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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 LED industry which contains GaN, it is expected that there will be a large amount of related wastes in the future. Especially the gallium has extremely high value of economic, therefore, it is necessary to establish the recycling system of the GaN waste. However, GaN is a direct-gap semiconductor and with high energy gap, high hardness, and high melting point make it difficult to recycle. Therefore, this study will analyze the physical characteristics of LED wastes containing GaN and carry out various leaching method to leach the valuable metals from the waste optimally. Different acids are used to find out the best reagent for leaching the gallium. Different experimental parameters are discussed such as the effect of the different acid agents , concentration, pressure, solid-liquid mass ratio, temperature, and time which influence the leaching efficiency of the gallium. In this study, various leaching methods which effect the leaching efficiency of the gallium are compared and the advantages and disadvantages are discussed. Finally, pressurized acid leaching method is preferred to leach the GaN waste, and hydrochloric acid is used as the leaching solution because of its better leaching efficiency of gallium. Eventually, the leaching efficiency of the gallium can reach to 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 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, are classified as significant from industrial application and critical from supply chain scarcity prospective [2,3].

Gallium is a soft, silvery metal which 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), including those in defense applications, high-performance computers, and telecommunications. Optoelectronic devices for use in aerospace and telecommunications applications, consumer goods, industrial equipment, medical equipment, and so forth, as well as a small amount for research and development, represented the remaining 30 percent of gallium

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consumption [5]. For current technological trend, gallium is irreplaceable by other materials /metals, unique performance, limited natural resources, ever growing consumers' demand and potential to substantially increase in the future demands for gallium, triggers global competitions to ensure steady supply[7]. According to a recent report published by the united nations environment programme (UNEP),less than 1% of EOL gallium and indium bearing materials 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]. A wide variety of products have microelectronic components that contain either gallium arsenide (GaAs) or gallium nitride (GaN)[5].

Due to low solubility of nitrogen in gallium and 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]. Explained technique reduces dislocation densities in their crystal structure; make the GaN a refractory material having a wide band gap[9].The compound gallium nitride (GaN) is used as a semiconductor in Blu-ray technology, mobile phones and pressure sensors for touch switches[4]. Owing to the large power-handling capabilities, highswitching frequencies, and higher voltage capabilities of GaN technology, GaN-based products, which historically have been used in defense and military applications, have begun to gain acceptance in the cable television transmission, commercial wireless infrastructure, power electronics, and satellite markets. 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 fourthgeneration (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 CAGR of 4.6% during the forecast period between 2017 and 2023 [12,13]. The total GaN semiconductors(including both, power and opto semiconductors) market revenue is expected to reach $2.6 billion by 2022, indicates massive production[14,15].

Recovery of gallium from the gallium rich waste MOCVD dust reported in literature are vary scarce, an important problem need 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, a material of interest as semiconductor material, which make GaN, either from the LED industry waste or from EOL GaN-bearing devices, difficult to treat and recycle. Several authors have reported that etching of GaN material is a challenge; hence, the chemical leaching of GaN is an essential and primary stage for recycling or treatment of the waste. Table I (adopted from Zhuang et. al) shows the leaching behavior of GaN with various mineral acids, organic acids, and alkalis at room temperature and higher temperature whih indicated that it is impossible to leach the refractory GaN without any pretreatment. [16].

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]Gallium nitride (GaN) principally was used to manufacture optoelectronic devices. ICs accounted for 60% of domestic gallium consumption and optoelectronic devices accounted for 40%. Approximately 70% of the gallium consumed in the United States was contained in GaAs and GaN wafers[11].Urban mining-For gallium context, the term means recovery

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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, 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 being used for industrial production [17e19]. Fang et al. studied recovery of gallium from coal fly ash by leaching followed by a precipitation edissolution process [20]. Xu et al. has reported 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], ITO waste target [27] has also been reported.

Swain et al. [28] has reported using acidic leaching method to recycle Ga rich metal-organic chemical vapour 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. 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 results of the two different methods, that the leaching efficiency of the gallium more than 70 w/w% could be achieved. In one process first LED industry dust has been acid leached at the optimum condition, subsequently leach residue was mixed with Na_2CO_3, ball milled followed by annealing, then again leached to recover gallium. In the second process, LED industry dust was mixed with Na_2CO_3, then ball milled followed by annealing and finally leached to achieve the quantitative leaching. However, the leaching process is too complicated which lead to the waste of the solvent and the leaching efficiency was too low.

