Pyrometallurgical Separation of Indium Phosphide through the Phosphorous Removal by Iron and the Chlorination Process Utilizing Ammonium Chloride

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Pyrometallurgical chlorination process has been employed for the recovery of elements from indium phosphide, InP, one of the important III–V semiconductor materials. It was found that both indium and phosphorous were converted to volatile species, indium chloride and phosphine, PH₃, by thermal treatment of InP powder in the presence of ammonium chloride. However, the recovery as volatile compounds reached ~60% at reaction temperature of 800°C. Based on these results we have employed the thermal treatment of the mixture of InP and iron powders. Phosphorous could be successfully converted to non-toxic iron phosphide, Fe₃P. The consequent chlorination reaction resulted in the indium recovery of ~100% in volatile form. The influence of reaction conditions, such as reaction temperature and composition of ammonium chloride, was examined. [doi:10.2320/matertrans.M2018007]

(Received January 9, 2018; Accepted March 27, 2018; Published May 11, 2018)

Keywords: indium phosphide, recovery, chlorination, ammonium chloride, pretreatment

1. Introduction

Indium phosphide is one of the III–V semiconductor materials with a bandgap of 1.35 eV at 23°C.¹ Their nanoscaled crystals or colloidal quantum dots are regarded as one of the promising candidates for the optoelectronics, lasers and biological imaging devices alternative to the toxic chalcogenides, such as cadmium or lead based materials.² The application of InP ranges also to the terahertz device³ and biological imaging devices alternative to the toxic chalcogenides, such as cadmium or lead based materials.² The utilization of ammonium chloride, NH₄Cl, as chlorination reagent is described elsewhere.⁷ A quartz horizontal reactor was used in mass ratio, or 1:22 in molar ratio. The experimental results were mixed in a mortal and were served for the chlorination experiment. Typical composition was 30 mg of InP and HCl gases. Some metal chlorides can be also used as chlorination reagents, though, in this case, high temperature is needed.

Our systematic study showed that the elemental separation was possible by the appropriate heating of the mixture of NH₄Cl and the targeted materials of mainly group 13 elements, which include indium tin oxide,⁵ bearing alloy,⁵ copper indium gallium diselenide,⁷ CIGS, one of the promising photovoltaic batteries, as well as gallium nitride,⁸ a major material of blue light emitting diodes.

In the present work, the chlorination process of indium phosphide is reported. The utilization of ammonium chloride involves the formation of hydrogen chloride (Reaction 1), which enables the chlorination of target elements. Therefore, the following chlorination is expected in the case of InP under the experimental conditions in the present work (Reaction 2):

\[ \text{NH}_4\text{Cl}(s) \rightarrow \text{HCl}(g) + \text{NH}_3(g) \]  \hspace{1cm} (1)

\[ \text{InP}(s) + 3\text{HCl}(g) \rightarrow \text{InCl}_3(s,l,g) + \text{PH}_3(g) \]  \hspace{1cm} (2)

Similar process based on the conventional hydrometallurgical treatment was reported in the past where InP was dissolved in hydrochloric acid and the dissolved indium and evolved PH₃ gas were recovered.⁹ On the other hand, phosphone or phosphane, PH₃, is extremely toxic and flammable compound,¹⁰ so that the direct chlorination of InP with HCl originating from NH₄Cl can cause significant environmental concern. We have, thus, examined pretreatment process utilizing iron to remove phosphorous from InP and then convert to stable iron phosphide. The reaction is described as:

\[ \text{InP}(s) + 3\text{Fe}(s) \rightarrow \text{In}(s) + \text{Fe}_3\text{P}(s). \]  \hspace{1cm} (3)

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 indium phosphide with a purity of >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 powders were mixed in a mortal and were served for the chlorination experiment. Typical composition was 30 mg of InP and 240 mg of NH₄Cl, i.e. corresponding to [InP]/[NH₄Cl] = 1:8 in mass ratio, or 1:22 in molar ratio. The experimental results at this composition will be presented, if not specified in the following.

2.2 Chlorination reaction and analytical method

The chlorination reactions were carried out in the same way described elsewhere.⁷ A quartz horizontal reactor (inner diameter 26 mm, length 700 mm) heated in an electric furnace. A sample specimen was put on a mullite boat, which was inserted into the hot zone of the furnace. The reactions were conducted under the flow of nitrogen gas. Typical carrier gas flow rate was 100 cm³/min and the reaction time was 30 min.

