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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Recovery of indium tin oxide (ITO) and glass plate from discarded TFT-LCD panel using an electrochemical method and acid treatments

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

The recovery of ITO and the glass substrate from discarded TFT-LCDs, without crushing the glass substrate, was done by using an electrochemical method and acid treatments. Anodic conditions did not show any redox reaction of the ITO except oxygen evolutions. The oxygen evolution lifted the ITO layer off the glass substrate with remaining colour filer and black matrix. Recovery of the ITO was 75%, but it showed an In/Sn ratio of 15.9:1. The recovered ITO could not be suitable for reuse directly. Maybe, it needed an addition of extra Sn. However, this work presented a new process for the resource circulation of the indium from discarded LCD panels. The free glass substrate was then recovered after removing colour filter and black matrix by using an acid solution. The optical transmittance of recovered glass substrate was about 90% in the visible region, and the average roughness was 0.96 nm.

Introduction

During the last two decades, many research groups have studied the specific characteristics of Indium Tin Oxide (ITO) such as transparency and conductivity because it could be applied to many important electronic industries. Recently, demands for ITO have increased because it has been used as a transparent conductive electrode (TCE) part in flat panel display (FPD). The consumption of ITO follows the display industry growth rate. Currently, the price of ITO has been increasing because the international production of rare element indium is limited. It has been reported that the current indium consumption rate will make the reservoir exhausted by the year of 2025.[1] As the consumption grows in industries, the price of indium will increase rapidly. In the year of 2013, the annual average New York dealer price of indium increased about 6% compared with the year before. Currently, Metal Bulletin shows that indium price increased by 26%. [2, 3] According to a report from Indium Corporation, the growth of FPD market has slowed, but a rapid increase in the solar industry is expected, especially in Copper Indium Gallium Selenide (CIGS). The indium demand for CIGS is expected to increase four times in 2016 than 2011. Therefore, it is expected that the consumption of indium will increase in the solar industry.

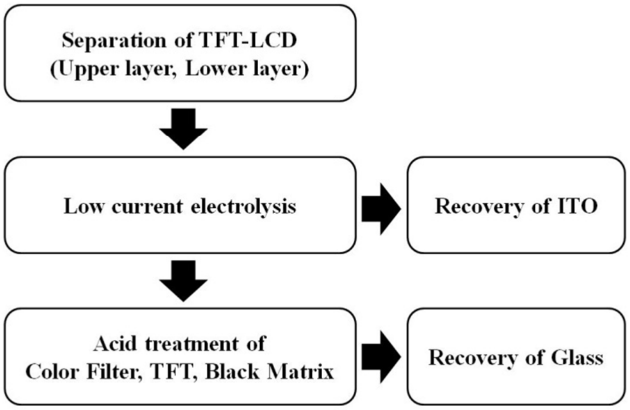
To combat the depletion of indium and tin resources, recycling of the elements from waste electrical and electronic equipment (WEEE) and waste sputtering targets have become important.[5] Glass plates, known as special non-alkaline glass, for the transparent electrode takes up about 8% of the total price of an LCD panel; most of them are discarded after final use. When the glass is discarded, it is a waste of resources, and of course, it is not environmentally friendly.[6] For these reasons, many research groups are trying to find recovery methods of indium (or ITO) and glass from discarded LCD for resource recycling.

Several methods are used for recovery of indium from discarded TFT-LCD panels including rough vacuum chlorinated separation[7, 8], dissolving assisted high energy ball milling (HEBM) [9, 10], and electrochemical machining (ECM).[11-15] Ma *et al.* [7, 8] reported the recovery of indium chloride from the waste LCD panels using rough vacuum-chlorinated separation methods, which showed high recovery yield of indium in the form of indium chloride. However, these methods require high temperatures and crushing of the LCD panel. Kang *et al.*[9] and Lee *et al.*[10] reported HEBM recovery of indium from used LCD panels. However, this method also involved crushing the glass. Separation of ITO from LCD panels without glass crushing was proposed by Pa[11-15] using electrochemical machining (ECM) that required very high currents and expensive apparatuses. However, Pa did not report the quality of removed ITO. As we discussed, glass substrate is another valuable material in LCDs. However, most of the indium recovery processes from discarded LCD adopted glass-crushing and destruction in order to collect ITO.

