

**Creating a circular supply base of gallium in the UK for use
in PEMD**

(ReGall: Recovery of Gallium using Ionic Liquids)

InnovateUK project number: 78550

Deliverable D3.2

Preferred Electrolytic Gallium Recovery Process

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1) Executive Summary

The ReGaIL project has a focus on the recycling of gallium from end-of-life light emitting diode lamps. More specifically, it has aimed to demonstrate the recovery of gallium using novel techniques that are more efficient, environmentally friendly and less costly than traditional routes such as smelting. New recovery methods have been demonstrated that use novel materials known as ionic liquids and deep eutectic solvents (IL/DES) instead of conventional aqueous chemistries based on strong oxidants and concentrated acids. These new materials possess a number of unique properties and they are also much more environmentally benign, which makes them ideal candidates for the types of metal recovery processes developed in this project.

The key challenges for any recovery process targeting a specific metal in an end-of-life electronic assembly include accessing, separating and dissolving the metal of interest from all the other materials present and then forming a solution that can be used to electroplate the dissolved metal of interest. Ideally, these process stages should have a good degree of selectivity, while being able to operate at low cost without the generation of expensive to treat waste products. In the case of LED chips, the gallium is typically present in the form of a thin film, but there are other metals present in the chips that can add to the value. These include indium, silver and gold and while the ReGaIL project has focused on gallium, recovery of these other metals has also been given due consideration.

Although each stage of the recovery process is critically important for the successful recovery of gallium, the early stages of the process have mostly been detailed in another deliverable, D3.1, which covers comminution and dissolution of the metals. The main subject matter for this deliverable is the specific electrowinning stage that allows the metal to be electroplated from an IL/DES solution. The focus is on the work carried out to demonstrate that gallium can indeed be recovered from end-of-life LEDs. It also contains a detailed analysis of the process variables that need to be optimised in order to achieve efficient plating, good yields and low costs. While many of these factors are known, it has become clear that there is a substantial amount of process optimisation work that needs to be pursued beyond the end of this short feasibility study before a preferred process can be defined. The deliverable thus concludes with a detailed list of recommendations for further work and process scale-up.

2) Introduction

2.1 General application of electrolytic recovery for metals

This deliverable has a focus on the electrowinning of gallium and it details the work carried out in the short ReGalL project to demonstrate that gallium recovered from end-of-life light emitting diode (LED) lamps can be recovered. More specifically, it covers the attempted plating of gallium from novel non-aqueous solutions that employ deep eutectic solvents rather than water. This is an innovative approach and one that has the potential to offer a number of advantages over conventional routes such as being more environmentally benign and producing less waste. For more information on electroplating from ionic liquids and deep eutectic solvents see the review paper by Abbot, Frisch and Ryder (1).

Electroplating processes are most commonly thought of in the context of depositing metals onto conductive substrates. The first example of the electroplating of a metal from a solution was reported over two hundred years ago. Since then, the process has become commonplace and is used for the deposition of a broad range of metals and alloys. It is widely used in industry to improve the surface qualities of objects, such as resistance to abrasion and corrosion, or to provide lubricity, reflectivity, electrical conductivity, or an enhanced appearance. It can also be used to build up thickness on undersized or worn-out parts, or to manufacture metal plates with complex shapes, a process called electroforming. Well known examples include the silver plating of cutlery, the gold plating of jewellery and the copper plating of printed circuit boards.

The actual term electroplating refers to the process that deposits a metal coating on a conducting substrate by the reduction of cations of that metal using a direct electric current. The substrate to be plated forms the cathode (negative electrode) of a cell in which the electrolyte is a solution of a salt of the metal to be coated. The cell also contains an anode (positive electrode) that is typically made of the same metal as that to be deposited, or an inert conductive material. A plating current is passed through the cell by connecting the anode and cathode to an external direct current power supply.

While electroplating is thus well known, there is a variation of the process that is used for producing or recovering metals and this is known as electrowinning. Electrowinning is essentially the electrodeposition of metals from their ores or other materials by a process

that involves them being dissolved into a suitable solution via leaching/dissolution. Once in solution the metals are plated onto a cathode in essentially the same way as for electroplating.

The electrowinning process has been long established as a good method for obtaining a wide range of valuable and useful metals. The metals most commonly obtained by electrowinning are lead, copper, gold, silver, zinc, aluminium, chromium, cobalt, manganese, and the rare-earth and alkali metals. Where the metal reacts with water, they can be recovered from a molten salt rather than by using an aqueous solution.

2.2 Plating from ionic liquids; benefits and challenges

The most common and well-established methods for recovering many metals involve the use of strong mineral acids and bases to dissolve oxides, and oxidising acids such as sulphuric and nitric, to solubilise the requisite metals. However, the reactivity of the electrolyte and the complex nature of the oxide/hydroxide chemistry of most metals makes many of these processes inefficient. They can also be not very environmentally friendly and lead to the generation of hazardous and expensive to treat effluent and waste. There has thus long been a motivation to introduce alternative, more energy efficient and environmentally sustainable chemical methods. While the vast majority of metals recovered by electrowinning are still plated from aqueous solutions (or molten salts), it is now possible to use other materials such as a wide range of ionic liquids and deep eutectic solvents instead. These materials have been known for some time to offer potential alternative routes to the established aqueous approaches and they form the basis of the method that has been demonstrated in the ReGall project. For example, deep eutectic solvents, that are mixtures of quaternary ammonium halides and hydrogen bond donors, have been utilised for the selective dissolution and electrowinning of metals both from ores and waste materials. Reline (a 1 : 2 mixture of choline chloride and urea) has been used to process the mixed metal oxide matrix from an electric arc furnace with zinc and lead subsequently being selectively removed and recovered from the liquid by electrowinning. Similarly, Ethaline (a 1:2 mixture of choline chloride and ethylene glycol) facilitates metal dissolution in the electropolishing of steels (2).

2.3 Prior art on gallium and indium electrowinning

Gallium has traditionally been produced as a by-product when processing the ores of other metals and its main natural source material is bauxite. It is thus obtained during the production of aluminium, although minor amounts are also extracted from sulfidic zinc ores such as sphalerite. However, if the gallium is being recovered from existing products, it will be present either as the metal itself or, as is the case in end-of-life electronics, combined with other elements in a range of semiconductor compounds such as gallium arsenide, gallium phosphide and gallium nitride. These materials are typically present in the form of thin films deposited on other substrate materials. Consequently, the best method for recovering the gallium is typically to dissolve the thin film as selectively as possible, and then modify the solution so that it can then be used to electroplate the metal.

However, while gallium can be electroplated from aqueous solutions (3), it is generally considered to be a difficult metal to recover, not least because of its low melting point (29.8 °C). It also easily forms alloys with other metals which can cause problems when selecting a suitable cathode material onto which it can be deposited. Finally, plating efficiencies are generally low and deposition is often accompanied by a significant level of hydrogen evolution if the current density is not optimised (4).

In the case of the ReGaIL project, the LEDs used as the source of the gallium also contained appreciable amounts of indium which made separate recovery difficult, since the standard reduction potentials are relatively similar. Electrodeposition of gallium from aqueous solutions requires large overpotentials. However, It has also been found that electrodeposition of gallium from an aqueous solution containing both indium and gallium, using a controlled current, begins only after most of the indium has been removed from the solution. In addition, it is known that indium and gallium can be separated by electrodeposition of indium from solutions with high sulfuric acid concentrations (5).

3) Dissolution of Target Metals

3.1 Oxidising solutions e.g. iodine in IL/DES

Unlike some metals such as silver and gold that are found in end-of-life electronics and related equipment (WEEE), the gallium is used as a compound semiconductor, which makes recovery more complex. In LEDs, the gallium is present in a variety of materials whose composition varies according to the wavelength (colour) of the light emitted. Examples here include gallium phosphide, gallium arsenide and gallium nitride. For LEDs that emit at the green and blue end of the spectrum, the preferred material is actually gallium indium nitride, where the ratio of indium to gallium is varied to tune the output wavelength. Consequently, end of life LEDs contain gallium in a variety of materials and formulations. This also means that they show variations in the ease with which the gallium can be extracted. Some compositions are more amenable to treatment with strong acids and oxidants than others, the more difficult to digest compositions requiring a high temperature roasting in air before they can be made to dissolve.

As detailed above, and in other deliverables, the approach taken in the ReGaIL project has been to use deep eutectic solvents where possible in place of the more conventional aqueous based reactants. This approach applies to both the electrowinning of gallium and the methods used for extracting the gallium into solution. In order to produce a solution of gallium suitable for electroplating the metal has to be oxidised into what will subsequently become the plating solution. The deep eutectic solvent (Ethaline) that forms the basis of the electrowinning solution is not, on its own, able to dissolve the gallium (and indium), so it is necessary to use an oxidant. Fortunately, it is possible to introduce a halogen such as iodine into the Ethaline to produce a good oxidising solution. Iodine is a powerful, yet relatively benign, oxidising agent and Ethaline can dissolve over 200 g of iodine per kg of solvent. Iodine in Ethaline is therefore a good matrix for metal dissolution. More importantly, the iodine can be used in a redox iodine/iodide couple where the iodine is regenerated at the anode of a suitably structured cell while the gallium is electroplated out as the metal at the cathode. In simple terms, the iodine oxidises the gallium to Ga^{3+} while itself being reduced to iodide. The gallium ions are then reduced to the metal at the cathode, while the iodide is oxidised back to iodine at the anode.

This process works for a number of metals and can thus be beneficial when recovering the key valuable metals found in LED chips i.e. gallium, indium, silver and gold. (Even gold can be recovered using iodine in this way, giving the opportunity to replace the traditional cyanide-based oxidation methods.)

