

The Removal of Tin from ITO-scrap Using Molten NaOH

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Indium demand has grown abruptly in the last few years at an average of ten percent per year. Consumption of indium is expected to increase throughout the next decade, especially by dint of growth for liquid crystal displays, high-definition television, semiconductor materials, batteries, low-temperature solders, and electronic application. Indium is used in various forms such as indium oxide/indium-tin oxide, indium metal and alloy, and indium compounds.^{1,2}

Indium-tin oxide (ITO) formed by doping indium oxide with approximately 10% of tin oxide, increases both electrical conductivity without significantly affecting transparency. Flat panel display applications for indium in the form of ITO are the most important end uses, more than one-half of the world's indium consumption. ITO, which has a high optical transparency and a high electrical conductivity, has been used as transparent electrodes for flat panel displays.

ITO films are generally fabricated by DC magnetron sputtering using ITO ceramic target. Magnetron sputtering is favoured because it is easily applied to large area with good uniformity. However, ITO targets should be replaced before a large portion of ITO material (60-70%) has been used because of race track formation.³⁻⁵ So, it might be said that the recycling of unused ITO target is indispensable as indium is a trace element and very expensive.

As shown in $\text{In}_{1.82}\text{Sn}_{0.18}\text{O}_3$ obtained by doping indium oxide with approximately 10% of tin oxide, tin is the major impurity in recovery process of indium metal from ITO target-scrap. Indium and tin are chemically very similar and separation one from the other in solution is a knotty problem. Tin has been removed from residue of acetate leaching by chemical replacement with zinc in 5-20% HCl.⁶ Another method concerns neutralization of solutions containing tin to pH 1 followed by cementation with indium^{7,8} or by treating with NaOH to a pH value of 2.8.^{9,10}

In this paper, I demonstrate a new method to remove tin and purify indium metal from ITO target scrap using molten NaOH.

Experimental Section

ITO target-scrap was obtained from Samsung Corning Co., Ltd. The sample was crushed and pulverized. A 100 g of powder sample was mixed with 100 mL of 50% NaOH solution in a round-shaped alumina crucible, and then heated in air at 500 °C for 8 h. The NaOH-treated powder was washed with distilled water until pH 7 of residual solution,

then filtered and dried at 150 °C in a dry-oven. The resulting powder was leached in 3 M H_2SO_4 solution at 80 °C for 1.5 h. The indium sponge was obtained by cementation in sulfuric acid solution with aluminum plate (pH \approx 3, 50 °C).

X-ray diffraction pattern of the sample was achieved by Schmadzu 6000 model with $\text{Cu-K}\alpha$ radiation. The elemental analysis was performed by inductively coupled plasma-emission spectroscopy (ICP) with Labtam 8400 model.

Results and Discussion

Figure 1 shows XRD patterns of ITO target-scrap powder before and after NaOH treatment. The XRD pattern (a) reveals that ITO target forms a single phase of In_2O_3 with cubic symmetry within a doping range of approximately 10% of tin oxide. After NaOH treatment at 500 °C, In_2O_3 phase (pattern a) is completely changed into Na_2SnO_3 phase (pattern b), which is due to the higher crystallinity of Na_2SnO_3 compared to indium compounds. Finally $\text{In}(\text{OH})_3$ phase (pattern c) is obtained after washing with distilled water on the powder of the pattern (b). It is probably due to the formation of amorphous indium oxy-hydroxide and Na_2SnO_3 after NaOH treatment at 500 °C, then the formation of $\text{In}(\text{OH})_3$ and SnO_3^{2-} in a highly alkaline solution. As SnO_3^{2-} can be easily removed in washing step, we obtain highly purified $\text{In}(\text{OH})_3$ as indicated in pattern c of Figure 1. This interpretation coincides with Pourbaix' E-pH diagram.¹²

