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RECYCLING OF GALLIUM FROM END-OF-LIFE LIGHT EMITTING DIODES

Nowadays Light Emitting Diodes (LEDs) are widely utilized. They are applied as backlighting in Liquid Crystal Displays (LCD) and TV sets or as lighting equipments in homes, cars, instruments and street-lightning. End of life equipments are containing more and more LEDs. The recovery of valuable materials – such as Ga, Au, Cu etc. – from the LEDs is essential for the creating the circular economy. First task is the development of a proper recycling technology. Most of the researchers propose fully chemical or thermal-chemical pathway for the recycling of LEDs.

In the meantime our approach based on the thorough investigation of the structure and composition of LEDs, and shown in this paper, is the combination of mechanical and chemical techniques in order to recover more valuable products, as well as to facilitate the mass transfer. Our laboratory scale experiments are introduced, the final aim of which is Ga recovery in accordance with our above approach. It was experimentally proved that the LED chips contain Ga and can be recovered by mechanical processes along with copper-product. Ga is presented on the surface of the chips in GaN form. Mechano-chemical activation in high energy density stirred medium mill and the following acidic leaching resulted in the enrichment of 99.52% of gallium in the pregnant solution.

Keywords: LED, LED recycling, LED chip, gallium, mechanical enrichment, mechano-chemical activation, leaching

1. Introduction

Nowadays Light Emitting Diodes (LEDs) are widely utilised. They are applied as backlighting in Liquid Crystal Displays (LCD) and TV sets or as lighting equipment in homes, cars and instruments. Their low energy consumption, diverse and unique properties and their long life time are turning them into reasonable choice for substituting other light sources in the future. Their usage has reached almost 300 Million units only in flat displays worldwide in 2015, and the market is forecasted to increase substantially to US $8.87 billion by 2018. End-of-life LEDs are at the meantime significant secondary sources of Rare Earth Elements (REE) and Ga which elements are on the European Union (EU) list of critical materials based on their relative importance and risk of availability for the European economy. Their recovery from the end-of-life products is a primary goal of European recycling industry according to Circular Economy action plan announced in 2011 [3].

GaN together with GaAs covers the largest proportion of Ga used in mainly integrated circuits, but significant portion is used for optoelectronic devices such as LEDs and solar panels [1,2]. According to Frenzel et al. [1] Ga annual demand increases in a rate of around 7.4%, considering the current recycling rate the primary production rates by 2050 are forecasted ten times higher. It has been found that Ga current supply potential is higher than today's production in form of by-products of Zn, bauxite processing and using coal sources worldwide. The supply security concerns for Ga are existing and their nature is mostly geopolitical and economic. These circumstances make the recycling of Ga from Waste Electrical and Electronic Equipment (WEEE) streams the desirable secondary path.

Sources of Ga in LEDs are GaAs, GaN and InGaN, depending on the type of the LED manufactured. It is also a difficulty of LED processing and Ga recovery that the most important part of the LED is its chip containing not only Ga, but various semiconductor materials incorporated as well into the resin along with plastics and different other metallic electrodes [4,5]. The recycling sources of Ga are originated mainly from the manufacturing of wafers of Integrated Circuit (IC), LED and Printed Circuit Board (PCB) products, but the end-of-life products are rarely considered as raw material sources in this regard.

For the LED recycling, several procedures have been tested mainly at laboratory scale. Most of the researchers propose fully chemical or thermal-chemical pathway for the recycling of LEDs.

Chen et al. [6] introduced several methods mainly focusing on the chemical-thermal processes. Their method applies nitric acid leaching of GaAs, then the coagulation and a dry annealing process that involves annealing, vacuum separation, and sublimation by heating up to 1000°C. As the result they reported condensed As_2O_3 with 99.2% purity, while the Ga_2O_3 powder produced was then dissolved and electrolyzed, allowing for 95.9% recovery of Ga with purity of 99.9%. Ahmed et al. [7]

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described method applying Cyanex 923 and Cyanex 925 solvent extraction reagents in kerosene for extracting Ga from HCl solution. Earlier, ion exchanging resin has been successfully tested for Ga recovery from alkaline solution [8]. They suggested to use their method to recover Ga during the Bayer-process, since it was found that Ga is selective over the Al. Another method to recover Ga from acidic solutions were supercritical CO_2 extraction, applying chelating agents in the process, which was reported by Chou and his research fellows [9].

