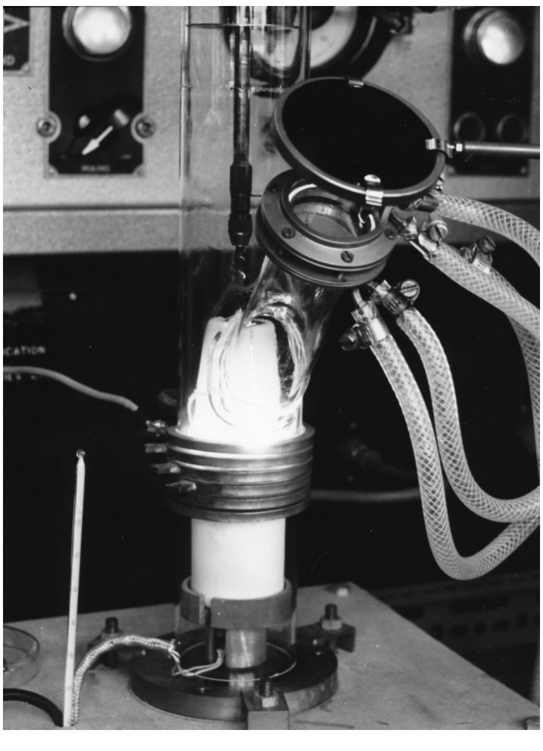
GROWTH OF SINGLE CRYSTALS AT STL

PIEZOELECTRIC ORGANIC-BASED CRYSTALS

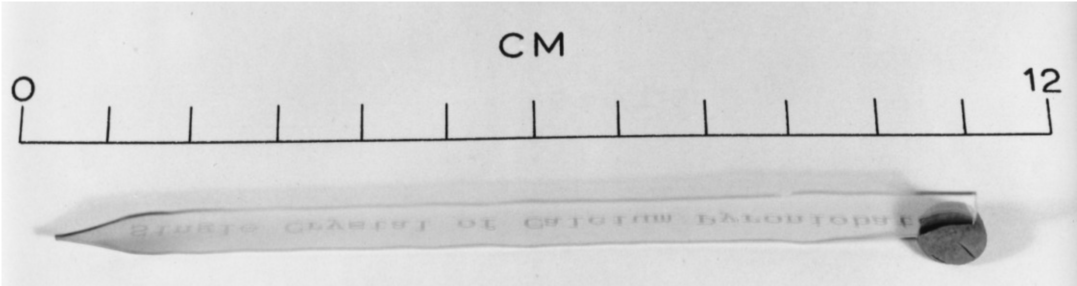
- During the 1940s there was a need to find alternative piezoelectric crystals to quartz because the latter largely came from Brazil. Organic compounds such as Rochelle Salt (potassium sodium tartrate) and ADP (ammonium dihydrogen phosphate) were known to be piezoelectric, so work was started by **Doc Foord** (possibly at STC North Woolwich in a pre-STL materials laboratory) to grow them. Production equipment was built to grow ADP, and **Bessie Hodgson** was the technician responsible for running the equipment.
- The single crystal was cut into slices and after metallizing were made into channel filters, and a set installed in a telephone exchange in Reading <or Slough>.

PIEZOELECTRIC & FERROELECTRIC INORGANIC CRYSTALS

- ITT Quartz Crystal Division (QCD) grew synthetic quartz by the hydrothermal process (**Ray Rabetts**) and made a range of quartz oscillators and filters.
- Quartz has a low electro-mechanical (e-m) coupling so a research programme was started at STL in 1965 to investigate single crystals with a higher e-m coefficient that could also be grown by a faster process.
- **Peter Graves** grew single crystals of piezoelectric calcium pyroniobate ($Ca_2Nb_2O_7$) and ferroelectric lithium tantalate ($LiTaO_3$) by the Czochralski method, whereby a crystal is pulled from the molten compound. The latter was contained in an iridium crucible heated by RF induction.