Some 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. Two glass
2.3 Pretreatment with iron for phosphorous removal

Solid products were connected to the reactor for the capture of more volatile products, not deposited inside the quartz reactor. First trap contained 200 mL of ion exchanged water, while the second 200 mL of 5 vol% NaClO, 1 vol% HNO₃ aq solution. The latter oxidative solution, which was originally developed for the hydrometallurgical recovery of InP,¹¹ was connected to ensure the capture of PH₃ gas for its conversion to phosphate, as the water solubility of PH₃ is not high (~0.03 g/100 g H₂O)¹². It should be, however, noted that the amount of the trap liquids is high enough to capture all the evolved phosphine, as the stoichiometric amount according to reaction (2) is ~7 x 10⁻³ g in an experimental run. The reaction residue in the boat was extracted by ion exchanged water, and then aqua regia heated at 250°C for 30 min.

The concentration of the elements in the solutions was determined by ICP spectrometer (SPS3000, SII). In the present paper the recovery of volatile compounds was focused. The recovery is, thus, defined as the ratio of element content in the condensate and traps to the total amount in the initial sample, i.e.

\[
\text{Recovery (\%)} = 100 \times \frac{m_{\text{condensate}} + m_{\text{traps}}}{m_{\text{total}}},
\]

where \(m\) denotes the mass and the subscript is the collected position.

Some of the gaseous products were captured during reaction in an aluminum gas bag and analyzed by gas chromatography–mass spectrometer, GC/MS, (GC/MS 6890/5973, Hewlett Packard) with HP-PLOQ column (\(\phi\) 0.32 mm, 30 m, Hewlett Packard), and XRD analysis was conducted with an Ultima-IV equipment (Rigaku) for the solid products.

2.3 Pretreatment with iron for phosphorous removal from InP

As mentioned in introduction, possible reaction products include PH₃ which is extremely hazardous, so that its removal prior to the chlorination reaction is desired. We have, thus, examined the reaction of the mixture of InP and iron as a pretreatment process of the chlorination. The powder of InP and iron (Wako pure chemicals, Particle size of 75 µm) was mixed in mortar. Typical composition was 30 mg of InP and 40 mg of Fe, corresponding to [Fe]/[InP] = 1.3 in mass ratio, or 3.4 in molar ratio, slightly higher than the stoichiometric ratio. The mixture was served for the reaction inside the horizontal furnace that was used for the chlorination reaction.

3. Results and Discussions

3.1 Products distribution by chlorination reaction of InP

Figure 1 shows the distribution of In and P after the reaction of InP with NH₄Cl at 600°C. Indium is mainly recovered from the reactor, while phosphorous from the traps. The results indicate that the products of phosphorous are more volatile than those of indium. If the chlorination takes place according to the reaction (2) described in the introduction, indium chloride and phosphine are the chlorination products. The vapor pressures, \(P_i\) of InCl₃ and PH₃ were calculated as \(\log_{10}(P_i/\text{Pa})\sim 3\) and 17 at 523°C, respectively,¹³ so that the present experimental result follows the vapor pressure data. The difference in the vapor pressures is, on the other hand, of 14 orders of magnitude, so that the reaction mechanism should be carefully examined. We have carried out a GC-MS analysis of the product gas which was captured during reaction by a gas bag without passing the liquid traps. The mass spectrometric analysis of the chromatograph (not shown) confirmed the formation of phosphine. The formation profiles at 400 and 800°C are shown in Fig. 2 where the peak area of PH₃ in the chromatograph of gas samples, collected for 3 min, sequentially, was plotted. The gas was captured between 3–12 min and 0–6 min at 400 and 800°C. It is clearly seen that the reaction increases with increasing temperature.

The results of products distribution also show the existence of the unreacted portion at 600°C.

3.2 Temperature dependence of the chlorination reaction

For the optimization of the reaction temperature, we have carried out the chlorination treatment at different temperatures. Figure 3 demonstrates the temperature dependence of the recovery of volatile compounds, i.e. reaction products collected from the reactor wall and the traps. The results of duplicate runs are shown in the figure. As the small amount of the sample was examined, relatively large error, >10% in some cases, should be considered, which is, however, not crucial for the later discussion.
At lowest temperature of 300°C indium recovery as volatiles was only \textasciitilde{5\%}. On the other hand, thirty percent of total indium was recovered from the reaction residue by ion exchanged water extraction. Thus, the chlorination of indium took place even at 300°C, because indium chloride is the only water soluble compound among the relevant compounds. This is plausible, because the mass reduction starts at 200°C, as found by thermogravimetric measurement of NH₄Cl (not shown), which causes the decomposition to ammonia and hydrogen chloride, reaction (1). As the vapor pressure of indium chloride is low, \( p = 1 \text{ Pa} \), at 300°C, the vaporization does not take place rigorously. If the chlorination reaction according to reaction (2) takes place, phosphine should be formed and be detected as volatiles, as the vapor pressure is exceedingly higher than that of indium chloride. Phosphorous recovery at 300°C (10\text{--}20\%) is slightly lower than the expected value, i.e. \textasciitilde{35\%}, which suggest that different reaction mechanism, other than reaction (2), may take place at low temperature. Further investigation may clarify the mechanism, although we focus on the improvement of the elemental recovery at higher temperature.

