Pyrometallurgical Recovery of Gallium from GaN Semiconductor through Chlorination Process Utilizing Ammonium Chloride

Kazuki Nishinaka1,*, Osamu Terakado2,*2, Haruki Tani1 and Masahiro Hirasawa1

1Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Nagoya 464–8603, Japan
2Department of Material and Environmental Engineering, National Institute of Technology, Hakodate College, Hakodate 042–8501, Japan

Pyrometallurgical chlorination process has been examined for the recovery of gallium from gallium nitride, GaN, a promising semiconductor material. It was found that gallium was successfully recovered as volatile gallium chloride by thermal treatment of GaN powder in the presence of ammonium chloride. All gallium could be recovered as volatile species at 500°C. The results indicate that gallium can be extracted from complex mixture of semiconductor materials or wastes through this process. The influence of reaction conditions, such as reaction temperature and composition of ammonium chloride, was examined.


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1. Introduction

Gallium nitride, GaN, is a semiconductor material with a bandgap of 3.4 eV, utilized mainly as blue light emitting diode1). It is also regarded as a promising material for power devices, such as converter and inverter, since it has high breakdown electric field, more than 10 times higher than silicon or GaAs2).

Some gallium ores are known in literature, although, because of their rarity, gallium is produced mainly as by-products of zinc or aluminum refining process3). It is, therefore, regarded as one of the critical metals in Japan. The recovery of the elements is commonly carried out in factories of semiconductor manufacturers. In the case of Japan, over 50 percent of gallium supply owes to the recycling of scraps in semiconductor manufacturers, while the import still accounts for ~40%4). The establishment of gallium recovery process from consumer wastes is, thus, considered to be important in conjunction with both resource strategy and interdisciplinary issue.

In our previous paper5), we reported the recovery process of elements from copper indium gallium diselenide, CIGS, through pyrometallurgical chlorination method utilizing ammonium chloride, NH4Cl. Hydrogen chloride and ammonia are formed in thermal decomposition of NH4Cl, the former of which is responsible for the chlorination of elements. The separation of the elements could be successfully achieved by the differences in the position of deposition inside the reactor according to the vapor pressure differences of the corresponding chlorides. However, it was found that the deposition of gallium product was close to the indium, which did not follow the order of the corresponding chlorides. The results indicate the formation of complex salt of gallium and indium. A systematic work can clarify the evaporation behavior of the chlorides of group 13 elements.

In the present work, we report the chlorination process of GaN by ammonium chloride. The influence of the reaction conditions, such as temperature and the composition, will be discussed in detail.

2. Experimental Procedure

2.1 Materials

Powder form of gallium nitride with a purity over 99.99% was supplied by Kojundo chemical laboratory Co., Ltd. The chlorination reagent was NH4Cl powder with a purity of 99.5% (Wako pure chem. Co., Ltd). The particles sizes, as observed with Scanning Electron Microscopy, were 1–2 μm and 0.5–1 mm for GaN and NH4Cl, respectively. The powders were mixed in a mortal and then pressed at a pressure of 10 MPa into a pellet of the diameter of 6 mm. Typical composition was 20 mg of GaN and 120 mg of NH4Cl, i.e., corresponding to [GaN]:[NH4Cl] = 1:6 in mass ratio, if not specified in the following.

2.2 Chlorination reaction and analytical method

The chlorination reactions were carried out in a quartz horizontal reactor (inner diameter 26 mm, length 700 mm) heated in an electric furnace5). Schematic figure of the reactor is shown in Fig. 1. A sample specimen was put on a mullite boat, which was inserted into the hot zone of the furnace. The reactions were conducted under nitrogen atmosphere. Typical total gas flow rate was 100 cm3/min. A preliminary work on the different reaction time showed that the mass change did not change after the reaction time of 30 min at 400°C. The reaction is considered to complete within 30 min. We set, therefore, the reaction time to 30 min, if not specified in the following.

Fig. 1 Schematic figure of the reactor.
following. Volatile products condensed at the cold part of the reactor during the reactions. The deposits were collected with ion exchanged water after the experimental run. Undissolved deposits could be collected by dissolving into aqueous HCl solution. A glass trap, containing 50 mL of ion exchanged water, was connected to the reactor which captures volatile products which did not deposited inside the reactor. As for the collection of the reaction products from residue in the boat, it was dissolved by ion exchanged water and then aqua regia.

The gallium contents in the solutions were determined by ICP spectroscopic analysis (SPS3000, SII). The recovery rate is defined as the ratio of gallium content to the total amount in the pellet.

