

Pseudo-direct gaps for efficient light emission and absorption

Mike Cooke reports on recent research seeking to develop optoelectronic devices based on indirect-bandgap semiconductors with a nearby direct gap.

Light emission from semiconductors usually depends on the existence of a direct bandgap (Figure 1). This is because the wave properties of the emitted light have to match those of the electron and hole states that recombine. In particular, the sum of the wave-vectors (of magnitude $2\pi/\text{wavelength}$) of the incoming electrons and holes combines into that of the outgoing photon. The relevant wavelength for the photon is hundreds (UV, visible) or thousands (infrared) of nanometers. By contrast, the relevant electron/hole wavelengths are atomic scale – i.e. tenths of nanometers. Given the large difference of scale and the inverse proportional dependence on wavelength, the photon has near-zero wave-vector.

In terms of the band structure giving the relation between energy (E) and wave-vector (k) of the electron states, one is looking for transitions between electrons in the conduction band to hole states in the valence band directly beneath. In semiconductors, the electrons tend to populate the lowest lying states in the conduction band and the holes populate the highest states in the valence band. The peak of the valence band is usually at zero wave-vector, but sometimes the valleys of the conduction band can be away from zero, giving an indirect gap.

While the conditions of light absorption are less stringent, photodetector and photovoltaic energy conversion (solar cell) devices show improved efficiency when constructed from direct rather than indirect semiconductors.

Researchers hope that, by exploring the potential of pseudo-direct gaps, new opportunities for optoelectronic application will arise. Here we look at three recent contributions to the research literature.

Electrically pumped light emission in germanium

The Chinese Academy of Sciences Institute of Semiconductors has been studying a lateral light-emitting diode (LED) and waveguide structure (Figure 2) based on the

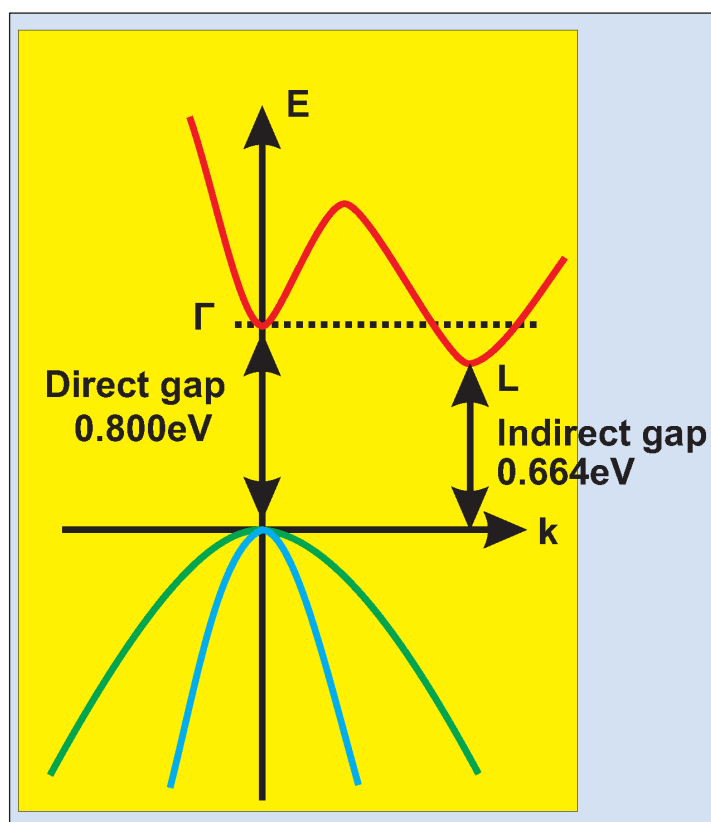


Figure 1. Rough sketch of germanium bandstructure along L direction showing direct and indirect valleys.

indirect-gap semiconductor germanium (Ge) [Zhi Liu et al, Appl. Phys. Lett., vol104, p191111, 2014]. The indirect gap should make efficient light emission difficult, but the band structure of Ge has a direct 'gamma' (Γ) valley in the conduction band that has a gap from the valence band only $\sim 140\text{meV}$ wider than the indirect gap of $\sim 660\text{meV}$. By contrast, silicon (Si) has an indirect gap of 1.12eV (the 6 'chi' or X valleys) and a direct Γ gap of 3.4eV .