4) Process and equipment requirements

4.1 Discussion

Electrolytic metal recovery, or electrowinning, is the recovery of metals from solution using the electroplating process. It has been applied in many plating processes such as metal finishing, PCB manufacturing, and rolling mills. Cadmium, tin, copper, solder alloy, silver, and gold are among the metals commonly recovered by electrowinning. The process involves an electrochemical cell where metal ions are reduced and deposited in metallic form onto a cathode, while oxygen is generally evolved at the anode. Two types of cathodes are used. In the first example, plate systems generate a solid metal that can be reclaimed by stripping off the metal from the cathode base. As the metal concentration in the solution decreases, the efficiency of metal removal decreases drastically. The second type of cathode that is used is the mesh cathode, providing a much greater surface area than a plate cathode and which generally allows the metal to be recovered from more dilute solutions. The use of a mesh cathode for the recovery of a metal from solution does however entail a secondary, usually pyrolytic or electrochemical, method to generate the metal in a pure form.

A typical electrowinning system consists of a tank that holds the electrolyte, sets of anodes and cathodes, a pump for transferring solutions from a feed tank to the electrolyte tank, a rectifier, and various process controls.

4.2 Electrowinning from Ionic Liquid Electrolytes

In respect of implementing metal recovery from ionic liquids containing a metal as a dissolved species, it is clearly desirable to deploy a system that has the greatest potential for adaptability across a wide range of viscosities and metal ion concentrations. While the essential concept of a metal being recoverable from a concentrated electrolyte may be translated into recovery from a dilute solution and may be held as equally viable for aqueous and non-aqueous media, their differing physico-chemical properties, which impact factors such as ionic mobility, must be taken into account. With specific reference to gallium, as with other metals, although the concept of pH has no significance within deposition from ionic liquids, factors such as solution viscosity and ionic mobility etc must be accommodated and they have a direct influence on the plating efficiency.

Another important factor when considering the use of ionic liquids in place of water as part of an electrolytic recovery process for gallium is that the ionic liquids are considerably more expensive than water. When using aqueous chemistries, the disposal and discharge of spent solutions is likely to have less of a financial impact than a process using ionic liquids. Discharge costs for ionic liquids are also likely to be relatively high, which means that attention will ultimately need to be focused on ways for recovering and reusing the ionic liquids and that methods for removing deleterious contaminants will need to be devised. For example, techniques such as electrodialysis, which are already used with aqueous chemistries, might also be suitable for use with ionic liquids. In aqueous solutions, small and highly charged metal cations are passed across a suitable exchange membrane and subsequently precipitated. It would be interesting to see if such techniques could also be used to recover relatively pure ionic liquids.

Several methods for the recovery of ionic liquids including distillation, extraction, adsorption, membrane separation, aqueous two-phase extraction, crystallization and external force field separation have been proposed historically but, within the context of any deployment other than full production, capture of ionic liquids from drag out may be accomplished via activated carbon adsorption.

4.3 Electrodes, cell design, sequential plating possibilities

Various materials are used in the fabrication of both anodes and cathodes. Historically, graphite and lead alloys were the preferred anode materials for electrowinning. However, their high overpotential requirements and degradable nature present significant drawbacks. More recently, anodes have often been manufactured from titanium and niobium and coated using the solid phase roll bonding method with precious metals, metallic oxides and/or their alloys and fluoride resistant metal composites. These types of electrodes are generically referred to as dimensionally stable anodes (DSA). The advantages of the newer anodes over the lead alloy anodes include;

- (1) production of higher purity product (deposit),
- (2) the low oxygen overpotential increases current efficiency,

(3) corrosion resistance provides higher durability and stability,

(4) halide resistance.

In the context of the ReGail project which is in essence a feasibility study and in which the electrodeposition experiments will be used primarily for verification (and not for an extended period in which any noticeable halide attack will be evidenced), it was considered that standard platinised titanium would suffice as a conventional anode system.

In respect of cell design, limits have been imposed by the amount of gallium which may be dissolved within the ionic liquid to generate a solution with an adequate concentration of gallium ions to facilitate electro-recovery. This translates to the electrodeposition being carried out in a solution volume of circa 100 to 150 mls to enable a concentration in the order of some 10 grams per litre of gallium to be present. For containment, a beaker would be utilised, albeit on a pilot or commercial scale either a polypropylene or PVDF tank would be the containment vessel of choice.

The equipment for process validation via electro-recovery would thus comprise an electrolyte (gallium present within an ionic liquid/deep eutectic solvent), a mesh or sheet anode of platinised titanium, a polished, degreased and cleaned copper sheet cathode, a rectifier capable of providing a smoothed DC output of sufficient capacity to generate metallic deposits across the cathode. By using a copper cathode, gallium, being a grey lustrous metal, would be readily identifiable as a cathodic deposit.

It should be noted that there exists the possibility of sequential electro-recovery in the instance where gallium is not the sole dissolved cationic species. In the specific instance of ReGAIL, and dissolution of gallium from used LED elements, indium will possibly be co-dissolved within the ionic liquid. Although the over-voltages for gallium and indium are close, it is likely that sequential deposition may be realised at differing applied voltages with an alloy being generated at applied voltages in excess of both over-voltages. This could thus provide a convenient method for recovering both of these valuable metals.

4.4 Cathode treatment, cleaning procedures

As already noted, for the purposes of electro-recovery within the ReGalL project, a sheet copper cathode was deployed. This was nominally of the same surface area as the inert anode i.e. to give a 1:1 ratio. The essential requirement for all substrates to accept an electro-deposited coating is that they are chemically clean and free of grease or other surface contamination. The degreasing is usually carried out on a commercial scale by hot caustic soda immersion, whilst chemical cleanliness is achieved by mild etching and acid immersion. The result is a clean, oxide-free nascent metal surface. For ReGalL the cathode was prepared by mechanical means and polished to afford high reflectivity.

4.5 Rectification Methods, agitation, temperature and membranes.

The plating current may be supplied to the solution, either as a constant direct current or via a pulse rectified supply. For the current project, a standard constant current/ constant voltage supply was utilised, although on a pilot or production scale, a pulsed supply would be investigated to ascertain the advantages of any enhanced efficiency and throwing power that might thereby be achievable.

Within any electro-recovery, or indeed standard plating operation, it is usually necessary to afford solution agitation. This is essentially to avoid or minimise any effects of concentration polarisation around the electrode surfaces caused by a depletion of metal ions in their immediate vicinity. When practicing electro-recovery from an ionic liquid it is even more necessary to introduce agitation, due to the high solution viscosities and the consequent effect upon ionic mobility. When dealing with electrolytes having low metal ion contents, it is likely that even more enhanced system features such as a mesh or three-dimensional cathode, or even a rotating cathode, may need to be deployed in order to achieve the requisite efficiencies.

4.6 Replenishment, Rinsing, Reusability – Closed Loop system

Within the context of ReGalL, it is anticipated that gallium and indium will be electro-recovered from a solution containing circa 7 – 8 g per litre of the metals. It should be noted

that this would be considered a relatively low metal ion concentration for the generation of coherent and consistent deposits. Whilst for a feasibility study this is perhaps of minimal consequence, for any larger scale, or pilot plant operation, it would be necessary to maximise the metal ion concentration levels within the electrolyte (within any limits imposed by solubility). Further, on the assumption that a fairly maximised gallium concentration is utilised within an electrolyte, it would be ideally necessary to replenish this solution to maintain such a relatively high metal ion concentration. This would have advantages in maintaining a constant deposition rate and further enabling maximum Faradaic electrodeposition efficiency to be realised. Without replenishment and operation on a batch basis down to residual metal ion levels in solution of <1000 mg per litre, such would be considered extremely difficult and the electrolyte viscosity would possibly negate the successful deployment of methodologies that have been developed for aqueous media to electro-deposit at such low metal levels.

In respect of rinsing the generated electrodeposited metal/s post electrowinning, the thus coated cathode would be rinsed in water with due observance of all developed methodologies of minimising drag out. These would include:

- extended dwell times over the electrolyte,

- use of a drag out with high velocity, low volume spray rinsing.

For the ReGaLL project itself, the amount of electrodeposition is small and the potential rinsing of perhaps less than one litre in total means that any issues regarding waste treatment or pollution control may be ignored.

However, the minimisation of drag out together with the maximisation of electrolyte life are essential pre-requisites within any future potential deployment of a system based upon ReGaLL technology. On a commercial scale, pollution will essentially arise from two distinct sources – that from drag out from the process bath, with such being contained within the rinse water outfall and any chemistry arising from the electrolyte being considered spent and necessitating discharge. This is driven by both a pollution control demand and the extremely high cost of the ionic liquid system compared to an aqueous based system. Approaches for control of outfall via rinsing would typically be discharge via activated carbon treatment or on

a larger and recyclable approach, using membrane techniques such as nano-filtration. Electrolyte reusability could also conceivably be realised via membrane technology.

4.7 Recovery of the Metals

Whilst in the context of the electrowon metals addressed in the ReGaIL project, the amount of metal actually deposited will negate any attempt to realistically remove it from the cathode to any reasonable level. It is anticipated that metal will be recovered from the ReGaIL electrolyte in potentially three distinct forms if both gallium and indium are being cathodically deposited. Dependent upon the separation efficiency, there will be a singular deposit of gallium, a singular deposit of indium and a smaller amount of an alloyed co-deposit (anticipated at <5%).

On a pilot or production deployment, where relatively large quantities of recovered metal are evident, it would be standard practice to deploy a polished stainless-steel substrate from which the metal/s may be peeled off to give a pure metal. It could of course be postulated in the instance of gallium, with a melting point of <30 °C, that the metal could be removed from the substrate by immersion in hot aqueous media. This would not be feasible with indium which has a melting point of circa 156 °C.

At this stage it is not possible to state the actual purity of the recovered gallium beyond it being oxygen-free electrolytic quality. There are a number of accepted methodologies for further refining gallium to an electronic grade material and these would be carried out subsequent to deposition.

