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**Extraction of indium-tin oxide from end-of-life LCD panels
using ultrasound assisted acid leaching**

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Abstract

In this report, indium-tin-oxide (ITO)-layer extraction from end-of-life (EOL) Liquid Crystal Displays (LCDs) was discussed by sulfuric acid leaching with simultaneous application of ultrasonication on the ITO-side of glass/ITO panels, exhibiting various dimensions. Applying this technique presents several advantages compared to the traditional leaching process such as fast and controllable kinetics, high extraction yield of indium and tin, selective recovery of these two metals possible, and the opportunity to recycle the neat glass separately avoiding additional separation processes. ITO-dissolution kinetics from EOL LCD panels were investigated as function of leaching time and acidity of sulfuric acid. At a temperature of 60°C, a nearly quantitative indium yield was obtained using an acid concentration of 18 mol/L by simultaneous application of ultrasonication, whereas only 70 % were recovered in the absence of ultrasound. Results from ICP-AES agreed well with SEM/BSE observations demonstrating the high efficiency of the ultrasound assisted process since only 3-4 min were required to obtain maximum ITO recovery.

Keywords: WEEE; recycling; LCD; indium tin oxide; indium; ultrasound.

1. Introduction

Since several decades, Liquid Crystal Displays (LCDs) were largely used in television sets, laptops, mobile phones, and other devices. Nowadays, great quantities of LCDs arrive in their phase of end-of-life (EOL), and are collected as part of WEEE (Waste Electric and Electronic Equipment), with strong impact from economic and environmental point of view [1-4].

Besides large amounts of various parts of valuable materials, the inner sides of LCD glass plates are covered by conducting Indium-Tin Oxide (ITO) electrodes in form of layers with a thickness up to 300 nm. Due to its excellent properties such as high optical transmission, good electrical conductivity, and strong adhesion to glass substrates, ITO is largely applied as electrode in LCD panels, as well as in Thin Film Transistors (TFT), cell-phones and other LC devices, and also in solar energy industry [5,6]. ITO usually consists of a mixture of indium (III) oxide In_2O_3 (90 mass%) and tin (IV) oxide SnO_2 (10 mass%), which is composed of 74 mass% indium, 8 mass% tin, and 18 mass% oxygen [7], where indium represents a high added value compared to tin.

Demand for indium mineral has grown strongly due to global consumer requests, with natural resources in the earth crust associated with zinc minerals such as sphalerite (ZnS , zinc blende) and with chalcopyrite (CuFeS_2), exhibiting average indium concentrations between less than 1 and 100 ppm [8-10]. The main world refinery production sites for indium can be found in Belgium, Canada, China, France, Germany, Japan, Peru, Republic of Korea, and Russian Federation. In 2015, the worldwide output was estimated to 755 tons, where China was the main manufacturer with 370 tons [11]. The ITO production continues to represent the majority of the global indium consumption. It was reported that the level of current indium use will exhaust the natural resources of this critical raw mineral material in 2025 [5].

After 2007, the quantity of indium produced starting from secondary raw materials was higher than that of primary raw materials. To fight against the depletion of indium resources,

recycling of WEEE became necessary [12-17], and in particular, ITO resulting from LCD waste can be regarded as the secondary raw material most important for the production of indium. Various methods of indium recovery starting from secondary sources were proposed, mainly on the basis of the hydrometallurgical technique [18]. Recycling of indium waste starting from ITO was also studied by pyrometallurgy [19], a complementary process to hydrometallurgy. Satoshi et al. [19] presented a process of indium recovery consisting of two stages: reduction of ITO with CO, and vacuum vaporization of the resulting indium-tin alloy. Ma et al. [20] investigated indium recovery starting from EOL LCD using vacuum pyrolysis followed by vacuum chlorinated separation, and obtained a high yield of indium species. Besides these processes, researchers reported [21-22] on the use of sub-critical water for the indium recovery from EOL LCD, at reaction temperatures up to 400°C. Lee et al. [23] applied the High Energy Ball Milling (HEBM) technique, implying LCD crushing at micron scale, followed by a treatment with hydrochloric acid (HCl). Choi et al. [24] developed an electrochemical method for ITO recovery followed by acid treatment, without glass crushing. ITO was obtained at a yield of 75 %, but the indium/tin ratio had been changed. The method of electrochemistry for indium recovery was also applied by Shindo et al. [25] on oxides composed of indium and zinc (IZO). During the electrolytic process, IZO waste as cathode was reduced to metals or suboxides, and high purity material was recovered. Higashi et al. [26] proposed microbial absorption of indium by “Shewanella” algae cells which revealed to be a fast process since 10-100 ppm of indium (III) ions were completely absorbed within 30 min using HCl under hydrothermal conditions.