The small difference between germanium's indirect and direct transitions raises the possibility for 'pseudo-direct' light emission through tweaking the band structure with strain and/or filling/doping the

four indirect 'L' valleys so that the Γ valley can become populated with electrons.

Fabricating effective Ge light emitters would have benefits for optoelectronics based on Si waveguides and silicon CMOS since Ge and SiGe alloys are already integrated in Si transistor mass-production processes, unlike the usual light emitters consisting of direct-gap III-V compound semiconductors.

The germanium film was grown on lightly-doped n^- -silicon (n^- -Si) substrates by cold-wall ultra-high-vacuum chemical vapor deposition (CVD). The precursor was pure germane (GeH_4). The 60nm buffer layer was grown at 290°C, and the main 740nm Ge layer at 600°C.

A 300nm silicon dioxide (SiO_2) film was grown by plasma-enhanced CVD (PECVD). The wafer was then annealed rapidly to improve crystal quality and to create tensile strain of between 0.20% and 0.22%. The Ge film was formed into $1\mu\text{m} \times 350\text{nm} \times 0.5\text{mm}$ ridge structures, with the SiO_2 forming a mask for the patterning process.

The regions by the ridge without SiO_2 mask were implanted with phosphorous and boron to create n- and p-type regions, respectively. The dopants were thermally activated and the SiO_2 mask removed. Between these steps a dilute solution of hydrogen peroxide and hydrochloric acid was used to smooth the sidewalls of the ridge. A new 700nm SiO_2 layer was applied using PECVD.

The metal electrodes were created and thermally activated for a good ohmic contact with the Ge film. The structures were cleaved across the $\langle 001 \rangle$ facet with waveguide lengths between 0.6mm and 1.3mm.

Using a lateral structure avoids the current having to cross the defect infested region of the Si/Ge interface. The researchers comment: "The device exhibited a good rectifying behavior and had excellent injection efficiency. The current density was about $100\text{kA}/\text{cm}^2$ with a 2V forward bias."

The waveguide peak emission wavelength of 1625nm at $30\text{kA}/\text{cm}^2$ injection current was significantly red-shifted compared with the 1590nm photoluminescence of 0.21% tensile-strained undoped Ge. The researchers suggest the red-shift could be due to

self-heating caused by the high injection current. The bandgap tends to shrink at high temperature. The halting of the red-shift trend beyond $110\text{kA}/\text{cm}^2$ is attributed to the low energy cut-off of the InGaAs detector that was used. Under $150\text{kA}/\text{cm}^2$ current injection, the light output power was around $1\mu\text{W}$.

The researchers also studied the emission from the top surface with a microscope at $10\text{kA}/\text{cm}^2$ (Figure 3). The emission peak in this case was 1587nm, consistent with the peak for 0.21% tensile-strained undoped Ge. The amount of emission was greatest near the n-contact region (position 'A' in Figure 2). The direct transition ' Γ ' valley is more likely to be populated near the n-type region than in the p-type region. As the current increased, the maximum emission region moved nearer to the intrinsic region.