The propose 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 motar grinding, ball milling for pre-treatment procedures. Material characteristic analysis accurately shows that the proportion and composition of metal which are investigated. Hydrometallurgy methods were being used for acid leaching process. In this consequence, the use of different parameters exactly discusses on leaching efficiency of gallium. Different parameters which affect the leaching efficiency of gallium were discussed such as the leaching agent, acidity, solid-liquid ratio, temperature and reaction time were experimented. Based on the discussion of the experiment results, the use of directly pressurized acid leaching will be effective. The leaching efficiency of gallium from the GaN wastes was expected to be over 99%.

2. Materials and Methods

2.1. Materials, reagents and instruments

The sample of GaN waste from LED industry was used for the experiments. The scanning electron microscope (SEM; Hitachi, S-3000N) and energy-dispersive X-ray spectroscopy (EDS; Bruker, XFlash6110) analyzed the surface characteristics of the GaN waste. The GaN waste powder was analyzed by X-ray fluorescence analyzer (XRF; Spectro XEPOS) as semi-quantitation analysis and X-ray diffraction (XRD; Dandong DX-2700) as qualitative analysis. In order to understand the thermal property of the GaN waste, TGA-DTG was utilized.The GaN waste was ball milled for the pre-treatment of 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=3mm) were used. The rotation speed was 150

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r.p.m. and milling time was 24 hours. After ball milling the samples were dried in an oven at 80 °C for 4 hours. The particle size distribution of the GaN waste after ball milling was tested by laser particles size analyzer (LPSA; HORIBA, LA-350). In order to fully dissolve, the GaN waste was put in aqua regia and hydrofluoric acid 5:1, at liquid-solid ratio 50(ml/g) under 23atm 220 ˚C for 4 hours. The chemical composition of the GaN waste was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES; Varian, 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 minutes to 270 minutes 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):

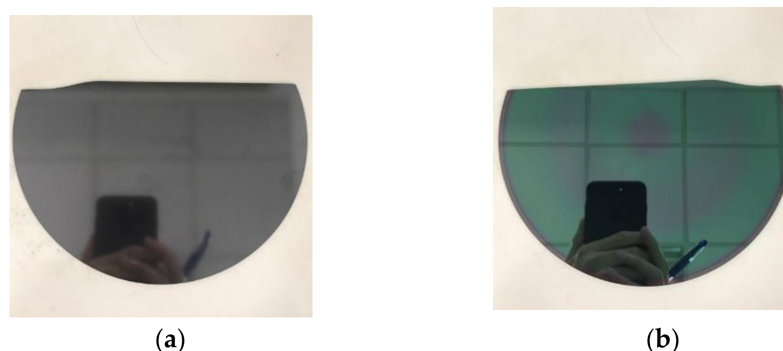
$$X_B = (m_1 / m_2) \cdot 100\% \quad (1)$$

where X_B is leaching rate, m_1 is actually quality of metal leaching, m_2 is metal quality of raw material.

3. Results

3.1. Waste Characteristic Analysis

The GaN waste is mainly divided into two sides in Figure 1. One side is based on Al_2O_3 for matrix layer and the other side is the coating layer which contains GaN about thickness of 50 um. Figure 2 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 2 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 3 shows the XRD diagram confirmed that the products 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 contains 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 1. (**a**) The matrix layer of the GaN waste (**b**) The coating layer of the GaN waste

