metals

Article

Recycling the GaN Waste from LED Industry by Pressurized Leaching Method

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Abstract: In recent years, with the increasing research and development of the light-emitting diode (LED) industry, which contains gallium nitride (GaN), it is expected that there will be a large amount of related wastes in the future. Gallium has an extremely high economic value, therefore, it is necessary to establish a recycling system for the GaN waste. However, GaN is a direct-gap semiconductor and with its high energy gap, high hardness, and high melting point, these make it difficult to recycle. Therefore, this study will analyze the physical characteristics of LED wastes containing GaN and carry out various leaching methods to leach the valuable metals from the waste optimally. Different acids are used to find out the best reagent for gallium leaching. Different experimental parameters are discussed, such as the effect of the different acid agents, concentration, pressure, liquid-solid mass ratio, temperature and time, which influence the leaching efficiency of gallium. Finally, acid leaching under high pressure is preferred to leach the GaN waste, and hydrochloric acid is used as the leaching solution because of its better leaching efficiency of gallium. Optimally, the leaching efficiency of gallium can reach 98%.

Keywords: gallium nitride; gallium; LED waste; LED recycling; leaching

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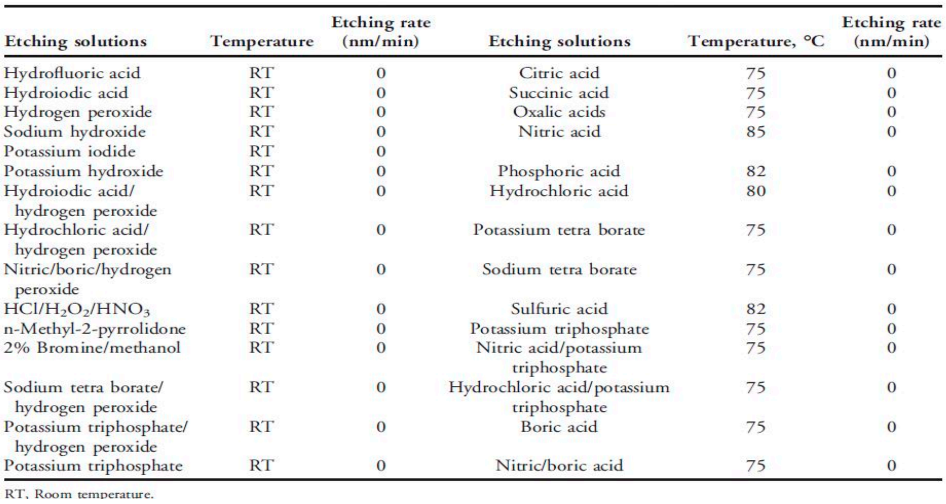
1. Introduction

Gallium and indium are essential ingredients for semiconductors and light-emitting diode (LED) LED chips, cell phones, photovoltaic generation panels, optical communication devices and computers [1]. Both of these metals are vital for the electronics industry because of their unique physical and chemical properties, and are classified as significant from an industrial application perspective and critical from a supply chain scarcity prospective [2,3].

Gallium is a soft, silvery metal which is used primarily in electronic circuits, semiconductors, and light-emitting diodes (LEDs). It is also useful in high-temperature thermometers, barometers, pharmaceuticals, and nuclear medicine tests [4]. Gallium technologies also have large power-handling capabilities and are used for cable television transmission, commercial wireless infrastructure, power electronics, and satellites. Gallium is also used for such familiar applications as screen backlighting for computer notebooks, flat-screen televisions, and desktop computer monitors [5]. In 2016, the global production of low-grade (99.99% pure) and high-purity (99.9999% and 99.99999% pure) Ga production was estimated to be 375 and 180 tons, respectively. Approximately 93% of low-grade Ga is refined in China. The principal producers of the high-purity metal were China, Japan, the United Kingdom, and the United States [6]. About 70 percent of the gallium was used in integrated circuits (both analog and digital). Optoelectronic devices represented the remaining 30 percent of gallium consumption [5]. For current technological trends, gallium is irreplaceable by other materials/metals, and triggers global competitions to ensure steady supply [7]. According to a recent report published by the united nations environment program (UNEP), less than 1% of end-of-life (EOL) gallium and indium bearing materials are being recycled [2,3]. Gallium is used in a wide variety of products that have microelectronic components containing either gallium arsenide (GaAs) or gallium nitride (GaN) [5]. Due to the low solubility of nitrogen in gallium and the high vapor pressure of nitrogen on GaN, the native substrate of GaN is not available in large quantities. The GaN is a crystal of high bond energy that is equal to 7.72 eV/molecule, which results in higher melting temperature and good thermal stability [8,9]. The value of sales for the GaN power device market was expected to reach $178 million by 2015 at an annual growth rate of nearly 29 percent [10]. In 2012, imports of gallium and GaAs wafers, which were valued at about $32 million, continued to satisfy almost all U.S. demand for gallium. GaAs and GaN electronic components represented about 99 percent of domestic gallium consumption [5]. The value of worldwide GaAs device consumption increased by about 7% to $7.5 billion in 2015 owing to a growing wireless telecommunications infrastructure in Asia; growth of feature-rich, application-intensive, third- and fourth-generation (3G, 4G) "smartphones", which employ up to 10 times the amount of GaAs as standard cellular handsets; and robust use in military radar and communications applications. Cellular applications accounted for approximately 53% of total GaAs device revenue and wireless communications accounted for 27%. Various automotive, consumer, fiber-optic, and military applications accounted for the remaining revenue [11]. By yearend 2016, the GaN radio frequency device market was expected to reach $340 million, a 13% increase from that of 2015, and was forecast to increase at an average annual rate of 17% to reach $630 million in 2020 [11]. The gallium nitride semiconductor device market is expected to reach USD 22.47 Billion by 2023 from USD 16.50 Billion in 2016, at a compound annual growth rate (CAGR) of 4.6% during the forecast period between 2017 and 2023 [12,13]. The total GaN semiconductor (including both, power and opto semiconductors) market revenue is expected to reach $2.6 billion by 2022, which indicates massive production [14,15].

