Environmental Research 140 (2015) 704–713

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

Valorization of GaN based metal-organic chemical vapor deposition dust a semiconductor power device industry waste through mechanochemical oxidation and leaching: A sustainable green process

Basudev Swain [a,*], Chinmayee Mishra [a], Chan Gi Lee [a], Kyung-Soo Park [a], Kun-Jae Lee [b]

[a] Institute for Advanced Engineering (IAE), Advanced Materials & Processing Center, Yongin-Si 449-863, Republic of Korea
[b] Department of Energy Engineering, Dankook University, Cheonan 330-714, Republic of Korea

ARTICLE INFO

Article history:
Received 4 April 2015
Received in revised form
9 May 2015
Accepted 2 June 2015
Available online 19 June 2015

Keywords:
Mechanochemical oxidation
Metal-organic chemical vapor deposition dust
Waste Valorization
Recycling
Gallium leaching

ABSTRACT

Dust generated during metal organic vapor deposition (MOCVD) process of GaN based semiconductor power device industry contains significant amounts of gallium and indium. These semiconductor power device industry wastes contain gallium as GaN and $Ga_{0.97}N_{0.9}O_{0.09}$ is a concern for the environment which can add value through recycling. In the present study, this waste is recycled through mechanochemical oxidation and leaching. For quantitative recovery of gallium, two different mechanochemical oxidation leaching process flow sheets are proposed. In one process, first the $Ga_{0.97}N_{0.9}O_{0.09}$ of the MOCVD dust is leached at the optimum condition. Subsequently, the leach residue is mechanochemically treated, followed by oxidative annealing and finally re-leached. In the second process, the MOCVD waste dust is mechanochemically treated, followed by oxidative annealing and finally leached. Both of these treatment processes are competitive with each other, appropriate for gallium leaching and treatment of the waste MOCVD dust. Without mechanochemical oxidation, 40.11 and 1.86 w/w% of gallium and Indium are leached using 4 M HCl, 100 °C and pulp density of 100 kg/m^{3,} respectively. After mechanochemical oxidation, both these processes achieved 90 w/w% of gallium and 1.86 w/w% of indium leaching at their optimum condition.

1. Introduction

GaN based semiconductor powder devices, namely laser diodes, power electronics, and radio frequency (RF) electronics, have provided significant growth in recent years for advanced GaN-based products. For the year 2012, the worldwide GaN-device market was approximately $100 million, and the value of the worldwide GaN power semiconductor market increased to an estimated $12.6 million in 2012, a fivefold increase from $2.5 million in 2011 (Jaskula, 2014). The metal-organic chemical vapor deposition (MOCVD) technique has been used for the epitaxial growth of GaN and InGaN for active layers in the fabrication of light emitting diode (LED) chips in the industry. The MOCVD has become the technology of choice for varieties of devices such as lasers, laser diodes, light-emitting diodes (LEDs), heterojunction bipolar transistors, photocathodes, photodetectors and solar cells. During the MOCVD manufacturing process in the semiconductor power device industry, gallium rich, nanosized and light black color dust particles are generated. Land filling should not be an option because of environmental hazard and various stringent environmental directives. The rapid growth of the optoelectronic market and the adoption of MOCVD as a well-established production technology have given rise to growing concerns over potential health hazard either to human, animal, and ecosystem, personnel and community safety, environmental impact (Shenai-Khatkhate et al., 2004). Health hazard of gallium and gallium compounds includes metallic taste, dermatitis, depression of the bone marrow function and large doses may cause hemorrhagic nephritis (Dierks, 2013). Domingo et al., and Gomez et al. have reported acute toxicity of gallium in rats and mice ([Colomina et al., 1993,Domingo et al., 1987,Gómez et al., 1992]). One should not be confused with bulk GaN non-toxicity.

World primary gallium productionwas 273 metric tons for the year 2012, which is less than 7% from the previous year (Salazar and McNutt, 2013). Gallium is a vital metal for the electronics industry, is classified as significant from the industrial application and critical from the supply chain scarcity perspective (Graedel, 2011; Graedel et al., 2011). For current technological trend, gallium is irreplaceable by other materials/metals. It has unique

* Corresponding author: Fax: +82 31 330 7113.
E-mail addresses: Swain@iae.re.kr, basudevswain@yahoo.com (B. Swain).

http://dx.doi.org/10.1016/j.envres.2015.06.003

performance, limited natural resources, ever-growing consumers' demand and potential to substantially increase the future demands for gallium, which triggers global competitions (Alonso et al., 2012). If the environmental concern, scarcity of natural resources, million-dollar industrial demands and the amount of waste generated or has to be generated are taken into consideration, treatment of MOCVD waste and gallium recovery through mechanochemical leaching is a feasible option.