The researchers believe that their results indicate the potential of Ge as a Si-based light-source. ▶

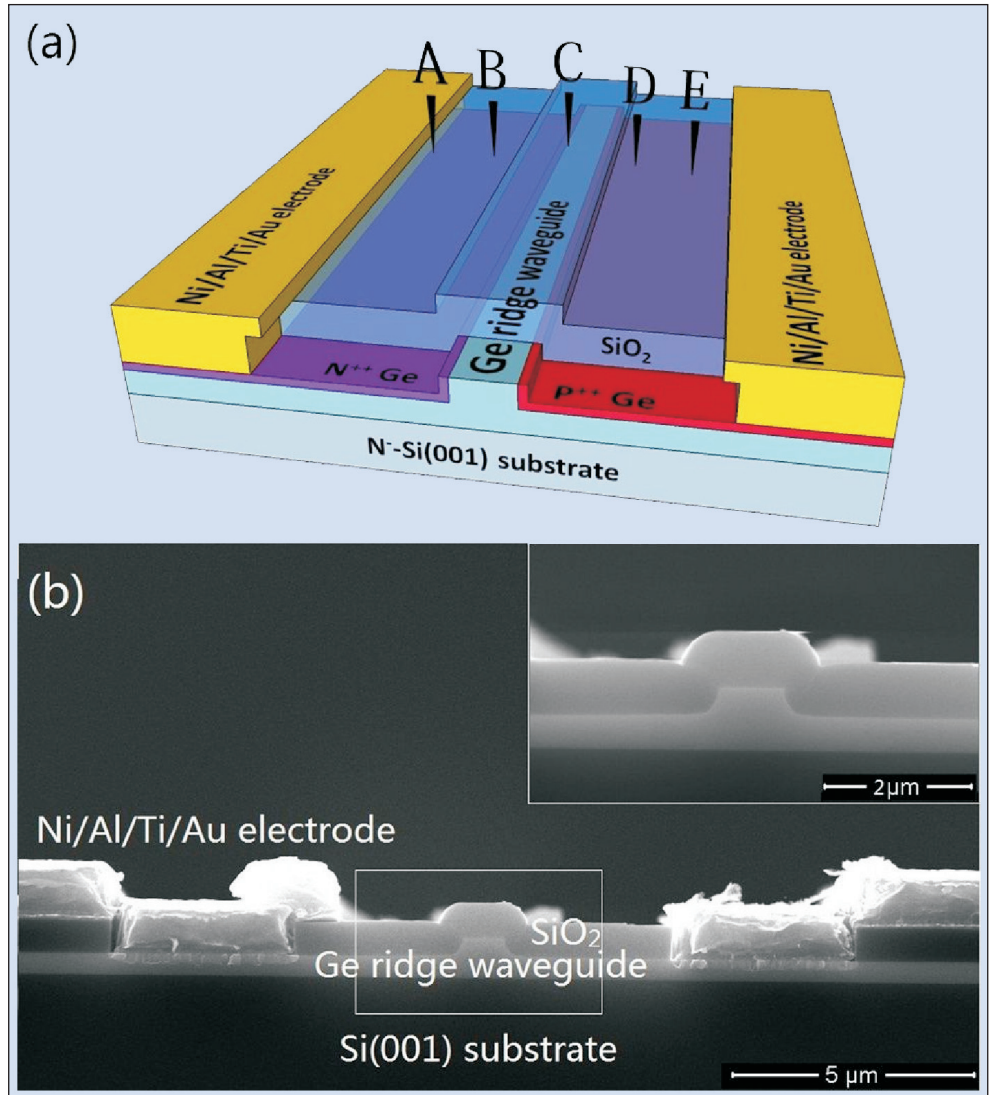


Figure 2. (a) Schematic of Ge p-i-n ridge waveguide LEDs on Si substrate. Top surface positions marked A to E for micro-electroluminescence measurement are shown. (b) Cross-sectional SEM of Ge p-i-n ridge waveguide LEDs and cleaved facet. Top width and height of the ridge waveguide are 900nm and 350nm, respectively.