Swain et al. [10] has reported using acidic leaching on Ga rich metal-organic chemical vapour deposition residues, rich in GaN, InGaN and other Ga-compounds. They have found that other than GaNGa phases were soluble in HCl, however solubilisation of GaN showed difficulties in leaching. Also Swain and their research group [11] have reported processing GaN rich dust originated from the LED manufacturing. They have proposed two different methodologies. According to the first, the original feed was acid-leached, the residue was mixed with Na_2CO_3, ball milled followed by annealing, then again leached to recover Ga. The second method is similar, but without the first leaching step. They have found along different benefits of the two different methods, that more than the solubilisation of 70 w/w% of Ga could be achieved.

While the above mentioned methods are processes applied either not only for the recycling, or used GaAs as Ga source and focused mainly on extraction of Ga from solution, Zhan et al. [4] used general white LEDs for their experiments containing GaN and InGaN as the source of Ga. According to their work, pyrolysis of organic plastic compounds was applied and the residue processed mechanically by secondary crushing and screening. The treated residue was introduced into vacuum furnace at temperature of 1373 K and vacuum pressure of 0.01-0.1 Pa, so that 93.48% of Ga recovery efficiency were achieved.

In the meantime our approach based on the thorough investigation of the structure and composition of LEDs, is the combination of mechanical and chemical techniques in order to recover more valuable products, as well as to facilitate the mass transfer. Mechanical pre-processing prior to the chemical one has many advantages. The chemical mass transfer in general is governed by the concentration gradient, the area exposed and the retention time. Nevertheless, the presence of the "alien" components in the mass transfer can dramatically decrease the concentration gradient, the contacting surface, as well as the diffusion rate. The mechanical pre-treatment provides the removal of such disturbing "alien" components. Furthermore, the lower the material flows to be submitted for the chemical processing, the lower the specific reagents requirement and, therefore the costs of the process [15].

Chemical mass transfer can be enhanced by mechano-chemical activation treatment [16]. Such enhancement can be successfully done using a stirred medium mill [17,18].

2. Experimental

Structure of LEDs

To recover the LED chips by mechanical methods, the structure, and the parts composition should be well known. Photos were made by optical microscope of LEDs, originated from LCD TV backlight. As an example a cross-section of an edge type LED is shown in Fig. 1, where the white LED package, the Cu parts coated with Ag, the LED chip on sapphire, the pure Au wires and the encapsulation of chip can be seen. The components were identified using SEM microscope with micro probe [5].

Sample

As a sample some new Surface Mounted Device (SMD) LEDs were procured. The type and the number of the processed LEDs are shown in Table 1, the total number of them was 705, the total mass was 32 g.

TABLE 1

Quality and quantity of the LEDs used for experiments

Type of LED	Colour	Number
SMD 5050 (with 3 chips)	coldwhite	147
SMD 5050 (with 3 chips)	warmwhite	147
SMD 2835	coldwhite	147
SMD 2835	warmwhite	147
SMD 3528	white	117
Sum		705

Flowchart of experimental processing

The tested process of the LEDs has two main parts. The first one is the mechanical preparation. During this preparation the LED chips containing Ga are physically liberated and separated from other parts of LED (Fig. 2, upper part).