Generally, pure strong acids like sulphuric acid (H₂SO₄), HCl, and nitric acid (HNO₃) were employed as ITO leaching agents, or mixtures of these compounds [27-32]. Virolainen et al. [27] developed a method of indium recovery from LCD by dissolution of ITO in these three acids, H₂SO₄, HCl, and HNO₃, followed by separation and condensation of indium by using

tributyl phosphate and bis(2-ethylhexyl) hydrogen phosphate (DEHPA) as extractants. These investigators showed that H_2SO_4 was not very corrosive compared to HCl for the process equipment. Kang et al. [28] recovered indium by solvent extraction with PC-88A which is a purified DEHPA, followed by electrolytic refining to obtain indium metal with high purity. Li et al. [29] developed a new hydrometallurgical process for indium recovery, including acid leaching and zinc cementing, and separation of tin by selective precipitation forming insoluble tin sulfide SnS_2 . Takahashi et al. [30] presented a process where crushed and incinerated LCDs from discarded cellular phones were treated with a HCl solution in order to obtain a chloride-induced indium compound which was vaporized at relatively low temperature, yielding an indium recovery rate of more than 80 %.

It should be mentioned that the oxidative behavior of the acids (H_2SO_4 , HCl, and HNO_3) together with other physico-chemical properties might lead to undesired side-reactions such as reactions with plastic waste attached to the LCD. It was shown for example that HNO_3 and HCl dissolved certain plastics during the indium extraction process [31]. In particular, highly concentrated HCl and HNO_3 , necessary for fast and efficient leaching capabilities, exhibit elevated volatility. For example, 37 % concentrated HCl represents a volatile liquid exhibiting a boiling point at $50^\circ C$, so that only a non-efficient 10 % concentrated HCl could be employed for leaching purposes (boiling temperature around $100^\circ C$) [33]. Moreover, HCl concentrations greater than 28 % can readily release hydrogen chloride gas. H_2SO_4 is stronger than nitric acid and presents low volatility due to the intense H-H bonding. For these reasons and other advantages [32], H_2SO_4 was chosen as ITO leaching agent for this investigation.

Swamy and Narayana [34] showed that ultrasound (US) assistance allows fast metal extraction compared to classical leaching processes. Beşe [35] studied copper dissolution by acid leaching applying US, and the author showed that the latter had a positive impact on the dissolution of copper and other metals. Deng et al. [36] used US activation for leaching heavy

metals of the sewage sludge, and they demonstrated that the extraction yield of Cu, Zn and Pb was enhanced with the increase of sonication time and HNO₃ concentration.

In this report, a simple efficient process has been proposed allowing fast ITO extraction from EOL LCDs. This process consists first in a series of coordinated disassembly sequences including separate recycling of printed circuit boards, backlight lamps which may contain mercury, metals, plastics, and other precious parts, and then exposure of the ITO-side of the remaining glass/ITO substrates to the acid surface. The interest of this leaching process supported by ultrasonication lies in the speed of ITO recovery in high yield without glass crushing, whatever the dimensions of the LCD panels. The effect of ultrasonication on ITO extraction from EOL LCD panels was investigated, by varying acid leaching time and acidity, while the acid temperature was maintained at 60°C.

2. Materials and methods

2.1 Materials

EOL LCD panels from WEEE were obtained from a recycling company located in the area called “Région Hauts-de-France”. The chemical products employed were concentrated H₂SO₄ (18 mol/L), and ultrapure water (resistivity 18.2 MΩ cm at 25°C and 1 atm pressure, corresponding to a conductivity of 0.06 μS/cm). H₂SO₄ (mass purity > 95%) was purchased from Verbièse laboratory (Merville/France). ITO, In₂O₃, SnO₂ and SnO nano-sized powders were obtained from Merck-Sigma Aldrich and used as received.

