

ReGall

Funded by InnovateUK: Project 78550

Issue 1
Q1 2021

Newsletter

Summary:

This exciting project will develop the required technology to recover gallium from end-of-life (EoL) LEDs to supply the uptake of Gallium Nitride (GaN) semiconductors in power electronics, machines, and drives (PEMD) by using Deep Eutectic Solvents (DESs).

During Q1 the consortium has confirmed that gallium can be recovered electrolytically from DESs and the technology will be refined during future periods. It has also carried out a literature survey and reviewed the current recovery practises for gallium, as well as assessing the future demands and potential market size for the metal and its salts. Details of these surveys and reviews will be available later.

Consortium Partners:



Gallium and its properties.

Gallium is a naturally occurring element that is only found as a trace element in conjunction with a variety of minerals, the most common of which are zinc and aluminium ores. It was discovered in 1875 by the French scientist Paul Emile Lecoq de Boisbaudran.

It is a Group 13 element and it has a density of 5.904g/cm^3 , an atomic number of 31 and it has 34 isotopes. The only stable isotopes are 69 and 71 and occur in the ratio 60 %:40 %, giving it an atomic weight of 69.723. Gallium has a very low melting point ($29.8\text{ }^\circ\text{C}$) but it has a very high boiling point ($2,204\text{ }^\circ\text{C}$).

It also has the unusual property of expanding by 3.1% when it solidifies; this characteristic is also seen with water, bismuth and germanium and, as a consequence, it should not be stored in glass or sealed containers. It has a thermal expansion of $18\text{ }\mu\text{m/m}^\circ\text{K}$ at 25°C and its thermal conductivity is 40.6 W/(m.K) ; its electrical conductivity is $7.1 \times 10^6\text{ S/m}$.

Pure gallium metal is soft and bright silver in colour, but its solid form usually appears as bluish-grey due to a passive layer on its surface. Solid has an orthorhombic crystal structure.

Gallium is totally miscible with metals such as aluminium, tin, indium and zinc and does not form any compounds, but it reacts with most other metals by diffusing into the metal lattice to create intermetallic compounds along the grain boundaries. This usually results in embrittlement of the metal.

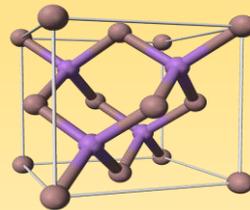
In the electrochemical series (ECS), gallium has a redox potential of -0.560V and reacts with acids to form the acid salt and discharge hydrogen.

Gallium salts are primary trivalent (Ga(III)), although there are a few monovalent salts (Ga(I)) known. There are also divalent salts such as GaCl_2 , but these are actually mixed salts of Ga(I) and Ga(III) .

Gallium and semiconductors (I)

When considering semiconductors, it is normal to think of silicon as it is the key material to make transistors, integrated circuits and other related components whilst it is the most common semiconductor in electronic device applications, it is not alone and other elements and compounds have also found use. In fact, the first transistor was made from germanium and throughout the 1950s it was the main material in transistors and other semiconductor devices. However, silicon was also known to be suitable for producing semiconductors and, once its processing was optimised, it rapidly replaced germanium, although it does still find use in some specialised applications.

Electronic devices don't have to be made from a single element; they can be fabricated from what are known as compound semiconductors. Instead of using elements such as silicon or germanium, a compound made by combining a group three and a group five element can be utilised. These so-called 'III-V' compounds have been developed for use in electronics since the 1970s, with the most popular one being gallium arsenide (GaAs). Gallium arsenide offers several advantages over silicon, making it more suitable for some applications and especially those requiring high frequency operation. GaAs components function up to around 250 GHz, meaning that they can support the signal speeds needed for the successful operation of 5G networks. They are also not affected as much by high temperatures as silicon and they generate less noise than silicon when operating at elevated frequencies, making them very attractive for use in mobile phones, satellite communications, microwave links and high frequency radar systems. GaAs is also used in the manufacture of Gunn diodes for the generation of microwaves.