Recovery of gallium from metal-organic chemical vapor deposition (MOCVD) dust reported in the literature are very scarce, so it is an important problem needing to be addressed and the hydrometallurgy process can be a solution to the issue. High refractive index, mechanical stability, high heat capacity, and thermal conductivity make the GaN waste difficult to treat and recycle. Several authors have reported that etching GaN material is a challenge; hence, the chemical leaching of GaN is an essential and primary stage for recycling or treatment of the waste. Figure 1 adopted from Zhuang, D. and Edgar, J. [16] shows the leaching behavior of GaN with various mineral acids, organic acids, and alkalis at room temperature and higher temperature which indicated that it is impossible to leach the refractory GaN without any pretreatment [16].



Etching solutions	Temperature	Etching rate (nm/min)	Etching solutions	Temperature, °C	Etching rate (nm/min)
Hydrofluoric acid	RT	0	Citric acid	75	0
Hydroiodic acid	RT	0	Succinic acid	75	0
Hydrogen peroxide	RT	0	Oxalic acids	75	0
Sodium hydroxide	RT	0	Nitric acid	85	0
Potassium iodide	RT	0			
Potassium hydroxide	RT	0	Phosphoric acid	82	0
Hydroiodic acid/ hydrogen peroxide	RT	0	Hydrochloric acid	80	0
Hydrochloric acid/ hydrogen peroxide	RT	0	Potassium tetra borate	75	0
Nitric/boric/hydrogen peroxide	RT	0	Sodium tetra borate	75	0
$HCl/H_2O_2/HNO_3$	RT	0	Sulfuric acid	82	0
n-Methyl-2-pyrrolidone	RT	0	Potassium triphosphate	75	0
2% Bromine/methanol	RT	0	Nitric acid/potassium triphosphate	75	0
Sodium tetra borate/ hydrogen peroxide	RT	0	Hydrochloric acid/potassium triphosphate	75	0
Potassium triphosphate/ hydrogen peroxide	RT	0	Boric acid	75	0
Potassium triphosphate	RT	0	Nitric/boric acid	75	0

RT, Room temperature.

Figure 1. Leaching GaN with Various Chemical Reagents.

GaN is employed principally in the manufacture of LEDs and laser diodes, power electronics, and radio-frequency (RF) electronics. Because GaN power transistors operate at higher voltages and with a higher power density than GaAs devices, the applications for advanced GaN-based products are expected to increase in the future [5]. The term urban mining-For gallium context means the recovery of valuables from waste electrical and electronic equipment, LED, and GaN waste from the semiconductor industry, which are known to contain appreciable amounts of this metal ingredient. Hence, the recycling of GaN-bearing EOL scrap is a sustainable, greener, and environment-friendly feasible option.

The research about recycling from gallium nitride around the world is very scarce. Especially, the literatures about recycling the valuable metals from the related waste are more rare, so it is important to develop and establish the recycling system from GaN waste. Recovery of gallium from secondary resources are well studied and are being used for industrial production [17–19]. Fang et al. studied recovery of gallium from coal fly ash by leaching followed by a precipitation & dissolution process [20]. Xu et al. has reported the recovery of gallium from phosphorus flue dust by leaching with spent sulfuric acid solution and precipitation [21]. Lee et al. has reported quantitative extraction of gallium from gallium arsenide scrap using HNO_3 as lixiviant at a concentration of 2.5 M [22]. Reductive leaching of gallium from zinc residue has been reported by Wu et al. [23], where quantitative leaching of gallium using SO_2 and H_2SO_4 as lixiviant has been reported. Furthermore, recovery of indium and (or) gallium through hydrometallurgical technique from thin-film solar panel [24], zinc sulfide concentrate [25], copper indium gallium diselenide [26], Indium Tin Oxide waste target [27] has also been reported.