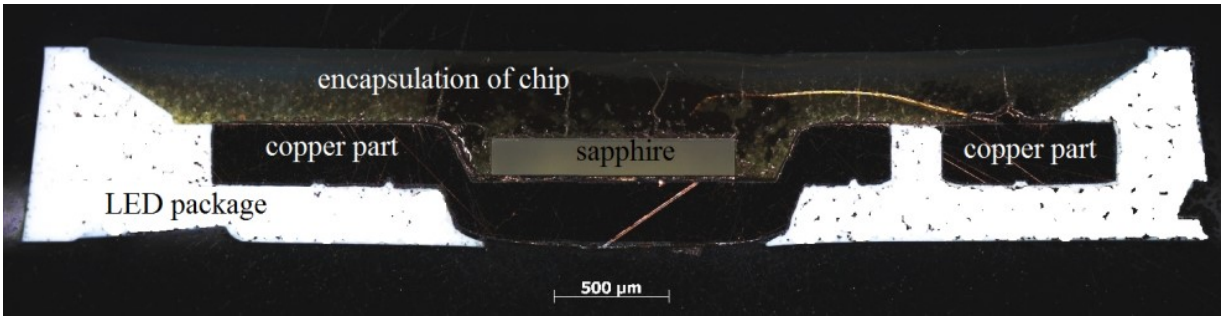

Fig. 1. Optical image of cross-section of edge type LED (polished section)

