MBE growth of GaAs-AlGaAs terahertz frequency quantum cascade lasers

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UNIVERSITY OF LEEDS

Outline of Presentation

- Molecular beam epitaxial growth:
  - Outline of MBE growth;
- Calibration of growth rates:
  - Flux Measurements;
  - RHEED;
  - Pyrometry;
- THz QCL growth at Leeds;
- Is everything straightforward?
  - Growth rate uniformity;
  - Doping;
  - Interfaces – roughness and asymmetry;
- Conclusions.

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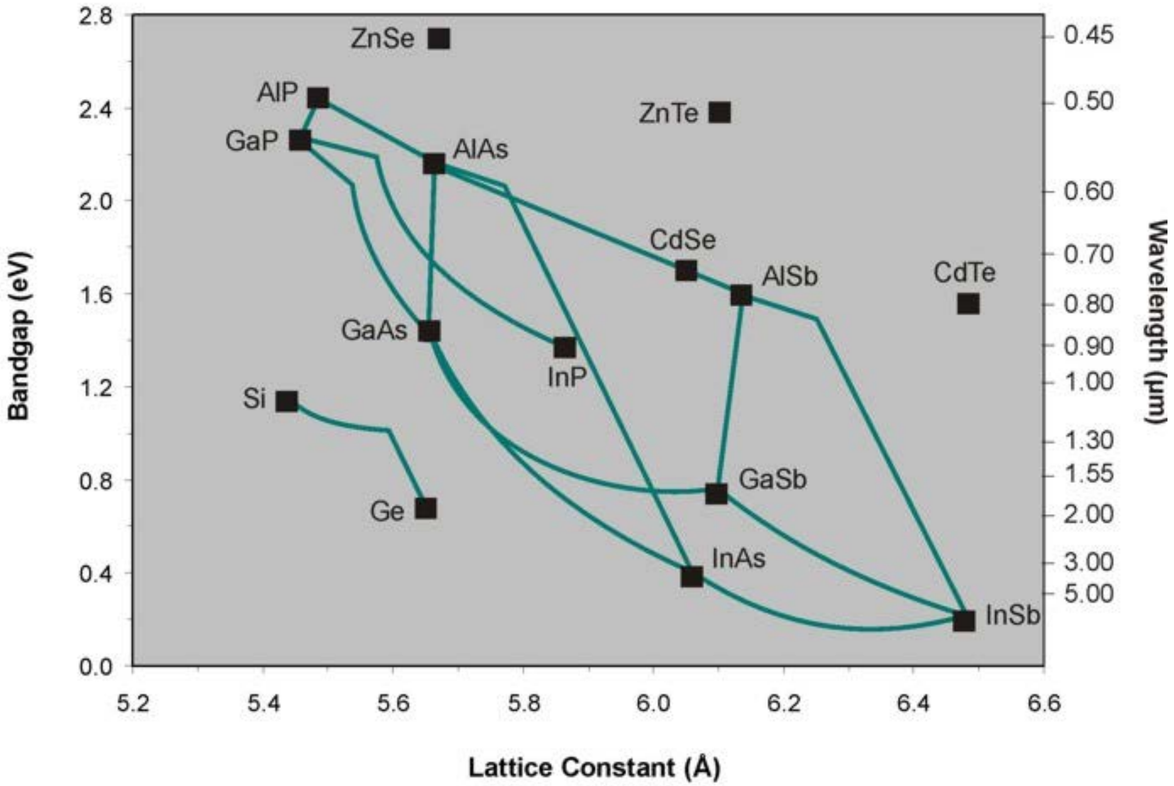
The requirements for bandstructure engineering (1)

- **What is required to produce sophisticated heterostructures?**



- **Appropriate semiconductors to combine and form a single crystal structure with differing band gaps;**

- **Good examples are:**
GaAs – AlAs;
InP – GaInAs – GaAlAs;
InAs– GaSb – AlSb.

- **Such semiconductor combinations can be grown, without defects and dislocations, as there is little strain.**

The requirements for bandstructure engineering (2)

What else is required?

- An ability to dope (add electrons/holes) the chosen semiconductor. For GaAs – AlAs, silicon (group IV) replaces gallium (group III) and adds electrons. Beryllium (group II) replaces gallium and adds holes;

- An ability to achieve switching between doping/semiconductors on an atomic scale;

- An ability to maintain pure crystal structures.

A clear need exists for epitaxial growth

- **Epitaxy refers to the method of depositing a monocrystalline film on a monocrystalline substrate. The deposited film is denoted as the epitaxial layer. The term *epitaxy* comes from *epi* = *'above'; taxis* = *'in ordered manner';***
- **The aim of epitaxial growth is to produce extremely pure semiconductor single crystals, in which the semiconductor composition (and hence band gap) and doping level can be changed with atomic monolayer precision;**

- **To allow accurate control, growth rates of 1 atomic monolayer per second are typical – but this leads to a problem:**

Contamination

- From kinetic theory, the number of atoms hitting unit area per second is given by:

$$I = Ap\sqrt{\frac{N_A}{2\pi k_B MT}}$$

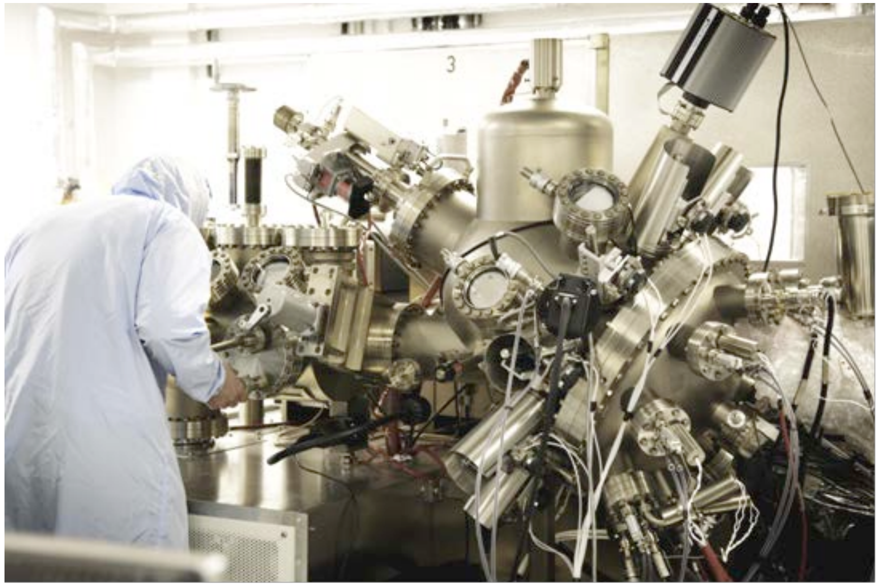
(p = pressure; M = mass of one mole of the gas; T = temperature).

- The number of nitrogen atoms hitting a 1 m x 1 m area in 1 s, at atmospheric pressure and room temperature thus far exceeds the flux of gallium atoms incident on the surface to form one atomic monolayer per second!

- To obtain high quality semiconductor growth – ultra-high vacuum conditions must be used.

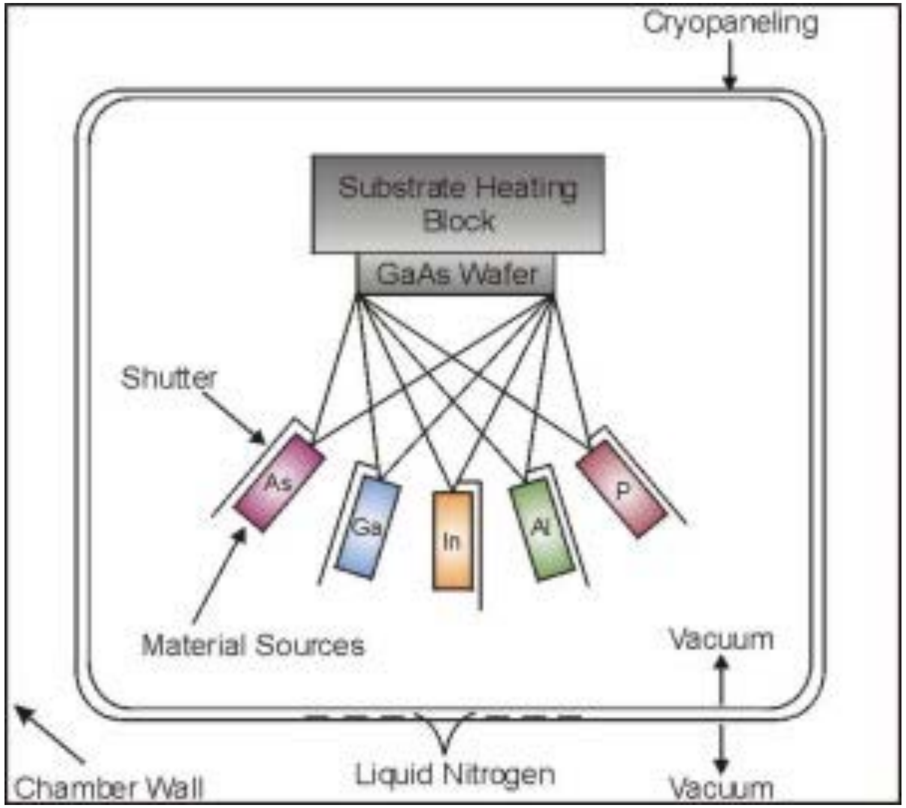
Crystal growth systems

- Growth of single crystals of semiconductors must thus be undertaken under ultra-high vacuum conditions:
- One technique is known as ‘molecular beam epitaxy’ – MBE;
- This talk will focus on the technique of MBE, and discuss its application to terahertz (GaAs-AlAs) quantum cascade lasers.



What is MBE?

- It is just a (very) expensive evaporator!



- **Key aspects:**

– Temperature controlled sources for individual materials;

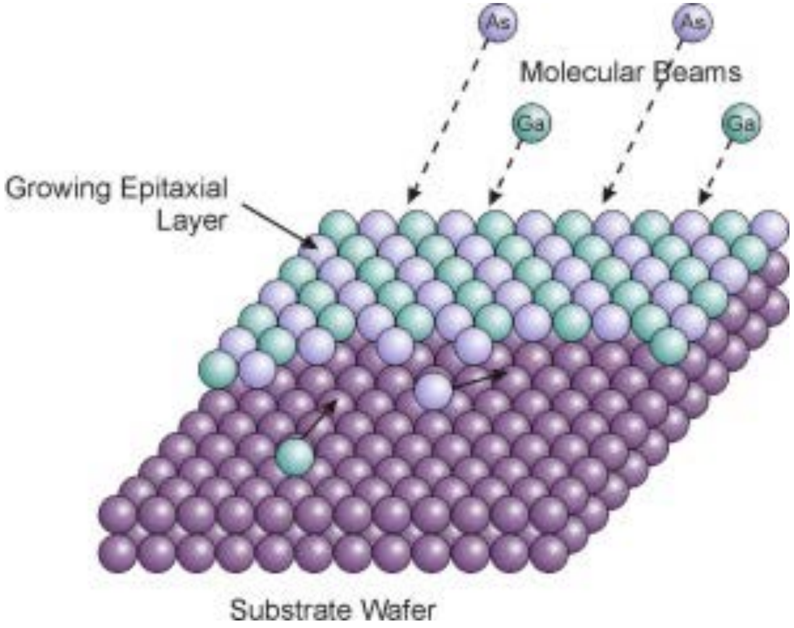
– Shutters for each source;

– Substrate (usually 0.5 mm thick) to support the thin epitaxial layers;

– Substrate heater;

– Vacuum.

The growth process



- Atoms/molecules hit the substrate at random (the random arrangement, in fact, leads to alloy scattering in AlGaAs);

- The substrate is heated (600 °C for GaAs) to ensure that the atoms have enough mobility on the surface to form a smooth layer in 1 second!

- In fact, for III-V semiconductors, growth is made easier by the fact that the group III atom (e.g. Ga, Al) normally sticks to the surface, whilst the group V atom (e.g. As, P) will only stick if the group III atom is present;

- An excess of the group V atom is thus used.