Swain et al. [28] has reported using the acidic leaching method to recycle Ga rich metal-organic chemical vapor deposition residues, rich in GaN, InGaN and other Ga-compounds. They have found that other than GaN Ga phases were soluble in HCl, however solubility of GaN showed difficulties in leaching. Also, Swain and their research group [29] have reported processing GaN rich dust originated from the LED manufacturing. They have proposed two different methodologies.

The purpose of this study will focus on the leaching efficiency of the gallium from the GaN wastes. In this study, the GaN wastes were crushed by mortar grinding, ball milling for pre-treatment procedures. Material characteristic analysis accurately shows the proportion and composition of metal under investigation. Hydrometallurgy methods were being used for the acid leaching process. Different parameters that affect the leaching efficiency of gallium were discussed, such as the leaching agent, acidity, liquid-solid ratio, temperature, and reaction time. Based on the discussion of the results, the use of directly pressurized acid leaching will be effective. The leaching efficiency of gallium from the GaN waste was expected to be over 99%.

2. Materials and Methods

2.1. Materials, Reagents and Instruments

A sample of GaN waste from the LED industry was used for the experiment. A scanning electron microscope (SEM; Hitachi, Tokyo, Japan, S-3000N) and an energy-dispersive X-ray spectroscopy (EDS; Bruker, Billerica, MA, USA, XFlash6110) analyzed the surface characteristics of the GaN waste. The GaN waste powder was analyzed by a X-ray fluorescence analyzer (XRF; Spectro XEPOS, Kleve, Germany) as the semi-quantitation analysis and a X-ray diffraction (XRD; Dandong DX-2700, Dandong Fangyuan, China,) as the qualitative analysis. In order to understand the thermal property of the GaN waste, thermogravimetric analysis date-time group (TGA-DTG) was utilized. The GaN waste was ball milled for the pre-treatment of the leaching process. The GaN waste was ground with a mortar and milled in isopropanol by a planetary ball mill (Wisemix programmable ball mill). Zirconia-coated grinding bowls (200 mL) and Zirconia grinding balls (diameter = 3 mm) were used. The rotation speed was 150 r.p.m. and the milling time was 24 h. After ball milling the samples were dried in an oven at 80 °C for 4 h. The particle size distribution of the GaN waste after ball milling was tested by a laser particle size analyzer (LPSA; HORIBA, Kyoto, Japan, LA-350). In order to fully dissolve it, the GaN waste was put in aqua regia and hydrofluoric acid 5:1, at liquid-solid ratio 50 (mL/g) under 23 atm 220 °C for 4 h. The chemical composition of the GaN waste was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES; Varian, Palo Alto, CA, USA, Vista-MPX) and mainly contained 89.91% Al, 3.39% Fe, and 3.38% Ga. Therefore, it is valuable and important to recycle the gallium from the GaN waste.

2.2. Leaching

Leaching procedures were carried out in standard laboratory leaching equipment. The GaN waste was leached by different kinds of acids like nitric acid, sulfuric acid, hydrochloric acid, and hydrofluoric acid for the best acids selection. Three different kinds of alkaline salts $LiBO_2$, NaOH, Na_2CO_3, were added to the GaN for alkali-roasting. Furthermore, the leaching parameters such as acidity, solid-liquid mass ratio, pressure, reaction temperature and reaction time were investigated. Acidity was set from 0.25 to 12 (mole/L) with liquid-solid ratio from 10 to 50 (g/mL). The effect of temperature was set from 25 °C to 220 °C and the reaction time was set from 60 min to 270 min to get better leaching efficiency of gallium. The concentration of gallium in the leach liquor was measured using ICP-OES (Varian, Vista-MPX). The leaching efficiency of gallium was calculated according to formula (1):

$$X_B = (m_1/m_2) \cdot 100\% \tag{1}$$

where X_B is leaching rate, m_1 is the actual quantity of metal leaching, m_2 is the metal quantity of raw material.

3. Results

3.1. Waste Characteristic Analysis

The GaN waste is mainly divided into two sides in Figure 2. One side is based on Al_2O_3 for matrix layer and the other side is the coating layer, which contains a GaN thickness of about 50 µm. Figure 3 shows the microstructure and the composition of GaN waste analyzed by the scanning electron microscope (SEM; Hitachi, S-3000N) and energy-dispersive X-ray spectroscopy (EDS; Bruker, XFlash6110). It is confirmed from Figure 3 that there are indeed two different layers in GaN waste. To ensure the waste contains GaN, X-ray diffraction (XRD; Dandong DX-2700) analysis was applied. Figure 4 shows the XRD diagram confirmed that the product contains Al_2O_3 and GaN. The composition of the GaN waste powder analyzed by X-ray fluorescence analyzer (XRF; Spectro XEPOS) is shown in Table 1. It could be found that the aluminum contained in the matrix layer is the main ingredient of the GaN waste and the waste also contains other metals such as iron, silicon chromium, nitrogen, and especially gallium.