We tried to develop a process that will recover ITO and the glass plate simultaneously from a discarded LCD panel. In this paper, we show this recovery of ITO and the glass plate without crushing by using an electrochemical method followed by treatment with acid.

Experiment

Sodium hydroxide (ACS grade, Sigma-Aldrich) and sodium nitrate (extra pure grade, Daejung Chemical & Metals, Korea) were used for the electrolyte. All electrolyte solutions and washing used high purity deionized (DI) water (18.2 MΩ·cm). Sulphuric acid (ACS grade, 96%, Sigma-Aldrich), hydrochloric acid (ACS grade, 37%, Sigma-Aldrich), and hydrogen peroxide (extra pure grade, 35%, Junsei Chemical Japan), were used as the acid treatment solution for removing the colour filter and black



SCHEME 1. Process of recovery of ITO and glass

matrix. Our recovery process of ITO and glass is shown in Scheme 1. First, the TFT-LCD plate was separated into upper and lower layers by using an edge-cutting method.[16] After separation, the polarizer film was removed by peeling, and the liquid crystal was removed using acetone and DI (deionized) water with sonication for 3 min. The upper layer which was cut into 1 × 4 cm^2 pieces in order to be used as electrodes for electrolysis. Basic electrochemical properties of the TFT-LCD upper plate were tested by cyclic voltammetry and chronoamperometry using a conventional three-electrode system. All of the electrochemistry was done by using a Potentiostat/Galvanostat (EG&G model 263A). The 1 × 4 cm2 pieces of the TFT-LCD upper plate were used as working electrodes. The reference electrode was a homemade Ag/AgCl electrode filled with saturated KCl. All potentials were compared to this reference electrode at room temperature. A platinum plate (1 × 6 cm^2) was used as a counter electrode. All cyclic voltammetry measurements were carried out at scan rate of 0.05 V/s in 0.1 M NaOH solution. Anodization and cathodization of the TFT-LCD upper plates were performed by applying potentials of 1.5 V for 5 min and -1.5 V for 5 min, respectively, in 0.1 M NaOH solution.

Low current electrolysis of the 1 × 4 cm^2 TFT-LCD piece was also performed using the Potentiostat/Galvanostat. In this experiment, the 1 × 4 cm^2 piece was used as the anode, and the Pt plate was used as a cathode. We applied a current density at 0.2 A/cm^2 in 15 wt% $NaNO_3$ electrolyte for 30min.[17] After the constant current electrolysis, the cut-piece was washed with DI water 4~5 times. After the washing, the used electrolyte and the washing waste were filtered together for the collection of ITO. The glass substrate, after removing ITO, was immersed in H_2SO_4 and then HCl: H_2O_2 (3:1) mixed solution for 5min in order to remove the colour filter and black matrix. After washing, the free glass plate was obtained. The optical transparency of this glass piece was tested with UV/VIS absorption measurements.

Surface morphology and size of the recovered ITO and glass surface were observed by an optical microscope (OM: DW-XJZ-6A) and a field-emission scanning microscope (FESEM: JEOL JSM-7000F). Chemical composition analysis was done by energy dispersive x-ray spectroscopy (EDS). The optical transmission spectra of the recovered glass were measured by UV/VIS spectrophotometer (HP 8453 Spectrophotometer). Surface composition and the chemical state of recovered ITO were investigated with X-ray photoelectron spectroscopy (XPS: VG Microtech ESCA2000) using Al Kα radiation as an exciting source. All binding energies (BE) were referenced to the C 1s peak at 284.6 eV. Surface roughness was investigated using an atomic force microscope (AFM: NX10 Park system)