The sources

- **Typical source construction:**

– Heater foils (normally tantalum) + stainless steel construction;

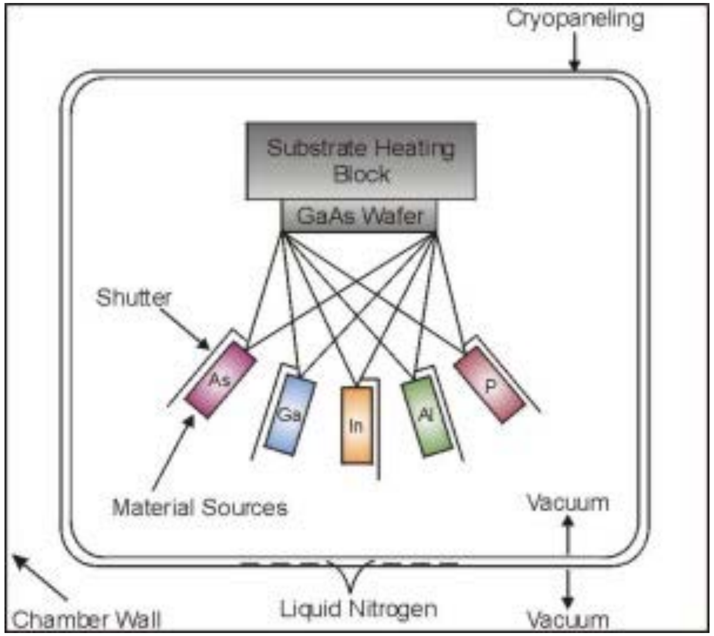
– Pyrolytic boron nitride (PBN) crucible for holding the material;

- **Thermocouple (for temperature control), heater connections, and (sometimes) water cooling;**
- **Materials are chosen to minimise contamination – PBN can be heated, for example, to > 1400 °C before starting to decompose;**
- **Sources are normally kept at a constant growth temperature giving a constant flux, rather than being changed, with shutters used to change the material composition.**

Obtaining ultra-high vacuum

- **A wide range of pumps can be used to achieve ultra-high vacuums:**
  - **Helium cryopumps;**
  - **Ion pumps;**
  - **Turbomolecular pumps;**
  - **Diffusion pumps;**
  - **Titanium sublimation pumps;**
- **But one of the most effective pumps is an internal shield, filled with liquid nitrogen!**

The use of ultra-high vacuum



- **Ultra-high vacuum is used to avoid contamination, but there is an additional advantage:**
- **The mean free path of a molecule in a gas is given by:**

$$L = \frac{1}{\sqrt{2}\pi n d^2} = \frac{k_B T}{\sqrt{2}\pi p d^2}$$

(where d is the average molecular diameter)

- **Atoms/molecules travel from the sources to the substrate without scattering! Hence the composition can be controlled of, say, AlGaAs by simply controlling the Al/Ga flux ratio.**

A typical growth campaign

- The growth chamber is let up to atmospheric pressure (under dry nitrogen to avoid oxidation);
- Components are repaired, cells are filled with materials;
- The whole system is baked at 200 °C for up to 2 weeks;
- The system is leak tested, reconnected up, and the cells are ‘outgassed’ for a period of about 1-2 weeks;
- Material growth starts, and the material quality will gradually improve over a period of 1 – 2 months;
- Growth will then hopefully continue for another 12 – 18 months, with perhaps 300 wafers being grown.
- Wafers are inserted through a load-lock, where they can be pumped down to 10^{-8} mbar. They are then transferred into a preparation chamber, where they can be degassed at over 450°C to remove water vapour and pumped down to 10^{-10} mbar.

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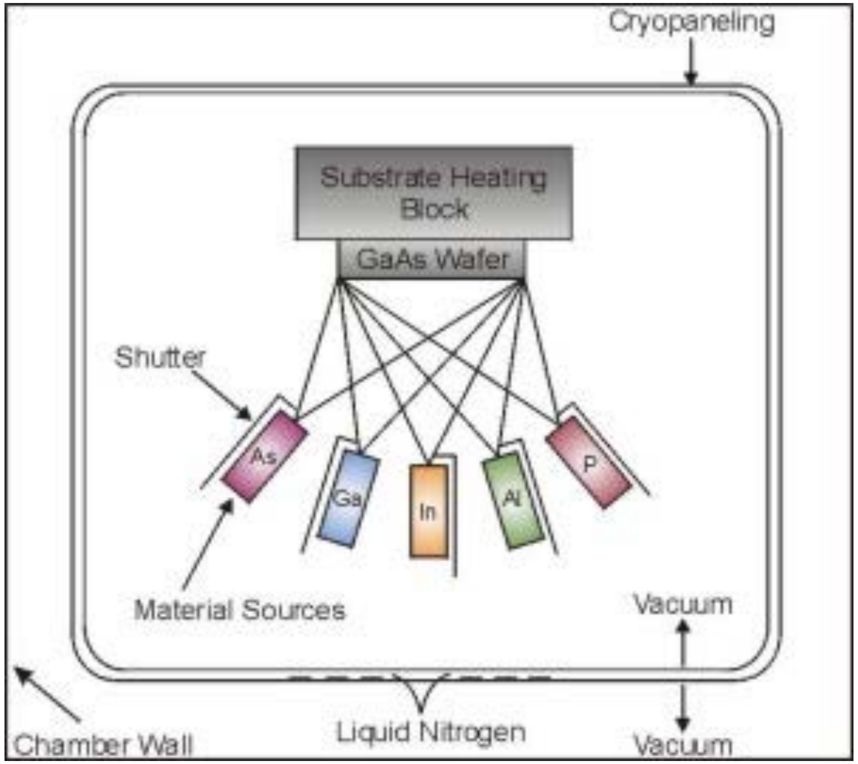
How can one tell what is going on?



- **What monitoring occurs *in situ*?**

– Mass spectrometry;

– Flux/Pressure measurements;

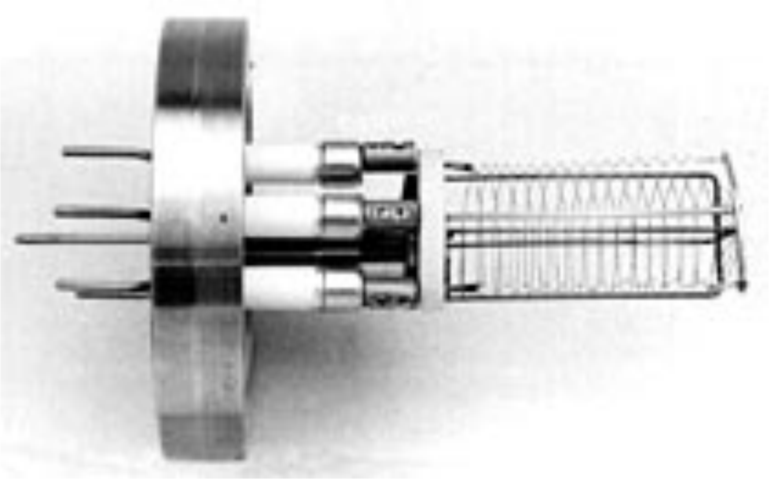
– RHEED;

– Optical pyrometry.

- **Mass spectrometry is used to monitor gas partial pressures, down to < 10^{-14} mbar. It is not used for monitoring growth itself normally. Oxygen levels are often < 10^{-13} mbar for an air tight system. Leaks are detected by looking for helium.**

Flux measurements

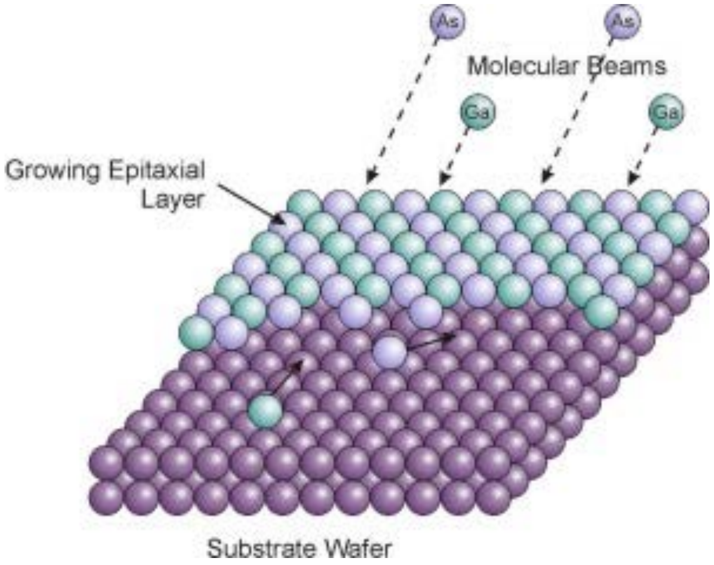
- Pressures in vacuum chambers can be measured using ionisation gauges:

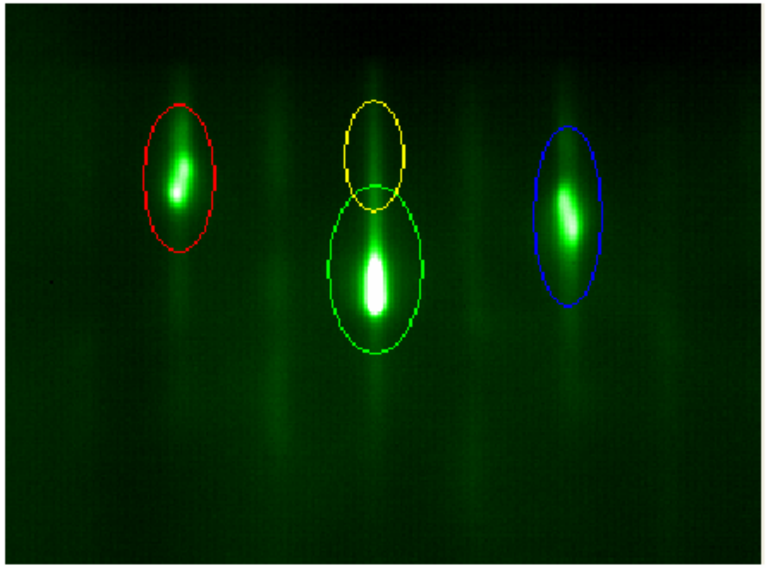


- These gauges consist of a filament and grid, which ionise the gas molecules. The ions are then detected on a collector, and this current can be calibrated as a function of pressure;

- The same gauges can be also used to set up growth rates by measuring atomic/molecular fluxes, and *ex situ* calibrations (using, for example, x-ray diffraction):
  - Growth rates of one atomic monolayer per second might give a current of (10 – 100) nA.

Reflection high energy electron diffraction (RHEED)

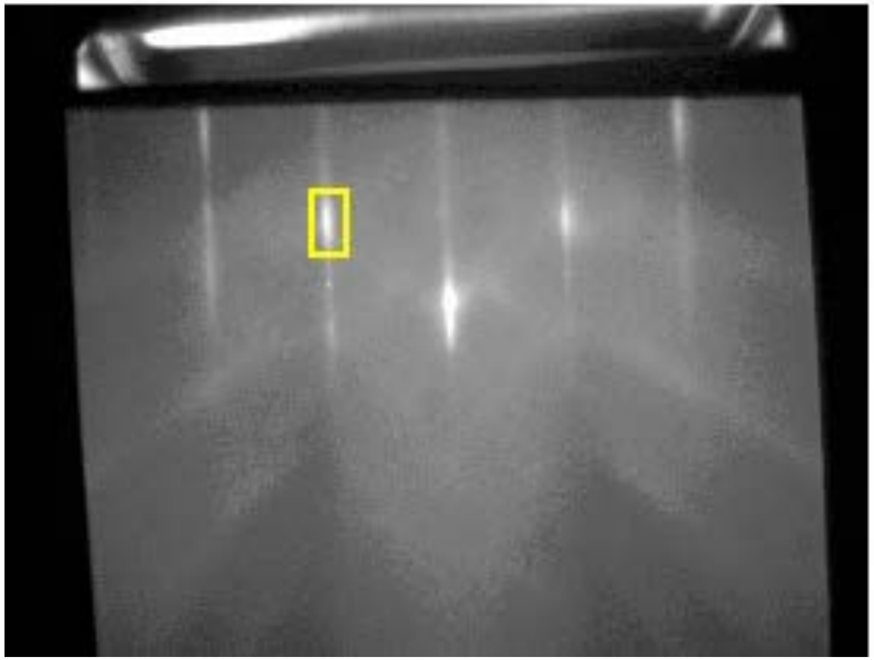




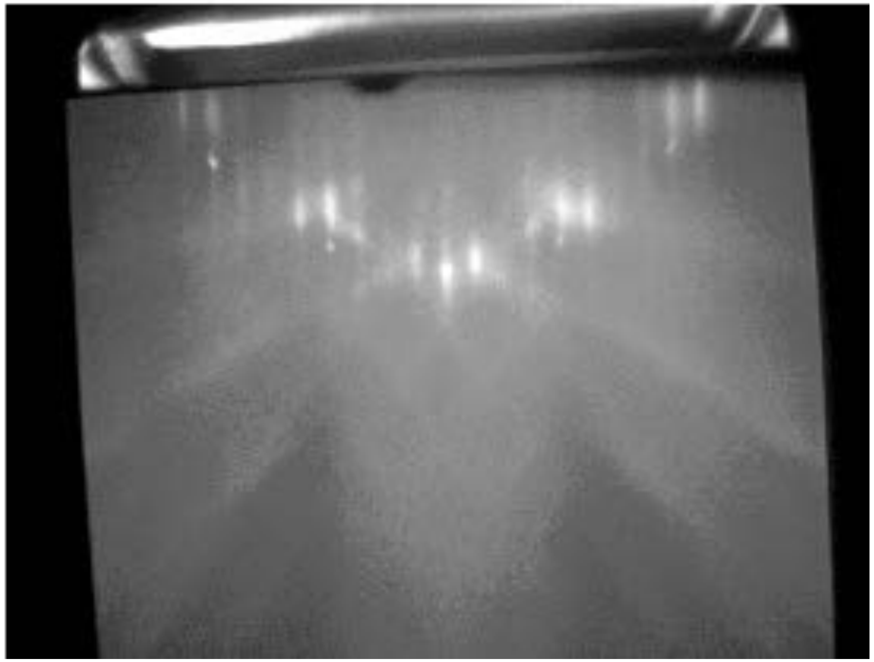
- As the growing GaAs structure is a single crystal, it gives rise to characteristic diffraction patterns. These can be seen by scattering electrons;
- The RHEED patterns depend on the precise kinetics of the surface, and reflect the substrate temperature; and ratio between the group V and group III atoms. In each case, different arrangements of atoms occur on the crystal surface.