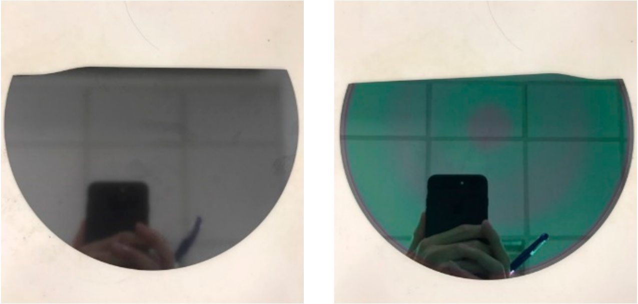
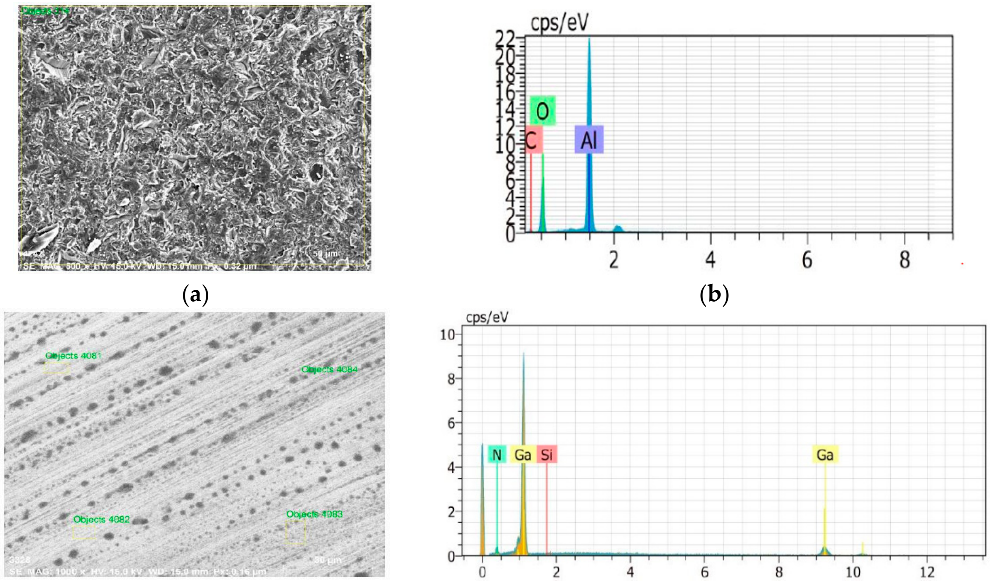

(**a**) (**b**)

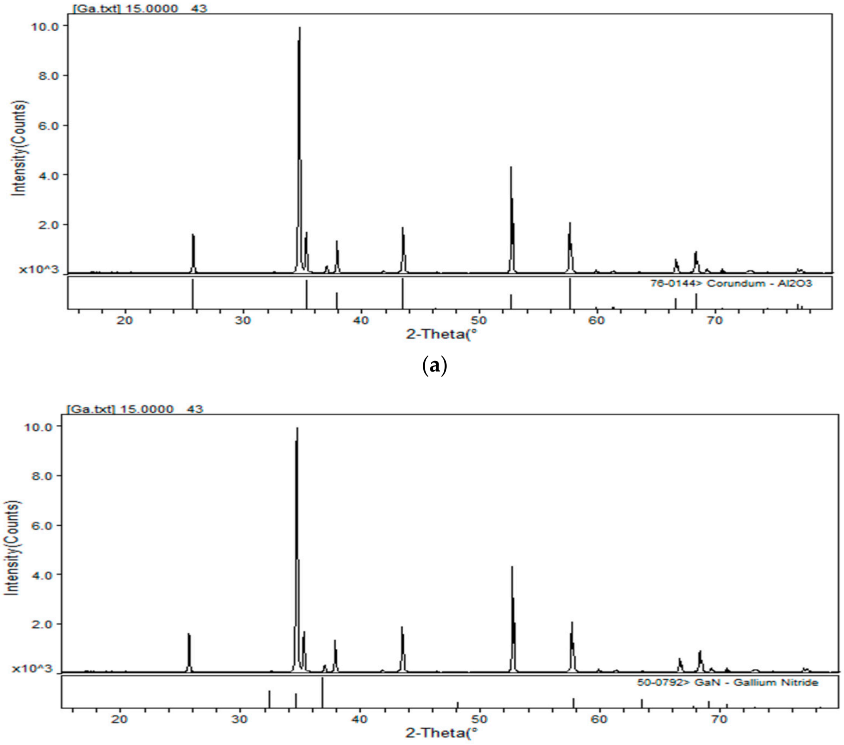
Figure 2. (**a**) The matrix layer of the GaN waste (**b**) The coating layer of the GaN waste.