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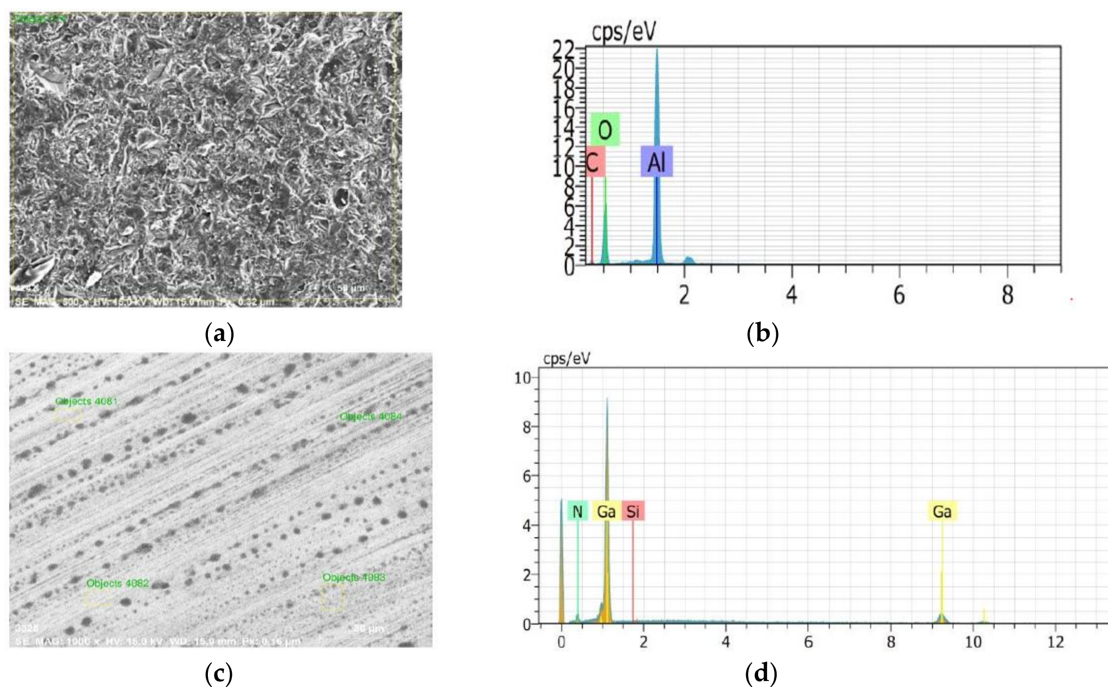
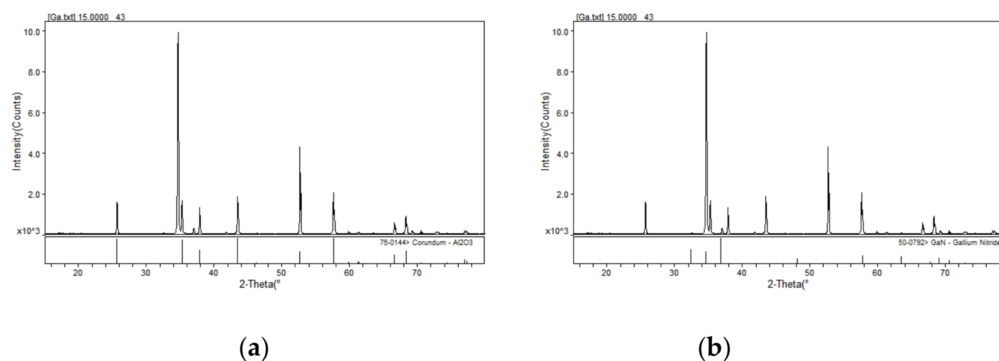


Figure 2. (**a**) Microstructure of matrix layer by scanning electron microscope (SEM) analysis. (**b**) The composition of matrix layer by energy-dispersive X-ray spectroscopy (EDS) analysis. (**c**) Microstructure of coating layer by scanning electron microscope (SEM) analysis. (**d**) The composition of GaN coating layer by energy-dispersive X-ray spectroscopy (EDS) analysis.



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

Figure 3. (**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	Fe	Ga	Si	Cr	N
Content(%)	89.9	3.39	3.38	1.91	0.96	0.45

Particle size distribution of GaN waste during a typical hydrometallurgical leaching process, particle size distribution might affect the reaction process. Generally, the smaller particles have greater average specific surface area, which can increase the contact area between reagents and leachate, and further to accelerate the reaction rate, and vice versa. Furthermore, extracted metals might be embedded into big particle and shredding or milling can liberated the small particles size. Therefore, a good understanding of particle size properties is essential for deciding that pre-treatments such as shredding or milling are needed. Particle size distribution was measured three times under parallel conditions using laser particles size analyzer (LPSA; HORIBA, LA-350). Figure 4 gives the mass distribution at different particle sizes of as-obtained GaN waste after ball milling. The results show that 1-60 μm size items form more than 70% of

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the total mass. In order to reach a better understanding of the particle size distribution of the GaN waste, the figure 4 give the cumulative mass fraction of as-received GaN waste. It is clear that 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.

