論 文 の 内 容 の 要 旨

論文題目　Extraction of Metals from Spent ITO, IGZO and CIGS targets for Recycling
（リサイクルのための ITO, IGZO, CIGS ターゲット材からの金属の抽出）

氏 名　顧　帅

1. Introduction

Indium-tin oxide (ITO), indium-gallium-zinc oxide (IGZO), and copper-indium-gallium-selenium (CIGS) targets are materials used in the production of solar cells. The utilization of these targets in a typical sputtering process is usually less than 50%, which means that less than 50% of target materials were utilized. The unused targets (also known as spent target) materials reach in indium (In), which is a key metal for the sustainable development of solar cells industry. The limited ore deposits of In and gallium (Ga) make it difficult to extract and recover these metals from primary resources, such as zinc sulfide mineral and bauxite residues. Since the spent target materials may contain up to 2900 ppm of In and 530 ppm of Ga, which concentrations are respectively 29 and 10 times higher than those in ores. The demand for In and Ga were estimated to be increased with 15% and 15-20%, respectively. These trend, in turn, requires a proper approach for recycling of spent targets would, which is becoming increasingly important.

2. Experimental

At present, the recycling approach for spent target materials were mainly solvent extraction (SX) and pyrometallurgy. Nevertheless, SX usually consumes an enormous amount of water and organic solvents, and produces wastes that need to be disposed of; while high temperature technique consumes large amount of energy and requires sophisticated equipment. Thus, an energy-efficient and environmental friendly approach are needed to recycle these spent targets.

After carefully analyzing and discussing the physical and chemical properties of ITO, IGZO and CIGS spent target materials, three different methods, namely: dissolution-distillation–dehydration -fractionation (DDDF), two-step solvent extraction, and dissolution-electrodeposition-dehydration -distillation (DEDD) were proposed and tested in this work, in an attempt to answer and shed light on the feasibility of recycling of these materials.

2.1. Extraction of In and Sn from the spent ITO target

Generally, HCl gas is utilized to react with In_2O_3 and SnO_2 at 373 K for 60 min to obtain $InCl_3$ and $SnCl_4$. The reaction products ($SnCl_4$ and $InCl_3$) were recycled respectively in a nitrogen atmosphere at 573 K and 673 K by evaporation. He et al., on the other hand, recycled ITO via a carbon (50 wt%) reduction at 1223 K under 1 Pa for 30 min, and pure In was recovered at around the condensing temperature. Yang et al. studied the recovery of In using several extractants: cyanex 923, cyanex 272, TBP and D2EHPA, respectively in hydrochloric and sulfuric acid solution, recovering ca. 99 wt% of In with a purity of about 90%. Swain et al. reported a recovery of 97.78% for Sn with 99% purity by using Cyanex 272. López-Díaz-Pavón et al. utilized the cationic ion-exchange resin Lewatit K-2621 to separate In from tin (Sn). Higashi et al. recovered In by adding the Shewanella algae into the leached solution to concentrate the In for 680 times. Unfortunately, all these methods mentioned above have several drawbacks. For example, vacuum-chlorinated separation ensures a low recovery rate and operates at high temperature, vacuum carbonization reduction process operates at even higher temperature and low pressure; SX consumes lots of water and organic solvents; ion-exchange and biological metallurgy are difficult to be employed in industrial operation.

In this work, a scalable, more economical and sustainable approach, namely dissolution-distillation-dehydration-fractionation (DDDF), was developed. The process can be divided into four steps: (1) dissolution, (2) distillation or crystallization, (3) dehydration, and (4) fractionation. First, the spent ITO powder was dissolved completely using 5M HCl, and then the leached solution was distilled to obtain the crystal of metal chloride hydrates. Next, the crystals were dehydrated by a dehydrating agent (i.e. $SOCl_2$) under refluxing at 76℃. Next, the resultant solution was fractionated to separate anhydrous $InCl_3$, $SnCl_4$, and $SOCl_2$. It is well known that anhydrous $SnCl_4$ is a liquid at room temperature. Anhydrous $InCl_3$ has no or little solubility in both $SnCl_4$ and $SOCl_2$, while $SnCl_4$ is soluble in $SOCl_2$ solution as shown in Eq. (1). In the fourth step, anhydrous $InCl_3$, $SnCl_4$, and $SOCl_2$ were separated from each other by simply fractionating the mixture. $SOCl_2$, which has the lowest boiling point (i.e. around 76 ^oC), was the first removed from the mixture. After that, $SnCl_4$ was removed at approximately 114 ^oC. At last, anhydrous $InCl_3$ powder (melting point: 586 ^oC, boiling point: 800 ^oC) was left at the bottom of the flask. The hydrates of indium chloride and tin chloride, obtained from the distillation process, and the anhydrous $InCl_3$, obtained from the fractionation process were then both analyzed by using XRD (Rigaku, Smartlab). In order to separate In from Sn, $SOCl_2$ was added to

dehydrate the crystals, and as a result, anhydrous $InCl_3$ and $SnCl_4$ can be obtained according to Eqs. (2) and (3).

$$2SOCl_2 + SnCl_4 \rightleftharpoons 2SOCl^+ + SnCl_6^{2-} \quad (1)$$

$$InCl_3 \cdot 4H_2O + 4SOCl_2 \rightarrow InCl_3 + 4SO_2 \uparrow + 8HCl \uparrow \quad (2)$$

$$SnCl_4 \cdot 5H_2O + 5SOCl_2 \rightarrow SnCl_4 + 5SO_2 \uparrow + 10HCl \uparrow \quad (3)$$