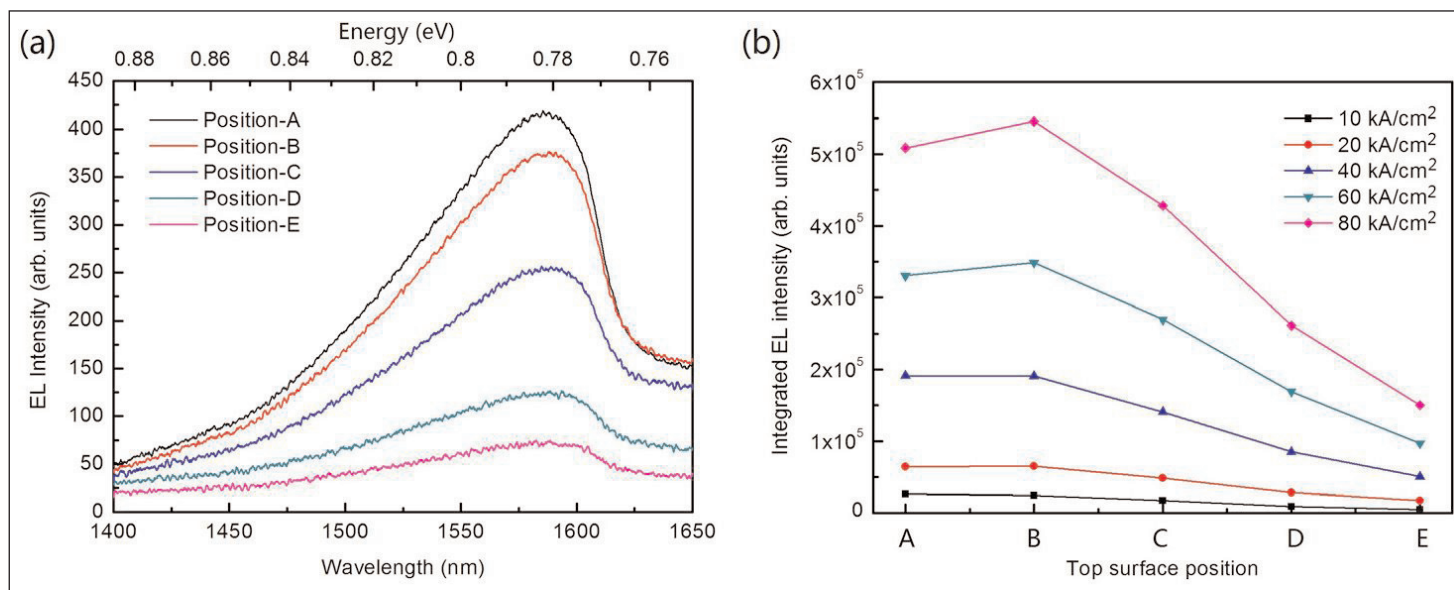


Figure 3. (a) Room-temperature top surface micro-electroluminescence spectra at various surface positions (Figure 2a) of Ge waveguide LED with fixed current density of 10kA/cm². (b) Integrated top surface EL intensities at different top surface positions (A–E) with varying current density.

Solar energy conversion

Yale University in the USA has developed indium gallium phosphide (InGaP) solar cells on gallium phosphide substrate [S. Tomasulo et al, Appl. Phys. Lett., vol104, p173903, 2014]. The aim of the researchers' work was to create a top-cell option for multi-junction cells with four or more junctions in monolithic or spectrum splitting architectures. It is hoped that such arrangements will be able to achieve conversion efficiencies up to almost 60%.

Such top cells need an energy bandgap of around 2.0–2.4eV. Gallium phosphide has such a bandgap, but unfortunately the 2.26eV gap is indirect, leading to inefficient conversion of photons into electrical energy. The InGaP alloy system has a transition from indirect to direct bandgap when the indium fraction exceeds 30%. However, the increase of indium content also leads to a reduction in the bandgap.

In fact, there are two valleys in the GaP bandstructure – a direct Γ valley with a gap of 2.78eV and an indirect 'chi' X valley. In InGaP, the Γ valley gap with the valence band decreases at the rate of 19meV/% of indium. The X gap reduces more slowly at 1.7meV/%.