RHEED patterns along different crystal directions

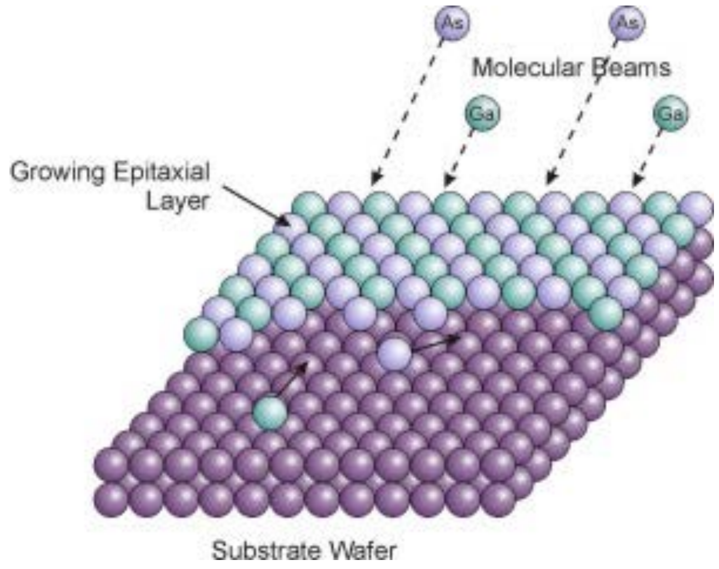
[110]

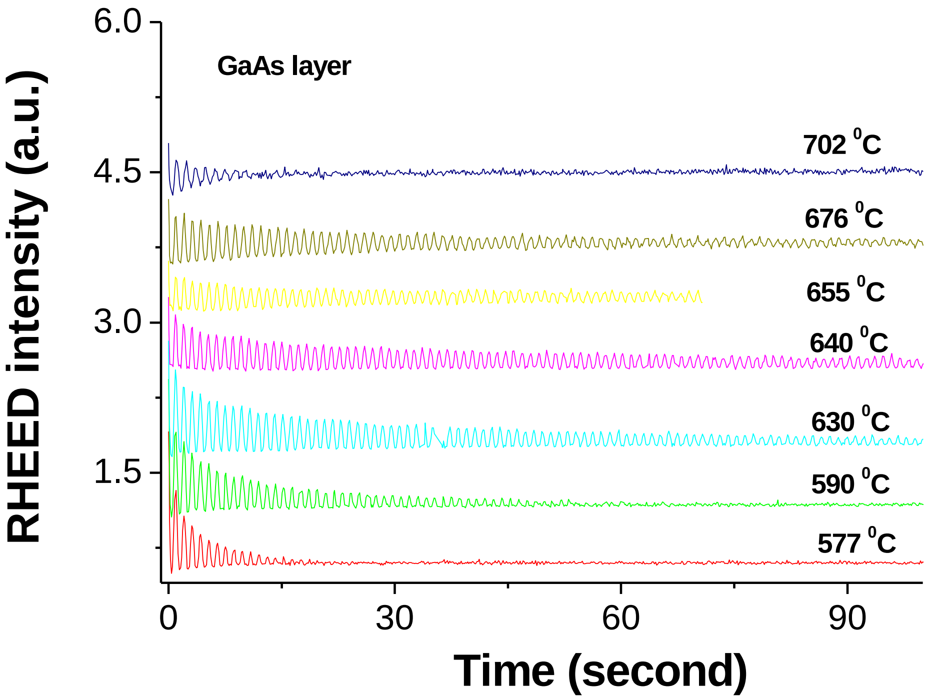


[1-10]



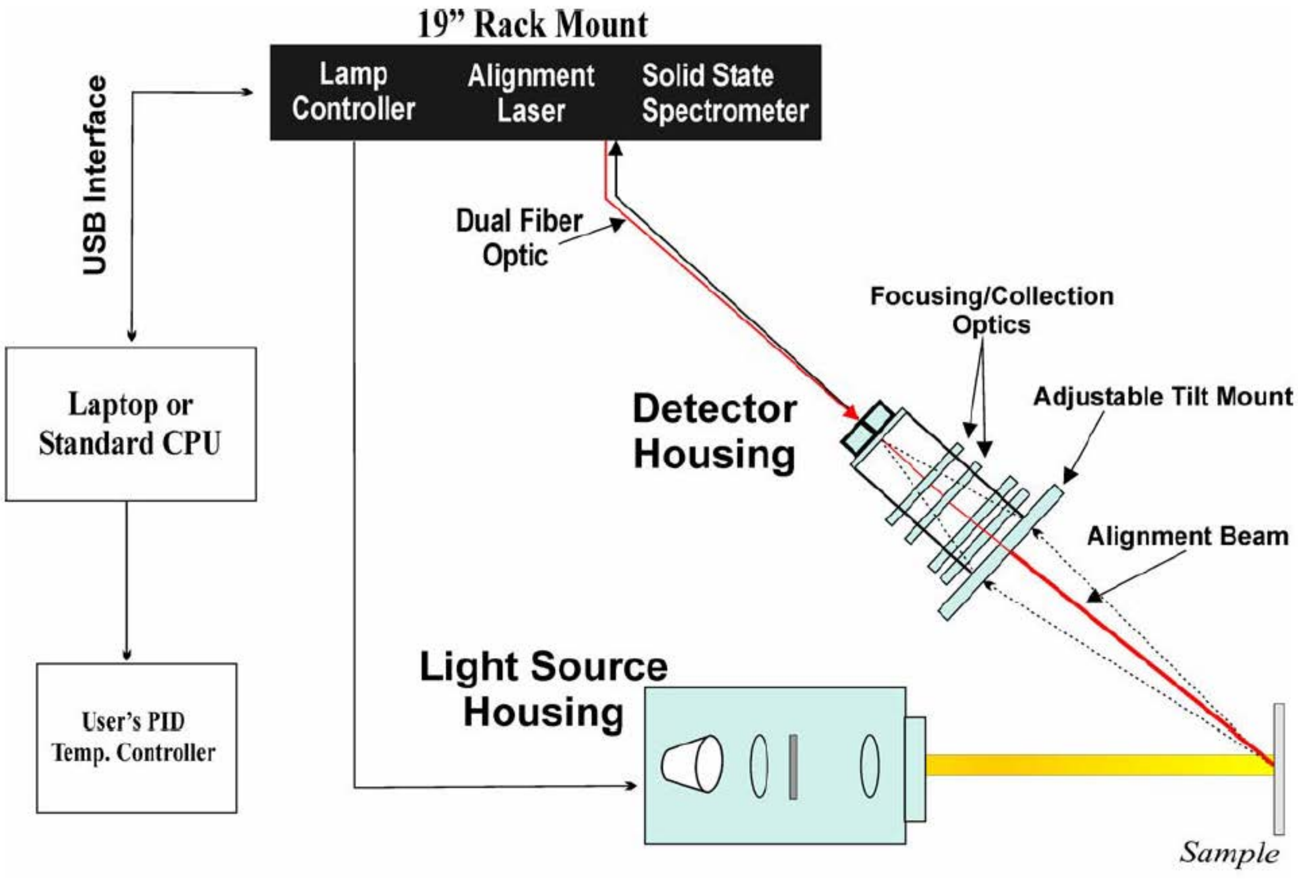
RHEED oscillations – measuring growth rates





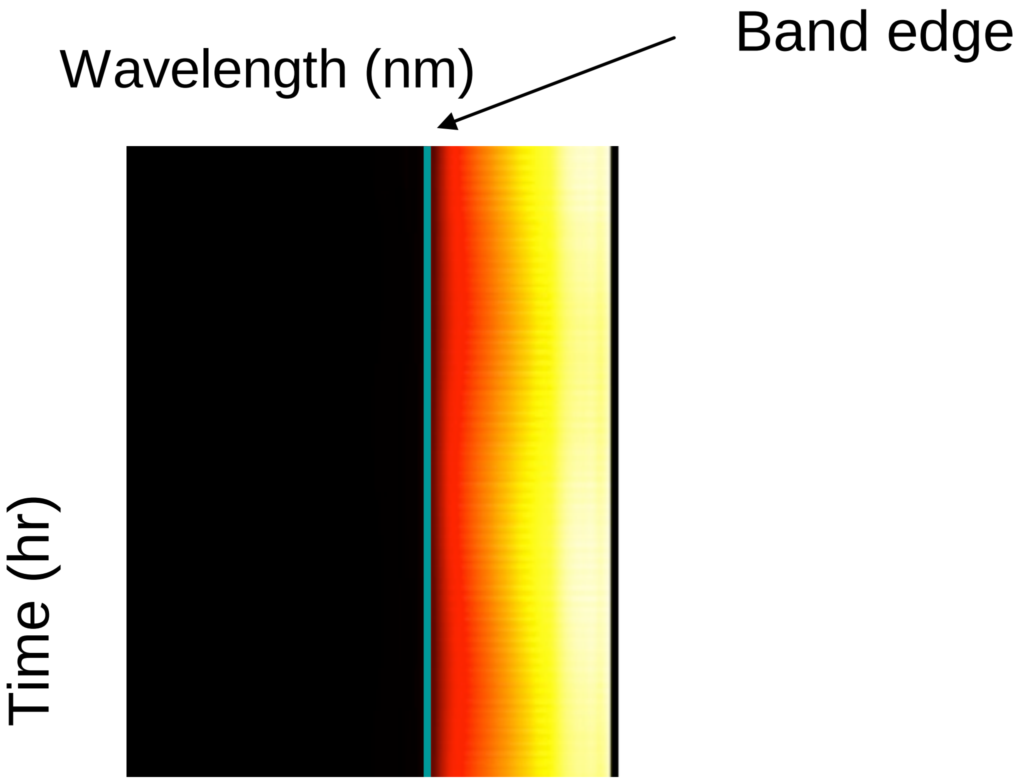
- **For deposition of a complete monolayer, specular reflection occurs; for an incomplete monolayer, the reflection is more diffuse;**
- **Oscillations occur in the reflected intensity and this can be used to calculate the growth rate (this won't come from the RHEED pattern alone).**

Optical pyrometry – an experimental arrangement



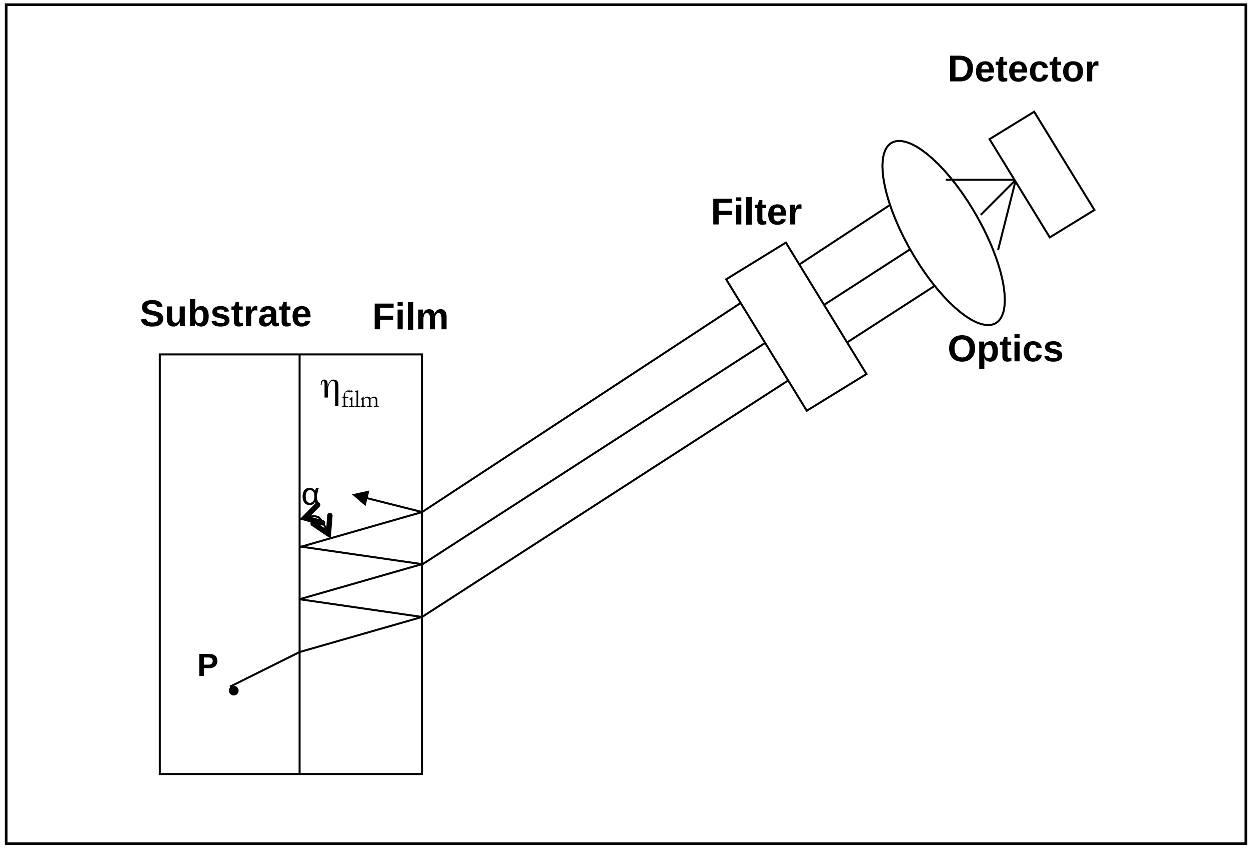
- From reflectivity (or transmission measurements), the wavelength dependent absorption can be measured.