2.2. Extraction of In, Ga and Zn from spent IGZO target

At presents, there are two main methods for separating In, Ga, and zinc (Zn) from IGZO for recycling, i.e. extraction resin and SX (SX). Liu et al. used the P507 resin (HR_2PO_3 where R is: 2-ethylhexyl phosphonic acid mono(2-ethylhexyl) ester) for separation of In, Ga, and Zn from sulfate solution. The results showed that a theoretical separation of In, Ga, and Zn from dilute solutions could be achieved by controlling pH and using different concentrations of hydrogen chloride as eluent, which consumes vast amount of water. Sasaki et al., on the other hand, utilized different extractants to separate In, Ga, and Zn from spent IGZO. He found that the α-dodecylaminobenzyl- phosphonic acid monobutyl ester with an aliphatic amine showed a relatively high selectivity towards In and Ga. In addition, the newly synthesized [*N*,*N*-di(2ethylhexyl)amino] methylphenylphos- phinic acid was found to be effective for the extraction of In, Ga, and Zn ions in nitric acid solution. Chen et al. used D2EHPA to separate In from Ga and Zn, after which the same extractant was used to separate Ga from Zn in nitric acid solution. In this work, the extraction of In, Ga, and Zn from spent IGZO target in HCl solution was studied in order to separate In and Ga from spent IGZO target in a sustainable and feasible manner. Based on the extraction behavior of D2EHPA and T-iso-BP, a novel process was proposed. The leaching solution was directly extracted with 30% T-iso-BP to separate the majority of Zn from In and Ga. The composition of the raffinate was 0.5% of In, 0.2% of Ga, and 86% of Zn. After which, the loaded organic (LO) phase containing 99.5% of In, 99.8% of Ga and 14% of Zn were stripped by HCl at pH= 2. It was found that 99.0% of In, 99.4% of Ga, and 12.53% of Zn were transferred into the resulting HCl solution. The residues remained in the organic phase. At this point, the majority of In and Ga with a small portion of Zn was successfully transferred into hydrochloride solution at low acidity.

2.3. Extraction of Cu, Se, Ga and In from spent CIGS target

Since selenium (Se) is the only nonmetal element in CIGS, the first recycling attempts started with the separation of Se, such as high-temperature oxidation. Other methods, such as high-temperature chlorination, nanofiltration, and SX were also utilized to recycle CIGS. High-temperature oxidation enabled the separation of Se from CIGS waste materials, while high-temperature chlorination separated the majority of $InCl_3$ (93 wt%) and $GaCl_3$ (97 wt%) at 340 and 260 ^oC, respectively. Nanofiltration and SX were employed for separating In from CIGS. High-temperature oxidation approach is capable of separating Se from CIGS, but it consumes enormous amount of energy, and is not capable of recycling

critical metals such as In and Ga; high-temperature chlorination approach is a relatively simple method for the recycling of In and Ga from CIGS, whereas it suffers from low recovery rate and high energy consumption. Although nanofiltration and SX is a scalable and easy method to industrialize the recycling of In, the final product was in an aqueous solution which needs a further process to separate Ga from CIGS. None of the approaches mentioned above can separate all the valuable elements from CIGS. Therefore, a more efficient approach to separate and recover copper (Cu), In, Ga, and Se from spent CIGS is highly desired. The dissolution-electro-deposition-dehydration-distillation (DEDD) process, not only enables the separation of high purity of In, Ga, Cu, and Se from CIGS, but also presents a reasonable approach for the recycling of CIGS materials in an environmental friendly manner. First, the spent CIGS powder was dissolved completely with HCl and H_2O_2. Based on their equilibrium electrode potentials, electro-deposition experiments were conducted in the leached solution with a Ti and Pt electrode to recover Se and Cu, respectively. Next, the solution was distilled and dehydrated with dehydrating agent (i.e., $SOCl_2$) under refluxing. Last, the resultant solution was filtered and distilled to separate anhydrous $InCl_3$, $GaCl_3$ and $SOCl_2$, respectively. In the last step, anhydrous $InCl_3$, $GaCl_3$ and $SOCl_2$ were separated from each other by simply filtering the mixture and distilling $SOCl_2$ solution in a rotary evaporator.

3. Conclusions

In brief, a scalable and environment-friendly process has been developed for efficient recycling of spent ITO, IGZO, and CIGS targets. The energy consumptions, reagents used, the amount of wastes generated, and final products were compared with the proposed DDDF approaches with SX and ion-exchange. It was found that the DDDF process consumes less energy, reagents, and produces the least secondary wastes, ensuring the highest recovery and purity of the products. The two-stage SX of IGZO could save enormous amount of water compared with the one-step conventional SX approach. Also, the DEDD approach utilizes electrochemical techniques to recover Cu and Se without adding any reduction reagents. Compared with other reported processes, this method has the following advantages: minimizing the reagents consumption, scalable mass production, higher recovery, and environmental benignity.

At the best of our knowledge, all these approaches, proposed in this work, are tested for the first time. Furthermore, due to the simplicity of these procedures, the method can also be employed to recover valuable metals from other target materials such as GZO and CIS.