ITO dissolution experiments were performed using either concentrated H₂SO₄ (18 mol/L) or less concentrated solutions, which were prepared with ultrapure water in the following acid/water volume percentages: 100/0 (18 mol/L); 90/10 (16.2 mol/L); 80/20 (14.4 mol/L); 70/30 (12.6 mol/L); 60/40 (10.8 mol/L); and 50/50 (9 mol/L), noted respectively as: S0, S1,

S2, S3, S4, and S5. In order to dilute S0 to the desired acid/water ratio, the correct amount of acid was added to ultrapure water in small doses.

2.2 Characterization techniques

Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES, Varian (VistaPro, Axial view)) was used for the quantitative analysis of indium and tin present in acid solution. The spectrometer was equipped with a pneumatic V-Groove nebulizer and an inert Sturmun-Master nebulization chamber (PTFE). The optimum conditions for the spectrometer for the analysis were the following: Plasma power 1.2 kW, integration time 5 s; baseline correction in dynamic mode; nebulizer pressure 300 kPa; auxiliary argon flow 1.5 Lmin⁻¹; argon plasma flow 15 Lmin⁻¹, and a rate of 15 rpm of the peristaltic pump to introduce the liquid sample. Each measurement was carried out three times. The acid solutions containing indium and tin were diluted with ultrapure water, and then analyzed. The metal content was quantified by calibration using external standards, and these standards were adapted to the sample matrix.

Scanning Electron microscopy (SEM, HITACHI S4700) equipped with Energy Dispersive Spectroscopy (EDS) microanalysis and a Back-Scattered Electrons (BSE) detector, was used for surface analysis and particularly imaging of LCD layers before and after ITO extraction. The samples were prepared by carbon coating in order to eliminate accumulation of electric charges, due to surface exposure by the electron beam. The magnification achieved during experiments was approximately 10000x using an acceleration voltage of 10 kV.

The optical microscope (OM) used was an Olympus BX-41 model, equipped with a digital camera that can record images with high resolution, conjugated with a PC. Sample analysis was carried out at room temperature

The chemical composition of ITO layers was examined by Time-of-flight secondary ion mass spectrometry (ToF-SIMS), using a TOF-SIMS 5 spectrometer from the company Ion-tof

GmbH (Münster, Germany). Before measurement, samples were cleaned with distilled water and dried with ambient air. The spectrometer was maintained under ultra-high vacuum of about 10^{-9} mbar. The ToF-SIMS experiments were operated in depth profiling mode to sputter the material. The in-depth distribution of elements was obtained from a sample surface of (300 μm x 300 μm). Primary Bi^+ ions (1 pA) were used for the analysis of a zone of (100 μm x 100 μm), and O^{2+} ions were applied for pulverization (1 kV), while the oxygen current was 284 nA. The depth profiles were then determined with a mechanical profilometer (IQ Alpha-Step, KLA Tencor).

2.3 Experimental procedure

EOL LCDs were dismantled manually for the separation of various precious components. Figure 1a illustrates schematically the process of disassembly and ITO recovery. Extraction of ITO layers was carried out in a container with dimensions (50 x 40 x 10 cm^3) possessing thus a solvent capacity of 20 L, but only a reduced volume of 5 L was used during the experiments. It should be pointed out that the inside of the basin was covered with an anticorrosive protection layer. This solvent container was equipped with an array of 8 ultrasonic plate-type transducers using piezotechnology, working at a frequency of 20 kHz. These transducers were glued at equal distances from each other at the upper outside of the container allowing uniform ultrasonic energy distribution. A NEXUS CASE SERIE 800 US generator from SinapTec company (Lezennes/France) was used applying a power of 320 W. The solvent container incorporated a valve located at the bottom of the tank allowing solvent evacuation and recovery of dissolved species, and a partially perforated insert was employed to maintain glass/ITO samples in the bath. Moreover, the container was secured by a retention tray, and a device allowed temperature control of the solution. ITO extraction experiments were carried out after reaching a constant temperature of $60^\circ\text{C} \pm 3^\circ\text{C}$.