5) Practical plating trials

5.1 Plating from model solutions

The initial work to electrowin gallium was carried out on model solutions. This was because the plating of gallium is known to be difficult from aqueous media and because the approach planned here used a deep eutectic solvent rather than water to form the electrolyte. In the proposed full process, it was the intention to use a more complex single stage approach to both dissolve the gallium from thin films deposited on the LEDs and to then electrowin the gallium from the DES-based solution. Additionally, other metals would be present on the LED chips and these included indium, silver and gold. They would also be oxidised into solution making the plating process more complex than would be the case for a simpler solution containing only gallium ions.

Therefore, it was initially necessary to confirm that gallium could indeed be electroplated from a DES before moving on to more complex electrolytes containing additional metals. A model plating solution was prepared using gallium chloride as the metal source along with Ethaline as the deep eutectic solvent. The main objectives of these initial trials were;

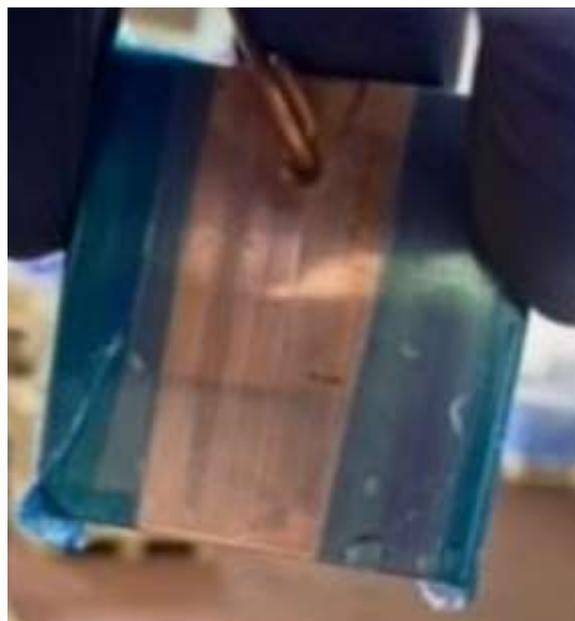
- to confirm that it was possible to plate gallium from such a DES based electrolyte,
- confirm the parameters needed to achieve optimised plating and deposits,
- identify any issues or problems that would need to be addressed prior to processing real samples obtained from LED chips.

These plating trials were carried out using an 'ideal' model electrolyte, i.e. one that utilised pure new gallium (gallium chloride) with no additives, additional metals or other contaminants in the solution. For convenience, and to avoid wasting material, the initial plating work was carried out at the beaker/hot plate scale. The cathode material onto which the gallium would be plated was copper and the anode was a platinised titanium mesh. This was chosen because the deposition of gallium would clearly be indicated by a change in colour. Also, gallium was known to alloy with copper and thus there were less likely to be issues with the gallium if it liquified during the deposition process (a known problem in aqueous plating of this metal.) The basic set up of the plating cell is shown below.



Plating cell showing two inert mesh anodes and a central copper cathode

The model plating solution was prepared by the University of Leicester and was essentially gallium chloride dissolved in Ethaline with the amount chosen to give metal concentration of 7 g/dm^3 . Initial plating trials were performed at room temperature, i.e. just below the melting point of gallium and a range of voltages (two to five volts), current densities and plating times (15 to 45 minutes) were evaluated. The current density was varied by masking off areas of the copper cathode.



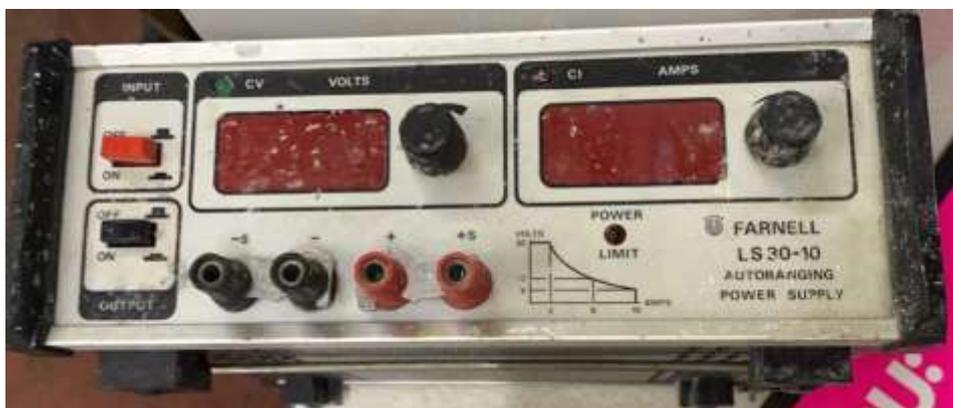
Cathode area masked off to adjust the current density

The initial trials were considered to be unsuccessful as there was no visible appearance of the expected grey gallium deposit on the copper anode, see below.



Typical initial appearance of cathode after plating i.e. no gallium present

Following the poor results obtained from the first set of plating trials, changes to the equipment and process were made. These included use of an improved rectifier with a smoother current output (Farnell LS30-10).



The improved rectifier used for the second batch of plating trials

The anode to cathode spacing was also reduced from the original distance of 5 cm to 1 cm, see below, and the cathode was given a wire brushing to clean and roughen its surface prior to plating.



Anode to cathode spacing reduced to 1 cm

There was also an investigation of the effects of giving the copper cathode an etch clean prior to plating. Nitric acid and sulphuric acid were both evaluated and it was found that nitric acid subsequently gave the best performance, so it was adopted as the preferred pre-treatment method. The nitric acid etch proved to be better so from hereon this will be used. During the plating trials it was noticed that crystallisation could take place in the electrolyte if the temperature dropped below allowed 8 °C. However, upon warming above this temperature the crystals were easily redissolved. It was also found that the gallium deposit could also redissolve immediately after plating and the plating solution needed to be rinsed off the cathode to avoid this happening.

6) Results and Discussion

6.1 Introduction

The gallium content of LED samples from a selection of sources was analysed. First, the sample waste stream was sorted for the particular type of LED light source (e.g. GU10). The lamp was then manually disassembled in order to isolate the active LED element (chips) of the device. The ancillary components were discarded, entering the standard recycling streams for these specific material types (e.g. glass, plastic and WEEE). The LED chips were received in three separate batches and the gallium content was assessed using two types of procedure addressing the key questions of;

- i) how much gallium is present in the sample?
- ii) where is it?

The first method was bulk homogeneous dissolution of the whole LED chip. This was achieved using aqueous acid digestion, followed by quantitative metal ion analysis using inductively-coupled mass spectroscopy (ICP-MS). In this case, it was possible to determine the total bulk content of the gallium within each batch of LED chips. In the second method of analysis, a representative sample of the individual LED chips was selected and elemental analysis was performed within a scanning electron microscope. This latter technique enabled both imaging of the LED sample, in order to understand the physical and topographical features of the device, as well as localised elemental analysis using energy dispersive analysis of x-ray emissions (EDAX). In particular, EDAX analysis enabled the spatial distribution of gallium in the sample to be mapped and potentially distinguished between samples of different origin, or to identify specific LED samples or component parts, that were gallium rich. This may be significant in guiding future recycling strategies if it is possible to identify particular sources or waste streams with high gallium content. Such gallium-rich sources would then be targeted for recycling and recovery over other less-valuable feedstock sources. The results below describe the analyses performed on two batches of LED chips supplied to the UoL. The first of these, batch 1, was a small batch (ca. 10 g) manually harvested from spent domestic GU10 units, the second batch, batch 2, was larger (ca. 200 g) and contained LED chips removed from a variety of lamp formats. Towards the end of the quarter, a third batch was also received,

batch 3, with chips extracted from high-power industrial aerospace lighting units. Analysis of these is ongoing and will be reported later.

6.2 Homogeneous dissolution and total content analysis (ICP-MS)

This section addresses the question of how much gallium is present in the waste stream. The metal content of a sample can be examined quantitatively using inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS achieves this by atomising the sample at high temperatures and has the ability to detect very low concentrations, including different isotopes of the same element. This instrument was used to detect the gallium content within end-of-life LED chips (batches 1 and 2). An example picture of these LED chips is shown in Figure 1 with a £10 note for size comparison. The samples shown here represent the second batch of LEDs supplied, but the sizes of the individual active elements were of similar dimensions in the first two batches.



Figure 1. Example LED chip size.

The sample preparation for ICP-MS involved a standard acid digestion to dissolve the solid sample. To accomplish this, an LED chip was placed in heated acids overnight until the entire sample dissolved. A cartoon schematic of this sample preparation is shown in Figure 2.

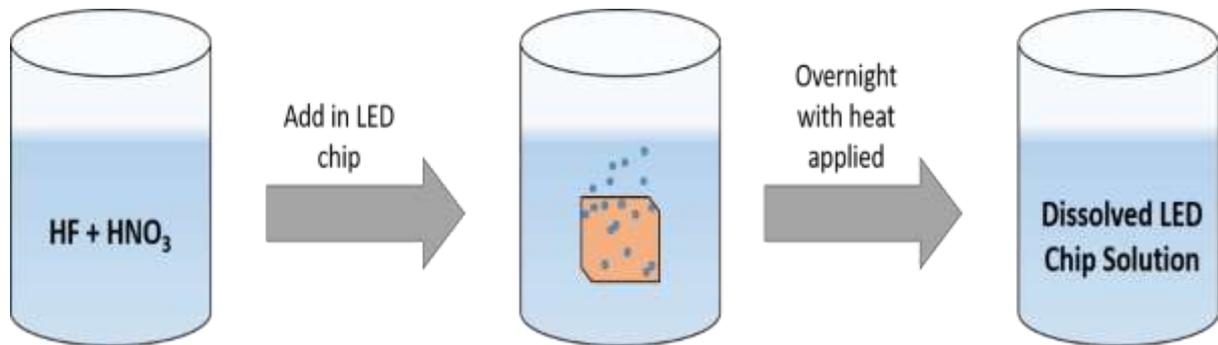


Figure 2. ICP-MS sample preparation method. A mixture of hydrofluoric and nitric acids was used to digest the LED chips until they completely dissolved.