Results and discussion

First of all, the electrochemical properties of the TFT-LCD upper plate need to be understood before separating ITO from the plate by using this electrochemical method. The electrochemical characterization of the upper plate was performed using a cyclic voltammetry method. Inset of Figure 1 (a) shows a cyclic voltammogram (CV) of the TFT-LCD upper plate carried out at the scan rate of 0.05 V/s in 0.1 M NaOH solution. The cyclic potential window was set between -0.6 and 0.6 V. When the potential scan was carried out in the positive direction, oxygen evolved, and in the other direction, hydrogen evolved.[18, 19] In this case, the on-set potentials of oxygen evolution and hydrogen evolution were seen at 0.6 V and -0.35 V, respectively. Figure 1 (a) also shows CV for the first 10 cycles between 0 and 1.4 V. The current was dramatically increased when the scan direction was in the positive direction, and gas evolution from the electrode was observed. The oxygen evolution current decreased as the number of cycles increased. On the other hand, the onset potential for oxygen evolution increased up to 0.8 V. This type of electrochemical behaviour of our TFT-LCD upper plate was quite similar to those of new ITO glass.[20] The electrochemical stability of TFT-LCD upper plate was evaluated before and after anodic and cathodic polarizations.[21] Anodization was done in 0.1 M NaOH with a constant potential of 1.5 V, and cathodization was done in the same electrolyte with a constant potential of -1.5 V for 5min. In Figure 1 (b), the CV after anodization of TFT-LCD upper plate is compared to the one before anodization. It showed that only charging current responses appeared in the potential range of -0.35 V to 0.6 V. This result indicated that no redox reaction except hydrogen evolution occurred at -0.35 V in that window. However, the CV after cathodization showed hydrogen evolution at about -0.4 V, and the oxidation reaction peak started at -0.3 V (Figure 1 (c)). In^{3+} and Sn^{4+} cannot be oxidized further because those values are the highest oxidation states respectively. However, during the cathodization, it might be possible to reduce them to the lower oxidation state. After cathodization, the chemical composition of ITO was changed, and an opaque film or In-Sn spherical particle was observed on the ITO surface.[22, 23] This result showed that the In^{3+} or Sn^{4+} can be reduced to a lower oxidation state. The oxidation peak came from reduced metal or a metal hydroxide. During the cathodization, metal or metal hydroxides of Sn and/or In deposited on the ITO surface.[24] Figure 1 (d) shows the CV of after cathodization for the first 10 cycles. During the cycles, the charging current decreased, and the oxidation peak also decreased continuously and disappeared finally. This finding showed that deposited materials were peeled off or dissolved easily from the ITO surface. According to these electrochemical behaviours, we decided to use anodic conditions for ITO recovery because electrochemical reactions of ITO would not take place. Figure 2 shows SEM images of the TFT-LCD upper plate after constant current electrolysis with the current of