The recovery increases at elevated temperature. It is considered that the faster kinetics of the reaction (1) causes the substantial increase in the local partial pressure of HCl at higher temperature, enhancing the chlorination reaction. Higher temperature is also favorable for the evaporation of the reaction products. However, the recovery reached at most 60 percent for indium.

The reason of the incomplete recovery is possibly due to the fact that the reaction (2) is thermodynamically unfavorable. The standard Gibbs energy change of the reaction was calculated by thermochemical software, FactSage Ver.6.4 (Thermfact and GTT-Technologies), as 80kJ/mol at 300°C, the value increasing to 200kJ/mol at 800°C. Thus, the increase in temperature does not straightforwardly lead to the enhancement of the recovery as volatile compounds.

### 3.3 Influence of the composition

As described in the previous section, the increase in the reaction temperature is not an adequate way to achieve the sufficient recovery of the elements. We have, thus, examined the influence of the NH₄Cl composition. Figure 4 shows the recovery of indium and phosphorous as a function of the mass ratio of NH₄Cl to InP at 600°C. On the basis of the reactions (1) and (2) or

\[
\text{InP}(s) + 3\text{NH}_4\text{Cl}(s,l) \longrightarrow \text{InCl}_3(s,l,g) + \text{PH}_3(g) + 3\text{NH}_3(g),
\]

the stoichiometric composition is 1.1 in the mass ratio of NH₄Cl to InP. The recovery is, however, only \textasciitilde{20\%} at the composition close to the stoichiometric ratio. The increase in ammonium chloride results in the improvement of the recovery, though the recovery reaches at most 60\% even at highest NH₄Cl composition of [InP]:[NH₄Cl] = 1:16 in mass ratio, or 1:44 in molar ratio. In consideration to the experimental errors (see Fig. 3 in the previous section), further increase does possibly not improve the recovery. In conclusion, the chlorination reaction according to the reaction (3) takes place, but it is not enough for the complete recovery of the elements from InP. One of the crucial reasons is that the reaction is thermodynamically unfavorable particularly at high temperature.

### 3.4 Pretreatment with iron powder

From the above results and discussion, full recovery of In and P was not realized by a simple chlorination treatment with ammonium chloride. It is strongly desired to find a different route for the recovery of the elements from InP. As discussed in literature,\textsuperscript{6} the indium recovery from indium-containing alloy was successfully done by the chlorination process. Thus, any pretreatments, which remove phosphorous from InP, should be promising methods. The resulted indium metal can be chlorinated in a facile manner.

For that purpose we considered a pretreatment with iron powder. Iron has high affinity to phosphorous, so that the reaction of InP with iron can take place according to the reaction (3), as mentioned in introduction.

This process has great advantage with respect to the repression of the hazardous compounds, such as phosphine in reaction (2) or (4). Iron phosphide is a stable solid compound at ambient temperature.

Figure 5 shows the XRD patterns of the mixture of InP and Fe heated at 400\text{--}800°C. At the lowest temperature the sample powders remain essentially the same. Some small
unknown peaks were observed, though the majors were InP and Fe. Above 600°C XRD peak of indium was visible, and those of Fe3P became more profound at 800°C. Thus, the phosphorous removal, reaction (3), can be achieved by the simple heating of the powder mixture of InP and Fe at slightly higher iron to InP mass ratio of 1.3, or 3.4 in molar ratio, than the stoichiometric mass ratio of 1.1, or molar ratio of 3. The calculated standard Gibbs energy of the reaction, \( \Delta G^\circ \), is \(-102\,\text{kJ/mol at 400°C, decreasing to } -108\,\text{kJ/mol at 637°C, at which solid-solid phase transformation of InP takes place.} \) Above this temperature \( \Delta G^\circ \) increases to \(-99\,\text{kJ/mol at 800°C.} \) The reaction behavior is not directly related to the temperature dependence of \( \Delta G^\circ \), although the reaction (3) is thermodynamically favorable in the examined temperature range. In the present work, variation of the composition of InP and Fe has not been studied. Further optimization in process parameters, such as particle size, can reduce the iron composition.