After the sample was fully digested, the solution containing the dissolved LED chip was then diluted to the ppm to ppb range for measurement, so as not to saturate the response of the instrument. Various acid dissolution regimes were attempted because the substrates of some of these LEDs were silicon-based and very difficult to dissolve. The most successful dissolution media were the most aggressive and contained hydrofluoric acid (HF). This was consistent with the fact that HF is very effective in etching Si-based materials (*e.g.*, glass). Interestingly, the gallium concentration varied significantly with the acid digestion procedure. Specifically, the first acid digest, *batch 1*, was performed using HCl and HNO₃ acids and gave 50-60 ppm gallium content (batch 1 LEDs). This was a relatively low content level, corresponding to 50-60 mg per kg of LED chips. In this case, some of the chip substrate material remained unresolved and so subsequent acid digestion was attempted using a more aggressive combination of HF + HNO₃ acids. In this case, the complete acid digestion resulted in a homogeneous solution which analysed to give a gallium content of 6475-8670 ppm (batch 1 LEDs) and 2388-3166 ppm (batch 2 LEDs), corresponding to a range of 2.4-8.7 g per kg of LED chips. Some of the magnitude of variance here is dependent on the measurement specifications (*e.g.* isotope of gallium) but a large part of this variation may be related to disparate levels of the metal in specific chip types. Initial results on the third batch (see above)

suggest further variation in these materials, but this will be presented and discussed in a later update of this report.

Key outcomes of this scoping survey are that;

- There are wide variations in Ga content for different types of LED chip
- The extent to which Ga can be brought into homogeneous solution is strongly dependant on the dissolution chemistry and conditions.
- There are large quantities of Ga (g per kg) available from common sources of spent LED elements that would potentially be commercially relevant.

6.3 Microscopy and distribution analysis (SEM-EDAX)

This section addresses the question of where is the gallium distributed in a selection of representative LED chips. Scanning electron microscopy energy dispersive x-ray analysis (SEM-EDX) allowed the acquisition of high-resolution images of the samples by rastering a focussed electron beam across the surface and detecting secondary or backscattered electron signals, the latter giving some indication of heavy-atom distribution in the image. An EDAX analyser was used to provide elemental identification and semi-quantitative compositional information.

Most of the LED chip elements were of a square / rectangular geometry (3-5 mm x 3-5 mm), Figure 1, with the active (light-emitting) face defining the upper surface. The chip thickness was typically 2-3 mm. In order to identify and quantify the position and distribution of gallium in the device, the chip elements were mounted edge-on in conductive epoxy resin then ground back to expose the cross-section. The sample preparation for SEM-EDX analysis began with mounting the LED chips sideways between a metal spring placed inside a cylindrical mould and curing in the epoxy resin overnight. This allowed the sample to be polished back through the side of the LED chip (and epoxy) to expose the inside layers of the LED chip. The sample could then be mounted bottom face up and analysed with SEM-EDX. The preparation is schematically shown in Figure 3.

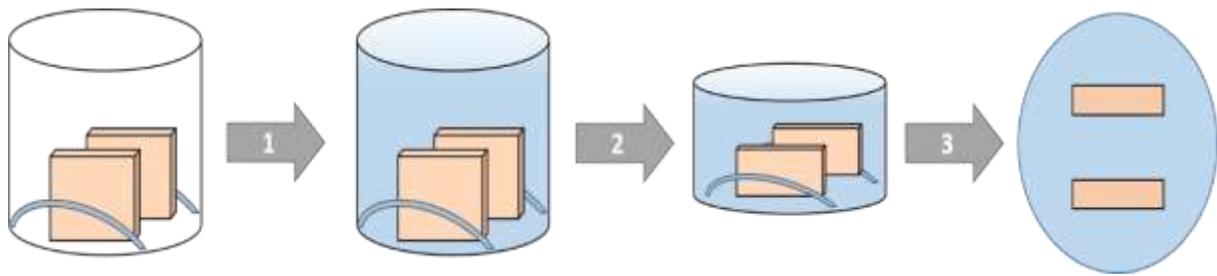


Figure 3. Cartoon schematic of SEM-EDX sample preparation. Step 1 involved mounting two LED chips with metal springs in a cylindrical mould and curing in an epoxy solution overnight. After the epoxy had solidified in Step 2 the sample was then polished back from the LED-facing side (bottom face in schematic) to expose the inner layers of the LED chips. The sample was then ready for SEM-EDX analysis in Step 3 (showing bottom face up).

It is worth noting here that the depth polished back on the LED chip was only qualitatively controlled and the depth may influence the available gallium to measure. Future work could try a few different polished depths to see if this significantly affects the SEM-EDX analysis.

Samples from batches 1 and 2 were mounted and sectioned in this way and then transferred to the SEM for analysis. Both batches showed similar features in terms of the gallium content and the distribution. However, the outcomes of the analyses for batch 1 guided the sample preparation for batch 2 and also the optimisation of parameters for SEM/EDAX analysis. Consequently, the images and figures shown below were selected from batch 2.

Figure 4 shows an SEM image of an entire LED chip section with the major elemental compositions from EDX analysis labelled on the image. The curved structures are the mounting springs and can be ignored. What is striking about this and other images, is that there are large parts of the internal structure of the chip element that contain no gallium at all. These regions contain mainly semiconductor substrate material (Si) as well as other metals (Au, Cu, Fe and Sn) that constitute the support and connectivity structures. From Figure 4 it can be seen that there are two distinct regions where elemental gallium was found and they are labelled with yellow arrows. In addition to the semiconductor materials, the copper substrate and tin solder used to join to external connectors are also clearly visible

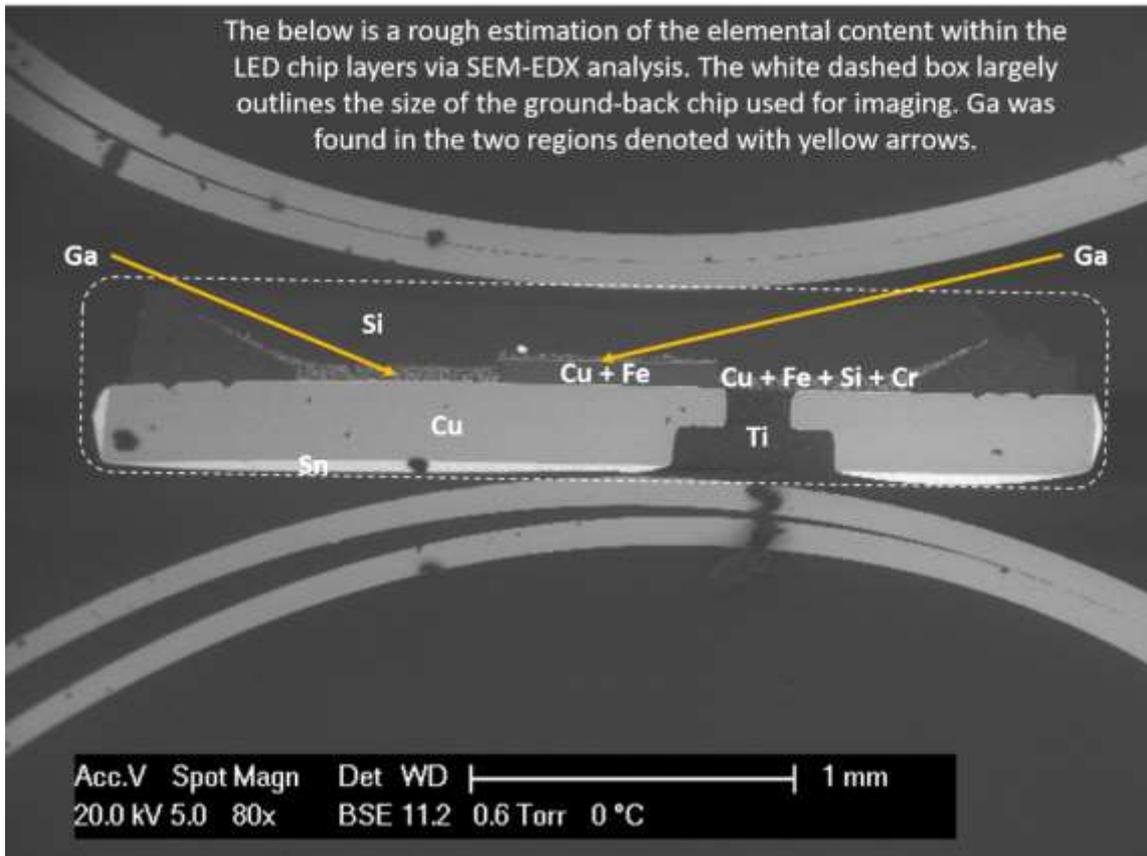


Figure 4. SEM image of an entire LED chip (outlined for clarity with a white dashed box) and the major elemental compositions are labelled.

A zoomed in region of Figure 4, highlighting the area where gallium was found is shown in Figure 5. The Ga content was found to reside in two discrete regions of the device. The first is in a region identified by globular features in a larger volume seen toward the top left-hand side of the cross-section. The second is in a thin white interfacial layer visible toward the top right-hand side of Figure 5. The electron beam of the SEM was focussed in both of these regions separately and EDAX spectra recorded in order to determine the elemental composition of those regions. These are identified as spectrum 11 and spectrum 12, Figure 5. The EDAX trace for the region identified as spectrum 11 (Figure 5) is shown in Figure 6.