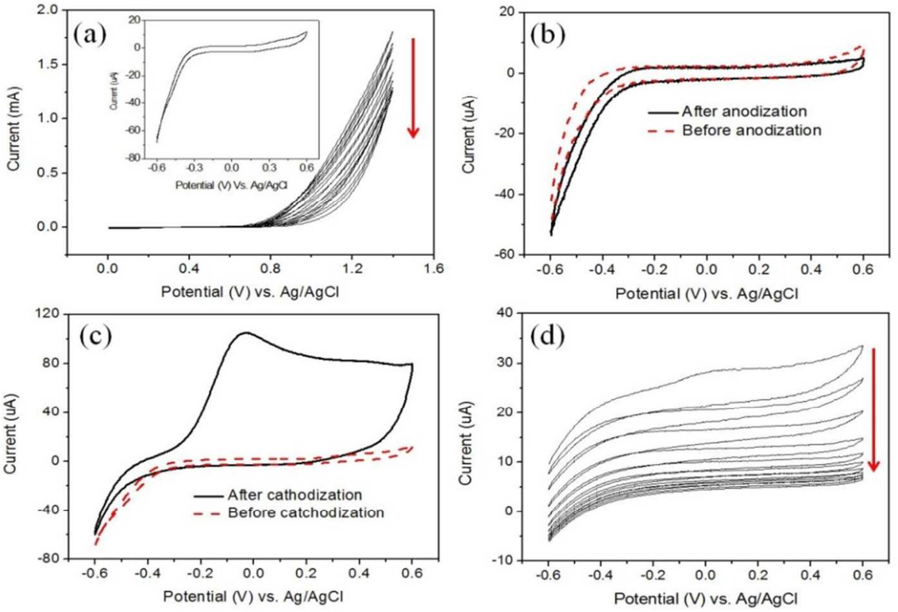


Figure 1. Cyclic voltammograms of TFT-LCD upper layer in 0.1M NaOH at 0.05 V/s (a) between 0 and 1.4 V for 10 consecutive cycles, (b) after anodization (1.5 V for 5 min), (c) after cathodization (- 1.5 V for 5 min), and (d) after cathodization for the first 10 cycles.

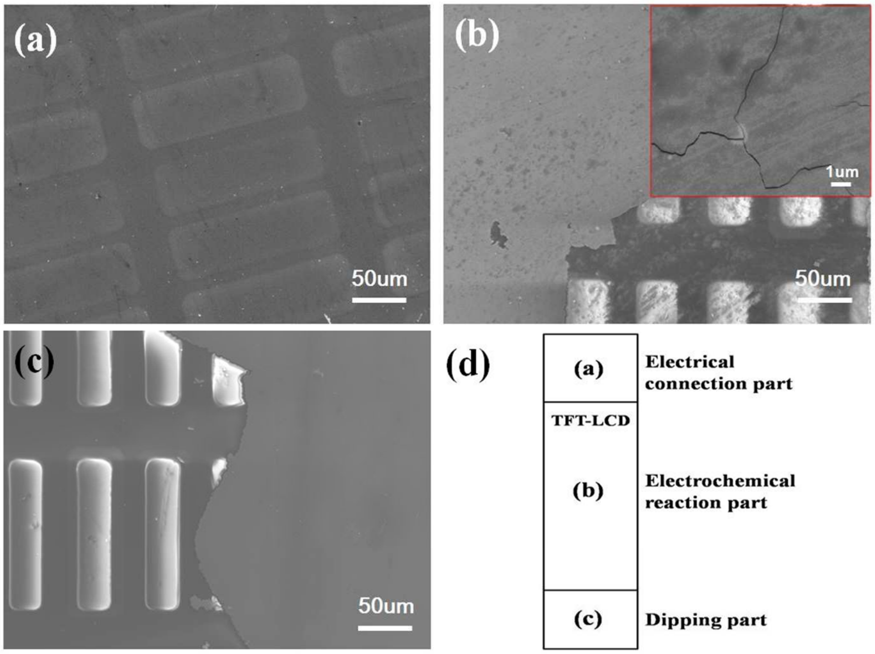
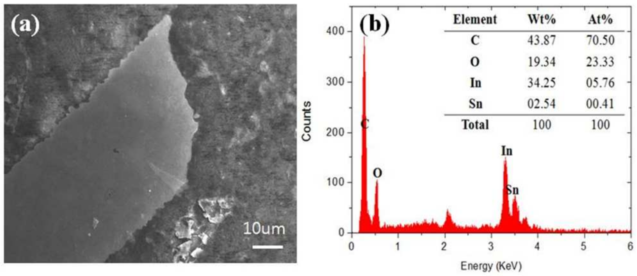


Figure 2. SEM image of the TFT-LCD upper layer after low current electrolysis (LCE): (a) electrical connection part, (b) electrical reaction part, and (c) dipping part. (d) The upper plate by parts is described in the schematic illustration.