Figure 1

During the extraction process, glass/ITO substrates from LCD were exposed to the acid bath with the ITO-side gently touching the liquid surface, allowing to limit the dissolution of other species which might contaminate the acid solution. Leaching experiments of the ITO layer were repeated several times and averaged results were given. The diagram displayed in Figure 1b presents a scheme of the experimental device used for ITO extraction.

3. Results and Discussion

Preliminary disassembly and acid leaching experiments were carried out on a series of EOL LCDs. The results presented hereafter from different analysis techniques were obtained from a single 17 inch LCD screen (4/3 format), which was chosen as representative example. Small area samples (2 x 2 cm²) were cut from this LCD, allowing to compare data from SEM/BSE, OM, and ICP-AES.

3.1 Surface analysis

Surface analysis of the open glass panels of a disassembled EOL LCD was carried out by SEM and OM techniques, after eliminating the LC from the inside of the sandwiched substrates. Both glass panels corresponding to Color Filter (CF) and TFT layers were analyzed and their morphologies are shown on Figure 2. Pictures a) and b) correspond to the CF layer, and illustrations c) and d) represent the TFT layer. SEM images (Figure 2a and 2c) present clearly the ITO layer on both CF and TFT substrates, since the ITO layer appears in gray and the glass substrate in black colors. In the case of the TFT panel, the white area corresponds to Molybdenum deposit. These results were confirmed by microanalysis via SEM/BSE. Figure 2a shows the ITO covering of the CF layer and the corresponding RGB colors (Figure 2b), and Figure 2d represents the ITO-layer of the TFT panel in relationship with the electrical circuits observed on Figure 2c.

Figure 2

The ITO layer thickness was determined by ToF-SIMS by surface erosion forming a crater, and then depth measurements of the crater corresponding to the whole ITO layer thickness were carried out by mechanical profilometry. Figure 3a shows the ToF-SIMS depth profile where only intensities from In, Sn, and Si fragments were displayed to clarify the graphical presentation. For sputtering times lower than 50 s, relatively low intensities were obtained due to the presence of a polymeric alignment layer and surface contamination. Above 50 s sputtering time, intensities from In and Sn ions increase strongly before reaching plateau levels corresponding to the ITO layer. A weak Si-based signal was observed which increases above an erosion time of 220 s to yield constant values in good agreement with the simultaneous decrease of intensities from In and Sn ions, indicating that the glass surface was reached after roughly 300 s sputtering time, which can be related to an average ITO layer thickness of 120 nm measured by mechanical profilometry (Figure 3b).

Figure 3

Knowing the average volume density of ITO ($7.14 \times 10^6 \text{ g/m}^3$), and keeping into mind that indium represents approximately 74 mass% of ITO, estimation of the theoretical indium quantity to be recovered can be carried out by taking into account the thickness of the ITO layer. By admitting as a first approximation that the ITO layer thickness could be considered as continuous on both sandwiched panels, Figure 4 represents calculated indium quantities to be recovered from EOL LCD panels as function of ITO layer thickness and LCD surface dimensions (CF and TFT layers). Three different ITO layer thicknesses were considered, i.e. 50 nm (particularly used for small devices), 100 nm, and 150 nm. The latter thicknesses can be found for recent and new computer monitors and TV screens, older LCD production could even exhibit ITO thicknesses up to 300 nm. Undoubtedly ITO removal from large screens is economically more attractive than from small displays, without taking into account their

commercial distribution. For example a large-size LCD screen of 85 inch in diagonal (16/9 format) represents a total ITO surface from CF and TFT layers of nearly 40000 cm², accounting for 2.1 g or 3.16 g indium, in case of ITO thicknesses of 100 nm and 150 nm, respectively. On the other hand, a standard popular LCD monitor of 19 inch in diagonal (16/9 format) includes roughly 105 mg (100 nm ITO thickness) and 157 mg indium (150 nm ITO thickness).

