

The Removal of Tin from ITO-scrap via Ozonization

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Indium is estimated to have an abundance in the earth's crust of 0.05 ppm, which is similar to that of silver. As with other comparatively rare metals, indium becomes more concentrated in by-products arising during the extraction of major metals such as zinc.¹

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.^{2,3}

Flat panel display applications for indium in the form of Indium Tin Oxide (ITO) are the most important end uses, more than one-half of the world's indium consumption. The glass plate coated with ITO which is formed by doping indium oxide with approximately 10% of tin oxide, exhibits electrical conductivity without significantly affecting transparency, and 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.⁴⁻⁶ 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. Rapid separation of indium from tin by sublimation has been reported.⁷ The procedure developed was based upon the volatility of indium acetylacetonate at moderate temperature. Another method concerns neutralization of solutions containing tin to pH 1 followed by cementation with indium^{8,9} or by treating with NaOH to a pH value of 2.8.^{10,11} Electrolytic recovery of indium from concentrated sulfate solutions has been suggested.¹² A two-stage electrolytic procedure was proposed involving recovery of indium in apparatus with flat cathodes and complete extraction on the flow-through porous cathodes. Numerous investigators have studied to recover indium from solution by solvent extraction.^{13,14} The newly developed method to remove tin and purify indium metal from ITO target scrap has been reported using molten NaOH.¹⁵

It is well known that ozone exhibits the strong oxidizing

power. Therefore, $\text{Sn(II)O} \cdot x\text{H}_2\text{O}$ are easily oxidized to the higher oxidation state $\text{Sn(IV)O}_2 \cdot x\text{H}_2\text{O}$ in solution by ozonization. Moreover, in an alkaline solution $[\text{HSn(II)O}_2]^-$ species are transformed into $[\text{Sn(IV)O}_3]^{2-}$ by ozonization. In the recovery process of indium metal, Sn species are readily removed in a washing step, which gives rise to highly purified indium metal.

In this paper, we demonstrate a new method to remove tin and purify indium metal from ITO target scrap via ozonization.

Experimental Section

ITO target-scrap was obtained from Samsung Corning Co., Ltd. The sample was crushed and pulverized. The resulting powder was leached in 3 M H_2SO_4 solution at 80 °C for 1.5 h, and then filtered to remove undissolved materials. The obtained solution was treated with NaOH, which resulted in suspension composed of metal hydroxide precipitates. The ozonization was performed using an ozonizer (Ozontech, LAB model) in this suspension. The ozonization was conducted for 2 h as a function of ozone concentration. The ozone concentration was verified with the variation of O_2 flow rate (0.5, 1, and 2 Liter per Minute (LPM)). For the recovery of purified indium metal, the indium sponge was obtained by cementation in sulfuric acid solution using aluminum plate (pH \approx 3, 50 °C). X-ray diffraction pattern of the recovered indium metal was achieved by Schmadzu 6000 model with Cu- K_α radiation. The elemental analysis was performed by inductively coupled plasma-emission spectroscopy (ICP) with Labtam 8400 model.

Results and Discussion

Table 1 shows the ICP elemental analysis result of ITO target-scrap as received. It reveals that ITO target composes a doping range of approximately 10% of tin oxide compared to indium oxide.

The powder of ITO target scrap was leached using 3 M H_2SO_4 at 80 °C for 1.5 h and filtered to remove undissolved materials. The obtained solution was treated with NaOH, which resulted in a suspended solution with metal hydroxide

Table 1. ICP elemental analysis of ITO target scrap as received

purity (%)		purity (ppm)									
In	Sn	Cr	Pb	Ni	Al	Zn	Cu	Cd	Fe	Mo	
74.84	7.50	<1	1	<1	<1	<1	18	<1	22	<1	

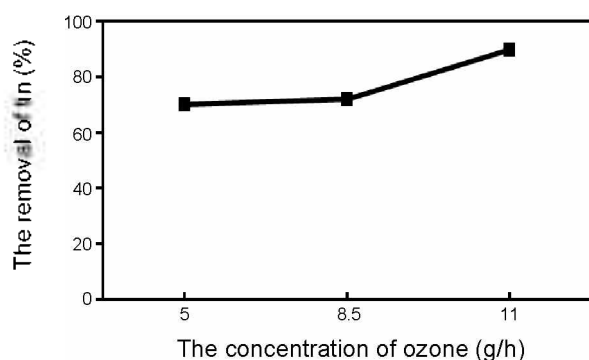
Table 2. ICP elemental analysis of metal hydroxide precipitates after ozone (or. oxygen) treatment^a

	In (%)	Sn (%)	Sn removal (%)
metal hydroxide precipitates after O ₂ treatment	60.95	1.320	82.40
metal hydroxide precipitates after O ₃ treatment	60.87	0.016	99.79

^aThe concentration of ozone: 11 g/h (O₂ flow rate: 2 LPM).

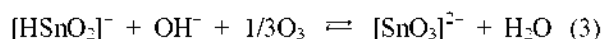
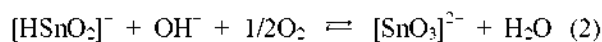
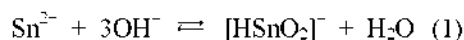
Table 3. ICP elemental analysis of the finally recovered indium metal

purity (%)	purity (ppm)													
	Sn	Cr	Pb	Al	Ti	Cd	Ni	Zn	Cu	Fe	Mo	Mg	Mn	Co
In	231	<1	5	7	<1	<1	36	13	16	50	<1	<1	<1	<1

**Figure 1.** The Sn removal (%) of the metal hydroxide precipitates as a function of O₃ concentration.

precipitates. The concentration of ozone was controlled and infused into the suspended solution for 2 h. Figure 1 shows the Sn removal (%) of the metal hydroxide precipitates as a function of O₃ concentration. It reveals that the higher the concentration of ozone, the Sn removal (%) of the metal hydroxide precipitates higher.

Based on the result of Sn removal *via* ozonization, it is recommended that the more effective Sn removal needs HNO₃ dissolution of ITO scrap because Sn²⁺ species are easily transformed into amorphous stannic acid, SnO₂·xH₂O which is readily removed under filtering process.¹⁶ As shown in Table 2, the ozone treatment is more effective in Sn removal compared to oxygen. More especially, a considerable Sn removal (99.79%) has been obtained in the ozone treated sample. The Sn removal by ozone treatment can be expressed by following chemical equations:



As ozone exhibits the higher oxidizing power than oxygen, Sn(II) species are more effectively oxidized into Sn(IV) in an

alkaline solution. Therefore, the finally stable [SnO₃]²⁻ can be easily removed. As Na₂SnO₃ is soluble in water and removed in a washing step high purity of In(OH)₃ can be easily recovered, which is well coincident with Pourbaix E-pH diagram indicating that Sn(OH)₂ and Sn(OH)₄ transform into HSnO₂⁻ or SnO₃²⁻ in an alkaline solution.¹⁷

The resulting In(OH)₃ powder was dissolved using 6 M H₂SO₄ solution. Indium was recovered as sponge metal through cementation with aluminum plate on the basis of standard reduction potentials (E° for In³⁺/In = -0.338 V, E° for Al³⁺/Al = -1.68 V) in H₂SO₄ 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 99.96% without any further purification step.

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