0.2 A/cm^2. In Figure 2 (a), no reaction was observed where the electrical connection was made. However, Figure 2 (b) and (c) show quite different images from that in Figure 2 (a). Figure 2 (b) shows the part between electrical connection part and the dipping part after electrolysis. Many cracks and lift-off parts of ITO were apparent, and the rectangular shapes of colour filters were exposed. The image of the dipping part appears in Figure 2 (c) and is quite similar to that of Figure 2 (b). However, unlike the electrochemical reaction part shown in Figure 2(b), the dipping part of the ITO showed clear lift-off. In these results, we considered that more electrolytes permeated into the space between the ITO and the colour filer layers in dipping part (c) than in part (b). During the electrolysis, cracks occurred on the TFT-LCD upper plate surface because of oxygen evolution between the ITO layer and the glass plate. As a result ITO was lifted off from the glass plate. After washing the glass plate, used



Element	Wt%	At%
C	43.87	70.50
O	19.34	23.33
In	34.25	05.76
Sn	02.54	00.41
Total	100	100

Figure 3. (a) FESEM image of the recovered ITO; (b) EDX analysis of the recovered ITO.

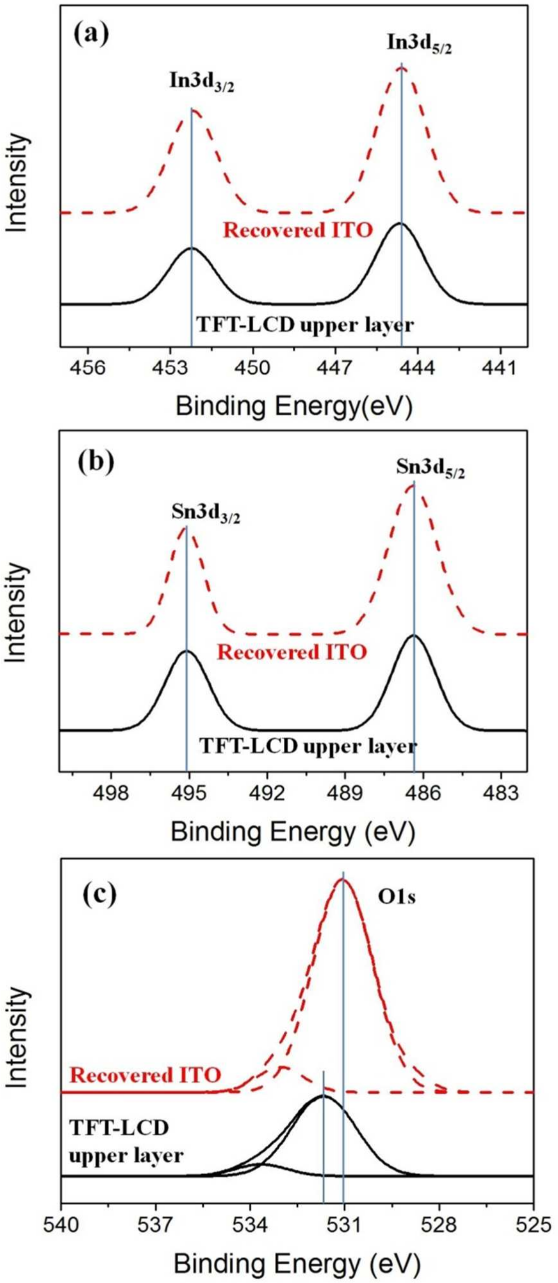


Figure 4. XPS spectra of TFT-LCD upper layer (black solid line) and recovered ITO (red dashed line); (a) Indium 3d, (b) Tin 3d, and (c) Oxygen 1s.

Table 1. Summarizes the binding energies and In/Sn atomic ratio.

Sample	In ($3d_{5/2}$) (eV)	Sn ($3d_{5/2}$) (eV)	O (1s) (eV)	In/Sn atomic ratio
TFT-LCD upper layer	444.6	486.3	531.7	9
			533.6	
Recovered ITO	444.6	486.2	531.1	15.9
			533.0	