Figure 4

A literature survey revealed a limited number of reports corresponding to depth analysis of the ITO layer, and more interesting, the recovered indium amount was often given as ratio of indium weight to glass/ITO weight, which makes comparison a difficult task, since independent of eventual impurity effects occurred during the shredding process, glass/ITO exists at least in 4 different thicknesses, 0.4, 0.55, 0.7, and 1.1 mm, the latter being the most common and cheapest one. Nevertheless, efforts were made to compare literature data in order to calculate the experimentally recovered indium quantities. These calculations were based on a 17 inch-LCD screen in 4/3 format presenting a surface of both layers of 1790 cm², a glass/ITO density of 2.498 g/cm³ [37], and a glass/ITO thickness of 1.1 mm. Wang et al. [38] reported about an indium content of 102 mg/kg (glass/ITO), which would correspond to 50.2 mg indium in the case of a 17 inch LCD screen. Lee et al. [23] determined the indium amount as 225 mg/kg, representing thus 110.7 mg for a 17 inch LCD screen. Li et al. [39] crushed 1 kg of glass/ITO in 500 mL acid solution and obtained under optimum experimental conditions a maximum indium concentration of 250 mg/L, corresponding to 61.5 mg indium for a 17 inch LCD.

3.2 Ultrasonic effect

Figure 5 presents ICP-MS results from acid treatment of glass/ITO panels. Indium and tin

dissolution kinetics were investigated as function of leaching time using concentrated sulphuric acid (18 mol/L) at 60°C in absence and presence of US activation. In all cases studied, the amount of indium and tin increased with leaching time reaching plateau levels within 3-10 min for indium, and 15-20 min for tin.

Figure 5

The ultrasonic effect is clearly visible on Figure 5a since practically no induction period was observed in this case, and a strong enhancement of the indium extraction efficiency could also be noticed. For example at 4 min leaching time, only 13 % indium was dissolved without ultrasonic treatment, whereas more than 82 % were obtained with ultrasonic activation. Plateau values indicating maximum indium quantities were already reached after 3 min leaching time in the latter case, while 10 min were necessary to obtain constant concentration values in the absence of US. The total indium recovery percentage was 70 % in the absence and more than 92 % in the presence of US activation. Applying ultrasonic power causes acoustic cavitation phenomena i.e. bubble formation and growth, and finally collapsing of these bubbles occur in the acid medium [40]. During their implosion, extremely high temperatures are generated and high-speed microjets and high pressure shock waves occur particularly at the interface between the acid solution and the solid ITO/glass matrix. As a consequence, ultrasonically assisted acid leaching intensifies solid/liquid mass transfer and particle diffusion. These phenomena improve considerably material extraction [41-42] in acid solution, thus ITO layer leaching will be facilitated. It was also found that tin extraction was less sensitive to ultrasonic activation than indium recovery. Indeed, Figure 5b shows, within experimental errors, roughly the same kinetics with slightly enhanced tin concentrations recovered applying US activation. Since US activation leads to strongly enhanced recovery especially of indium, extraction experiments described below will be conducted applying this procedure.

3.3 Influence of acidity

Figure 6 shows the dilution effect of H_2SO_4 on indium and tin extraction, as function of leaching time. Dissolution kinetics strongly depend on acid concentration for both indium and tin. A rapid increase of indium concentration with leaching time was found for the highest acid concentration (Figure 6a), whereas successive reduction of the acidity slowed down indium dissolution. The decrease of reactivity was found to be in good agreement with the decrease of acid concentration, in the following order: S0-S1-S2-S3-S4-S5. Interestingly, after a leaching time of 30 min, plateau values were obtained for the efficiency of indium extraction situated between 89 and 96 % (Figure 6a), independent of the initial acidity.

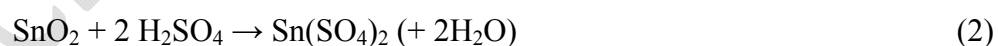
Figure 6

A literature survey shows that the results reported here are in good agreement with published data; i.e. an increase of the acid concentration leads to enhanced indium extraction from ITO [29]. It should be highlighted that literature data report on large time scales for acid leaching under different operational conditions: Starting from ITO powder, Virolainen et al. [27] obtained 100 % yield of indium and tin within 6 h leaching time using 1 mol/L H_2SO_4 at room temperature. Yang et al. [31] estimated the maximum indium efficiency to 80-90 %, achieved after 4 h leaching time applying a 6 mol/L H_2SO_4 solution at $T=20^\circ C$. An indium extraction rate of 85 % was reported by Li et al. [29] after a leaching period of 80 min at $T=65^\circ C$. The same operational temperature was chosen by Wang et al. [32] together with a H_2SO_4 concentration of 0.6 mol/L and a leaching time of 42 min.