(**a**) (**b**)

(**c**) (**d**)

Figure 3. (**a**) Microstructure of matrix layer by scanning electron microscope (SEM) analysis; (**b**) The composition of matrix layer by energy-dispersive X-ray spectroscopy (EDS) analysis; (**c**) Microstructure of coating layer by scanning electron microscope (SEM) analysis; (**d**) The composition of GaN coating layer by energy-dispersive X-ray spectroscopy (EDS) analysis.



(**a**)

(**b**)

Figure 4. (**a**) X-ray diffraction (XRD) analysis of the GaN waste with Al_2O_3 peak; (**b**) X-ray diffraction (XRD) analysis of the GaN waste with GaN peak.

Table 1. The composition of the GaN waste analyzed by X-ray fluorescence analyzer (XRF).

Element	Al_2O_3	Fe_2O_3	Ga	SiO_2	CrO_3	N
Content (%)	89.9	3.39	3.38	1.91	0.96	0.45

During a typical hydrometallurgical leaching process, particle size distribution affects the reaction process. Generally, the smaller particles have greater average specific surface area, which can increase the contact area between reagents and leachable material and accelerate the reaction rate. Furthermore, extracted metals might be embedded in big particles and shredding or milling can liberate the small particles. Therefore, a good understanding of particle size properties is essential for deciding whether pre-treatments such as shredding or milling are needed. Particle size distribution was measured in triplicate using a laser particles size analyzer (LPSA; HORIBA, LA-350). Figure 5 gives the mass distribution at different particle sizes of as-obtained GaN waste after ball milling. The GaN waste is in the range of 1–100 µm (more than 90%) after ball milling, indicating that it can be used as feed when utilized in conventional leaching.

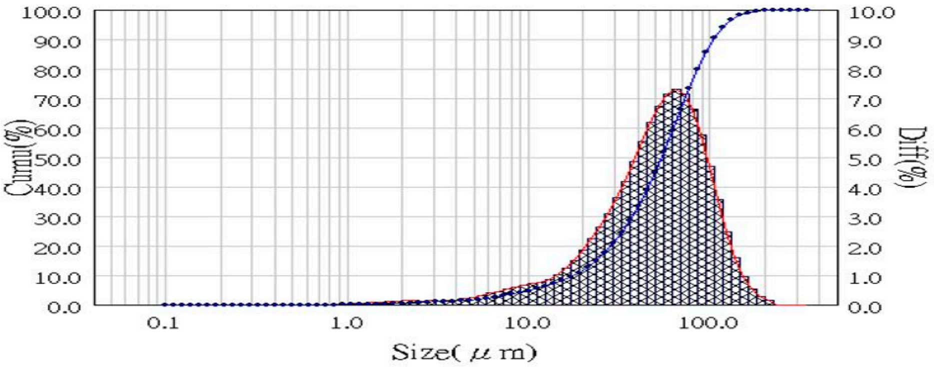


Figure 5. Particle size of the GaN waste by particle size distribution analyzer after ball milling.

To explore the phase change behavior and understand thermal property of the GaN waste, TGA-DTG was analyzed under air atmosphere with the heating rate 10 °C/min. Figure 6 depicts the corresponding TGA curve. Oxidation of metals from the GaN waste can be distinguished. The oxidation of metals starts at a low temperature (500 °C) and the weight increases at a relatively constant rate because the GaN waste contains other elements such as Fe, Si and Cr. The weight increases slightly between around 1000–1200 °C. Under an air atmosphere, the weight of the raw GaN waste increases continuously until the end of the analysis process at 1000 °C. This is owing to the oxidation of the GaN waste and the degraded temperature being around 750 °C.

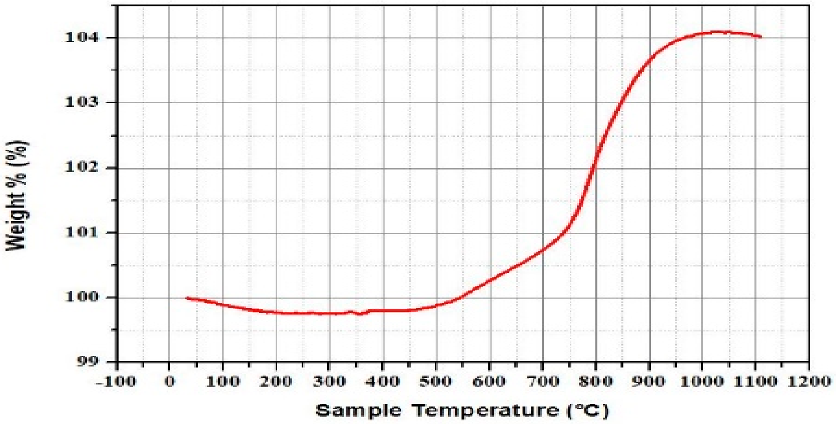


Figure 6. The thermogravimetric analysis (TGA) analysis of GaN waste with the heating rate 10 °C/min.