The Yale group explored how moving the composition towards the crossover point increases conversion efficiency. In fact, the conversion efficiency improves even in the indirect region as the Γ valley comes in range of the X valley.

Previous work with InGaP has tended to grow the material on gallium arsenide (GaAs) substrate. Unfortunately, the InGaP is then placed under tensile strain, which, according to the researchers, "leads to faceted trenches and cracks, and extremely thick graded buffers are required to minimize these efficiency-diminishing defects". The Yale group chose GaP substrates so that the InGaP was under compressive strain to avoid these problems.

The epitaxial structures (Figure 4) were grown on p-GaP substrates in a Veeco Mod Gen II solid source

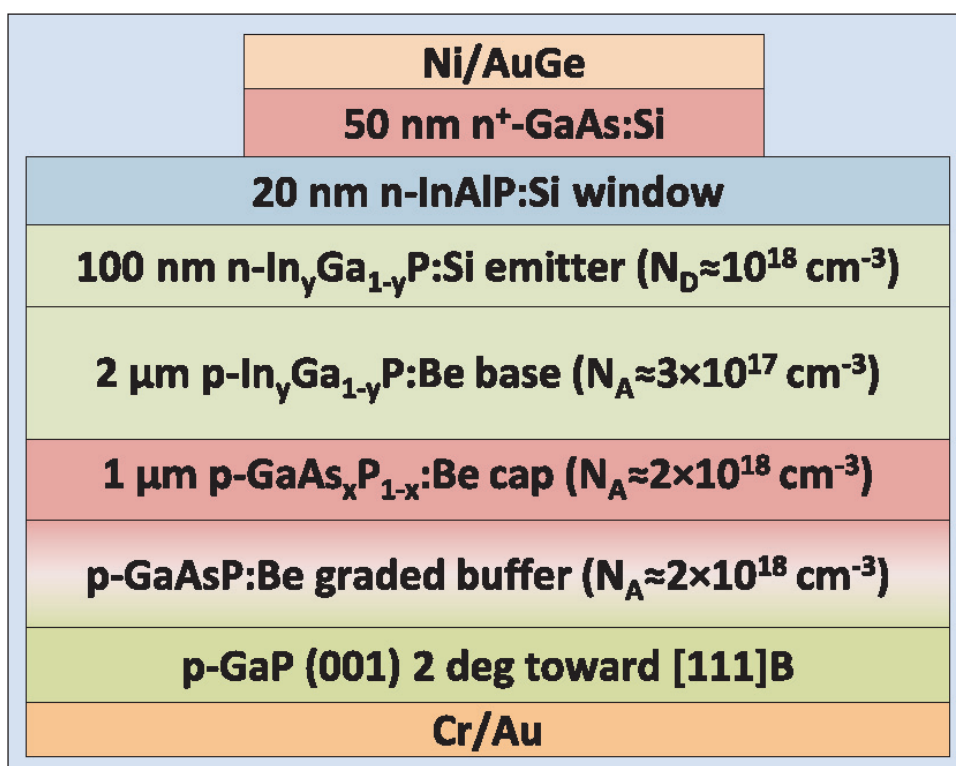


Figure 4. Schematic of InGaP solar cells.

Table 1. Summary results: bandgap energy (E_g), threading dislocation density (TDD), open-circuit voltage (V_{oc}), bandgap-voltage offset ($W_{oc} = E_g/q - V_{oc}$), short-circuit current density (J_{sc}), ratio of J_{sc} to theoretical maximum for infinite base and unity collection probability ($J_{sc, ratio}$), fill factor (FF), and conversion efficiency (η).