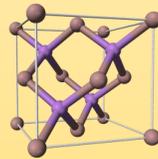


Gallium and semiconductors (II)

One of its drawbacks is that gallium arsenide is much more expensive than silicon, but the industry is increasingly demanding performances that require GaAs has to be used. This increasing demand for GaAs devices is reflected in the prediction of a 12.5% compound annual growth rate between 2021 and 2026, when the device market will be valued at \$22 billion.

While gallium arsenide is the second most popular material after silicon for fabricating semiconductors, gallium is also used in some other III-V materials and these include gallium nitride (GaN), gallium phosphide (GaP) and gallium antimonide (GaSb). These compounds have all found extensive use in LEDs, but they are sometimes also employed in the manufacture of a wide range of specialist and emerging semiconductors.

There is currently great interest in gallium nitride, which like gallium arsenide, has many advantages over silicon. This in part is due to the fact that it has a wide band gap compared to silicon, which imparts properties useful in optoelectronics. GaN components have the ability to operate at much higher voltages and frequencies reaching up into the terahertz region. Consequently, they are increasingly used in radio and radar related applications such as air traffic control. Due to its high-power density and high voltage breakdown limits, GaN is also being used in 5G cellular base stations.



GaN devices are able to operate at temperatures up to 400 °C, making them very attractive for use in high power electronics, such as power converters. Because of its high efficiency, GaN-based electronics offer significantly reduced energy consumption in applications such as power transmission and management. This is becoming an increasingly important product area, especially as the world moves towards much greater use of renewable energy sources. The currently used silicon-based converters are only around 90% efficient, with the remaining energy being lost as heat. Switching to GaN will enable smaller, lower cost, more efficient power converters to be used and for significant energy savings to be made.

Structure of a LED Lamp:



Period 1 progress:

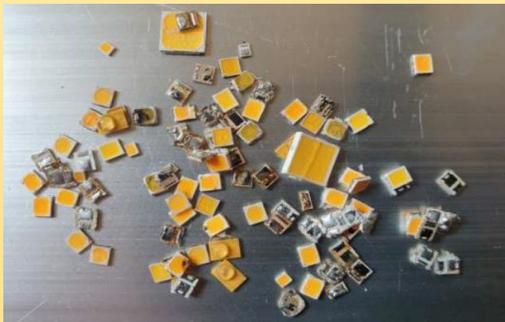
Initial trials have been carried out with different WEEE sources including LEDs, TVs and office lights.



Samples vary in both gallium content and its ease of access. For example, lamps are easier to access LEDs than are TVs .

Period 1 progress:

Disassembly of GU 10 LEDs

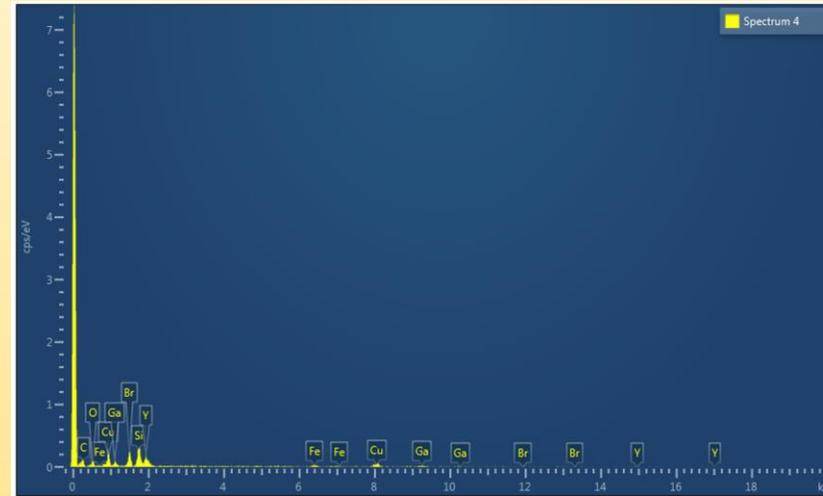
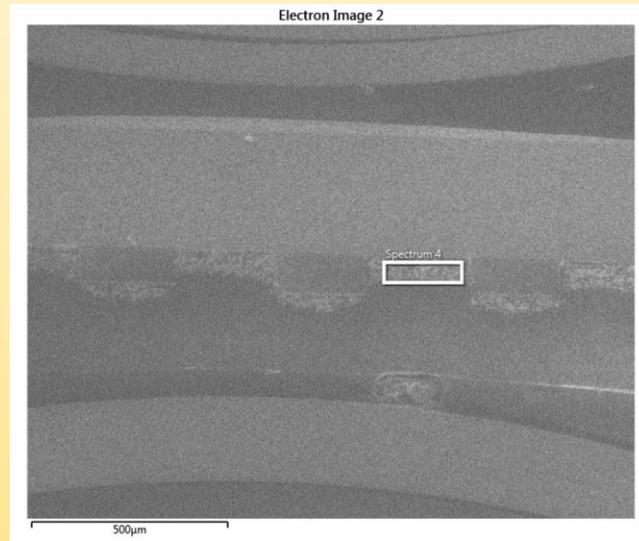


Manual disassembly of GU10 LED lights has identified many different metals and non-metals, including copper, aluminium, iron, gallium, yttrium, glass, plastics and electronic circuit boards. There is an opportunity for the recovery of multiple materials. Gallium has been identified in discrete layers.



Period 1 progress:

Gallium has been located in discrete layers in LEDs.



Analysis has been done by SEM and EDX.

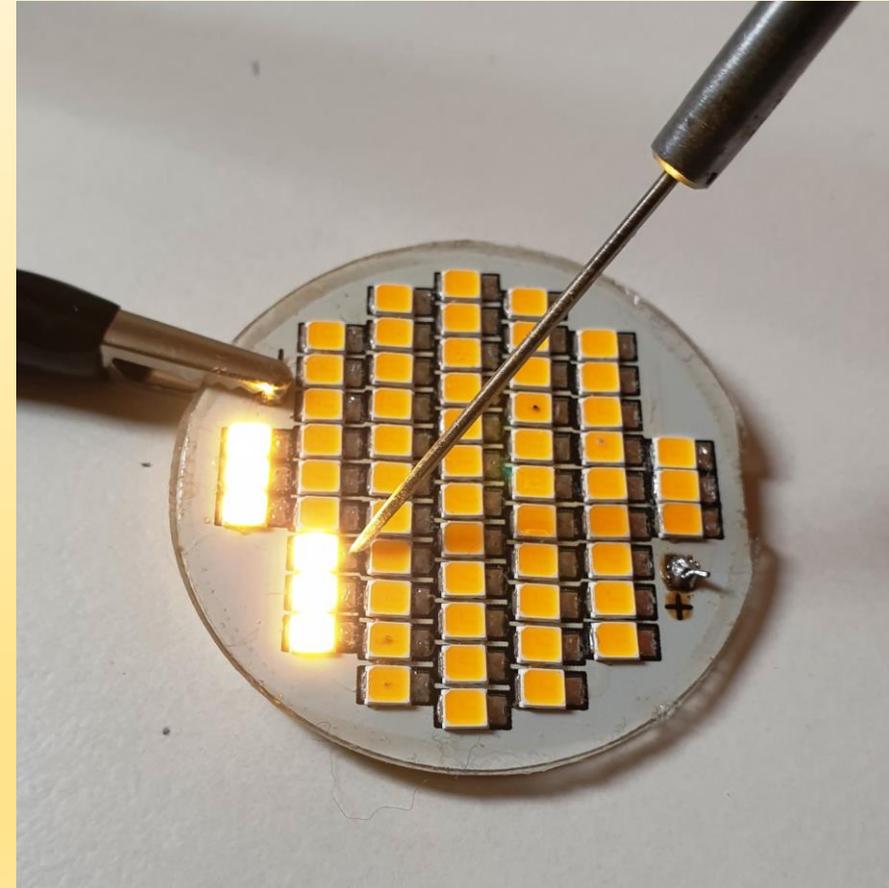
Period 1 progress:

A potential threat to the supply chain for the recovery and recycling of gallium is the reuse of LEDs. ReGaIL has found that when a lamp fails, most of the LEDs are still working; for instance in one failed lamp, only one in 58 LEDs had failed.



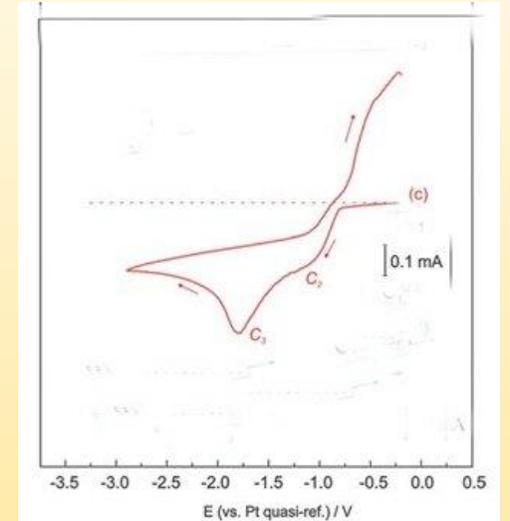
In the hierarchy of waste, the preferred option is to reduce waste, followed by reuse of the waste stream, then repair and recycle the failed unit.

With improved design and manufacturing methods, LEDs could be tested and any failed bulbs could be replaced, thereby reusing the whole light unit.

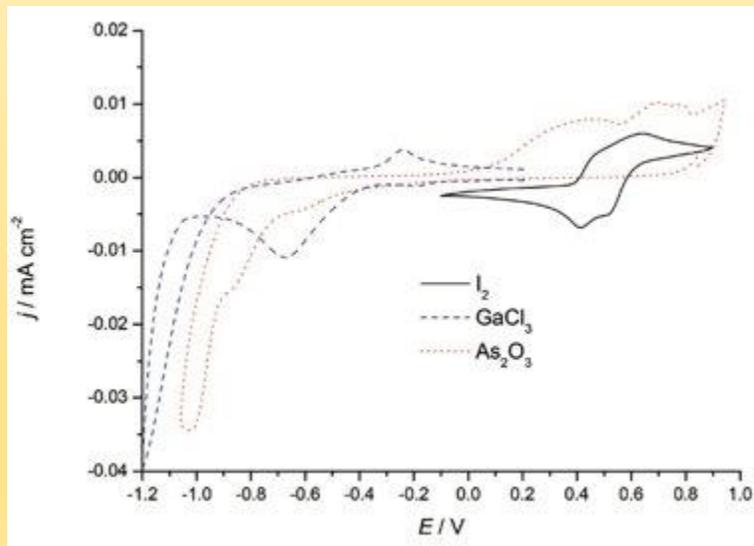


Period 1 progress:

It has been demonstrated by other workers using Deep Eutectic Solvents (DES), such as $[\text{Py}_{1.4}]\text{Tf}_2\text{N}$ (1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)amide) that gallium can be electrodeposited at room temperature and its cyclic voltammogram is:



Ga in $[\text{Py}_{1.4}]\text{Tf}_2\text{N}$



Ga, As and I_2 in ReGaIL DES

The cyclic voltammogram of gallium in the ReGaIL DES also shows electrochemical activity but at different potentials to those in $[\text{Py}_{1.4}]\text{Tf}_2\text{N}$.