3.2. Leaching under Atmospheric-Pressure

In this section discusses the effects of nitric acid, sulfuric acid, hydrochloric acid, and hydrofluoric acid on the leaching efficiency of gallium from GaN waste at atmospheric-pressure(<1 atm).

The pre-treated GaN waste powders were reacted with four acid concentrations of 10 M at a liquid-solid ratio of 50 (mL/g) at 25 °C and 90 °C for 4 h respectively. Using ICP-OES analysis determines the leaching efficiency of gallium in different kinds of acid agents.

The results of Table 2 indicated that hydrochloric acid had the most effective leaching reaction for gallium under the same reaction conditions. With the increased temperature from 25 °C to 90 °C, the leaching efficiency of gallium in hydrochloric acid is much higher than that of other three acids. Therefore, hydrochloric acid was selected as a leaching agent. But the leaching efficiency of gallium is still very low (<10%) at atmospheric-pressure(<1 atm).

Table 2. The leaching efficiency of gallium (%) with four acid with concentrations 10 M at liquid-solid ratio of 50 (mL/g) at 25 °C and 90 °C for 4 h respectively.

Temperature	**HNO_3**	**H_2SO_4**	**HCl**	**HF**
25 °C	0.17	1.04	3.16	1.13
90 °C	1.36	3.28	8.9	2.73

3.3. Alkaline-Roasting Leaching

From the method of alkali-roasting, three different kinds of alkaline salts, $LiBO_2$, NaOH, and Na_2CO_3, were added to the GaN waste with the mass ratio of 10:1, respectively, at 1000 °C for 8 h. After the alkali-roasting, dissolving these samples in H_2O, HNO_3, H_2SO_4, HCl, and HF with concentrations of 10 M, respectively, at a liquid-solid ratio of 50 (mL/g) at 90 °C for 4 h.

From Table 3 it could be found that the alkaline-roasting leaching method with pre-alkali roasting is better than leaching at atmospheric-pressure. The leaching efficiency of gallium in HCl is higher than that of other acid agents. NaOH is the most effective alkaline flux, and $LiBO_2$ is the least. This is because NaOH melts at a much lower temperature than $LiBO_2$ or Na_2CO_3, so the NaOH has more opportunity to attack the material. However, the use of HCl after alkali-roasting could not dissolve the GaN waste completely at one time because the residues after filtration must be calcined with the alkaline salts and added to the HCl for several times in order to completely dissolve the GaN waste according to B. Swain [28].

Table 3. The leaching efficiency of gallium (%) with acid concentrations 10 M at liquid-solid ratio 50 (mL/g) at 90 °C for 4 h after alkali roasting.

Acid Agent/Alkali Agent	**$LiBO_2$**	**NaOH**	**Na_2CO_3**
H_2O	17.3	24.5	21.6
HNO_3	36.6	45.2	41.7
H_2SO_4	37.8	47.5	43.7
HCl	52.9	73.3	62.4
HF	34.4	52.5	43.1

3.4. Pressurized Leaching

3.4.1. Effect of Concentration and Pressure

This section explored the effects of different concentrations of HCl on the leaching efficiency of gallium. Figure 7 shows that the leaching efficiency of gallium is very low at 1 atm (25 °C). But when the pressure is raised to 23 atm (220 °C), the leaching efficiency of gallium increased significantly at the same concentration of HCl, so the pressurization method can reduce the amount of HCl used in the leaching reaction and achieve a higher leaching efficiency. Therefore, this experiment will use the pressurized leaching method.

In order to examine the effect of the HCl concentration on the leaching efficiency of gallium in GaN waste, the concentration of HCl was varied from 0.05 M to 12.0 M at a liquid-solid ratio of 50 (mL/g) at 25 °C (1 atm) and 220 °C (23 atm) for 4 h, respectively. Figure 7 indicates that when the temperature is 25 °C (1 atm), the leaching rate is very low for all concentrations of HCl, even up to 10 M. However, when the temperature rises to 220 °C and the vapor pressure is at 23 atm, the leaching efficiency can be very high (>98%) until the concentration of HCl is diluted from 12 M to 0.25 M. Therefore, 0.25 M HCl was used as the best concentration parameter for the pressurized leaching method because all the gallium was leached at this condition.