Numerous articles have been published in the literature for recovery of gallium from primary resources (Mihaylov and Distin, 1992; Moskalyk, 2003; Zhao et al., 2012). Recovery of gallium from coal fly ash (Fang and Gesser, 1996), phosphorus flue dust (Xu et al., 2007), gallium arsenide scrap (Lee and Nam, 1998), and gallium from zinc residue (Wu et al., 2012) has been reported in the literature. Reports on the treatment of MOCVD waste and the recovery of gallium from the GaN waste by hydrometallurgy is scarce. In our current study, we have investigated the recovery of gallium from MOCVD waste dust. These waste dusts generated during the MOCVD process are primarily rich in gallium content along with significant amounts of indium, which is an important resource for recovery of these important industrial metals. The GaN scrap from various resources like MOCVD dust, gallium bearing end of life (EOL) waste electronics and electrical equipment are the important resources. As recycling technology for recovery of gallium and indium from these waste resources is not well established, the same needs to be developed. Chemical oxidation through annealing followed by a leaching process can be techno-economic environment friendly process for the waste treatment and value recovery.

We have investigated different processes for treatment of MOCVD waste dust and quantitative recovery of gallium from the waste. To treat the waste MOCVD dust and recover gallium, leaching followed by metal recovery by the hydrometallurgy process can be the cleaner and greener technology. To treat the MOCVD waste dust, oxidation of GaN is an important process as the GaN is neither easily oxidized nor easily leached. To recover gallium leaching is the primary stage. In order to recover gallium, leaching is the primary step to follow up. Two different processes are proposed for treatment of waste MOCVD dust and quantitative recovery of gallium from the MOCVD waste. In one process first of all the MOCVD dust was leached at the optimum condition, subsequently leach residue was mixed with Na_2CO_3, ball milled followed by annealing, and again leached to recover gallium. In another process, MOCVD waste dust was mixed with Na_2CO_3, and then ball milled, followed by annealing and finally leached to achieve the quantitative gallium leaching. The novelties of the MOCVD waste treatment and the gallium recovery process developed are listed below.

(1) Both the treatment processes proposed are novel; resource material used for the purpose is a challenging industrial waste which needs treatment and a promising secondary resource targeted for gallium and indium recovery.
(2) Thermal analysis, phase properties and oxidation chemistry of GaN toGa_2O_3 and GaN to $NaGaO_2$ revealed in this paper are the rudimentary and novel information, which has never been reported in the literature.
(3) More importantly, the solid-state chemistry involved in this process is an important discovery worth reported, presented in Section 3.2.
(4) The developed process can address the waste electrical and electronic equipment (WEEE) directive (became effective on 14 February 2014) (European-Union, 2012), and restriction of the use of hazardous substances in EEE (RoHS) directive (European-Union, 2011).
(5) Our developed process also addresses United Nations Environment Programme (UNEP) E-Waste Management strategy (UNEP, 2007) and the waste management strategy of extended producer responsibility (EPR).

2. Materials and methods

2.1. Materials

Enco Co. Ltd., the Republic of Korea, supplied the waste MOCVD dust. Other chemicals like H_2SO_4, HNO_3, HCl, NaOH, and Na_2CO_3 were of analytical grade supplied by Daejung chemical and metal Co., Ltd., the Republic of Korea.

2.2. Mechanochemical treatment and oxidation through annealing

The MOCVD dust was mixed with Na_2CO_3 at one-to-one weight ratio, milled in an air environment by a planetary ball mill (Wisemix programmable ball mill). Zirconia-coated grinding bowls (200 ml) and Zirconia grinding balls were used. The rotation speed was 150 rpm and milling time was 24 h. After ball milling, the samples were dried in an oven at 60 °C for 6 h. The requisite amount of the ball-milled sample was placed in the center of a horizontal tube furnace using an alumina boat. The furnace temperature increased linearly at 10 °C /min until it reached the requisite temperature (in the range of 800–1200 °C). The entire oxidation through the annealing process was carried out for 4 h (including the time required to reach desired temperature). After turning off the furnace, the sample was cooled to room temperature. From here onward, those samples which were mixed with Na_2CO_3, and followed by ball milling process are called mechanochemically treated waste MOCVD dust. Those were not treated mechanochemically as the above process is called raw waste MOCVD dust.

2.3. Leaching

A leaching reactor used for leaching of the mechanochemically treated waste MOCVD dust and raw waste MOCVD dust samples is presented elsewhere (Swain et al., 2014), also given as a Supplementary information (SI), SI Fig. S1. The main reactor vessel was of a 0.5 L three necked round bottom flask, equipped with an overhead stirrer driven by a variable-speed motor. Heating mantle with asbestos covered over coil was used for heating and a thermostat was attached to control the reactor temperature. Thermocouple equipped with digital display during continuous operation of the reactor was used to monitor the temperature during leaching. Through a preliminary study, 1 h leaching time was found to be enough to attend the optimum possible leaching. Throughout the leaching studies, reaction time was maintained at 1 h.

2.4. Analytical procedures

Both mechanochemically treated and raw waste dusts were characterized by SEM (scanning electron microscopy, JSM-6700F, JEOL), EDS (energy dispersive spectroscopy), XRD (X-ray diffraction, Shimadzu XRD-6100), and TGA–DTA (thermogravimetric analysis–differential thermal analysis, Shimadzu DTG-60H). Metal concentration of leach liquor was analyzed using ICP-AES (OPTIMA 4300DV, Perkin-Elmer, USA) after suitable dilution using 5% HCl. The maximum deviations permitted were about ±3% in ICP-AES analysis, but for temperature controlled leaching the deviation was ±2 °C.