Measuring substrate temperature



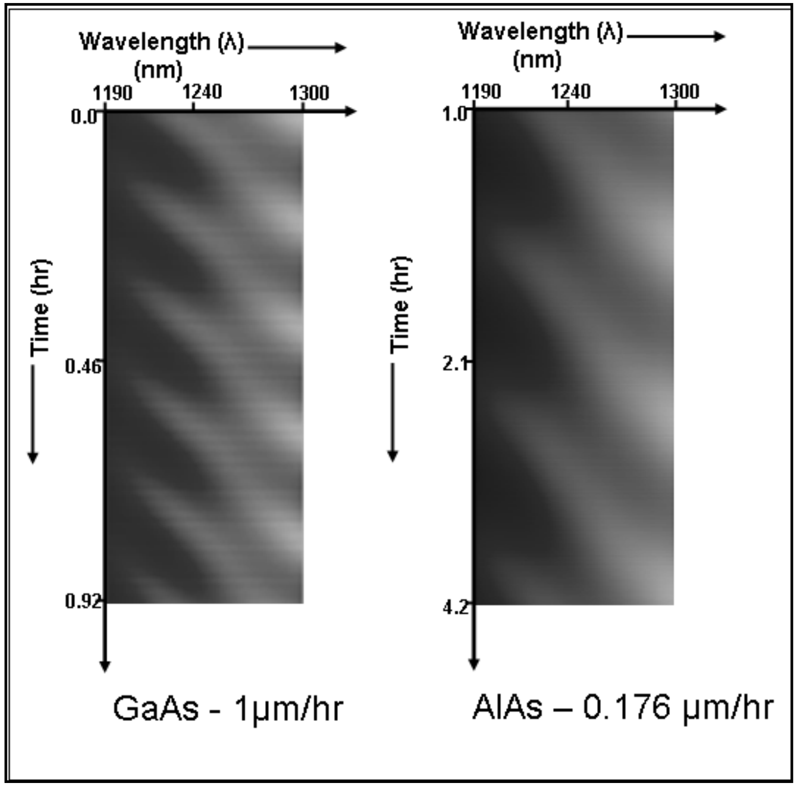
- By measuring the position of the band edge, the temperature of the semiconductor can be deduced from prior calibration. This allows monitoring of the temperature during growth (as can be achieved with a pyrometer).

But we can also deduce growth rates…



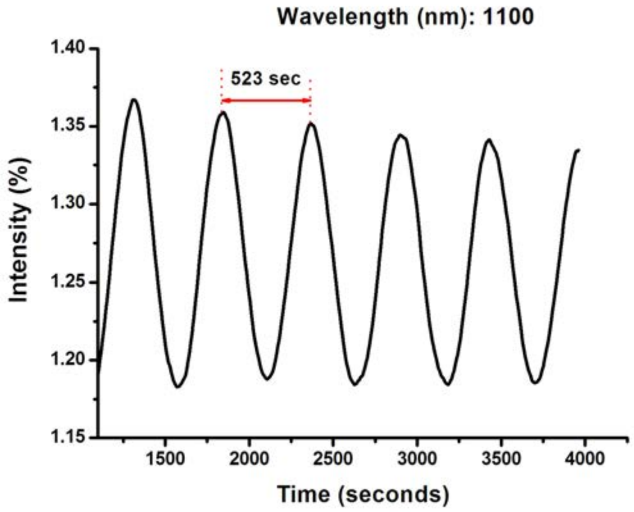
- Interference effects occur owing to the reflection and refraction of the thermal radiation from the substrate at the faces of the growing epitaxial layer.

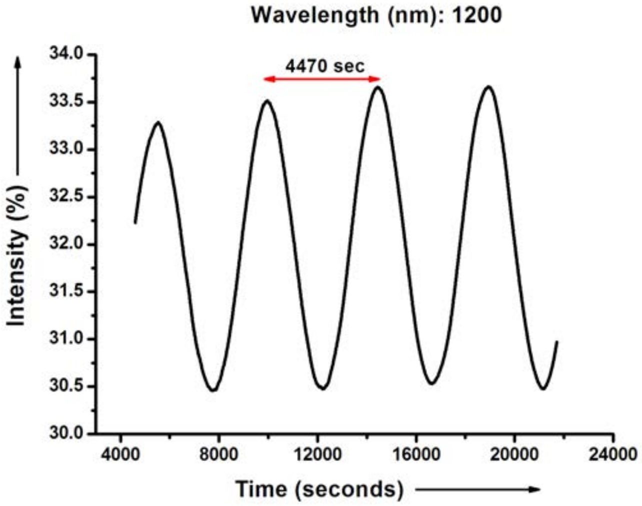
Growth rate determination by interferometry



GaAs - 1μm/hr

AlAs – 0.176 μm/hr

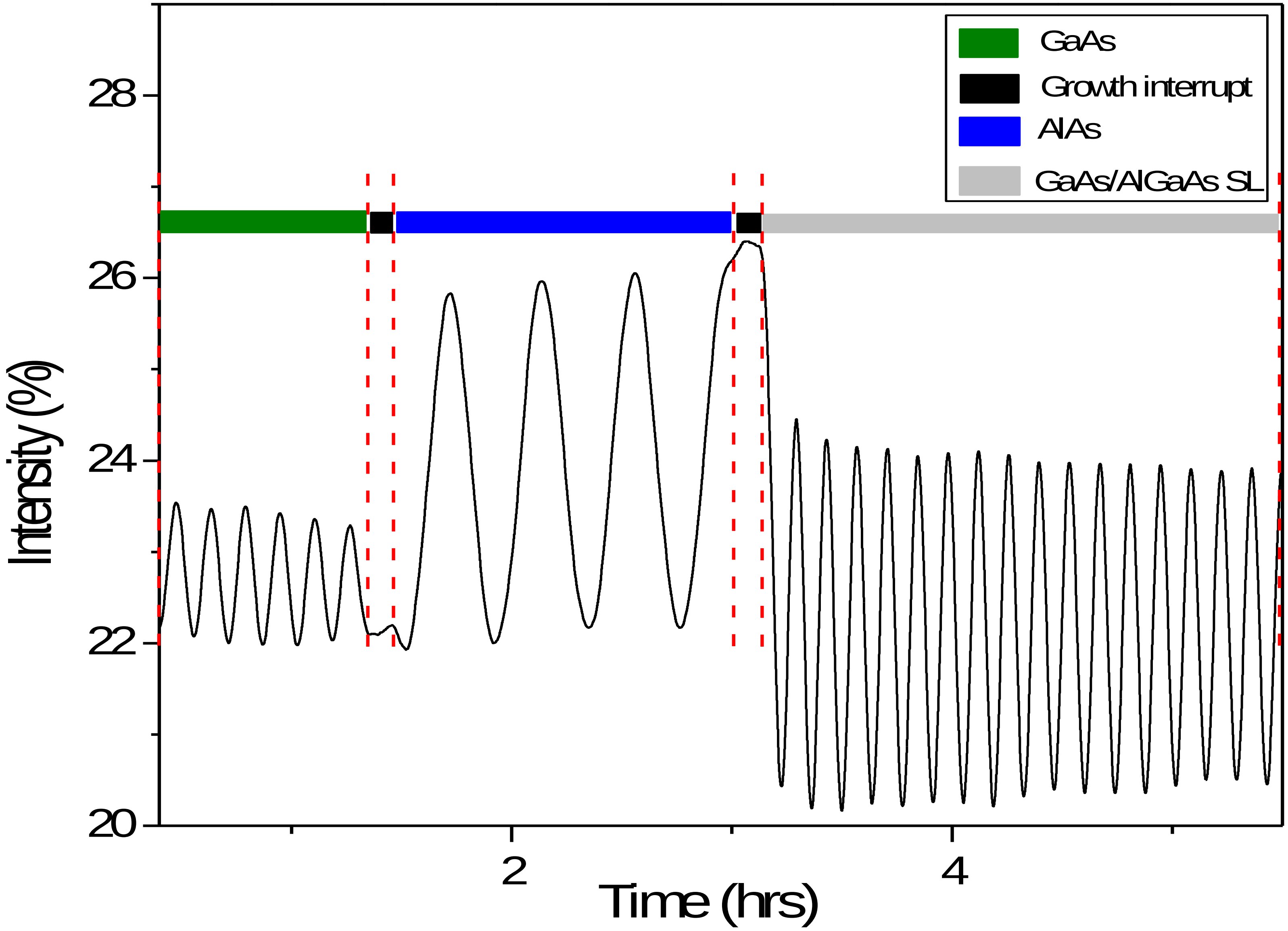




$$G = \frac{1}{T} \times \frac{\lambda}{2\eta}$$

G = growth rate
T = period
λ = wave length
η = refractive index

And one can monitor real time during growth



How do you measure doping levels *in situ*?

- **You can't!**

  All *in situ*, measurement instruments do not have the necessary sensitivity;

- **The doping is measured outside the MBE growth chamber (using, for example, Hall measurements or capacitance-voltage measurements);**

- **Results are then fed back into a calibration curve on the MBE computer, which allows doping levels to be set accurately;**

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  - **Doping;**
  - **Interfaces – roughness and asymmetry;**
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THz QCL growth at Leeds

- We like to grow GaAs at 1μm/hour (~ 1 monoloyer per second);

- For a standard QCL, with a 15% AlGaAs mole fraction, the AlAs growth rate is then 0.176 μm/hour.

[NB For mole fractions around 30-35%, we would normally calibrate for 33%; i.e. 1μm/hour of GaAs, 0.5 μm/hour of AlAs]

- Calibration is undertaken using pyrometry oscillations (although approximate values are obtained by flux measurements/RHEED):

– Averages cell fluxes over 1–5 hours (unlike RHEED/flux measurements), and gives greater accuracy than flux measurements (gauge sensitivites can change with exposure to arsenic, and Al fluxes are low).

- Flux measurements are used to calibrate the more approximate concentrations in etch stop layers.

A QCL growth

- Warm cells from idling temperatures, and measure fluxes for Ga, Al and As(1 hour);
- Calibrate Ga and Al using pyrometric oscillations (1-2 hours for Ga, 4-5 hours for Al (low growth rate);
- Check fluxes of Ga, Al, and As;
- Grow QCL overnight (> 10 hours), automatically, ramping down cells at the end of growth;
- Grw high electron mobility transistor structures to monitor chamber quality, and also regular bulk doping structures to check doping levels.

[Costs for a THz QCL are higher than many optoelectronic devices, owing to the length of time taken to grow and calibrate the structures.]

Can I have multiple aluminium mole fractions?

This can be achieved in one of three ways:

- **Interdigitated – Al and Ga cells are shuttered open and closed rapidly, with the average mole fraction being given by the relative amount of time the shutters are open:**

Problem: If two cell fluxes are set up, there are only a certain number of permutations that are possible. Also what effect do the interfaces have on electron and phonon transport.

- **Ramp the cells between different temperatures.**

Problem: It takes time for cells to settle down, so interrupts are needed. Not ideal with 100 repeat periods, and will calibrations drift?

- **Use two Ga or two Al cells – they are on the system.**

Problem: A system issue may then end the growth run.

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What can go wrong?

- I am not discussing any exotic material system…
  - the focus is on GaAs-AlGaAs;
- Can there be anything interesting to say about the growth?
  - I have worked on this material for over 20 years!
- I too can remember the problems we faced with:
  - material purity and defects;
  - reliability of components (e.g. substrate manipulators);
  - growth rate uniformities, and interface quality;
  - calibrations between laboratories.
- But surely all is sorted…
  - *We’ll see!*

Actually the technology is still demanding…

- **Consider the design problems of MBE:**

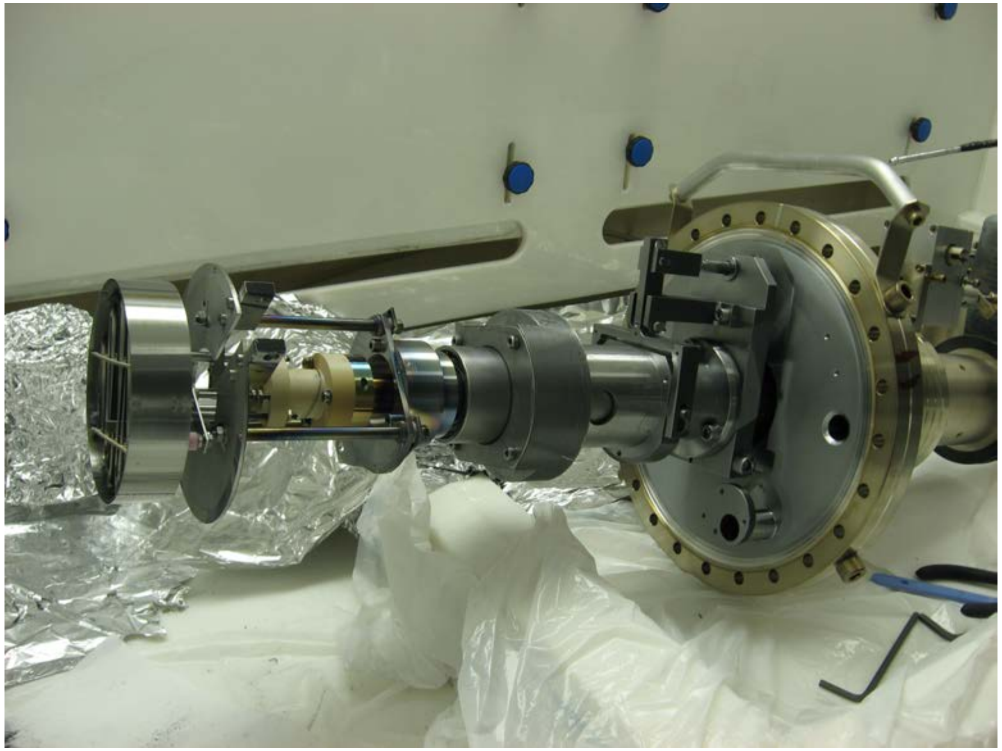
Design a substrate manipulator, it needs to:

– Heat a substrate to over 600 °C, whilst being coated;

– Rotate a wafer to achieve uniformity;

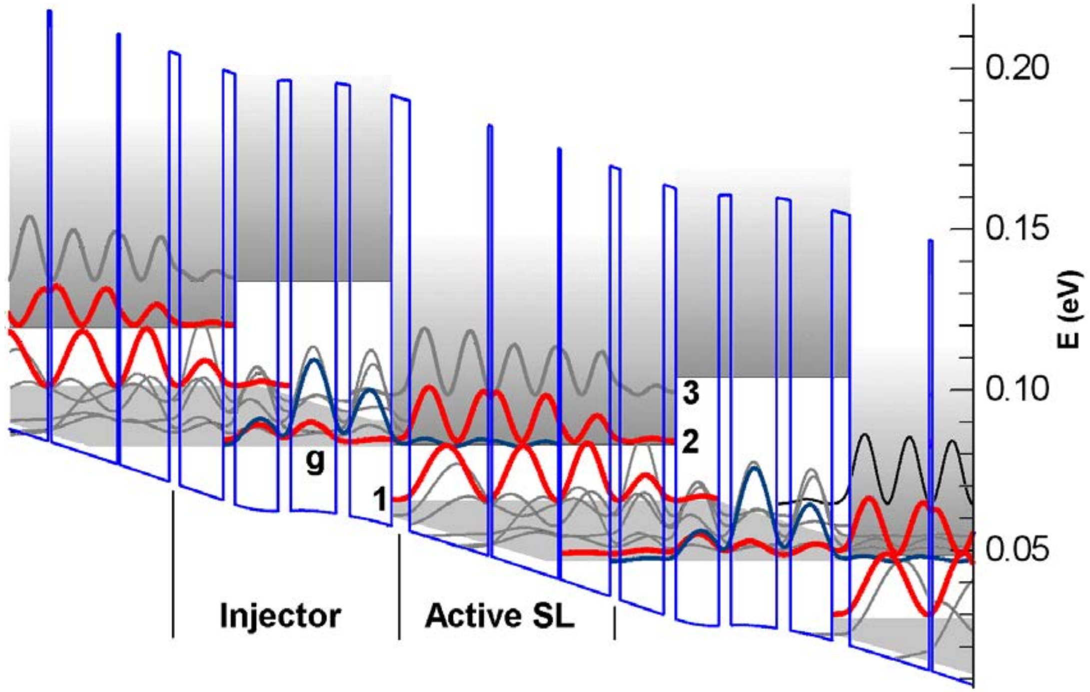
– Operate uninterrupted for up to 2 years;

– Allow substrate loading and unloading.



… but you can’t use any lubricant!

And THz QCL is quite challenging..



R. Köhler *et al.*, *Nature* 417, 156 (2002)
The Economist, August 10th, 73 (2002)

- The first THz quantum cascade laser had:

104 repeat periods of active layer and injector;

Each period was 104.9 nm long, and contained barriers only a few atomic monolayers thick;

- Uniformity of structure (to < 2%) was maintained over the > 10 hours taken to form it.

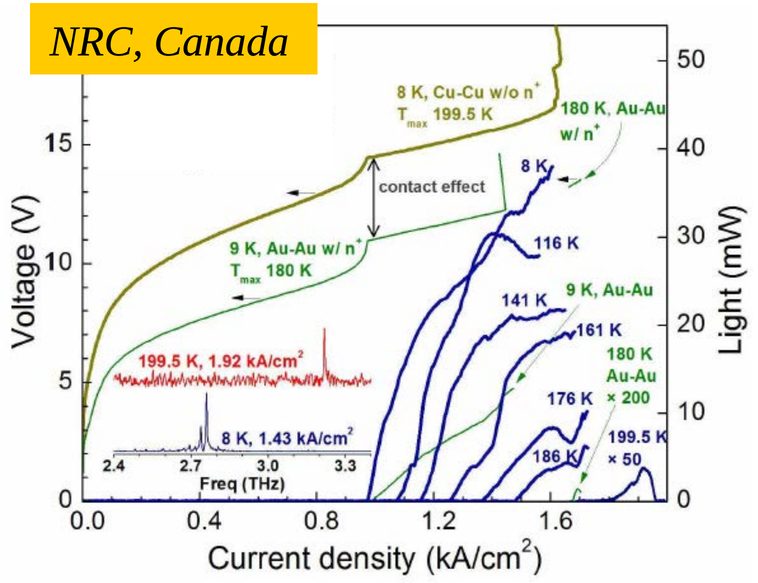
- System reliability is critical!

Let’s just think about the design

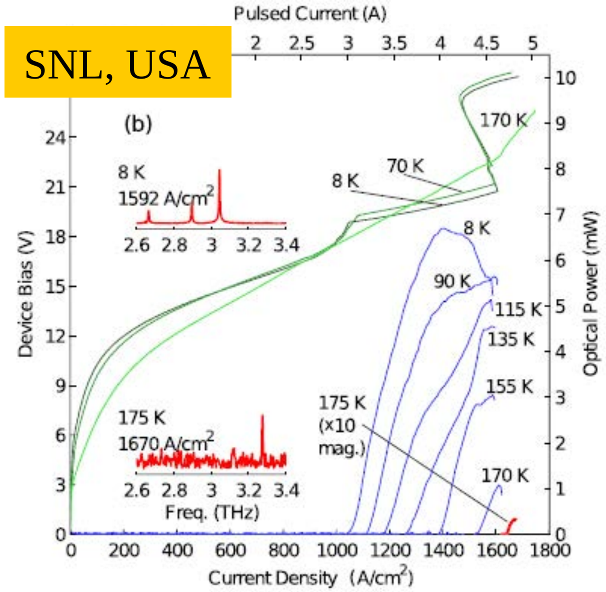
- There are >1000 interfaces…
  - Are we sure about our growth rate uniformities?
- What about doping?
  - Average doping levels are typically a few 10^{15} cm^{-3};
- Are the interfaces good, is the structure ‘as grown’?
  - Interface quality really will effect electron transport, as can asymmetry of interfaces in devices;
- How accurate are the calibrations between laboratories?
  - Can we copy a literature recipe?
  - *Let’s look at an example…*

How are we doing (same QCL design)?

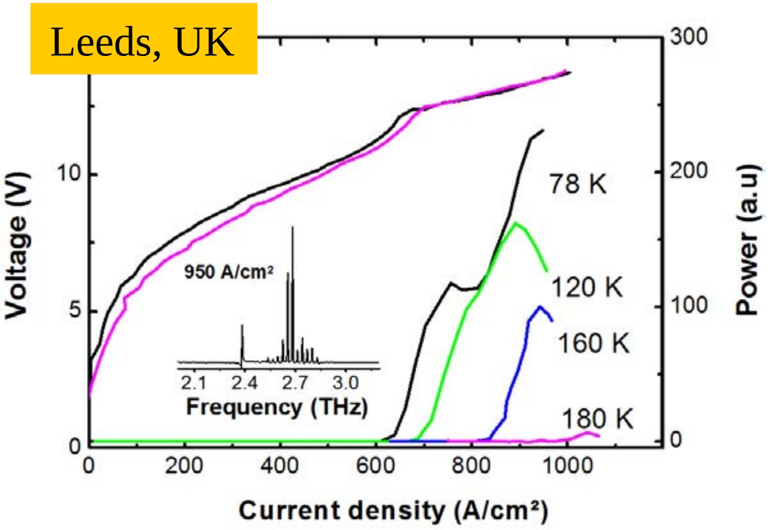
NRC, Canada



SNL, USA



Leeds, UK



Lab	J_{th} (A/cm²)	J_{max} (A/cm²)	T_{max} (K)	ν@8K (THz)
NRC	890	1520	199.5	2.73
SNL	1030	1400	175	3.02
Leeds	600	950	185	2.68

1. **S. Fathololoumi et al, *Opt. Express*, 20, 3866 (2012)**
2. ***C.* W. I. Chan et al, *Appl. Phys. Lett.*103, 151117 (2013)**

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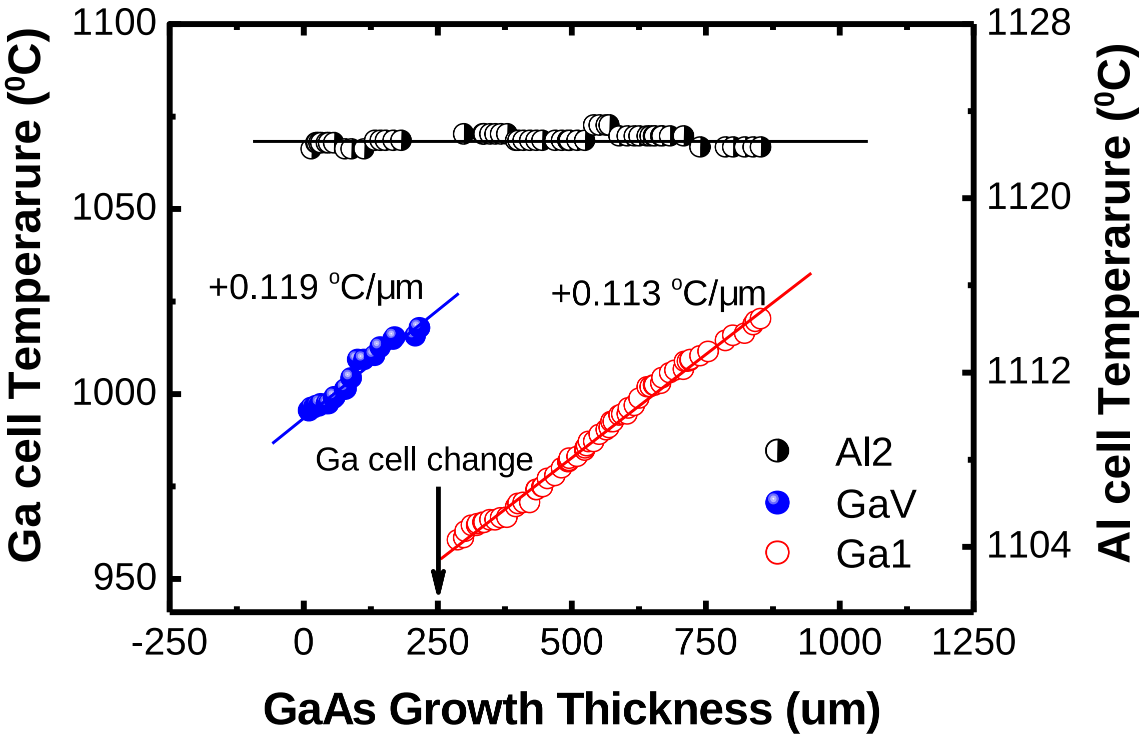
Growth reproducibility from Leeds

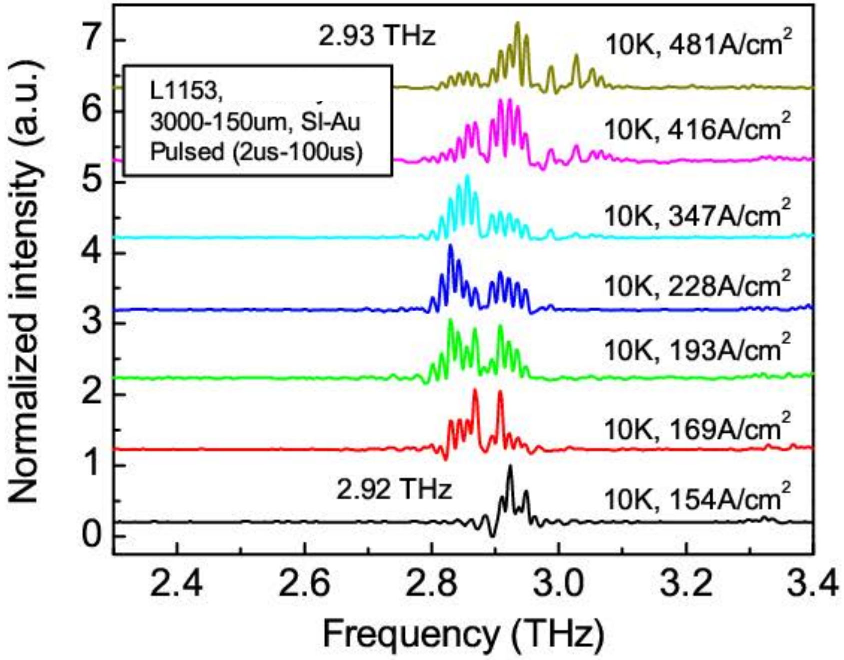


- To grow gallium at 1 μm/hour requires the gallium cell temperature to change by ~0.11 °C/μm, whereas the Al cell temperature remains almost constant for a 15% mole fraction owing to a smaller consumption of material;

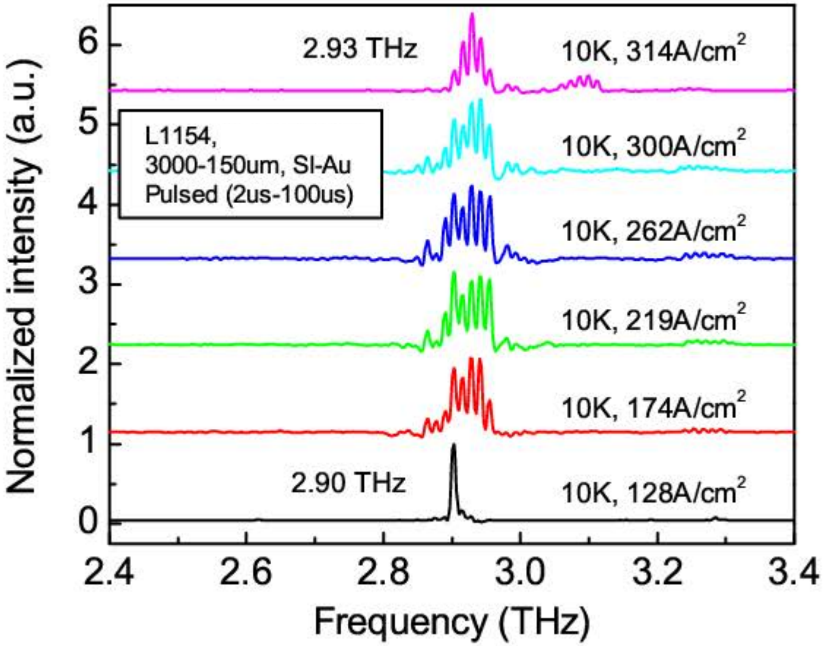
- Compensation of the flux drift is therefore really needed.