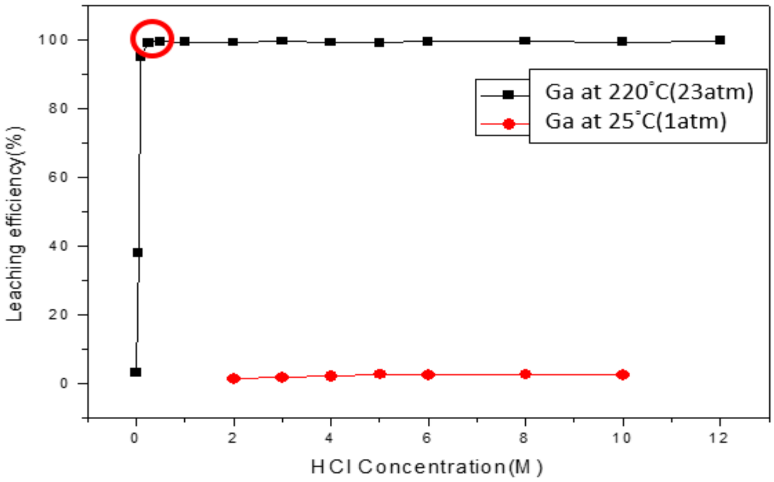


Figure 7. Effect of HCl concentration on the leaching efficiency of gallium at liquid-solid ratio 50 (mL/g) at 25 °C (1 atm) and 220 °C (23 atm) for 4 h respectively.

3.4.2. Effect of Liquid-Solid Ratio

Figure 8 is the effect of liquid-solid ratio on leaching efficiency of gallium from the GaN waste using 0.25 M HCl at 220 °C for 4 h. The leaching efficiency of gallium was dramatically increased while the liquid-solid ratio increased from 10 (mL/g) to 30 (mL/g). The reason was that when the liquid-solid ratio was low, there was insufficient acid to react in the process. In other words, when the liquid-solid mass ratio was high, there was more acid ready to react and available to obtain a higher leaching efficiency. While the liquid-solid ratio was from 30 to 50 (mL/g), the leaching of gallium was complete. Hence, the liquid-solid ratio of 30 (mL/g) was chosen as optimum to save the amount of HCl used. Because at this condition all gallium could be leached, the addition of more acid could not leach more gallium.

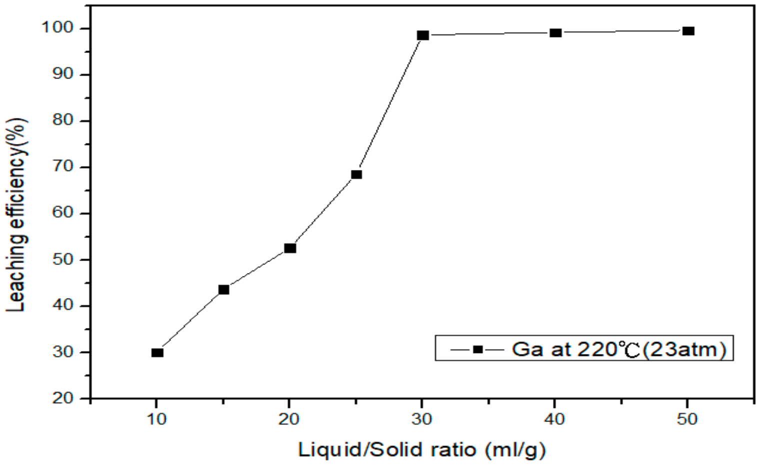


Figure 8. Effect of liquid/solid ratio on the leaching efficiency of gallium in 0.25 M HCl at 220 °C for 4 h.

3.4.3. Effect of Temperature

The effect of temperature on the leaching efficiency of Ga from the GaN waste using 0.25 M HCl with the liquid-solid ratio 30 (mL/g), for 4 h is shown in Figure 9. The leaching efficiency of gallium increases with the increasing temperature because the temperature has a great effect on the leaching process. The higher temperature could raise the speed of molecular motion and enlarge the energy of the particle collision. The vapor pressure also increased with temperature, which leads to the HCl reacting more thoroughly with gallium under the same reaction time. The result determined 200 °C for the best parameter to leach because it displayed no significant increase of leaching efficiency while the temperature increased above 200 °C (15 atm).

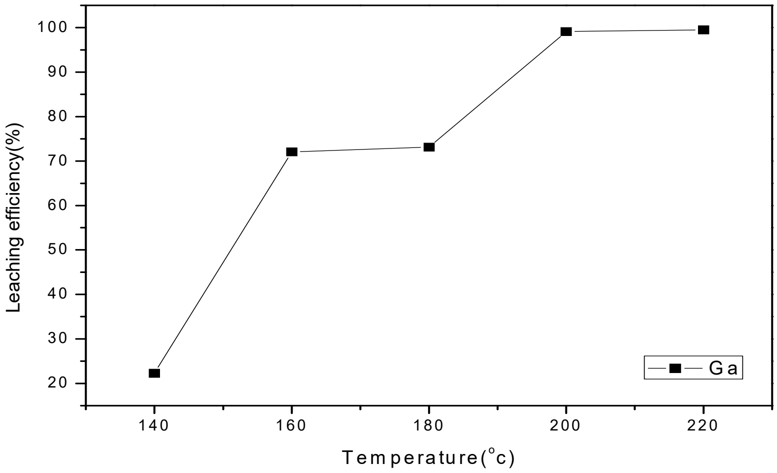


Figure 9. Effect of temperature on the leaching efficiency of gallium in 0.25 M HCl with the liquid-solid ratio 30 (mL/g), for 4 h.