- The $Ca_2Nb_2O_7$ had a peculiar growth habit such that long crystals with very flat surfaces were grown, and overall was similar to mica.

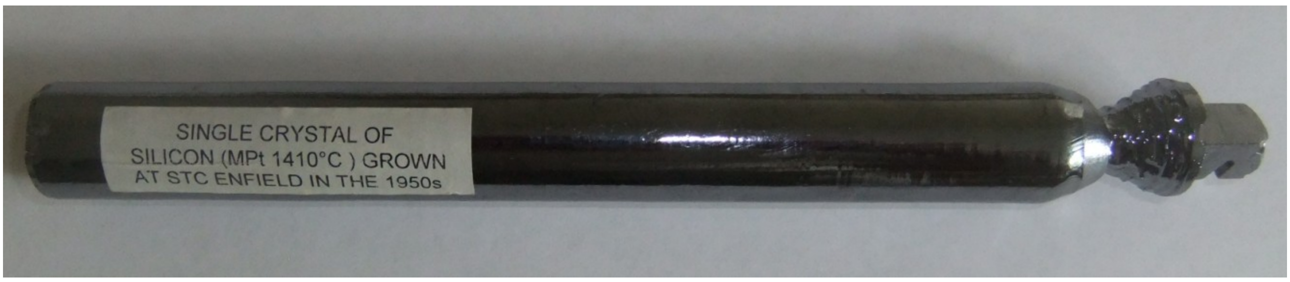


Single Crystal of Calcium Pyroniobate

- **David Smith** of QCD found that $Ca_2Nb_2O_7$ had an e-m coefficient of about 20, but was not a viable material for production because of its susceptibility to cleavage.

SEMICONDUCTOR MATERIALS

- In the 1950s, with the discovery of the transistor, STL Enfield started research into growing high purity single crystals of germanium and silicon.
- Germanium was grown by the Czochralski method of pulling a single crystal from the melt.
- A team comprising of **Eric Bush, Henley Sterling, Reg Warren** and **Ernie Workman** was set up to grow single crystal silicon.
- High purity polycrystalline silicon was prepared using gaseous silane (SiH_4), which was consolidated into rod using the silver boat process <*see other display boards*>.
- The rod of pure silicon was placed in a vertical position in an RF coil, and the tip melted by induction, from which a single crystal was grown by the Czochralski method.