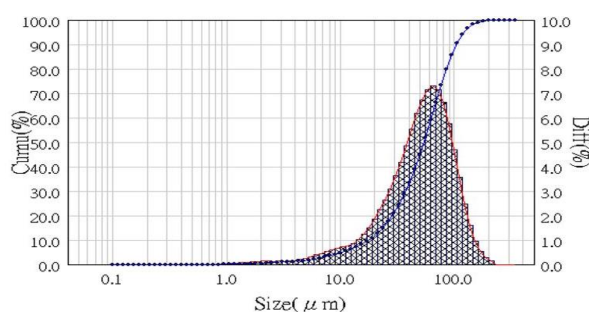

Figure 4. Particle size of the GaN waste by particle size distribution analyzer after ball milling.

To future explore the phase change behaviour and understand thermal property of as-obtained GaN waste, TGA-DTG was analyzed under air atmosphere. Figure 5 depicts the corresponding TGA curve. Under air atmosphere, the weight of the raw GaN waste increases continuously until the end of the analysis process. Two main stage, i.e. oxidation of metals and oxidation of GaN (from around 750 °C) can be distinguished. The oxidization of metals starts at a low temperature and the weight increases at a relatively constant rate. The oxidation of GaN generally starts at around 750 °C, and the weight increases slightly between around 1050-1200 °C. This is owing to the full complete oxidization of GaN. From the TGA thermal analysis, it can be known that the melting point of the GaN waste is above 900℃.

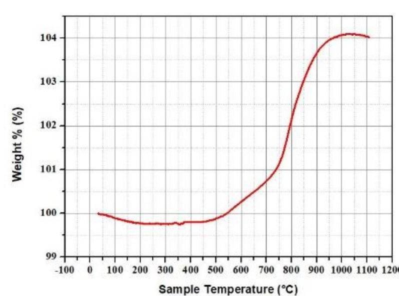

Figure 5. The TGA analysis of GaN waste.

3.2. Atmospheric-pressure Leaching

In this section discusses the effects of nitric acid, sulfuric acid, hydrochloric acid, and hydrofluoric acid on the leaching efficiency of gallium in GaN waste on atmospheric-pressure(<1atm). The pre-treated GaN waste powders were reacted with four acid with concentrations 10M at liquid-solid ratio of 50(ml/g) at 25°C and 90°C for 4 hours respectively. Using ICP-OES analysis to require the leaching efficiency of gallium in different kinds of acid agent.

The results of Table 2 and Table 3 indicated that only hydrochloric acid had obvious 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 leaching agent. But the leaching efficiency of gallium is still very low (<10%) on atmospheric-pressure(<1atm) because of the low solubility of gallium in nitrogen .

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Table 2. The leaching efficiency of gallium in different acids at 25°C

Acid agent	HNO_3	H_2SO_4	HCl	HF
Leaching efficiency of Ga(%)	0.17	1.04	3.16	1.13

Table 3. The leaching efficiency of gallium in different acids at 90°C

Acid agent	HNO_3	H_2SO_4	HCl	HF
Leaching efficiency of Ga(%)	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 LiBO2, NaOH, Na_2CO_3, were added to the GaN waste with the mass ratio 10:1 respectively at 1000℃ for 8 hours. After the alkali-roasting, dissolving these samples in H_2O, HNO_3, H_2SO_4 , HCl, and HF with concentrations 10M respectively at liquid-solid ratio of 50(ml/g) at 90°C for 4 hours.

From table 4. 5. 6. 7 .8. it could be found that alkaline-roasting leaching method with pre-alkali roasting is better than the atmospheric-pressure leaching method. The leaching efficiency of gallium in HCl is higher than that of other acids agent. However, the use of HCl after alkali-roasting couldn't 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 which can completely dissolve the GaN waste. Therefore, the residue after alkaline-roasting leaching must be roasted with alkaline salt repeatedly to dissolve the gallium nitride waste completely. It takes a lot of time to dissolve the GaN waste from alkaline-roasting leaching method.

Table 4. The leaching efficiency of gallium in H_2O after alkali roasting.

Alkali agent	LiBO2	NaOH	Na_2CO_3
Leaching efficiency of Ga(%)	17.3	24.5	21.6

Table 5. The leaching efficiency of gallium in HNO_3 after alkali roasting.

Alkali agent	LiBO2	NaOH	Na_2CO_3
Leaching efficiency of Ga(%)	36.3	45.2	41.7

Table 6. The leaching efficiency of gallium in H_2SO_4 after alkali roasting.

Alkali agent	LiBO2	NaOH	Na_2CO_3
Leaching efficiency of Ga(%)	37.8	47.5	43.7

Table 7. The leaching efficiency of gallium in HCl after alkali roasting.