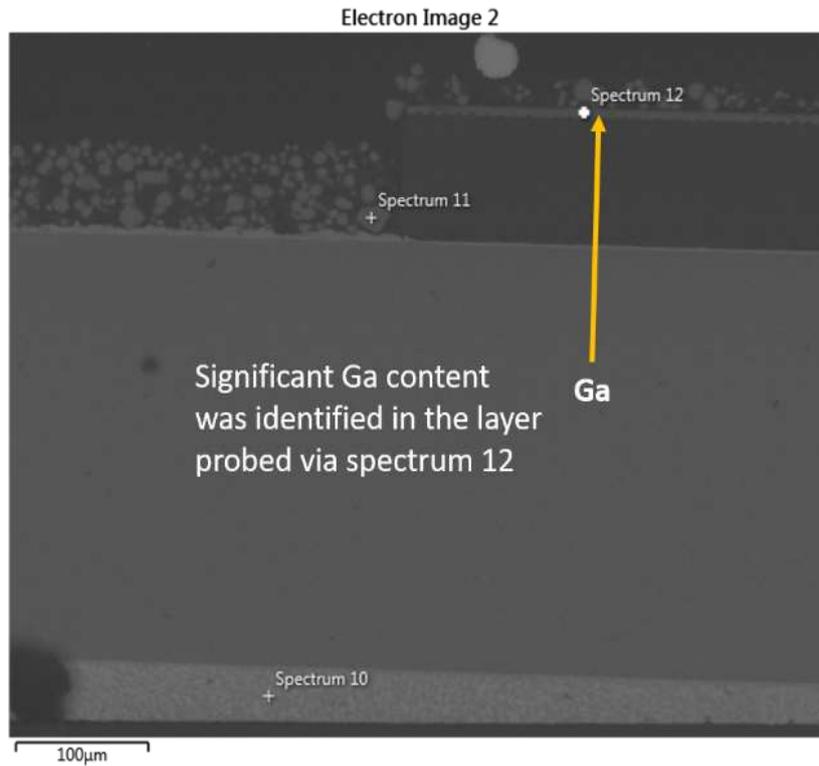


Figure 5. Zoomed in region from Figure 4 showing the small layer where Ga was identified.

The EDAX spectrum shown in Figure 6 contains peak emission features that can be identified with the major elemental components as labelled. At this particular measured location, the gallium content made up nearly 80 % of the elemental content.

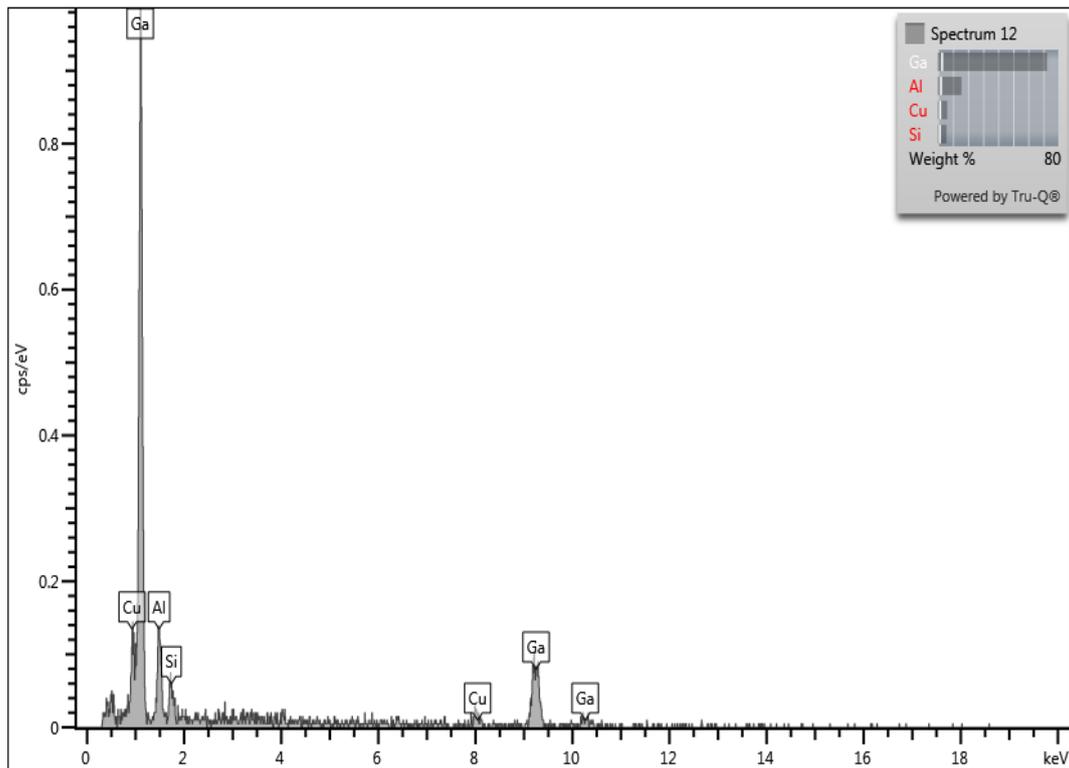


Figure 6. Exemplar EDX spectrum showing Ga detection in the LED chip.

While this is only a semi-quantitative measure of the gallium content, it has been possible to identify that the gallium appears to be tucked away within different, discrete volumes within the LED chip. Also, this analysis has allowed other metals to be identified, such as Au, that could also be potentially recovered from these chips.

Of further note is that the internal structure (as evidenced from the cross-section) of some of these devices is quite complex. Similar distributions of phase separated materials on a number of chips has been observed. An example of this is shown in Figure 7. In this case, the globules are shown distributed in the bulk semiconductor phase consisting mainly of silicon.

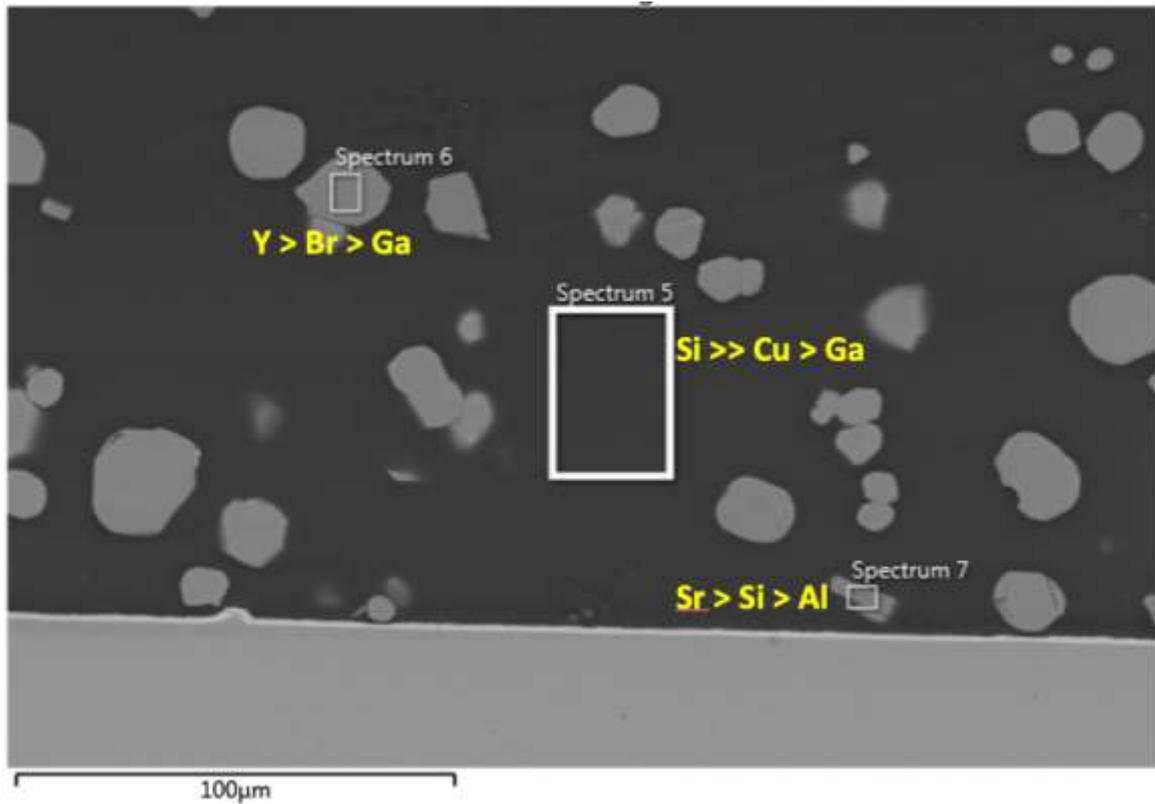
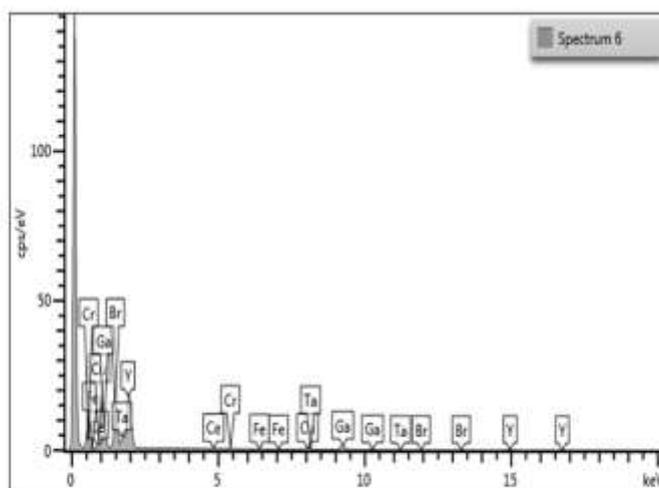


Figure 7. SEM image of phase-separated regions of internal LED material.

EDAX analysis of the globule marked as spectrum 6 (Figure 7) shows high gallium content at 13.6 % indicated in the spectral data and semi-quantitative integrals, Figure 8.



Element	Wt%	Wt% Sigma
Cr	0.23	0.06
Fe	0.69	0.06
Cu	2.78	0.11
Ga	13.70	0.20
Br	28.93	0.19
Y	51.66	0.28
Ce	0.89	0.12
Ta	1.13	0.28
Total:	100.00	

Figure 8. EDAX analysis of the region labelled spectrum 6 shown in Figure 7.