In fraction	E_g (eV)	TDD (/cm ²)	V_{oc} (V)	W_{oc} (V)	J_{sc} (mA/cm ²)	$J_{sc, ratio}$	FF	η
0%	2.26 ^a	...	1.46	0.80	1.64	17%	0.64	1.53%
18%	2.23 ^a	2.28x10 ⁶	1.46	0.77	2.29	23%	0.74	2.47%
24%	2.21	4.02x10 ⁶	1.43	0.78	2.75	26%	0.73	2.87%
30%	2.12	7.60x10 ⁶	1.42	0.70	3.65	30%	0.75	3.89%

^a Indirect gap.

molecular beam epitaxy (MBE) chamber. The use of a gallium arsenide phosphide (GaAsP) graded buffer reduced threading dislocations that arise from the lattice mismatch between the substrate and overlying epitaxial structure. The compressive grading was achieved using between 10 and 16 steps of 360nm thickness and increased arsenic molar fraction of four percentage points per step. The aim was a grading rate of stain over buffer thickness of 0.4%/μm. The indium aluminium phosphide (InAlP) window layer was lattice-matched to the InGaP active emitter/base material.

The epitaxial samples were formed into 1mmx1mm solar cells. The devices were patterned with photolithography and wet etched down to the n-InAlP window layer through the top n⁺-GaAs used to achieve good ohmic contact with the metal n-type electrodes. No anti-reflective coatings were used in any device. A reference GaP device with Al_{0.25}Ga_{0.75}P window was also produced.

The current and voltage characteristics were measured under AM1.5G solar simulation conditions (Table 1). Also, the threading dislocation density (TDD) was estimated using electron-beam induced current (EBIC) measurements. The TDD increased by 3x with indium fractions between 18% and 30% — a factor that Yale plans to address in future work.

Although the devices are in the ambiguous direct-indirect bandgap region, their external quantum efficiency (EQE) behavior is similar to that of a direct-gap In_{0.49}Ga_{0.51}P device with a sharp turn-on at the band edge. The bandgap-voltage offsets (W_{oc}) were higher than for InGaP on GaAs cells. The researchers comment: "We speculate that the wide- E_g solar cells presented here, as well as GaP devices, possess increased point defect densities, resulting in elevated W_{oc} . It is possible that as y decreases, the growth conditions that were chosen for $y = 0.49$ are no longer appropriate, suggesting that growth condition optimization should be performed for each composition."

The main improvement of the InGaP structure is an increase in short-circuit current density (J_{sc}), leading to a 2x improvement in conversion efficiency (η) over a GaP cell.

Wurtzite gallium arsenide nanowires

Researchers in Switzerland and Norway have used strain to alter the light-emitting properties of gallium arsenide (GaAs) nanowires [G. Signorello et al, Nature Communications, vol5, p3655, published online 10 Apr 2014]. The researchers from IBM Research-Zürich, Norwegian University of Science and Technology (NTNU) and CrayoNano AS found that different strain conditions cause a transition in the band structure from a direct to pseudo-direct gap.

The GaAs nanowires were grown in the wurtzite (WZ) rather than the zincblende crystal structure usual with