3.4.4. Effect of Reaction Time

Figure 10 shows the effect of leaching efficiency with reaction time utilizing 0.25 M HCl with a liquid-solid ratio of 30 (mL/g) at 200 °C. The leaching efficiency of gallium increased dramatically from 60 min to 150 min. The reason is that with the increase of leaching time, more and more surfaces of unreacted particle cores would react with the HCl. The leaching efficiency of gallium was complete and stopped increasing after 180 min. Consequently, the leaching time was carried out at 180 min.

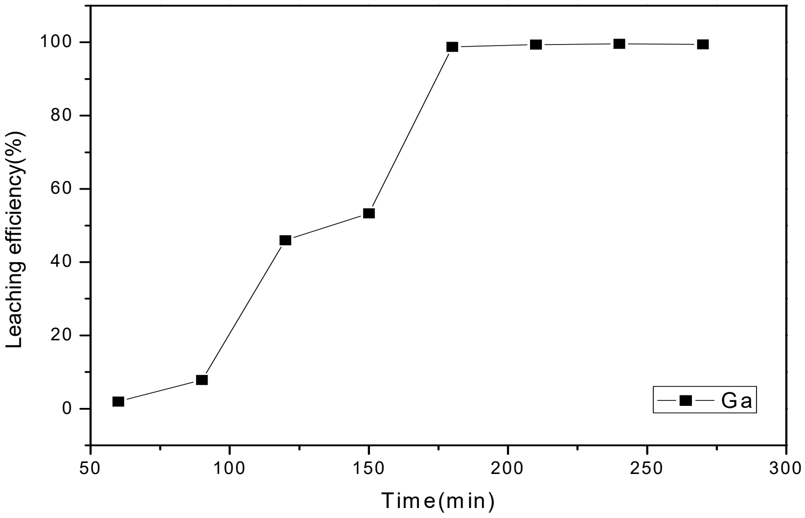


Figure 10. Effect of reaction time on the leaching efficiency of gallium in 0.25 M HCl with liquid-solid ratio 30 (mL/g) at 200 °C.

4. Conclusions

The leaching method of gallium from the GaN waste has proven in this work to be successful and effective. The experimental flowchart of the best leaching method is shown in Figure 11. In this study, several leaching methods were used to discover the most efficient leaching rate of gallium in GaN waste. The GaN waste, generated from industrial GaN manufacturing, is a refractory material, but it can also be considered an important secondary resource of gallium. The particle size of the pre-treatment GaN waste is concentrated in the range of 1–100 μm (>90%), indicating that it can conduct in the leaching experiments. Although alkali-roasting leaching can leach the GaN waste, it takes a lot of complicated procedures and time to completely leach gallium. Comparing various leaching methods, the recovery of gallium from GaN waste under high pressure has proven to be the most effective leaching method in this study. Table 4 shows the optimal conditions of the leaching procedure is 0.25 mol/L of HCl with a liquid-solid mass ratio of 30 mL/g at 200 °C (15 atm) for 180 min and about 98.46% gallium was leached. This study indicated that those parameters were significant to analyze the leaching behavior. Overall, the recovery of gallium from GaN waste by acid leaching under high pressure was effective.

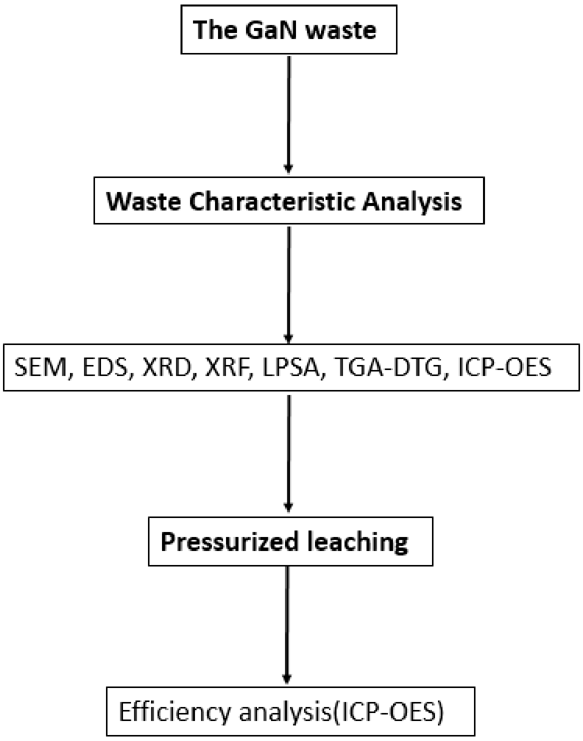


Figure 11. The flowchart of the best leaching method.

Table 4. The optimal parameters of the leaching process.

Material	[HCl]	Liquid-Solid Ratio	Temperature	Leaching Time
GaN waste	0.25 M	30 mL/g	200 °C (15 atm)	180 min

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