Pete Graves August 2014

THREE-FIVE BASED COMPOUNDS

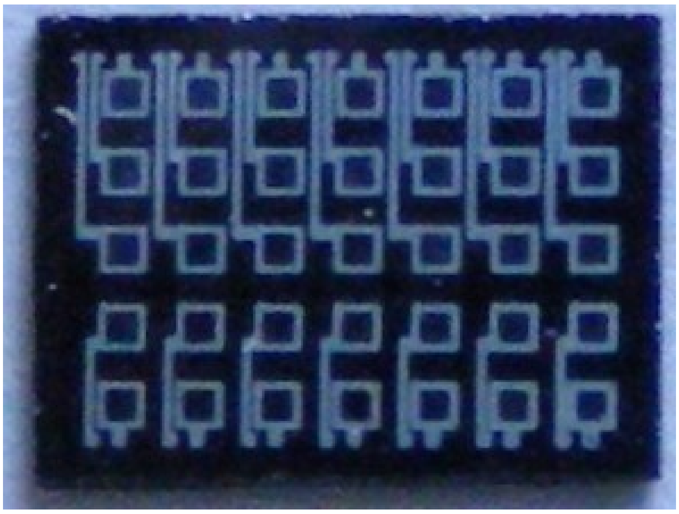
SINGLE CRYSTAL GROWTH

- **Colin Goodman,** who joined STL about 1960, directed toward the compound semiconductor gallium arsenide (GaAs), which has a melting point of 1238°C.
- The technique adopted was the horizontal gradient-freeze method, supervised initially by **Albert Langton** and assisted by **Dick Upson**. Gallium was melted in a silica boat in an evacuated silica tube that also contained enough arsenic metal to react with and saturate the gallium at 1250°C. The temperature gradient in the surrounding furnace was arranged so that as the temperature was slowly reduced, the gallium arsenide solidified, initially from one end, progressing to the other. The proportion of single crystal material was not very good, but it did produce enough to allow the development of devices and of the vapour phase 'epitaxial' processes which were becoming important.
- **Derek Bolger** took over supervision of the growth of GaAs process about 1964 when Albert left and continued until 1974 when he became STL Safety Officer. Then **David Greene** took over supervision, with **Joe Hopkins** as his assistant, with the aim of GaAs ingots with a very high free electron concentration, required for substrates for the single heterostructure lasers that were being made in Paignton after development at STL. Wafers were cut from the ingots by **John McArthur** in the Model Shop and polished by **Win Spellane**. In 1980 the work finished, as there were commercial sources of the required material.

EPITAXIAL GROWTH

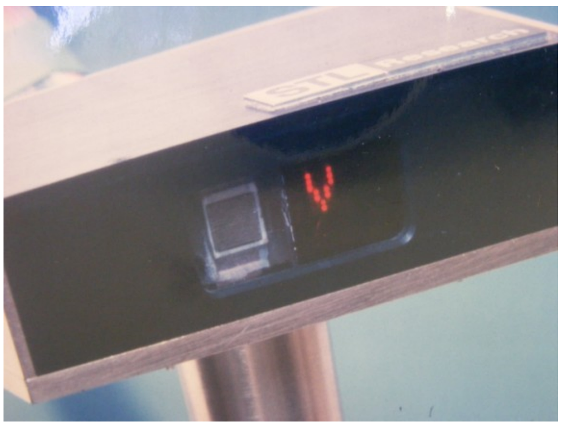
- In 1962 development work on the epitaxial process of growing thin layers on a single crystal substrate of GaAs was started by **Derek Bolger**, based on the process originally developed by **George Antell** when he was at Plessey Caswell. The process involved the high temperature reaction of Ga and the vapour of arsenic trichloride ($AsCl_3$). The latter was only one of many highly unpleasant and dangerous chemicals involved in materials processing at that time.
- **Brian Barry** and **Derek Bolger** managed to make a small sample of aluminium arsenide in around 1962, and **John Whitaker** was able to make appropriate electrical measurements on it.
- The growth and development of single crystal GaAs provided the basis of solid state laser technology which was subsequently key to developing fibre-optic systems.

- **Clive Stewart, Sue Wheeler** and **Mike Wright** used vapour phase epitaxy (VPE) to deposit a layer of GaAsP on a polished GaAs wafer, to fabricate the first red discrete Light Emitting Diodes (LEDs).
- Epitaxial wafers were also processed into discrete monolithic 5x7 alpha-numeric LED displays first by depositing an insulating layer, then defining the LED array, diffusion to produce the p-n junctions, metallization to provide the contacts and finally cleaving. These devices developed by **Jack Peters, Bill Bourne and Alan Brisbane** were the first, certainly within the UK, monolithic alpha-numeric LED display.



- A coding matrix of p-n junctions was used to address the display using thin silicon (mechanically thinned to 10-20 μm), which had unique properties of transparency and flexibility (**Derek Mash, Bessie Hodgson, Brian Eales** and **Gordon Henshall**). The addressed alphanumeric display was demonstrated at the Harlow Town Show, circa 1970.

- LED line arrays were produced at STC Paignton for use on photographic film. Eventually GaAsP LEDs were used as displays in calculators as manufactured by Hewlett Packard. *<Of course the use of LEDs burgeoned for use in large arrays, headlamps and tail lamps in automobiles, in cameras – the list is endless>*.



Derek Bolger, David Greene and
Gordon Henshall, September 2014