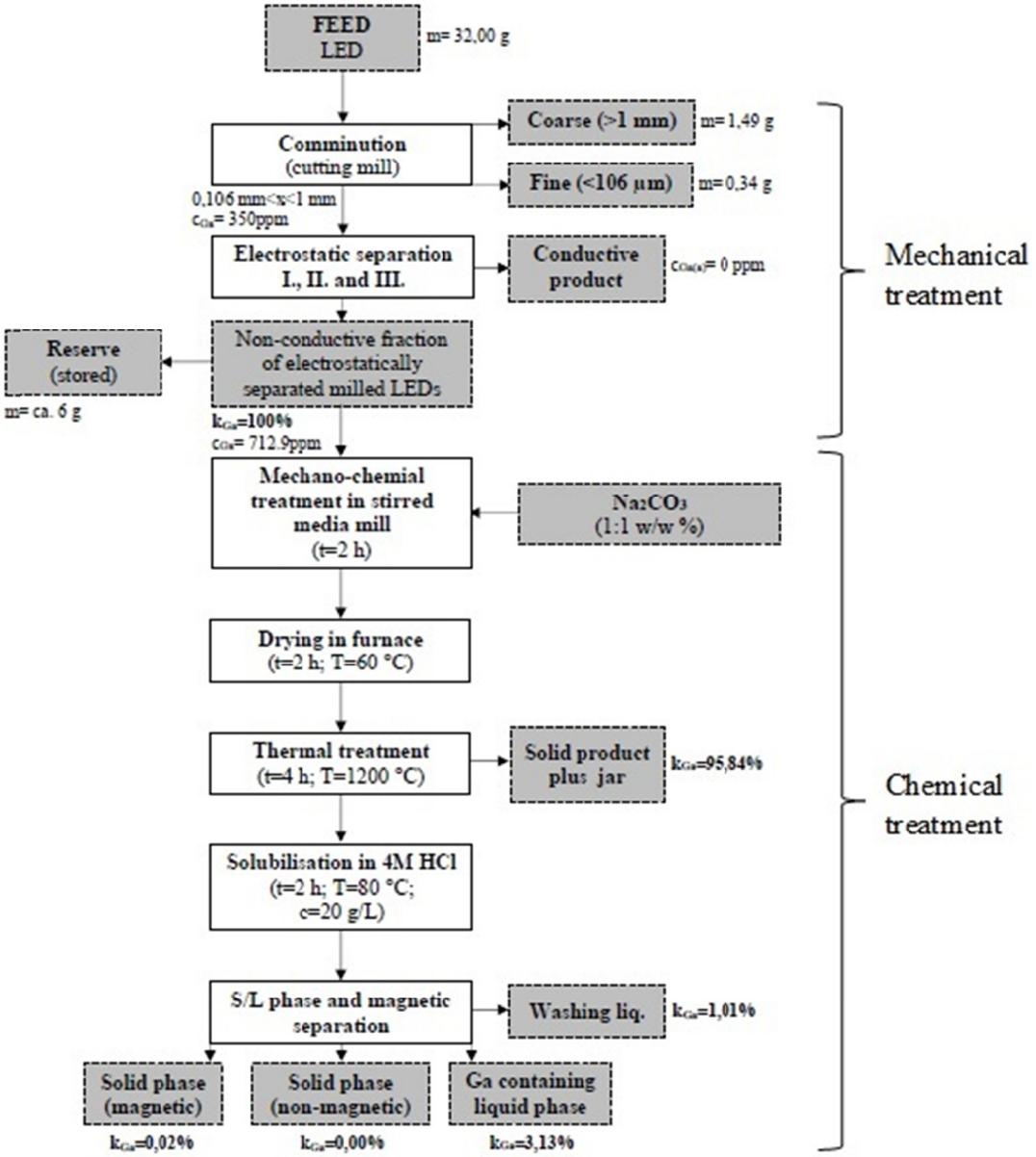

Fig. 2. Flowchart of processing. Notes: m-mass; c-concentration, k-component yield

Firstly the collected sample of 32 g LEDs was ground in cutting mill (type: RETSCH SM2000) with 1 mm sieve holes. The coarse (>1 mm) and the fine (<106 µm) fractions were removed, because it was revealed earlier that the chips are concentrated in the 106...1000 µm fraction (Fig. 3).

For the electrostatic separation ERIEZ separator was used (drum diameter: 200 mm, U = 30 kV). This non-conductive fraction was fed on electrostatic separator in three steps: conductive product was further fed twice to recover the non-conductive LED chips. The non-conductive fraction (LED chips) was the feed for the further experiments on the chemical treatment.

The second part of our recycling concept is the chemical treatment as it is shown in the lower part of Fig. 2. Since our approach was to facilitate the chemical reaction by mechano-chemical activation treatment of mechanically processed LED in presence of Na_2CO_3 in an energy-intensive stirred medium mill, such a mill was constructed in our Institute. The parameters of the mill are as follows: total volume: 126 cm^3; grinding media size: 0.6-0.8 mm; grinding media density: 3.8 kg/dm^3; grinding media filling ratio: 60 V/V%; circumferential velocity: 6 m/s. $Na_2CO_3$was added in the 1:1 (w/w) stoichiometry. It was planned to run the stirred media mill for 8 hours, but the unexpected warming up forced us periodically switch off the mill, so that the total mechano-chemical treatment lasted for 2 hours. The solubilisation was carried out in 4M HCl for 2 hours at temperature 80°C and solid concentration 20 g/L in shaking flasks.

3. Results and discussion

Mechanical preparation

The main aim of this research was to investigate the recovery of the Ga from the LEDs, locating on the surface of the chip. As it can be seen on the cross sectional image (Fig. 2) the