Alkali agent	LiBO2	NaOH	Na_2CO_3
Leaching efficiency of Ga(%)	52.9	73.3	62.4

Table 8. The leaching efficiency of gallium in HF after alkali roasting.

Alkali agent	LiBO2	NaOH	Na_2CO_3
Leaching efficiency of Ga(%)	34.4	52.5	43.1

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3.4. Pressurized Leaching

3.4.1. Effect of Concentration and Pressure

This section explored the effects of different concentration of HCl on leaching efficiency of gallium. The figure 6 shows that the leaching efficiency of gallium is very low at 1atm(25 ˚C). But when the pressure rised to 23atm(220 ˚C), the leaching efficiency of gallium increased significantly at the same concentration of HCl, so pressurization method can reduce the amount of HCl used in the leaching reaction and achieve a higher leaching efficiency. Therefore, this experiment will use pressurized leaching method.

In order to examine the effect of HCl concentration on leaching efficiency of gallium in GaN waste, the concentration of HCl was varied from 0.05 M to 12.0 M at liquid-solid ratio 50 (ml/g) at 25 ˚C(1atm) and 220 ˚C(23atm) for 4 hours respectively. The figure 6 indicates that when the temperature is 25 ˚C(1atm), the leaching rate is very low even the concentration of HCl rise up to 12M. However, when the temperature rise to 220 ˚C and the vapor pressure is at 23atm, the leaching efficiency can be very high (>98%) until the concentration of HCl is diluted from 12M to 0.25M. Therefore, 0.25M HCl was used as the best concentration parameter for pressurized leacheing method because all the gallium was leached at this condition.

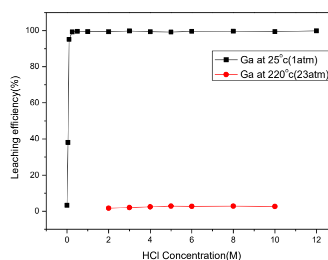

Figure 6. Effect of HCl concentration on the leaching efficiency of gallium.

3.4.2. Effect of Liquid-Solid Ratio

Figure 7 is the effect of liquid-solid ratio on leaching efficiency of gallium from the GaN waste using 0.25M HCl at 220 ˚C for 4 hours. The leaching efficiency of gallium was dramatically increase while 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 no sufficient 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 higher leaching efficiency. While the liquid-solid ratio was from 30 to 50(ml/g), the leaching rate of gallium was saturated. Hence, the liquid-solid ratio was chosen 30 (ml/g) as optimum to save the amount of HCl used. Because at this condition all gallium could be leached, the addition of more acid couldn't leach more gallium.

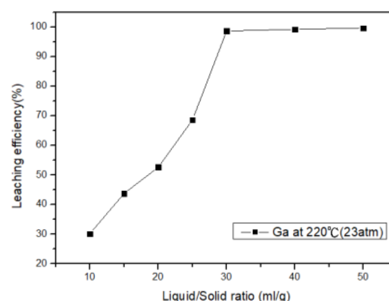

Figure 7. Effect of liquid/solid ratio on the leaching efficiency of gallium.

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3.4.3. Effect of Temperature

The effect of temperature on leaching efficiency of Ga from the GaN waste using 0.25M HCl with the liquid-solid ratio 30(ml/g), for 4 hours is shown in figure 8. 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 lead to HCl can reacts more thoroughly with gallium under the same reaction time. The result determined 200 ˚C for the best parameter to leach because no significant increase of leaching efficiency while temperature increased above 200 ˚C(15atm).

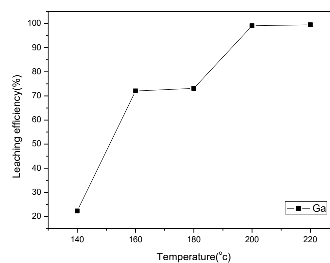

Figure 8. Effect of temperature on the leaching efficiency of gallium.

3.4.4. Effect of Reaction Time

Figure 9 shows the effect of leaching efficiency with reaction time utilizing 0.25 M HCl with liquid-solid ratio 30(ml/g) at 200 ˚C. The leaching efficiency of gallium rise dramatically from 60 min to 150 min. The reason is that with the increase of leaching time, more and more surface of unreacted particle core would react with HCl. The leaching efficiency of gallium increased slightly from 120 min to 150 min because the reaction was overcoming the energy barrier at this time. The leaching efficiency of gallium was in balance and stopped increasing after 180 min. Consequently, the leaching time was carried out at 180 min.