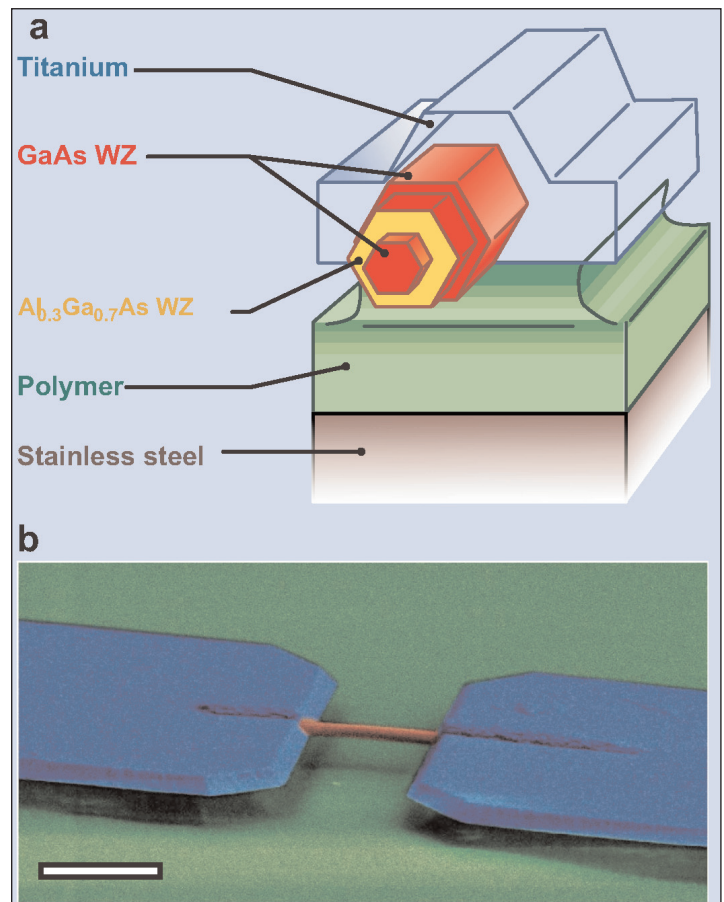


Figure 5. Wurtzite GaAs nanowire strain device. (a) Schematic cross-section of nanowire strain device. Device dimensions not to scale. (b) False-color scanning electron micrograph of nanowire strain device. Scale bar 1mm.