What is clearly illustrated by these data and images is that there is a substantial quantity of gallium embedded within the structure of these devices. The gallium is not generally located within the top facing layer of the device, but distributed within the substrate. This undoubtedly makes it more difficult to extract the gallium, as it is necessary to dissolve and disperse the underlying silicon-based semiconductor. The bulk analytical measurements have shown that this can indeed be accomplished by using strong inorganic oxidative aqueous acids. However, in this work the aim is to develop comminution and dissolution protocols using ionic liquids as an alternative to such conventional aqueous methods.

6.4 Extraction and recovery from ball-milled samples

Samples of ball-milled LED chips prepared by S2S were subjected to a range of leaching conditions. An example of the physical appearance of the finely divided sample, compared to the parent LED chips is presented in Figure 9.



Figure 9. LED chips from dismantled light lamps (right) and ball-milled powder (left).

Although, on the scale of the photograph, the powder appears quite finely divided, in fact there is a range of particle sizes and the distribution is quite large. In this study, the work was limited by time scale and, going forward, it would be a benefit to the dissolution process kinetics to have a more even distribution and smaller particle size.

A range of Type III DES liquids were selected for dissolution trials with the ball-milled powder. These were based on a combination of choline chloride, $\text{HO-CH}_2\text{-CH}_2\text{-N(CH}_3)_2\text{Cl}$, with a range of protic alcohols and acids including ethylene glycol (*Ethaline*), oxalic acid (*Oxaline*), lactic acid (*Lactaline*) and urea (*Reline*). Here the trivial, commercial names for the DES liquids are used for brevity. The liquids used along with the dissolution conditions are summarised in Table 1. In general terms, a weighted amount of powder was added to 50 mls of DES and stirred for a 24-hour period. The remaining solids were then filtered and the leachate liquid analysed. As a result of the varying distribution of particle sizes, similar volumes of powder had differing masses.

=	Quantity LED powder added (g)	Dissolution time allotted (hr)	Dissolution temperature (°C)	Dissolution stirring speed
<i>Ethaline</i>	0.5	24	50	3
<i>Oxaline</i>	0.5	24	50	3
<i>Ethaline</i> + <i>Oxaline</i>	0.5	24	50	3
<i>Ethaline</i>	5	67	50	3
<i>Reline</i>	0.5	20	50	3
<i>Lactaline</i>	5	45	50	3

Table 1. Dissolution conditions for leaching of the LED chip ball-milled powder with various DES liquids. The trivial names of the DES are used for brevity.

In these limited trials, leaching was performed at constant temperature of 50 °C and with moderate agitation. More aggressive methods are certainly available including higher temperatures and additional mechanical agitation including ultrasound. Moreover, the high thermal degradation points and low vapour pressures of DES lend themselves well to this type of approach. A photograph of the leachate solutions following the 24-hour period for the range of liquids is presented as Figure 10. The picture below shows the solution colour change after dissolution of the ball milled LED chip powder in selected DES. The table below also lists the order (from left to right) and dissolution parameters.



Figure 10. Samples of leachate liquid following the procedures indicated in Table 1. The liquids are (L-R) Ethaline, Oxaline, Ethaline+Oxaline, Ethaline (higher loading), Reline, Lactaline.

The native DES liquids are colourless and so the colour changes evident in Figure 10, whilst quite subtle, indicate dissolution of some components of the powder; this is quite encouraging. Interestingly, the most convincing colour change was observed for the lactaline liquid. This is almost certainly due to both the oxidising power of the organic acid and the coordinating capability of the lactate anion. Also, by comparing the images for dissolution of 0.5 g powder in *Ethaline* with 5 g powder in *Ethaline*, the extent of total dissolution, as evidenced from the qualitative colour change, seems to be insensitive to the total mass loading of powder under these conditions.

In addition, the leachate samples were analysed by UV-Vis spectroscopy over a range of wavelengths covering the near UV, through the visible spectrum into the near IR. The spectra for the leachates in all the liquids are presented in Figure 11. Here, all the absorption appears in the region between 250 nm and 350 nm and can be assigned to the presence of metal ion species not present in the native liquids. Hence, there is evidence of leaching from the powder sample in all but the *Reline* liquid. The greatest amount of total leached metal species, as judged from the absorbance scale in the spectra, was observed in the case of the *Lactaline*. This was consistent with the subjective colour based assessment (above). The absorbance peak present at ca. 335 nm, or at least one component of it, may be due to copper salts present in the liquid. Qualitatively, this is responsible for the pale yellow colour.

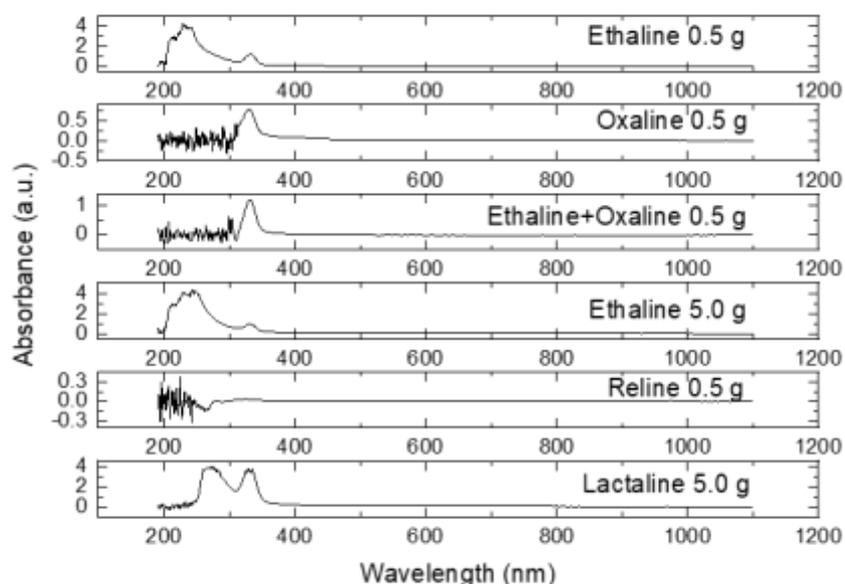


Figure 11. UV-Vis spectra of the leachate liquids from Table 1 and Figure 10.

Given that the *Lactaline* electrolyte seemed to have been the most effective of those trialled, this was selected for the targetted recovery of metals through electrowinning. Subsequently, an electrochemical cell was set up with a copper cathode material using the *Lactaline* DES leachate. An image of the experimental set-up during electrolysis is shown in Figure 12. The indicated set-up was used to plate from the *Lactaline* dissolution sample. There is a visible deposit on the $2 \times 2 \text{ cm}^2$ designated electroactive plating area. A voltage ramp up of the potential from 1.00 V to 2.10 V was used to generate the plated sample; quiescent solution, 50 mA limit, and 2.20 V limit. An overall picture of the rectifier is also included showing the deposition in real time after ca. 10 minutes of plating. There are visible bubbles on the surface of the cathode and a clear colour change of colour/texture in the submerged predefined plating area.

The *Lactaline* DES contained a high concentration of acidic protons and so the observed bubbling was the result of hydrogen evolution. This limited the Faradaic yield of metal recovery and, given the low concentrations of metals indicated in the leachate, resulted in a relatively small coating on the cathode. Despite this, there was a visible coating on the surface of the cathode after the electrolysis and this is shown pictorially in Figure 13. Here the *Lactaline* cathode sample is shown after removal from the plating solution and rinsing with DI water. This sample was then subjected to further surface analysis using SEM-EDX in order to determine the chemical nature of the visible deposit.



Figure 12. Experimental set-up for electrowinning from the Lactaline DES during electrolysis and showing clear colouration on the electroactive region of the Cu cathode.



Figure 13. Cathode piece removed from initial electrowinning experiment shown in Figure 12 having been rinsed in DI water and dried.

The cathode piece (Figure 13) was transferred to the analysis chamber of the SEM and the secondary electron image was recorded, as well as the EDX spectrum of selected areas of interest. An exemplar secondary electron image is shown in Figure 14. This image shows that the coating is uniform but indeed very thin and that the surface features remain those of the underlying copper substrate. Visual colouration suggests that the coating is of the order of around 1 μm , or less in thickness. This is perhaps not surprising given the mild conditions and limited time scale both for dissolution and electrowinning.

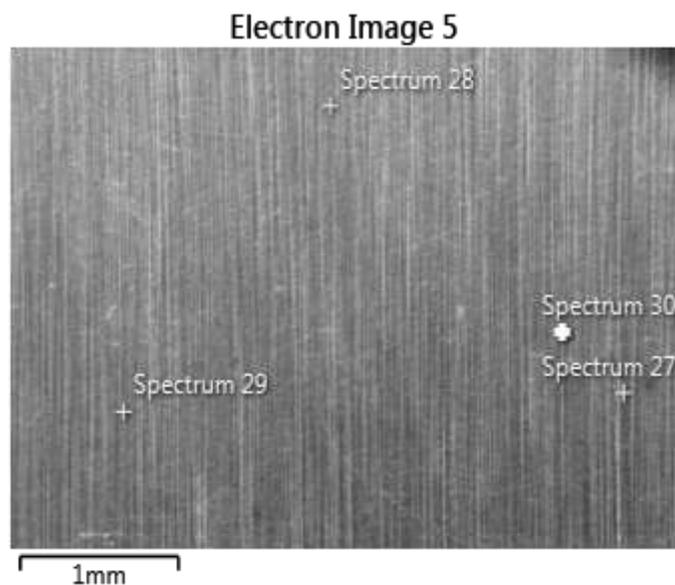
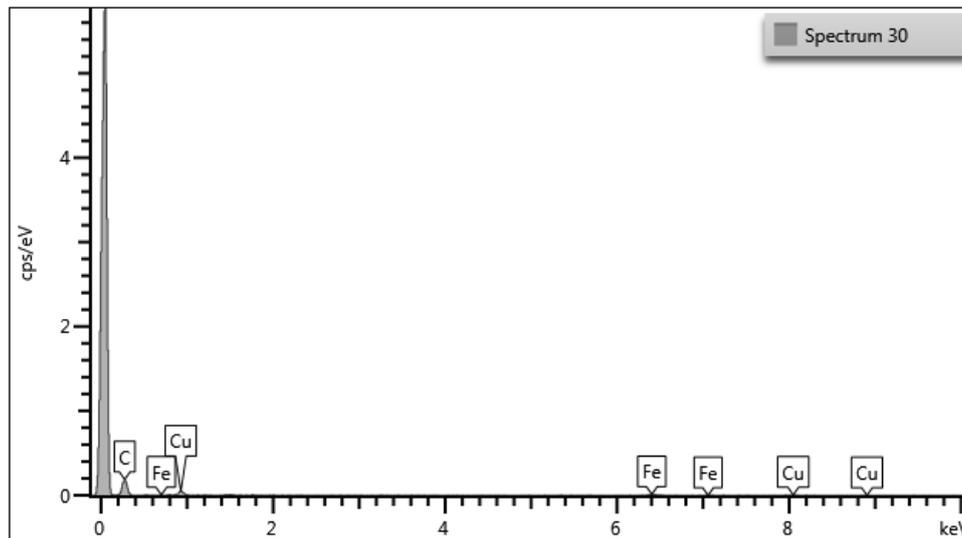


Figure 14. Secondary electron image (SEM) of the coloured region of the cathode piece removed from initial electrowinning trials.