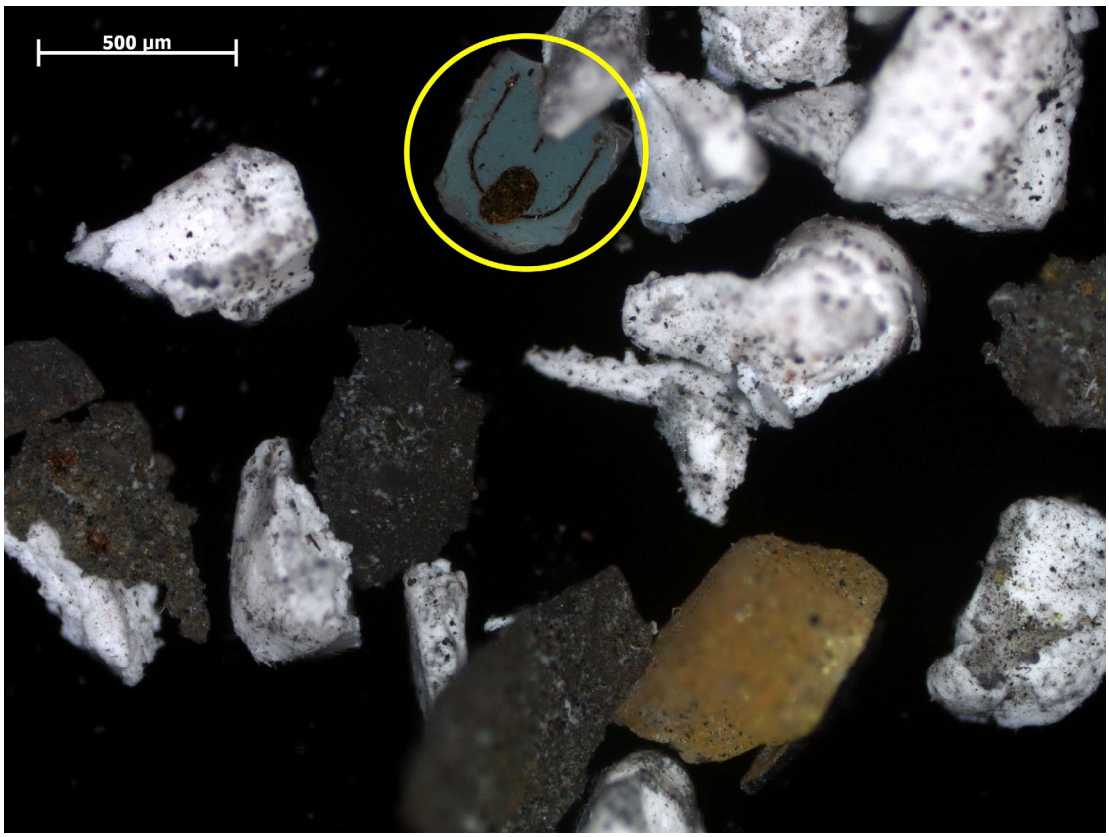

Fig. 3. LED chip in 106...1000 µm fraction (chip marked with circle)

parts of LED are merged, so the physical liberation of them by a proper mill is necessary. The cutting mill was found as an appropriate tool for this purpose. The measured Ga concentration after milling was 253 ppm in the relevant 106...1000 µm fraction [12]. After the milling aimed at the physical liberation, the different parts can be mechanically separated. Separation by the electric conductivity ensures that the metallic parts (e.g.: Cu) can be removed before the chemical treatment, and it can be also a valuable by-product. The non-conductive product contains the LED chips (the calculated Ga-concentration was as high as 516 ppm) with other non-metallic parts (e.g.: housing). It was revealed that in this step the concentration of Ga can be increased approximately by two magnitudes if the product contains only chips [12].

This fraction should be further chemically treated to remove the Ga containing layer.

Chemical solubilisation of GaN

Ga is represented in the tested samples as GaN. According to many authors [13] it is a refractory material towards solubilisation in various lixiviants. This statement was proved also by our recently carried out experiments on chemical solubilisation of GaN using H_2SO_4, HCl and HNO_3in various concentrations and combinations, as well as NaOH [12]. The reason of the refractory is that GaN is a high bond energy crystal.

It was thermodynamically established by Ellingham and Pourbaix diagrams that the GaN can be transformed into soluble $NaGaO_2$ by oxidative roasting in presence of Na_2CO_3 [14]. Our own thermodynamic calculations using HSC Chemistry 5.0 Software fully proved that.

Fig. 4 illustrates the photo of the sample after 2 hours mechano-chemical activation treatment. The excess of soda, as well as plastic particles can be seen.

An unexpected technical problem happened during the oxidative thermal treatment too: the tested material stuck to the porcelain jar, and even penetrated into that. As the ICP chemical analysis revealed, the majority (95.84%) of the Ga could be found in this form.

The removable from the jar tested material was then solubilised in shaking flask in 4M HCl for 2 hours at temperature 80°C and solid concentration 20 g/L. After solid-liquid separation the solid residue was magnetically separated, the magnetic solid residue had 5.27 ppm Ga-concentration, while the non-magnetic had a very low mass yield.

The solubilisation of the mechanically pre-processed and mechano-chemically activated LED waste in the 4M HCl, removable from the porcelain jar, even within technical problems, was very successful: 99.52% of Ga diffused into solution as related to the operation unit. The concentration of Ga in the liquor of the solubilisation was 6.75 mg/L.

Although, there is still a lack in the experimental data and much to experimentally continue, the obtained previous results are promising and open wider opportunity for the establishing the recycling technology for GaN from the end-of-life LEDs.