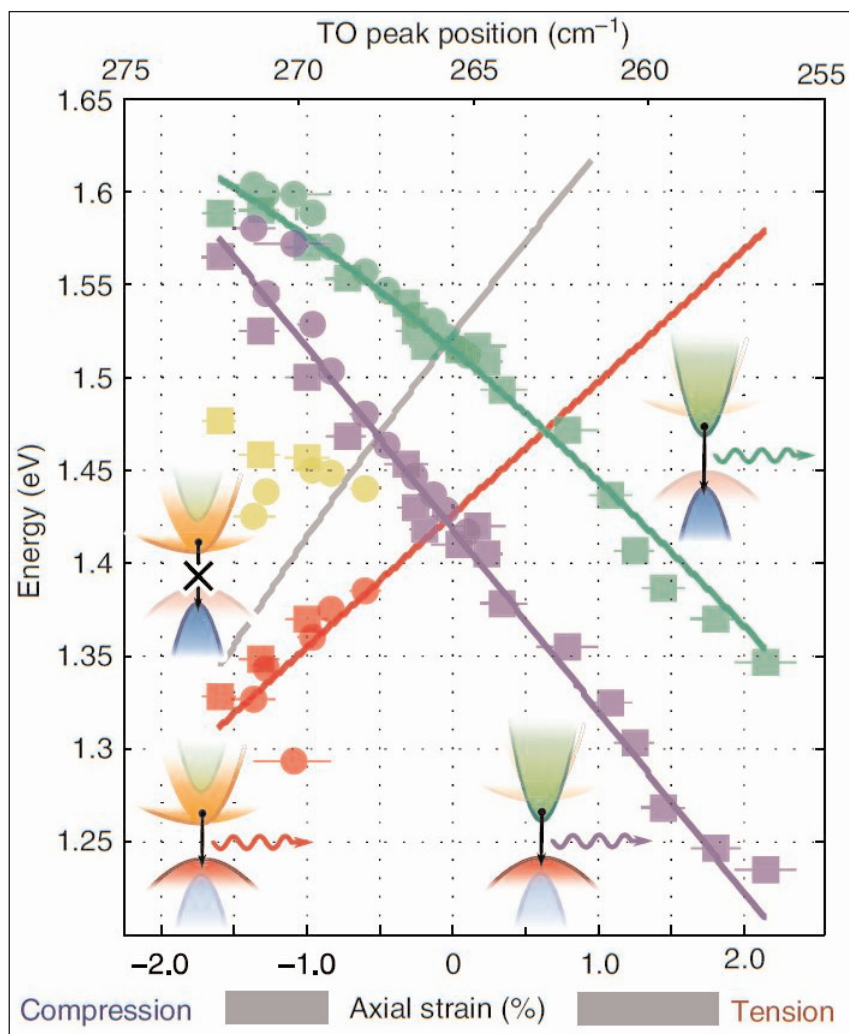


Figure 6. k.p model of uniaxial stress effects in wurtzite GaAs. Energy of optical transitions, extracted from fits of photoluminescence spectra are plotted as function of Raman transversal optical (TO) phonon peak position (top abscissa) and of inferred axial strain (bottom abscissa). Squares and circles represent values obtained from two different nanowire devices. Continuous lines correspond to uniaxial strain dependence of photon energy expected from k.p model. Transitions between bright conduction band and heavy- and light-hole states, purple and green, respectively. Transitions between dark conduction band and heavy-hole band are in red, whereas forbidden transitions between dark conduction band and light hole are represented by grey line. The researchers also found dark conduction band transition (yellow data points) that follows nonlinear energy shift that differs between the two nanowire devices, "whose origin is not yet clear".

bulk GaAs. The researchers found bright photoluminescence under tension but decreasing brightness under compression. This is interpreted as signaling the transition between a direct to a pseudo-direct energy gap.

There are two conduction bands in WZ GaAs — one offering a direct gap with strong photon emission with transitions to the valence bands of heavy- and light-hole states and the other with simple photon emission to the light-hole band forbidden by symmetry considerations. The direct/pseudo-direct transition occurs

when one of these gaps becomes smaller in energy than the other.

The researchers see the use of such strain effects as being potentially useful to increase carrier lifetime and quantum efficiency of photodetectors, as well as to decrease dark currents and generation-recombination noise. Further, they comment: "These results pave the way for a new generation of devices that can simultaneously serve as efficient light emitters and efficient photodetectors by leveraging the uniaxial strain degree of freedom."

The c-axis wurtzite (WZ) nanowires were produced in an MBE reactor using a gold-catalyzed vapour-liquid-solid method. The nanowires consisted of a $\sim 40\text{nm}$ GaAs core, and further shells of $\sim 40\text{nm}$ $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ and $\sim 3\text{nm}$ GaAs. The core and AlGaAs shell are lattice-matched. The GaAs shell protects the structure from oxidation.

The nanowires were fabricated into free-standing structures clamped with titanium to a flexible substrate of stainless-steel covered in polymer (Figure 5). Bending the structure created tensile or compressive strain in the nanowire.

Under unstrained conditions, the researchers estimated an optical bandgap of $1.417\text{eV} \pm 8\text{meV}$ ($\sim 875\text{nm}$ near-infrared wavelength), by using a model that combines data from Raman spectroscopy and photoluminescence (PL) with a k.p model of the strain-dependent effects on the energy bands (Figure 6). The temperature of the measurement was estimated to be in the range 300–480K due to laser-induced heating on the relatively thermally isolated nanowire structure.

Lead author Giorgio Signorello comments: "The laser power was chosen to be as low as possible for compatibility with the measurement of the PL spectra and, especially, of the Raman spectra (which impose the tightest requirements in terms of laser power). I want to emphasize that using the same laser power for PL and Raman is very important to plot correlated Raman/PL data [as in Figure 6]."

The difference between the bright and dark conduction bands was estimated at $33\text{meV} \pm 47\text{meV}$. For comparison, zincblende (ZB) GaAs has a gap of $1.376\text{eV} \pm 15\text{meV}$ for temperatures of $398 \pm 32\text{K}$.

The researchers hope to combine these discoveries with nanowire growth methods on graphene developed by Crayonano to produce improved solar cells and LEDs. NTNU and Crayonano also plan to grow gallium nitride nanowires on graphene with a view to creating flexible, strong, lightweight white LEDs with better optical properties. ■