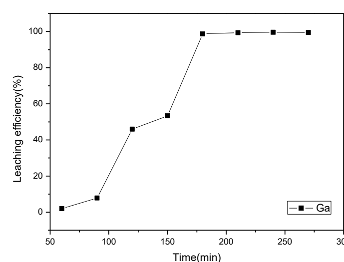

Figure 9. Effect of reaction time on the leaching efficiency of gallium.

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4. Conclusion

The leaching method of gallium from the GaN waste has been proven in this work to be successful and effective. The suggested leaching process is shown in Figure 10. In this study, several leaching methods were used to find out the most efficient leaching rate of gallium in GaN waste. The GaN waste, generated from the industrially of GaN manufacturing, is a refractory material, but it can be considered as an important second resource of gallium. The particle size of 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 gallium nitride waste, it takes a lot of complicated procedures and time to leach gallium completely. Comparing various leaching methods, the recovery of gallium from GaN waste which used pressurized acid leaching has been proved to be effective. The optimal conditions of leaching procedure are 0.25 mol/L of HCl with liquis-solid mass ratio of 30 ml/g at 200 ˚C (15atm) for 180 minutes and about 98.46% gallium was leached. The statistical investigation demonstrated that the selected parameters were the high level of linear relationship in leaching process and indicated that those parameters were significant to analyze the leaching behavior. Overall, the recovery of gallium from GaN waste by pressurized acid leaching was effective.

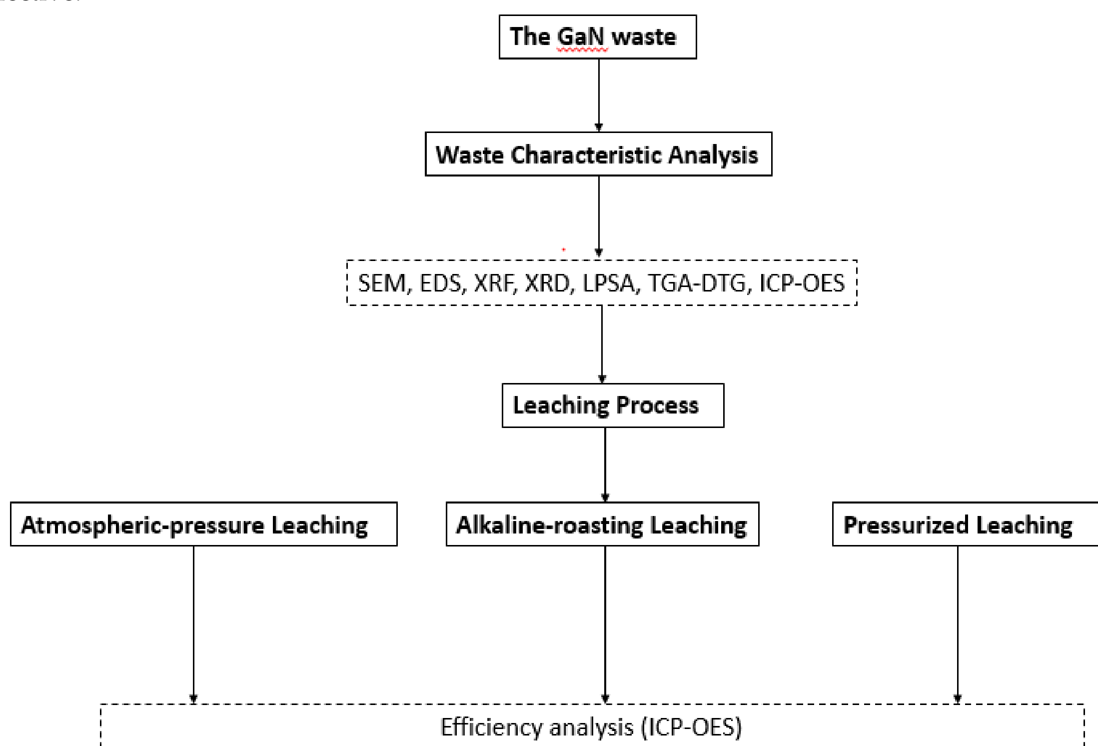

Figure 10. The flowchart of this study.

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