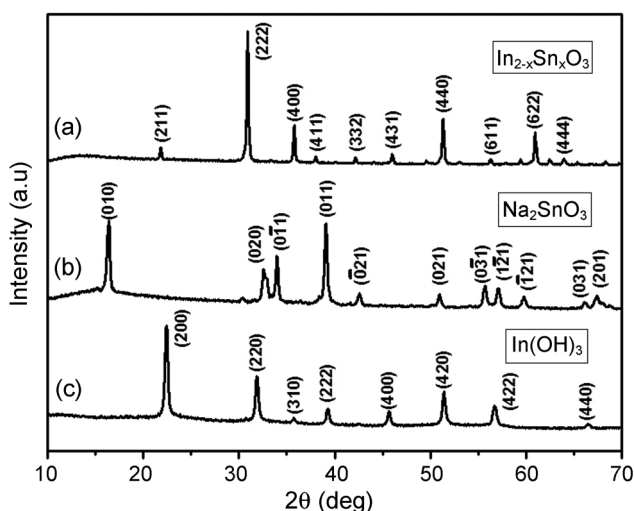


Figure 1. XRD patterns of ITO scrap powders: (a) before NaOH treatment; (b) after NaOH treatment with (a) sample; (c) after washing with (b) sample.

Table 1. Chemical composition of ITO scrap obtained by ICP analysis*

	In (%)	Sn (%)	Al (%)	Mo (%)	Cu (%)	Ni (%)	Co (%)
as received ITO powder	75.302	8.453	0.023	0.008	0.012	0.011	0.001
washed powder after NaOH treatment	78.959	0.621	0.013	0.004	0.002	0.021	0.001

*The samples are dissolved in aqua regia solution.

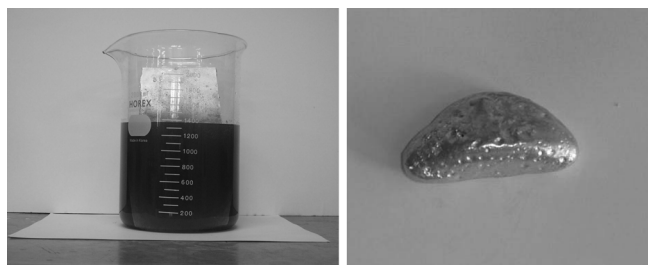


Figure 2. The cementation set-up (left) and obtained indium metal (right).

As shown in Table 1, ICP analysis reveals that the removing rate of tin for washed sample after NaOH treatment is approximately 93% compared to as received ITO target powder. It should be pointed out that molten NaOH breaks chemical bonds of $\text{In}_{2-x}\text{Sn}_x\text{O}_3$ compound, which results in the formation of Na_2SnO_3 and corresponding indium hydroxides. As Na_2SnO_3 is soluble in water and removed in a washing step, high purity of $\text{In}(\text{OH})_3$ can be easily recovered,¹¹ which is well coincident with Pourbaix, E-pH diagram indicating that $\text{Sn}(\text{OH})_2$ and $\text{Sn}(\text{OH})_4$ transform into HSnO_2^- or SnO_3^{2-} in an alkaline solution.¹²

Based on the XRD and ICP results, the roles of molten NaOH can be described as follows:

- i) bond dissociation of $\text{In}_{2-x}\text{Sn}_x\text{O}_3$ phase at elevated temperature
- ii) the formation of water soluble Na_2SnO_3 phase in high pH region
- iii) the removing agent for tin impurity in $\text{In}_{2-x}\text{Sn}_x\text{O}_3$ compound.

The resulting $\text{In}(\text{OH})_3$ powder was dissolved using 6 M

H_2SO_4 solution. Indium was recovered as sponge metal through cementation with aluminum plate on the basis of standard reduction potentials (E° for $\text{In}^{3+}/\text{In} = -0.338$ V, $\text{Al}^{3+}/\text{Al} = -1.68$ V) in H_2SO_4 solution with pH value of 1.5 at 60 °C. Indium sponge metal is smelted at 400 °C by excess NaOH which is used for preventing indium from oxidation and absorbing metal impurities. ICP analysis reveals that the purity of indium metal is found to be approximately 99.2% without any further purification step except NaOH treatment. Figure 2 shows the cementation set-up and obtained indium metal.

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