Regions of the coating identified in the SEM image (Figure 14) were selected for compositional analysis using EDX, these are indicated as crosses (labelled *Spectrum XX*) on the SEM image, Figure 14. A sample EDX spectrum and compositional analysis, corresponding to position *Spectrum 30* (Figure 14), is presented below as Figure 15.



Elemental composition of the SEM-EDX sample analysis.

Element	Wt%	Wt% Sigma
O	21.31	
Fe	43.18	10.00
Cu	35.51	10.98
Total:	100.00	

Figure 15. EDX spectrum and compositional data for the coloured region (Spectrum 30) of the cathode sample from Figure 13 and Figure 14.

Unfortunately, the only elements present in the EDX analysis were copper and iron. Copper was the substrate material and the appearance here is evidence that the thickness of the coating is substantially less than the spallation integration depth of the primary electron beam. The presence of iron was unexpected, but most probably originated not as a component of the original LED matrix, but from the walls of the ball-mill which were made from stainless steel. However, this preliminary analysis does not conclude that gallium is not present in the deposit, merely that we are not able to detect it using SEM/EDX for this sample.

In fact, EDX is notoriously insensitive to thin coatings because of the penetration of the electron beam into the substrate.

Subsequent trials must, therefore, focus on achieving thicker deposits through more aggressive dissolution conditions (as well as longer time scales) and longer periods of electrodeposition. In addition, leaching efficiency can be improved by more consistent, homogeneous and finer comminution. In the short-term, this can be achieved by mechanical sieving of the existing ball-milled powder and processing of the finer fractions to improve leaching conditions. This work is currently underway and the results are pending.

Further, ICP-MS analysis of the existing leachate samples is currently underway in order to quantify and identify the metal ion content of the different liquids; these data were also pending at the time of writing and will be included later.

6.5 Fractionation

In order to increase the efficiency of the leaching of gallium and other metals, the ball-milled sample was fractionated by physical separation using filter cans with different mesh sizes, Figure 16.



Figure 16. Fractionation of ball-milled powder, filter cans (left) and fractionated powders (right).

The powders were separated into fractions with varying average particle sizes from 1000 μm , 300 μm , 150 μm , 75 μm and $< 75 \mu\text{m}$. These were each subjected to leaching and the ICP-MS quantitative analysis. At the time of writing (13/08/21) the results of these analytical measurements are still awaited. If they become available by the 18th August they will be added and discussed at the project Q3/close out meeting on the 19th August 21.

6.6 Extraction and recovery of other CRM metals

In addition to gallium and the substrate metals, there are other precious components contained within the LED WEEE. One of the most important metals present is indium, which is also categorised as a critical raw material. In additional experiments, work was carried out to examine if both gallium and indium could be recovered together from DES-based electrolytes and leachates. In order to determine if this was possible, an experiment was performed using a model DES solution containing both GaCl_3 and InCl_3 salts. This is shown in Figure 17.



Figure 17. Experimental set up for the test recovery of both In and Ga from a model DES solution containing 0.1 M GaCl_3 and 0.1 M InCl_3 in Ethaline 200 (left), Ga/In coated cathode piece (right).

The joint electrowinning of gallium and indium was achieved on a copper cathode, however, the overpotential for indium recovery is around 0.5 V less cathodic than that for gallium. This offers the possibility to selectively recover both metals from a mixture obtained in the DES leachate. A coated

cathode is also shown in Figure 17. The silver grey coating on the copper is the co-deposited layer of gallium and indium. This was confirmed using EDX analysis, and the results shown in Figure 18, clearly show the presence of both metals in the deposit.

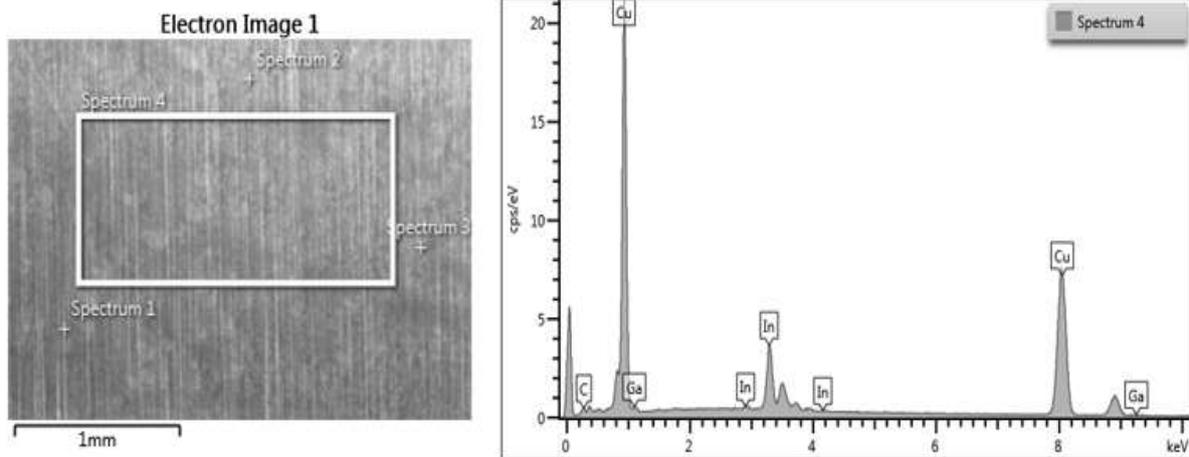


Figure 18. SEM image and EDX analysis results from the silver-grey region of the deposit on the copper cathode shown in Figure 17 which confirm the presence of both gallium and indium.

6.7 Conclusions

- LED active components have been extracted from waste whole-devices (e.g. GU10 lamps) by manual disassembly to reveal the active elements (chips). These are a relatively small part (by mass) of the total device and the value stream of the other recyclable materials (glass, plastic, copper, WEEE and so on) is noted.
- Bulk elemental analysis of the LED chips has been achieved by dissolution of the samples in aggressive aqueous acids and using ICP-MS quantification. These results showed that the gallium content of the sample chips was as high as 2.4 - 8.7 g per kg. These figures will be used as input values for further modelling and techno-economic assessment.
- Elemental mapping has been carried out through cross-sectioned LED chip elements and has shown that the gallium identified by bulk analysis was distributed unevenly in

the active chip elements. It was primarily embedded within phase-segregated regions of the silicon-based substrate semiconductor.

- The localised distribution of the gallium in the chip will necessitate targeted methods in order to maximise its extraction. Such methods will include mechanical comminution like ball-milling of the LED chips in order to reduce the structures to a fine powder. This will break open the semiconductor substrate and expose the embedded gallium. Further ball-milling of samples from the existing batches will be attempted later. It is anticipated that this method will also enable the use of milder methods for gallium extraction that may leave behind the extracted silicon substrate as a valorised powder for a separate recycling stream.
- Leaching of the ball-milled material in a range of DES liquids has been trialled and has been shown to be partially successful.
- Electrowinning trials on the DES leachates have yielded thin-layer metallic deposits, but EDX analysis has been inconclusive. These trials are on-going.
- Electrowinning of other CRM metals including In is possible offering the opportunity to selectively recover both Ga and In from WEEE leachate.

6.8 Acknowledgements

We greatly appreciate the technical support from Graham Clark (Advanced Microscopy Facility, School of Engineering, University of Leicester) on SEM-EDX analysis and Adam Cox (School of Geography and Geology, University of Leicester) for practical help in performing the ICP-MS analysis of samples and for helpful discussions.

7) **Basic Costs and Economic Viability of the Process**

This section is intended to give a basic introductory overview of the important cost factors that need to be considered when assessing the economic viability of the proposed new recovery process. At this early stage of development (the work reported here was a basic feasibility study) it is not possible to make any accurately quantifiable assessments of the integrated process stages or indeed the individual elements. Such an analysis is planned for a follow-on project, where the process will be scaled-up to allow larger quantities of the target metals to be recovered and more data to be collected specific to the key cost factors such as energy and materials consumption, waste generation and treatment costs, along with process efficiency and equipment costs. However, it should also be noted that a more detailed preliminary process assessment has been undertaken by HSSMI and the results of their study are reported elsewhere in another project deliverable.