Another advantage of this process is that indium has low solubility to iron. The Fe–In system is characterized by a large range of liquid immiscibility (3.4–91 at% In), the absence of compounds and low mutual solid solubility. Thus, this iron pretreatment is profitable for the subsequent chlorination reaction, as the possible decrease of the activity of indium is avoided.

### 3.5 Chlorination reaction for the iron-pretreated sample

The compounds involved in reaction (4) have different magnetic properties. Iron and Fe3P are ferromagnetic, while indium and InP, are non-magnetic. Thus, it should be, in principle, possible to separate indium and Fe3P by conventional magnetic separation technique. We employed a preliminary experiment in which the reaction products were dispersed in water in a glass beaker and then magnetic field was applied by a small neodymium magnet from outside of the beaker. As a result, most of the powders were attached to the magnet through the glass wall of the beaker. Non-magnetic portion in the solution was collected and the elemental analysis showed that it contains only indium. Therefore, the formation of indium takes place by heating of the mixture of iron and InP, as confirmed by XRD measurement. The recovery of non-magnetic indium metal reached, however, less than 10% in the preliminary test. The main reason of the low recovery owes to the entanglement of indium particles by unreacted iron and/or Fe3P particles. Further optimization can improve the indium recovery.

In the present paper, iron-pretreated sample powders were employed for the chlorination reaction. After the chlorination reaction yellow deposits were detected inside the cold part of the reactor. The recovery is plotted against the reaction temperature in Fig. 6, together with the data without pretreatment. The composition of the initial InP and NH4Cl was 1:8 in mass ratio, or 1:22 in molar ratio, where all of the pretreatment mixture of InP and Fe was mixed with NH4Cl. Obviously, the iron-pretreatment improved the indium recovery significantly. The recovery of phosphorous and iron from the volatile phase was fully suppressed by the iron-pretreatment. Both iron and phosphorous remained in the residue possibly as iron phosphide, as mentioned in the previous section.

It is concluded that iron-pretreatment is effective for the separation of elements from InP, fixing the phosphorous as stable and non-toxic iron phosphide, which cannot be dissolved in water and dilute acid. Essentially all indium was collected as volatile compounds by the iron pretreatment followed by chlorination reaction. For further optimization of the process the influence of the composition of NH4Cl was examined. The recovery is plotted in Fig. 7. Drastic increase was observed for the recovery with increasing the composition of ammonium chloride. Approximately eighty percent of the recovery was achieved at the composition of [NH4Cl]/[InP] = 2.1 in mass ratio, or 5.5:1 in molar ratio, four times larger than that without iron pretreatment. Further increase in the ammonium chloride content lead to the slight improvement in the recovery of indium, reaching \( \sim 100\% \) at the mass ratio of [NH4Cl]/[InP] = 16:1, or 44:1 in molar ratio. Thus, indium was fully converted to volatile chloride. The recovery of iron and phosphorous as volatile, on the other hand, was almost zero, indicating that these elements remain as iron phosphide in the reaction residue.

### 4. Conclusions

We studied the pyrometallurgical process for the separation of the elements from a semiconductor material, InP, by the chlorination reaction with ammonium chloride. The increase
in reaction temperature and NH₄Cl composition improved the recovery of both indium and phosphorous as volatile compounds. This is possibly explained by the promotion of reaction kinetics as well as the increase in the vapor pressure of the reaction products, chlorides, at elevated temperature. The higher NH₄Cl composition causes the apparent increase in the local partial pressure of HCl formed by the thermal decomposition of chlorination reagent. As phosphine was detected in the gas phase during the chlorination treatment, the reaction is supposed to be described as reaction (4).

The efficiency of the direct chlorination was at most 60 percent of indium even at the mass ratio of NH₄Cl to InP of 16, or molar ratio of 44, at the reaction temperature of 600°C. Moreover, the emission of highly toxic phosphine can be of great concern to the environment. In order to avoid the formation of the toxic gas, we have examined a pretreatment process utilizing iron powder. It was found that phosphorous in InP could be converted to stable and water-insoluble iron phosphide by thermal treatment of the sample in the presence of iron powder. Further chlorination treatment with ammonium chloride could separate indium as volatile compound from the mixture, achieving the ~100% recovery. Thus, the iron pretreatment is a promising process in the view of environmental-friendly separation of the semiconductor material.

Acknowledgments

The authors acknowledge Messrs. Shoji Takai, Takaaki Jinno, and Kentaro Tsuzuki, Nagoya University, for their kind supports on ICP measurements.

REFERENCES