tools\(^17\) to probe the effects of the design or process technology variation on the electronic band structure\(^28\). The ultra-sensitivity to strain-induced band-structure changes, which are demonstrated for the electronic Raman technique, can make this technique a valuable tool in such applications. It can also be a valuable tool for probing electronic-structure changes induced by single dislocations\(^28\), strain engineering of ultra-thin semiconductor crystalline layers\(^30\) and unconventional approaches to heteroepitaxy\(^31\).

**Figure 4 | Electronic Raman scattering in GaAs x N.** (a) The 1.7-K electronic Raman scattering frequency for a set of GaAs x N samples with various N concentrations. The frequency was determined from spectra similar to those shown in Fig. 3b, and the much lower required power (0.1–0.28 mW) was also measured using molecular beam epitaxy on GaAs substrates. Because all epilayer thickness values were much lower than the critical thickness for the grown films, the films were assumed to be perfectly pseudomorphically strained to the substrate. The film compositions reported here were determined using PLE in the case of AlGaAs x As or X-ray diffraction in the case of GaAs x N.
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Acknowledgements
The work performed at NREL is supported by the U.S. Department of Energy Office of Science, Basic Energy Sciences under DE-AC36-08GO28308. This work was partially performed at the Center for Integrated Nanotechnologies, which is a user facility of the U.S. Department of Energy, Office of Basic Energy Sciences. Sandia National Laboratories is a multi-program laboratory that is managed and operated by Sandia Corporation, which is an entirely owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000. The dilute nitride samples were provided by A. Ptak as part of a previous BES project.

Author contributions
D.A.R. and J.L.R. grew the samples; B.F. discovered the low-frequency Raman feature; A.V.M. modelled the effect of strain on the measurements; A.M. interpreted the electronic Raman data and wrote the manuscript.

Additional information
Competing financial interests: The authors declare no competing financial interests.
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How to cite this article: Fluegel, B. et al. Electronic Raman scattering as an ultra-sensitive probe of strain effects in semiconductors. Nat. Commun. 6:7136 doi: 10.1038/ncomms8136 (2015).

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