In this work, high efficiency for the indium extraction was obtained by application of US within short time scales (only 4 min to reach a yield of more than 82 %). To the best of our knowledge, such fast reactions for ITO leaching from LCD supports were not reported up to date.

In the case of tin extraction displayed in Figure 6b, the acid concentration dependence on the extraction yield did not follow a clear tendency, since the following decreasing efficiency order was found: S5-S1-S3-S4-S2-S0. Figure 6b shows that the strongest tin extraction was observed with the lowest acid concentration and vice-versa, but the intermediate data do not agree well to this trend. On the other hand, these leaching curves exhibit plateau values beyond 20-25 min exposure time, in a range of extraction efficiencies comprised between 68 % (S0) and 100 % (S5).

Some investigators mentioned that SnO₂ was found to be insoluble in H₂SO₄ [13, 23, 29], causing thus a certain reduction of ITO recovery, since SnO₂ represents roughly 10 mass% of the total ITO weight. The presence of oxides with weak tin and indium valence, such as SnO, InO and In₂O, was also reported, which might show better solubility in H₂SO₄ than SnO₂. On the other hand, other literature references indicate that due to their amphoteric character, SnO₂ as well as SnO dissolve either in strong bases or acids [43-44]. In particular, reactions between tin (II)- and tin (IV) oxides with highly acidic H₂SO₄ give the corresponding tin (II) and (IV)-sulfates, where Sn(SO₄) remains soluble in H₂SO₄, but Sn(SO₄)₂ could precipitate to form tin (IV) sulfate dihydrate Sn(SO₄)₂·2H₂O. The principal reactions of sulfuric acid dissolution of ITO from glass/ITO substrates can be written as [43]:



It should be mentioned that these reactions (1)-(3) possess an irreversible character. In order to clarify the findings from literature, additional dissolution experiments using separately ITO, In₂O₃, SnO₂ and SnO nano-sized powders were conducted in our laboratory, applying the same conditions used for leaching experiments of EOL LCD panels under US assistance. Nano-sized powders were selected for this purpose in order to conduct this study on a size

scale comparable to the thickness of the ITO layers (< 300 nm). Since this investigation was focused on the acid treatment of one single 17 inch LCD screen (4/3 format) in a total volume of 5 L, dissolution experiments were carried out taking into account maximum quantities to be recovered for this case, supposing an ITO layer thickness of 300 nm; i.e. for ITO: 383 mg, and consequently for In_2O_3 : 307-345 mg (80-90 mass%); for SnO_2 : 38-77 mg (10-20 mass%); for SnO: 30 mg. As result, all solubility limits were found to be above these limits, so that eventual immiscibility effects could be excluded in the present investigation.

3.4 Chemical analysis by SEM/BSE

Figure 7 displays a selection of SEM pictures obtained from the ITO-side of small glass/ITO samples (2×2 cm²) which were cut from the same 17 inch LCD used for Figures 5-6. These samples underwent the same acid leaching procedure as those investigated by ICP-AES technique, allowing thus a direct comparison of the results achieved from ITO-extraction kinetics considering both methods. Chemical surface analysis was carried out on each SEM picture presented on Figure 7 via data recovery from a BSE detector. As a result, signal intensities related to certain colors/grey scales could be specifically attributed to In, Sn and Si containing compounds, allowing to follow ITO dissolution from In/Sn oxide coverage up to the final glass surface represented essentially by SiO_2 compounds.

Figure 7

SEM pictures were acquired from treated glass/ITO samples as functions of leaching time and acid strength, showing fast dissolution kinetics especially in the case of S0: In/Sn signal intensities went to zero within only 3 min leaching time, corresponding to complete dissolution of the ITO layer, and 5 min were necessary to get only Si-based signals in the case of S1.

As expected, successive reduction of the acidity (S1 → S5) leads to continuous slowing down of the extraction kinetics; and complete dissolution of the ITO layer was achieved for S2, S3, S4, S5 at 12.5 min, 15 min, 25 min and 30 min leaching time, respectively. The acidic conditions employed in this investigation were generally suitable for ITO recovery, with important differences in leaching time, necessary to reach the same maximum ITO quantity in all cases considered here.