### 2.3 Spatial separation of the elements

Spatial separation of the elements is one of the major advantages of the chlorination metallurgy. Our previous work on the chlorination of CIGS revealed that the gallium deposition took place close to that of indium, though the vapor pressures of gallium (III) chloride and indium (III) chloride are different from 3–4 orders of magnitude. We deduced the complex formation of indium and gallium chlorides. Study on the chlorination of GaN can clarify the evaporation behavior of gallium species.

We have, therefore, examined the chlorination reaction under the same condition of the CIGS experiments. The reaction was done under the atmosphere of 20 vol% oxygen in nitrogen at the flow rate of 100 mL/min. Fifteen pieces of quartz tube (outer diameter 25 mm, inner diameter 23 mm, length 10 mm or 20 mm) were put along the inner wall of the reactor side by side. Volatile products deposited on every tube were collected by 3 mL of aqua regia and diluted to 25 mL by ion exchanged water, and then analyzed by ICP spectrometer.

### 3. Results and Discussions

#### 3.1 Change in gallium distribution as a function of reaction temperature

We observed the deposition of white products after the chlorination reaction. One of the products is NH₄Cl, which is deposited after the sublimation of the initial ammonium chloride or by the recombination reaction of the thermal decomposition products, that is

\[
\text{NH}_4\text{Cl} \rightarrow \text{NH}_3 + \text{HCl}. \tag{1}
\]

As will be discussed later, gallium compound was also detected in the deposits. It is obvious that the reactant GaN does not evaporate in the examined temperature range, since the vapor pressure of GaN is considerably low (Fig. 2). The vapor pressure of gallium, which can be formed in the reducing atmosphere, is also low. On the other hand, the gallium chloride has very high vapor pressure, about 1 atm at 250°C. It is, therefore, plausible that the chlorination products are responsible for the white deposits.

Figure 3 shows the gallium distribution for the chlorination reaction at different temperatures. A satisfactory mass balance of Ga was achieved for the present experiments. At 250°C the evaporation of gallium compounds was not observed. Gallium remained mostly in the reaction residue; around half of the element was water soluble and the rest water insoluble compounds. As gallium nitride is not dissolved in water, water-soluble compound is gallium chloride. As reported in our previous work on the chlorination reaction using NH₄Cl, the accurate determination of the deposits could be hardly carried out because of the coexistence of a large amount of ammonium chloride, resulting from the sublimation of the initial NH₄Cl in the sample mixture or the recombination reaction of ammonia and hydrogen chloride (Reaction 1).

At elevated temperature the gallium distribution shifted to the quartz tube and the trap, indicating the formation and the evaporation of volatile species. The portion of reaction tube increased significantly, accompanied by the drastic decrease in the water-insoluble portion from 250°C to 300°C. As seen in Fig. 2, the vapor pressure of GaCl₃ is very high, so that the chlorination product can be easily evaporated under the present experimental condition. On the other hand, the complete evaporation was not achieved, ca. 30% of gallium remaining as chloride inside the reaction boat. Above 400°C no gallium was detected in the reaction residue, and the complete evaporation was observed. The recovery of ~100% as deposit species was achieved for the reaction at 500°C. The change in gallium distribution can be explained by the enhanced decomposition and the consequent increase in the HCl partial pressure at elevated temperature. From the practical point of
of gallium as a function of mass ratio of NH₄Cl to GaN for the composition of the reactants. Figure 4 shows the recovery of the reaction conditions we have examined the influence of GaN and NH₄Cl at elevated temperature. For an optimization of the reaction conditions we have examined the influence of GaN and NH₄Cl at elevated temperature. For an optimization of the chlorination, which was considerably higher than the stoichiometric composition for the reaction at 500°C. It is clearly seen that the portion of gallium captured in the reactor tube increases with increasing the amount of ammonium chloride, indicating the enhancement of the chlorination as well as the evaporation of gallium products at higher NH₄Cl composition. Water-insoluble residue was detected at the mass ratio of 2, above which no residue portion was observed.

For the interpretation of the results it is necessary to explore the reaction mechanism. A possible reaction pathway in the present experiments is

$$\text{GaN} + 3\text{NH}_4\text{Cl} = \text{GaCl}_3 + 4\text{NH}_3,$$

where the standard Gibbs energy change of the reaction, $\Delta G^\circ$, is $\approx -4.3 \text{ kJ} \text{ at } 500^\circ \text{C}$. For this reaction the mass ratio of 2 is the stoichiometric composition. The present result shows that excess amount of NH₄Cl is necessary for the sufficient evaporation of gallium chloride. However, the recovery of $\approx 70\%$ could be achieved at the stoichiometric composition for the GaN chlorination, which was considerably higher than the reactions in our past study², where only $\approx 40\%$ of gallium recovery was achieved for the chlorination reaction of CIGS at over 10 times more amount of NH₄Cl composition than the stoichiometric composition.