Growth reproducibility from Leeds

QCL GR=1.020 um/hr



QCL GR=1.017 um/hr



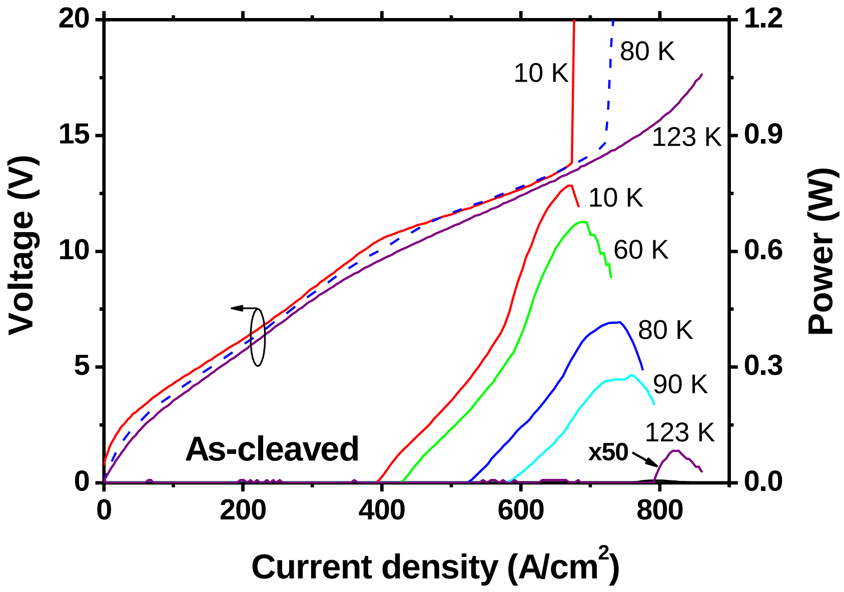
- **Nominally the same QCL design, with pyrometer determined thickness controlled to ±5%;**

- **Leads to almost identical emission frequency.**

QCL design is from M. Wienold et al., *Electron. Lett.* , 45 , 1030 (2009)

And reproducibility between two campaigns

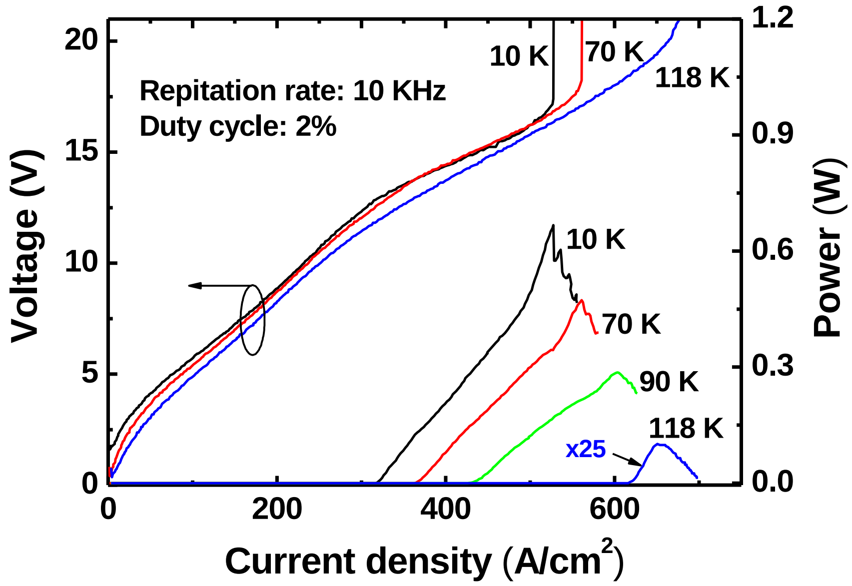
2013 growth campaign



- **Peak output power of 0.78 W**
- **Lases up to 123 K**
- **Lasing around 3.4 THz**

2014 growth campaign

(After refurbishment)

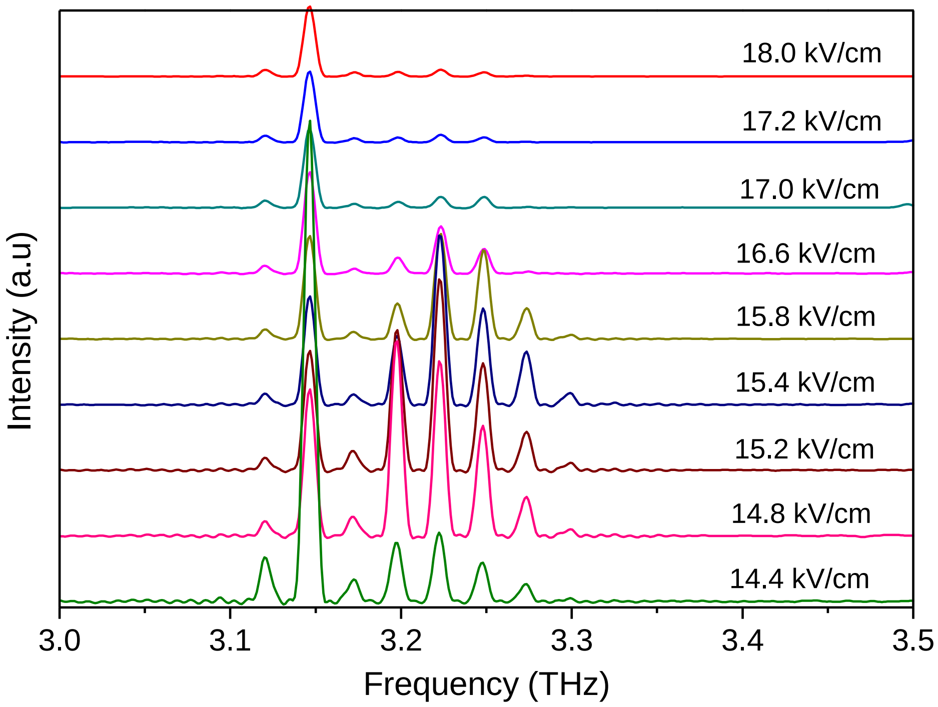


- **Peak output power of 0.67 W**
- **Lases up to 118 K**
- **Lasing around 3.3 THz**

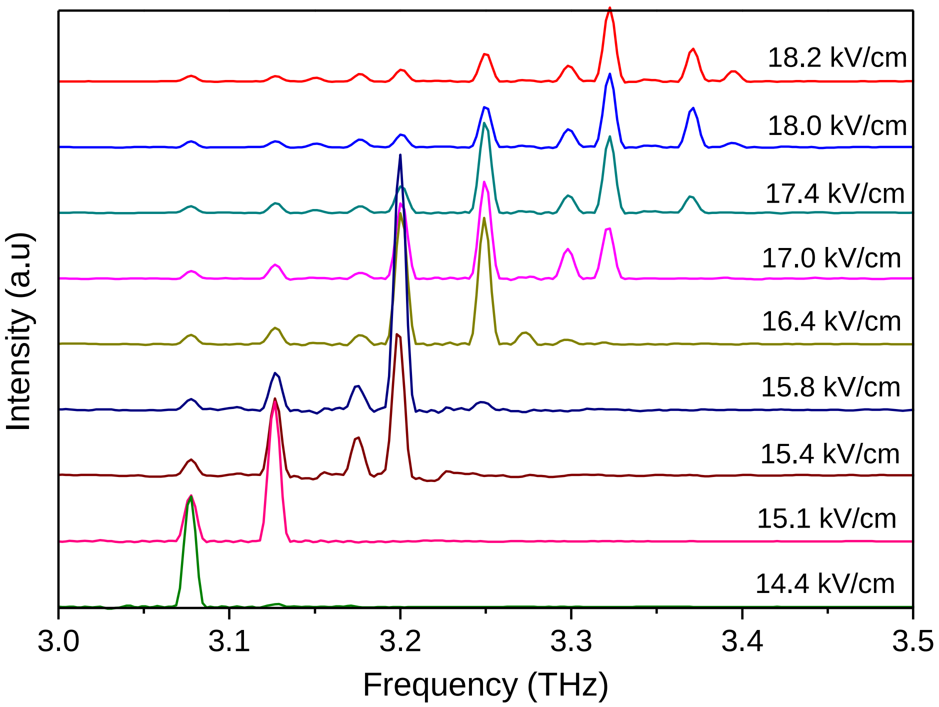
See: L. H. Li talk (Wednesday) at IQCLSW, to given by Y. Han.

A controlled flux drift

- A (single plasmon), resonant-phonon depopulation structure was designed, where the Ga flux was changed from +6% to –6% in the active region;