In order to compare both analysis methods (ICP-AES and SEM/BSE), data treatment of SEM/BSE pictures shown in Figure 7 was carried out using a standard image processing program. The obtained results were presented in Figure 8 together with ICP-AES data from Figure 6. Leaching percentages of 0 % and 100 % correspond to a completely covered ITO surface (situation before leaching) and to total ITO removal, respectively. As a result, data processing of SEM/BSE pictures was found to be in good agreement with the kinetics determined by ICP-AES technique. It should be mentioned that the latter technique represents an indirect determination method for ITO layer removal, whereas chemical analysis via BSE detector of glass/ITO surfaces corresponds to a direct method indicating presence or absence of indium and tin containing compounds on the glass surface.

Figure 8

4. Conclusions

In this report, ITO-layer extraction from EOL LCD was discussed by sulfuric acid leaching with simultaneous US application on the ITO-side of glass/ITO panels exhibiting various dimensions. Applying this technique presents several advantages such as high extraction yield of indium and tin, fast and controllable kinetics, selective recovery of indium and tin possible, and the opportunity to recycle the neat glass separately avoiding additional separation processes. It should be highlighted that LCD-glass belongs to a special category containing

low ion concentrations, presenting thus a certain economic value added. In particular it was demonstrated that by using 18 molar sulfuric acid at a temperature of 60°C, the percentage of recovered indium reached nearly quantitative yield applying US, whereas without US assistance, only 70 % indium were obtained after 20 min leaching time. It should be underlined that maximum ITO recovery could not be achieved in the absence of US activation.

Variation of the sulfuric acidity in the range from 9 mol/L to 18 mol/L affects strongly ITO extraction kinetics, but the whole ITO layer could be finally removed for all acid concentrations employed here. The best conditions for fast and maximum ITO recovery were determined as: sulphuric acid (18 mol/L) leaching of the ITO side of glass/ITO panels during 3-4 min at 60°C under sonication.

The approach presented in this report to investigate the ITO recycling process provides essential information to monitor and to control indium and tin recovery qualitatively and quantitatively. Further studies will be performed to investigate upscaling feasibility from experiments conducted at the laboratory to pilot and industrial applications.

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Figure captions

Figure 1: a) Diagram illustrating the extraction of the ITO layer from EOL LCD panels.

b) Schematic presentation of the experimental device used for ITO extraction from the glass/ITO substrates.

Figure 2: Microscopic observations of a dismantled EOL LCD. Pictures a) and b) correspond to the CF layer, and images c) and d) represent the TFT array layer. Illustrations a) and c) were obtained by SEM whereas b) and d) were observed by OM.

Figure 3: a) ToF-SIMS depth profile of the ITO layer thickness as function of sputtering time. In order to simplify the graphical presentation, only the evolution of In, Sn and Si cations were considered.

b) Result from mechanical profilometry of the ToF-SIMS profile shown in a).

Figure 4: Calculated indium quantities to be recovered from waste LCD panels as function of ITO layer thickness and LCD surface (CF and TFT layers).

Figure 5: Ultrasonic effect and influence of leaching time on a) indium and b) tin extraction of a 17 inch LCD (3/4 format) using concentrated sulfuric acid (18 mol/L) (S0) at $T=60^{\circ}\text{C}$. The dashed lines stand for the calculated maximum concentration taking into account an ITO layer thickness of 120 nm (cf. Figure 3).

Figure 6: Influence of the acidity on the extraction of a) indium and b) tin from 17 inch LCD, assisted by US at a temperature of 60°C . S0, S1, S2, S3, S4, and S5 correspond to sulfuric

concentrations of 18, 16.2, 14.4, 12.6, 10.8, and 9 mol/L, respectively.

Figure 7: SEM/BSE pictures from the ITO-side of small glass/ITO samples ($2 \times 2 \text{ cm}^2$) which were cut from the same 17 inch-LCD support. The time scale corresponds to different leaching times, and S0-S5 stand for various acid strengths as mentioned before.

Figure 8: Comparison of ITO-leaching kinetics analysis obtained by ICP-AES and SEM/BSE techniques. Closed symbols belong to ICP-AES results, whereas open symbols represent SEM/BSE data. Only four acid concentrations S0 (18 mol/L), S1 (16.2 mol/L), S3 (12.6 mol/L), and S5 (9 mol/L) were considered here to clarify graphical presentation.

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