### 3.3 Evaporation kinetics

In this section we will consider the evaporation kinetics of gallium compounds. Figure 5 shows the recovery as a function of nitrogen gas flow rate for the reaction at 500°C. The total recovery decreased at elevated flow rate. Similar result was observed in our past study on the chlorination reaction of bearing alloy containing indium³, where slight decrease in the evaporation of indium chloride was observed from $\approx 60\%$ at 100 cm³ min⁻¹ to $\approx 50\%$ at 500 cm³ min⁻¹. In the present case the recovery of gallium is more significantly affected by the carrier gas flow rate (−100% at 100 cm³ min⁻¹ and $\approx 70\%$ at 300 cm³ min⁻¹). The increase in the carrier gas flow rate results in the decrease in the apparent partial pressure of HCl. Thus, the chlorination reaction rate might be slower for the GaN system than the indium alloy which has possibly lower activity of indium. In order to clarify the detailed reaction mechanism, further studies are needed.

The reaction at 300°C showed that the water-soluble compounds of gallium, i.e. chlorides, remained in the residue. Therefore, we have examined the evaporation kinetics by examining the reaction time at the temperature of 300°C. Defining the evaporation ratio, $R$, as the mass of gallium captured outside the mullite boat divided by the total gallium mass in the sample, we observed $R$ value of $\approx 57\%$ and $\approx 80\%$ at the reaction times of 30 and 60 min, respectively. Therefore, the increase in the reaction time has positive effect for the recovery of gallium from GaN. On the other hand, full recovery of gallium was not possible, as the $R$ value was slightly lower ($\approx 80\%$) than the value from the result at higher temperature, $R > 90\%$ at 500°C (see Fig. 3). The present result suggests the existence of another reaction pathway where non-volatile compound formation takes place inside the reaction boat. Its existence is plausible, as the reaction (2) is less favorable at high temperature according to the $\Delta G^\circ$ value. Further studies should be required to clarify the details.

The above results suggest the existence of an optimum gas flow rate. The decrease in the flow rate leads to, on one hand, the increase in the recovery. On the other hand, it results in the formation of non-volatile products, which leads to the decrease in the recovery.

### 3.4 Spatial separation of the elements

Figure 6 shows the deposition profile of the element and the average temperature plotted as a function of the distance from the exit of the furnace for the reaction at 400°C under 20% oxygen – 80% nitrogen atmosphere. Gallium was, on the one hand, mostly detected close to the exit of the furnace at $\approx 2 \pm 2$ cm, where the deposition temperature was around 130°C. On the other hand, sixteen percent of gallium was detected in the water trap.

The result of the deposition inside the quartz reactor is sat-
isfactorily in accordance with that of the chlorination reaction of CIGS\(^5\). The present result suggests that the complex formation does not play an important role, as it is not the case for the chlorination of GaN. The decrease in the vapor pressure of gallium product was also observed in the chlorination reaction of de-selenized CIGS\(^8\), in which the authors suggested two possibilities: the impeding of gallium chloride evaporation in the excess amount of ammonium chloride and the formation of complex between \(\text{GaCl}_3\) and \(\text{NH}_4\text{Cl}\), such as \(\text{NH}_4\text{GaCl}_3\).

It is interesting to note that parts of gallium were detected also in the water trap, indicating the formation of highly volatile species. Taking the vapor pressure of the gallium compounds into account, we consider that \(\text{GaCl}_3\) is responsible for the compound in the trap. Therefore, several product species with different vapor pressures may exist in the chlorination reaction utilizing ammonium chloride. As a matter of course, the oxygen partial pressure can play a significant role in the chlorination reaction. The chlorination behavior as well as vapor species can differ from those of the present result at 20% oxygen atmosphere. Thus, further studies under atmospheres at different oxygen partial pressures should be carried out in the future work.

4. Conclusions

In the present work we studied the pyrometallurgical recovery of GaN through chlorination reaction with ammonium chloride. It was found that the increase in reaction temperature and \(\text{NH}_4\text{Cl}\) composition lead to the increase in the evaporation of gallium compounds, possibly gallium chloride. All gallium could be recovered by the reaction at 500°C with the composition of \([\text{GaN}]:[\text{NH}_4\text{Cl}] = 1:6\) in mass ratio. The increase in the carrier gas flow rate resulted in the decrease in the gallium recovery. This is presumably due to the decrease in the apparent partial pressure of \(\text{HCl}\), the decomposition product of ammonium chloride.

It was also found that the gallium was mainly deposited at \(\sim 130^\circ\text{C}\) in reasonably agreement with the result of the chlorination of CIGS. The result shows that the complex formation of gallium and indium is not plausible, indicating the dependent deposition of the element from different kind of semiconductor wastes. Further studies, such as the examination of the reaction (2) in section 3.2, are required for the optimization of the process.

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