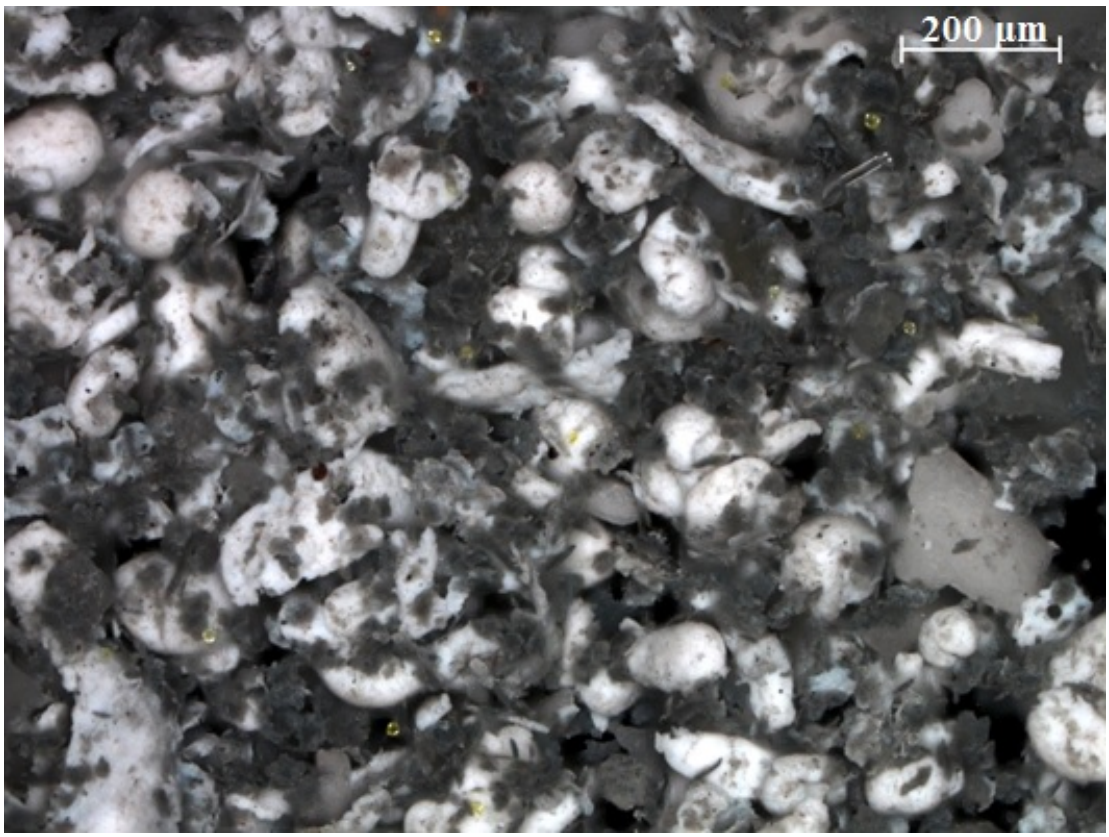

Fig. 4. LEDs sample after 2 hours mechano-chemical activation treatment in stirred medium mill

4. Conclusions

The aim of our work was to investigate the possibility of the recovery of Ga from end-of –life LEDs at labor scale combining the mechanical pre-treatment with the following chemical-thermal techniques. Quite a large number of different, in electronic equipment typical LEDs (705 pieces) were processed during our experiments. By the mechanical preparation, after physical liberation the conductive parts (Cu) were successfully removed. The non-conductive part contained the GaN layer on the surface of the LED chips, the calculated Ga concentration was as high as 516 ppm. It was experimentally proved that the mechano-chemical activation in stirred media mill is an effective tool to obtain high recovery of Ga in the pregnant solution after the following chemical leaching using HCl: 99% of Ga recovery can be reached. Although, there is still a lack in the experimental data and much to experimentally continue, the results obtained are promising, prove our concept of combined mechanical-chemical-thermal treatment as a proper, and open wider opportunity for the establishing the recycling technology for GaN from end-of-life LEDs.

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