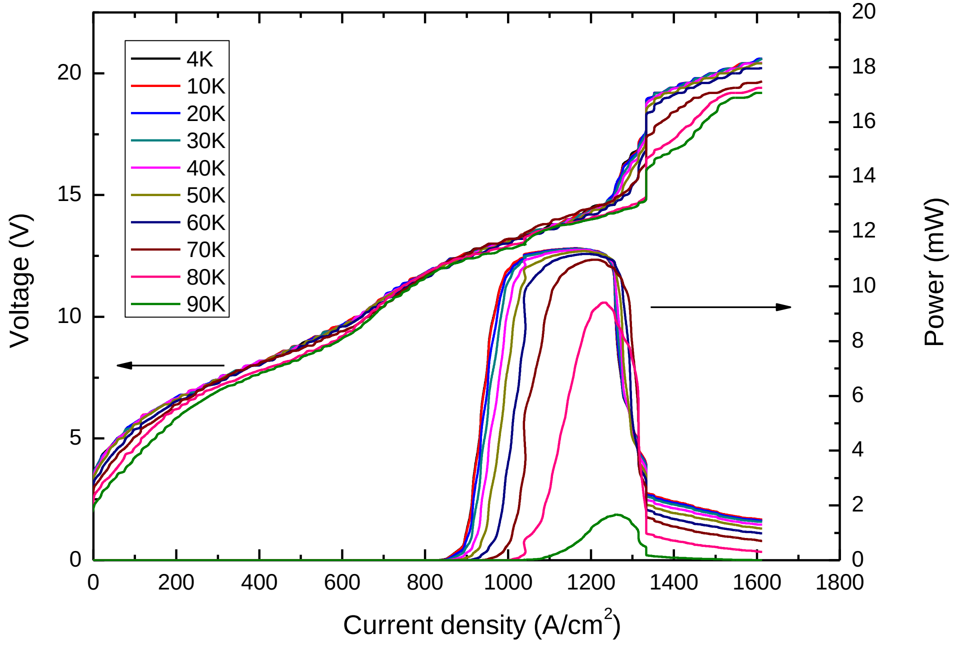
Standard Growth



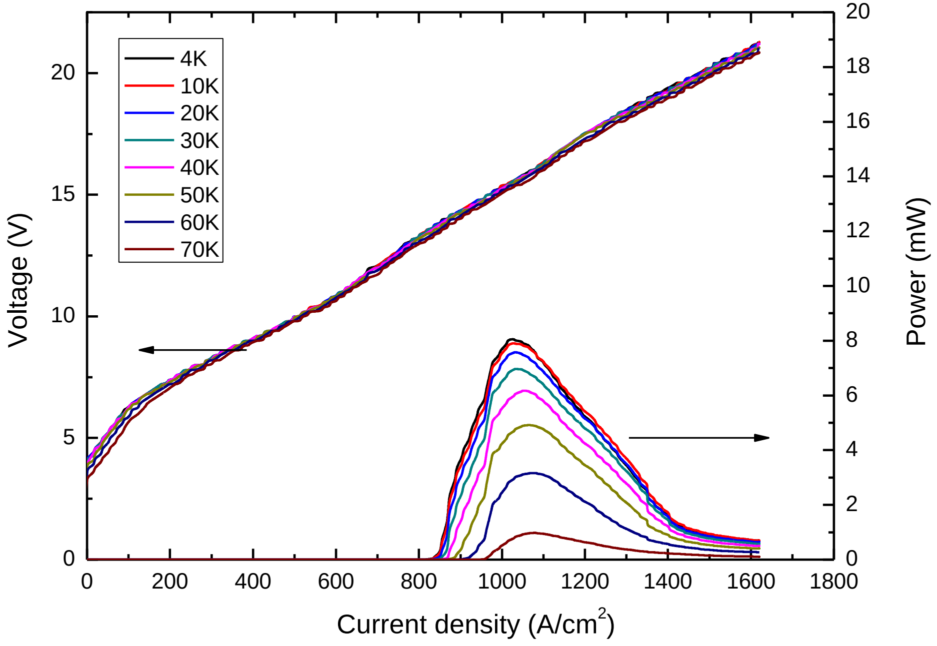
Chirped Growth

S. P. Khanna *et al*, *Appl. Phys. Lett.* 95, 181101 (2009).

LIV Characteristics



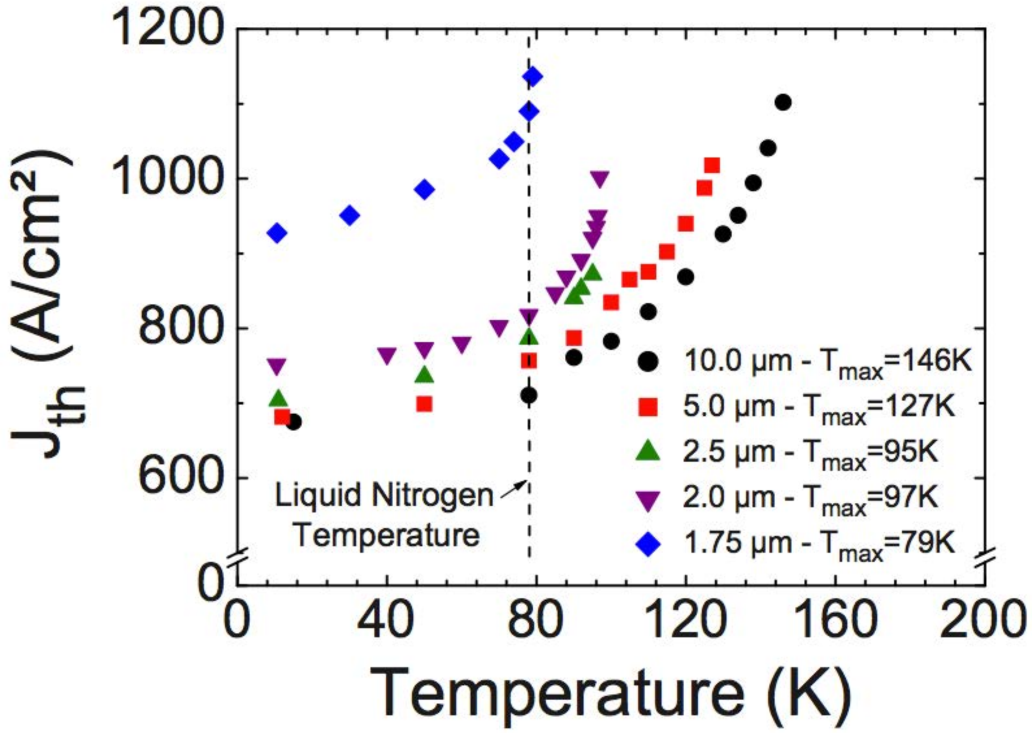
Standard Growth



Chirped Growth

- **If deliberately changing the growth thicknesses leads to < 50% drop in output power, then how much of the active region actually contributes to lasing?**

In fact, the active region can be shrunk to 1.75 μm!



E. Strupiechonski *et al*, *Applied Physics Letters*, 98 (2011).

- **So how uniform are the fields in this structure?**
- **Are domains forming? (see D. Ban talk at IQCLSW)**

Much needs to be done to optimize performance, but if one can reduce the 10 μm growth thickness – that would help!

Let’s just think about the design

- There are >1000 interfaces…
  - Are we sure about our growth rate uniformities?
- What about doping?
  - Average doping levels are typically a few 10^{15} cm^{-3};
- Are the interfaces good, is the structure ‘as grown’?
  - Interface quality really will effect electron transport, as can asymmetry in devices;

Doping is a significant issue in THz QCLs

- **THz QCLs are extremely sensitive to the active region doping level. Changes of ~ 10% can make significant differences;**
- **Yet doping is typically low; e.g. one GaAs layer is doped at ~4 x 10^{16} cm^{-3}, but the average doping is only ~ 6 x 10^{15} cm^{-3};**
- **This can cause problems, since background doping levels in a growth chamber can be ~ 1 x 10^{15} cm^{-3}, either n- or p-type (depending on growth conditions, and cleanliness of chamber);**
- **Unfortunately, with the 10 hour growth, it is often not realistic to grow a series of QCLs with systematic changes in doping;**
- **Many THz QCLs are, therefore, almost certainly not optimised.**

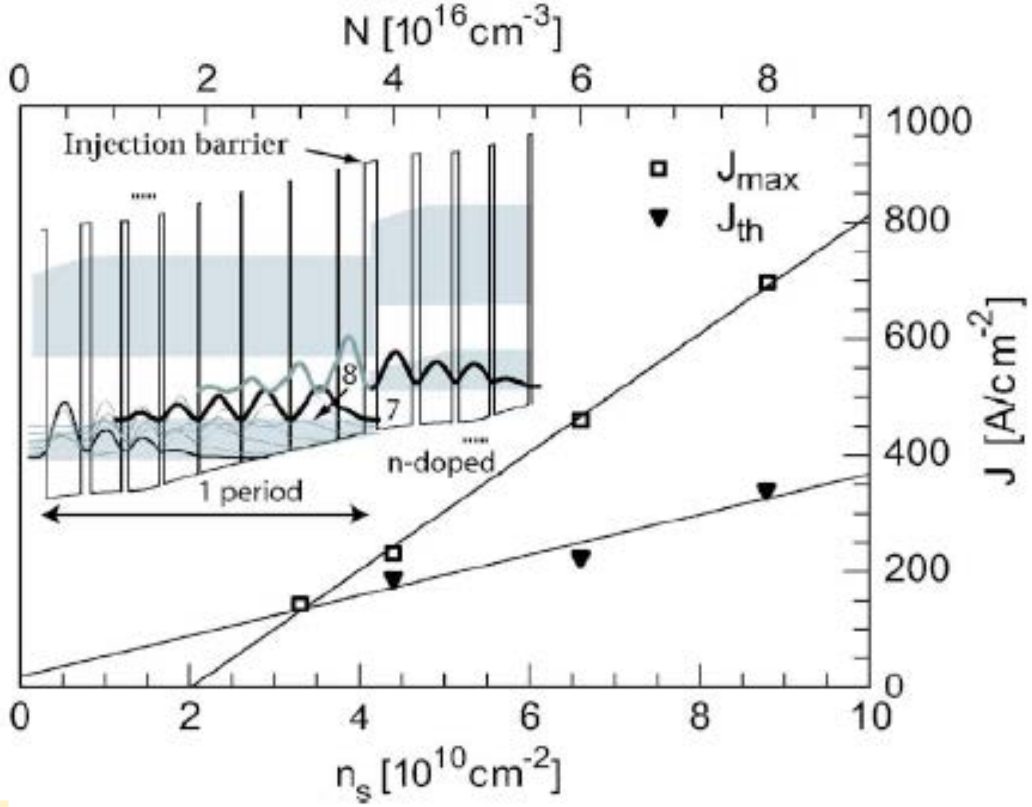
(To check background doping levels, one needs to grow thick (>10 µm) undoped GaAs – time consuming. HEMT structures are thinner.)

Effects of doping level on THz QCLs

$$J_{th} = (\alpha_m + \alpha_w)\cdot(\Gamma\cdot g)^{-1}$$

$$g = \tau_3\cdot\left(1 - \frac{\tau_2}{\tau_{32}}\right)\cdot\frac{4\cdot\pi\cdot e\cdot z^2}{\lambda\cdot\varepsilon_0\cdot n_{eff}\cdot L_p(2\cdot\gamma_{32})}$$

$$J_{max} = \frac{e\cdot N_s}{2\cdot\tau_3}$$



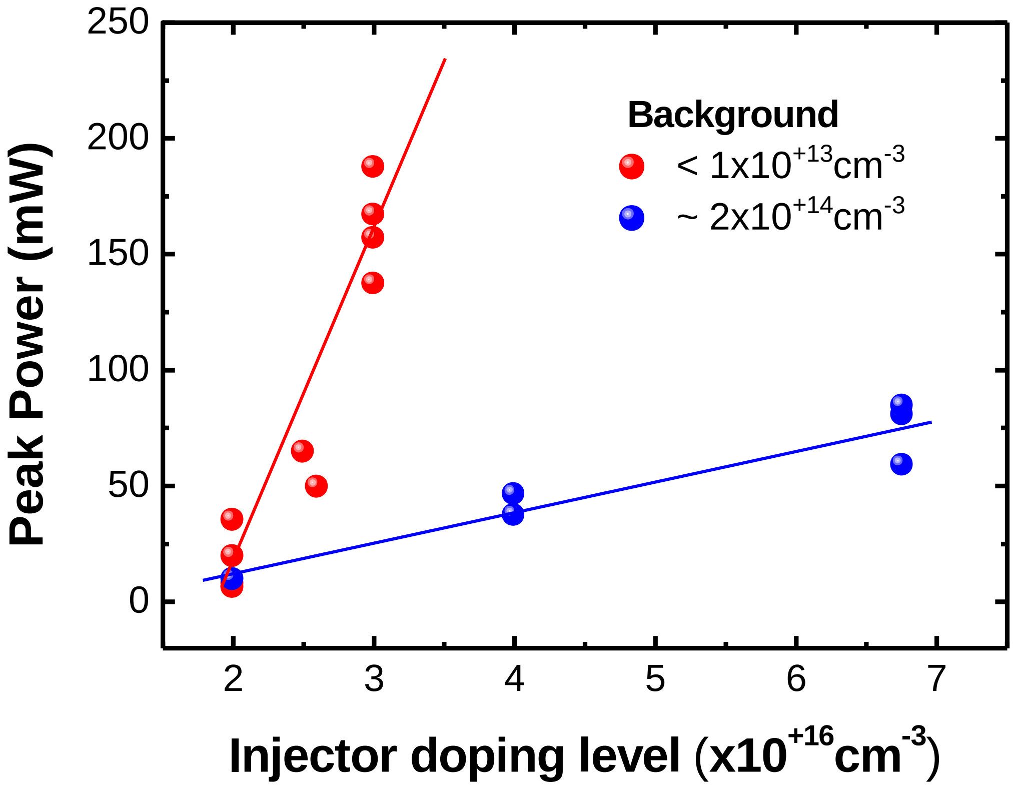
Doping density increases

$\rightarrow \alpha_w$ and $\gamma_{32}\uparrow\rightarrow J_{th}\uparrow$

$\rightarrow J_{max}\uparrow$

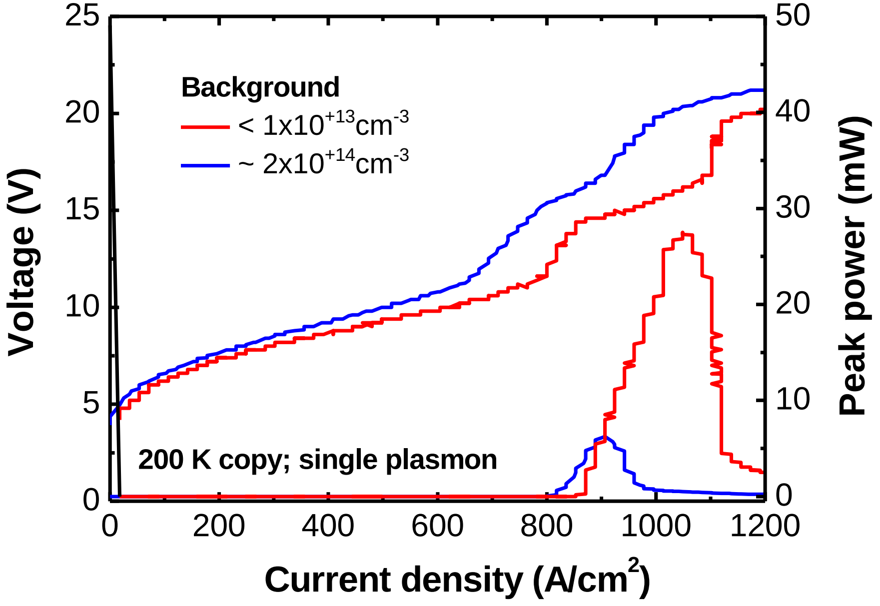
L. Ajili, J. of Appl. Phys., 100, 043102 (2006)

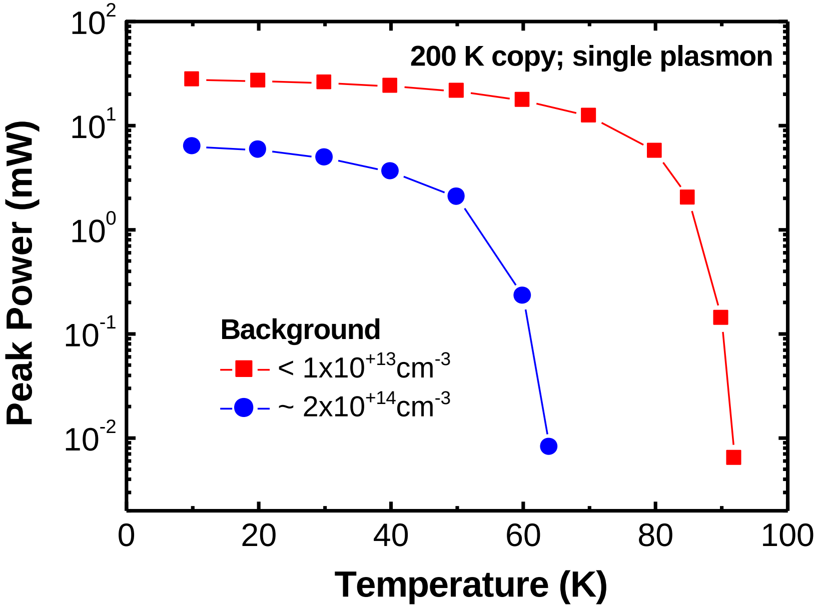
Effects of doping level on THz QCLs



- Same QCL active design, different background and injector doping;
- Dynamic range and output power scale with doping.