In any basic assessment of the economic viability of a metal's recovery process, the fundamental consideration is not how much the recovery process costs, but is it more cost effective than any current alternatives. More specifically for the recovery of gallium from end-of-life LEDs, if the proposed process is to be successful, it should be possible to obtain the metal at a lower cost than producing it as a by-product of primary metal extraction from ores. Of course, the actual reality of the economics around gallium recovery are not quite so straightforward. Firstly, gallium is a critical raw material that is sourced predominantly from China. Therefore, there may well be strategic reasons for recovering gallium locally, even if it does cost more than metal produced from primary sources in the Far East. Secondly, gallium is present in LED lamps along with a range of other materials that have a value. In terms of the ReGaLL process for recovering gallium from the LED semiconductor chips themselves, the metal is typically found in the presence of indium, silver and gold. The proposed ReGaLL process is capable of recovering both gallium and indium, which are typically found combined in the compound semiconductors used to form the actual light emitting diodes. Given that the price of indium is typically slightly greater than that of gallium, the ability to recover both metals in a single process will significantly improve the process economics. The additional presence of silver or gold adds further value. The following brief analysis covers the key elements of the overall ReGaLL process that will need to be fully assessed and optimised in

order to enable the most cost-efficient operation and thus for the gallium and other metals to be economically recovered.

Input materials

The source of the gallium in the ReGaIL project has been end of life LED lamps. These are complex structures with a wide range of materials and components. The gallium (and indium) are found in one specific site in the lamps, namely the light emitting semiconductor chips themselves. Ideally, in order to have an efficient process, it would be preferable to be able to separate these chips from all of the other components. Dismantling trials have shown that this is indeed possible and relatively straightforward, with no requirement for complex or expensive tools and equipment. However, when performed manually, it is time consuming and the labour costs exceed the value of the recovered gallium. There is thus a need to improve the efficiency of this process, probably by implementing some form of automation. This is perfectly feasible and would probably utilise developments of techniques that are already widely implemented by WEEE recyclers. Such approaches could be explored in a follow-on project from this one, where the ReGaIL process would be enlarged to the pilot plant scale.

Once the LED chips have been isolated, they can then be treated to extract the gallium and other valuable materials e.g. indium. Currently, in order to improve the efficiency of the chemical dissolution of gallium, the LED chips have been subjected to comminution using a ball milling process. This works well and generates a powder with a much larger surface area that is better for facilitating subsequent gallium dissolution using the iodine/deep eutectic solvent approach detailed elsewhere in this report. Ball milling is a scalable process, but it is also relatively slow and consumes energy. There are thus opportunities to improve the efficiency of this part of the process. Alternatively, it may be possible to extract the gallium from the chips without the need for ball milling. For example, the use of higher temperatures and longer times for the dissolution part might be viable but an evaluation of the various potential processes would be needed to identify the best combination of process variables. Again, these aspects can be more fully explored in a subsequent larger follow-on project to this one.

Gallium Dissolution

A novel element of the ReGaIL approach is that it uses a single stage process to both dissolve the gallium and to electroplate it out of the deep eutectic solution. The preferred method uses iodine as an oxidising agent in a deep eutectic solvent, and its *modus operandi* is more fully detailed elsewhere. Although the potential of the process has been demonstrated, there are clearly a number of areas where it should be possible to improve the efficiency and thus reduce the costs. Firstly, it is important to ensure that the iodine-based dissolution operates as efficiently as possible. Factors here will include temperature, solution agitation, reactor design, iodine concentration and the efficiency of the anodic regeneration process. The cost of the deep eutectic solvent will also be important, so the choice of a relatively low-cost material would be advantageous. There will be costs associated with the possible loss of the DES due to drag out, but these could be reduced via implementation of standard drag out minimisation procedures such as the use of air knives. There will also be the cost of treating and disposing of any waste materials, e.g., the remains of the chips after the valuable materials have been removed from them. This will typically be a mixed inert oxide material and it may be possible to find secondary uses for the residues rather than consigning them to landfill, for example.

Gallium Recovery

In the ReGaIL process, the gallium and, possibly, other metals are recovered by electrolysis and thus one of the main costs will be directly related to the amount of electricity needed to recover a specific amount of the metals. For the electrolytic recovery of some metals from aqueous solution, e.g. copper, the processes are highly efficient and it is relatively straightforward to calculate the cost of the electricity needed to produce a specific mass of metal. Unfortunately, gallium is not one of these metals and its electrowinning is known to be inefficient, even from aqueous plating media. Additionally, the plating efficiencies achieved when using deep eutectic solvents are low, so achieving the best possible performance via the use of optimised plating techniques will be an important aspect determining the economic viability. Fortunately, there are various approaches that can be used to enhance plating efficiency, these include key factors such as the make-up of the electrolyte, the plating cell configuration, the electrode materials and their design. The electroplating current can be

applied directly or using a pulsed waveform and here alone there are many variables that can be optimised to achieved enhanced efficiencies. Another consideration is plating temperature and the solution viscosity; deep eutectic solvents tend to be quite viscous, so it is important that solution viscosity does not cause any metal transport/diffusion related problems. Finally, gallium has a low melting point which can also be the cause of problems when seeking to electrowin it. By carefully choosing appropriate anode materials, e.g. copper, it may be possible for the deposited gallium to form an alloy. This could be a viable way of enabling higher temperatures than would be otherwise possible to be used.

These are just some of the many factors that can influence the efficiency and hence cost of the gallium recovery process. They need to be studied and optimised, along with any other relevant impacting factors. Consequently, it is proposed that these variables would be evaluated as part of a follow-on project, where there is a move up the technology readiness levels and an increase in the size of the process towards pilot plant scale operation.

8) Recommendations for Further Work and Scale-up

The work carried out in this feasibility study has been conducted on a relatively small scale and has essentially been undertaken to confirm that the recovery of gallium from end-of-life electronics is possible using an alternative novel non-aqueous process. The work has involved a significant level of manual intervention, especially in the early stages of the process where the intention was to use a source of gallium that was relatively concentrated. Consequently, a manual process was used for dismantling LED lamps and collecting individual LED chips, while enabling all of the other parts of the lamp to be separately recovered and processed to recover maximum value. Clearly, while such an approach is appropriate for an initial feasibility study, it is unlikely to be economically viable on a larger scale. Indeed, some preliminary assessments of the economics of using such a manual approach have confirmed that the costs of manual disassembly would be too high to enable an economic return. The average time for disassembly after practice and fine tuning was found to be around five minutes per lamp across all lamp types i.e. around 12 per hour. At a labour cost of £30 per hour including overheads, the dismantling cost per lamp was therefore ~£2.50. Using the average numbers of chips recovered from a typical selection of waste lamps, the mass of chips per lamp would be around 5 g. The current market price of gallium is close to \$300/kg, so even if the whole of the LED chip was gallium its value would be \$1.50. However, this is not the case and the actual level of gallium present is much less than this figure. Consequently, it would appear that manual disassembly is unlikely to be economically viable, unless there is a very significant increase in the price of gallium. Of course, the LED chips do contain other metals such as indium, silver and gold, and there is also value in the rest of the LED assembly but even with all this additional added value, it is highly likely that some level of automation will therefore be necessary.

While an automated method is likely to be needed to improve the economics of recycling, careful consideration will need to be given to the specific approaches to be adopted. There are a number of established processes used by recyclers for separating different types of materials such as metals from plastics, as well as different types of metals and plastics. However, in this case, the main aim should be to isolate the LED semiconductor chips from the wide range of other materials that are present in end-of-life lamps, as these can then be treated using the established conventional methods.

9) Summary and Conclusions

In this project, the work carried out to recover gallium has been focused on the use of electrowinning techniques. However, the approach has utilised a novel method whereby the gallium was dissolved into a solution that employed a common deep eutectic solution rather than by using a typical conventional aqueous approach. This helped the process to be more sustainable and to avoid the generation of hazardous and expensive to treat waste. It also offered the possibility to implement a novel, single stage process that could be employed for both the dissolution and recovery of the gallium in a single reactor/plating cell design. Furthermore, this method was also amenable to the recovery of indium, which is also present alongside gallium in end-of-life LEDs. By using this approach, having the ability to recover gallium, indium and possibly other metals, it should be possible to improve the economics of the process, while avoiding the loss of additional scarce and valuable metals (e.g. gold and silver).

In the first stages of the work, a model solution of gallium in the deep eutectic solvent Ethaline was utilised to demonstrate that the metal could indeed be electroplated. Reasonably standard plating conditions were used, including an inert anode and a copper cathode. The copper cathode was useful in that the deposition of the silvery grey coloured gallium could easily be seen on the electrode. Also, it allowed the gallium to form an alloy with the copper, thereby avoiding problems associated with gallium's low melting point. The recovery of gallium from an Ethaline solution was clearly demonstrated, although further work will be needed to optimise the efficiency and to define the specific equipment and process conditions etc.

Early in the project, it became clear that the end-of-life LED chips contained other valuable metals, including indium, silver and gold. Indium is often used alongside gallium in the compound semiconductor materials that are used to emit light and the amount found varies depending on the specific wavelength of light needed. Given that indium is also a group three metal that is both reasonably valuable and widely used in electronics, it is clearly worth recovering at the same time as the gallium. Therefore, before electrowinning trials were performed on solutions prepared using LED chips as the source of the metals, a second model

solution was made using equimolar amounts of gallium chloride and indium chloride in Ethaline.

In the final part of the project, the recovery of gallium and indium from actual LED chips was then attempted. The challenge here was in getting the metals into solution when they were in the form of a gallium/indium compound semiconductor film deposited onto the LED substrate. Typical techniques that have previously been utilised included a high temperature roasting in air followed by dissolution in strong aqueous acids. In the method utilised here, the chips themselves were removed from end-of-life lamps and then ball milled to produce a fine powdered material that would make the metal extraction easier. Dissolution was then performed using iodine in the deep eutectic solvent as an oxidising agent (which was anodically regenerated in a closed loop process). Once in solution the gallium and indium were recovered electrolytically by plating onto a copper cathode.

At the time of writing this work was continuing, even though the project had officially concluded, and it has thus not been able to include details here. This report has been completed and issued on the final official day of the project. Depending on the results obtained in the following two weeks or so prior to the final progress meeting, a final update of this deliverable may be prepared.

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