Effects of doping level on THz QCLs





- Lower background doping gives larger output power/dynamic range;
- > 2×10^{15} cm^{-3}, devices are rarely lasing

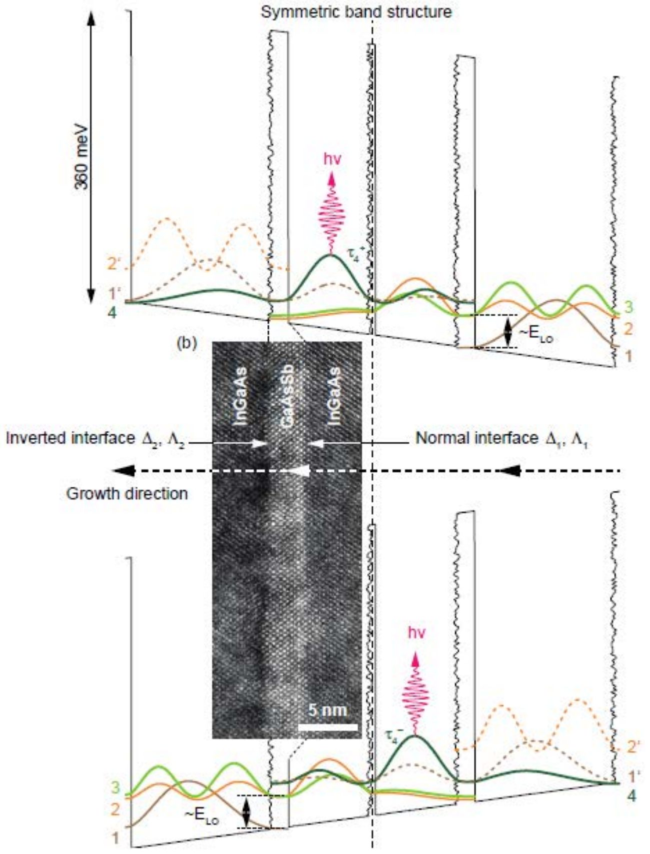
Are there other issues?

Well yes!

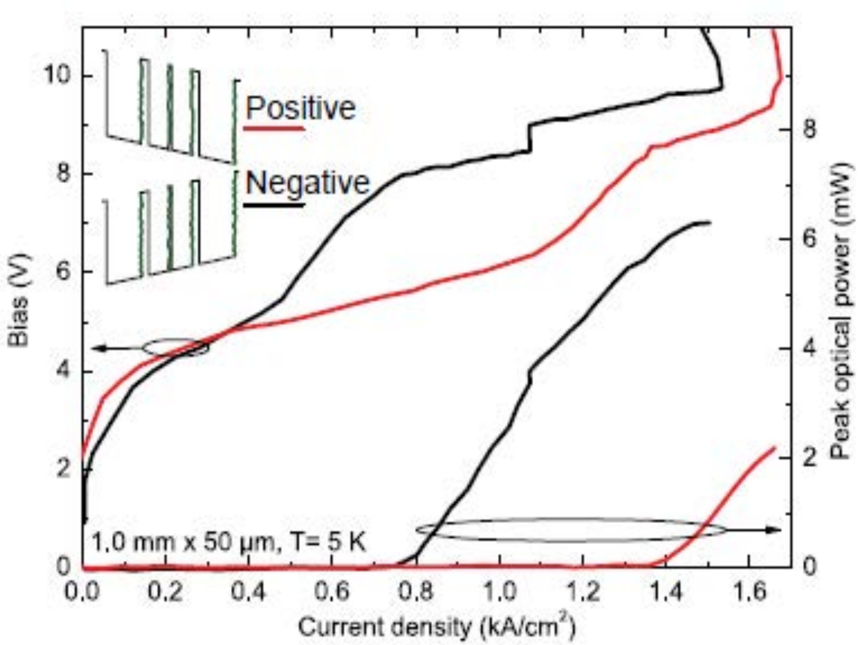
- **Substrate temperature and the V/III ratio can not only change background doping levels and dopant activation, but can also alter interface quality. Are the interfaces smooth? Are the barriers symmetric?**

- **How is doping incorporated? Bulk or delta doped? In the wells or barriers? What are the implications of dopant diffusion/segregation?**

Impact of rough interfaces on THz QCLs



Example: InGaAs/GaAsSb THz QCL

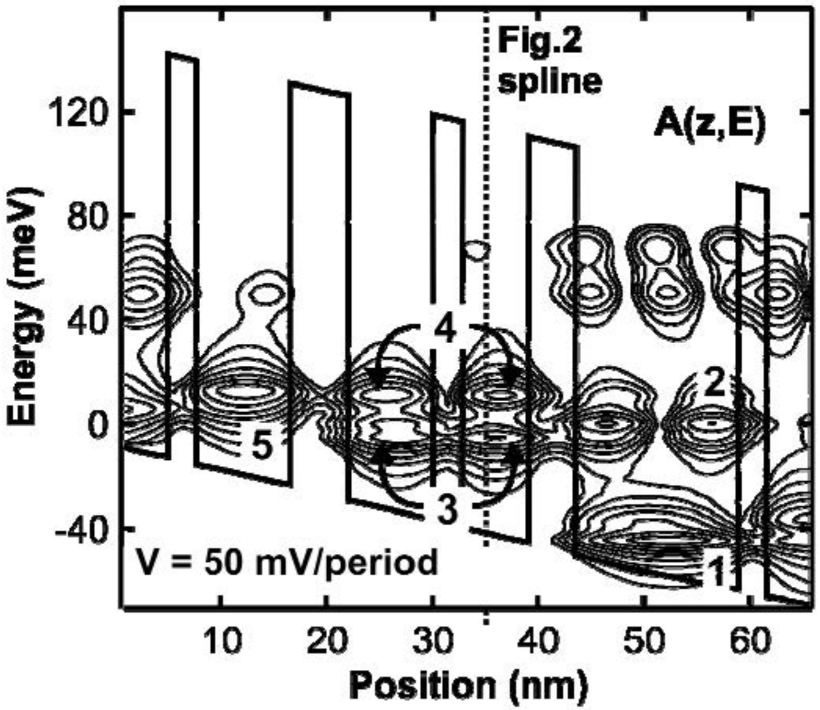


C. Deutsch, *Optics Express* 21*, 7209 (2013*)

(see G. Strasser talk at IQCLSW)

- **Pronounced interface asymmetry**
- **Better performances in negative bias**

Impact of rough interfaces on THz QCLs



T. Kubis et al., *14th International Workshop on Computational Electronics (IWCE)*, 2010

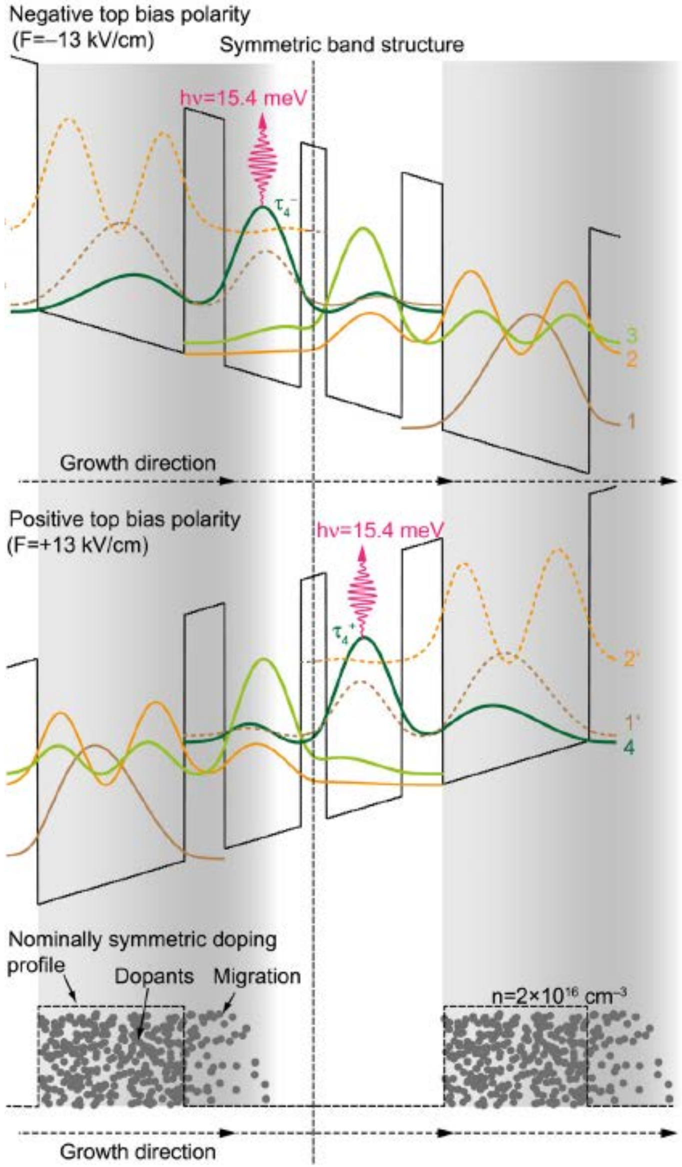
Rough interfaces scattering:

Broadens confined states;

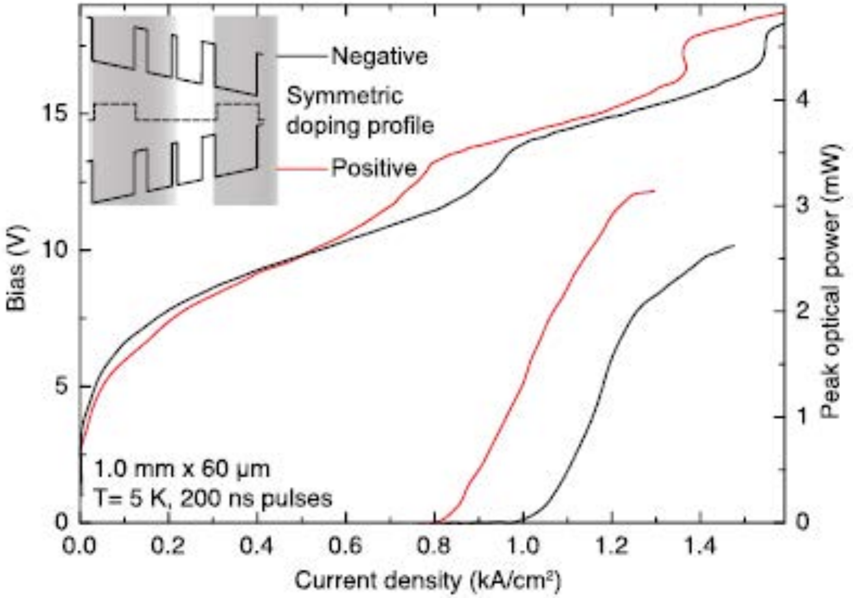
Changes the state occupancy.

(see presentations at IQCLSW by, for example, M. Lindskog, X. Lu, A. Grier, K. Krivas)….

Effects of dopant migration on THz QCLs



Symmetric GaAs/AlGaAs THz QCL



C. Deutsch, *Appl. Phys. Lett.* 102, 201102 (2013)

- **Dopant migration causes scattering**
- **Better performances in positive bias**

So, yes there are issues still to address…

The challenge:

- How do we model and interpret ‘non perfect growth?
- How can we address this during growth?
- Can we achieve reproducibility between laboratories, given the difficulty in absolute calibration of growth temperatures, fluxes, and the growth kinetics?

There appears much materials work still to be done!

Outline of Presentation

- Molecular beam epitaxial growth:
    - Outline of MBE growth;
- Calibration of growth rates:
    - Flux Measurements;
    - RHEED;
    - Pyrometry;
- THz QCL growth at Leeds;
- Is everything straightforward?
    - Growth rate uniformity;
    - Doping;
    - Interfaces – roughness and asymmetry;
- **Conclusions.**

Conclusions

- **The technique of MBE growth has been reviewed;**
- **Techniques for calibrating growth rates have been discussed;**
- **There remain many challenges in growing state-of-the-art, reproducible THz QCLs;**
- ***A significant issue in optimizing THz QCLs is the length of time needed to grow and process a THz QCL – it is difficult to optimize a single THz QCL, even in the 'well established' GaAs-AlGaAs materials system, let alone other materials systems.***

Thank you to the organisers for the invitation to speak at this conference, and for your attention.