electrolyte and the washing waste were filtered together for the collection of the ITO. The shape and composition of the recovered ITO were characterized by using FESEM and EDS. Figure 3 (a) shows the FESEM image of the of the irregularly shaped, recovered ITO. According to the EDS analysis in Figure 3 (b), the recovered ITO consists of oxygen, indium, and tin. The In and Sn atomic ratio was estimated to be 14:1, which is a little different from the original value of 10:1. XPS spectra of TFT-LCD upper plate (black solid line) and recovered ITO (red dashed line) are shown in Figure 4. Table 1 summarizes the binding energies and the In/Sn atomic ratio. The In 3d binding energy from the recovered ITO was precisely the same values from the TFT-LCD (Table 1). In 3d spectra, Figure 4 (a) shows two peaks located at 444.6 eV and 452. 3 eV that correspond to In $3d_{5/2}$ and In $3d_{3/2}$ state, respectively. These values are associated with In^{3+} bonding state in the form of In_2O_3.[25-28] We also measured the Sn 3d XPS of the TFT-LCD upper layer and the recovered ITO in Figure 4 (b). The Sn $3d_{5/2}$ and Sn $3d_{3/2}$ peaks were found at 486.3 eV and 495.2 eV, respectively. These values indicated that Sn is in the Sn^{4+} bonding state from SnO_2.[26] The BE values of the recovered Sn were the same as in the original TFT-LCD layer. These results indicated that In and Sn of chemical states were not changed after constant current electrolysis treatment. However, the O 1s spectrum from the recovered ITO showed a little discrepancy. The oxygen binding energy shifted by about -0.6 eV, and the In/Sn atomic ratio increased (Table 1). A.Kraft *et al.*[29] reported that oxygen was incorporated into the In_2O_3 lattice during the oxygen evolution. This finding would lead to a decrease of charge carrier concentration or decrease of oxygen vacancies. In this result, we considered that oxygen evolution was comparable to O_2 plasma treatment on ITO glass. In general, O_2 plasma or UV-ozone treatments on ITO surface increase the work function and the In/Sn ratio of ITO.[26, 30] ITO is a degenerate n-type semiconductor where Sn^{4+} donates one free electron and the oxygen vacancy donates two free electrons.[25, 31] After the O_2 plasma treatment on the ITO surface, the concentration of Sn^{4+} and the concentration of oxygen vacancies decreased. Moreover, chemical composition and the work function of the ITO were changed.[32] The mechanism of the In/Sn ratio change was not clear at this moment. However, we suppose that the In/Sn ratio changed because of a decrease in oxygen vacancies during the oxygen evolution; this result is under further investigation.

The glass substrate is an important and valuable material that needed to be recovered from the WEEE. The TFT-LCD upper plate usually consists of ITO, a colour filter (CF), and a black matrix (BM). After recovery of ITO, the CF and BM were removed by using acid treatments to recover the free glass substrate. Figure 5 shows the optical microscope images of the TFT-LCD upper plate after LCE treatment. Figure 5 (a) does not show any electrochemical reaction because no permeation of electrolyte to this part occurred. However, in Figure 5 (b), after LCE treatment, only ITO was separated, thus leaving CF and BM

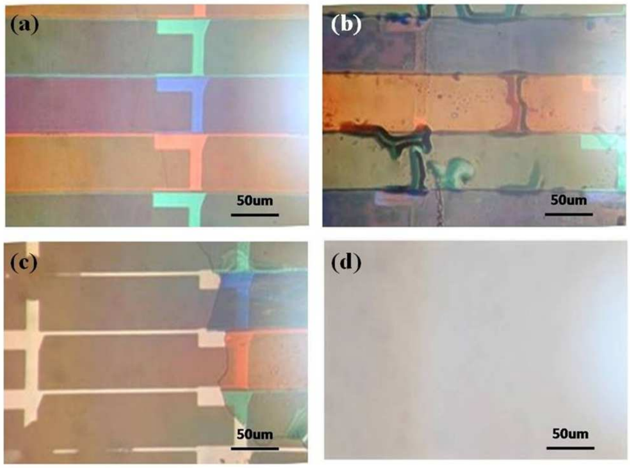


Figure 5. Optical microscope images of TFT-LCD upper plate after LCE treatment; (a) electrical connection part, (b) after removing ITO, (c) after removing CF, and (d) after removing BM.

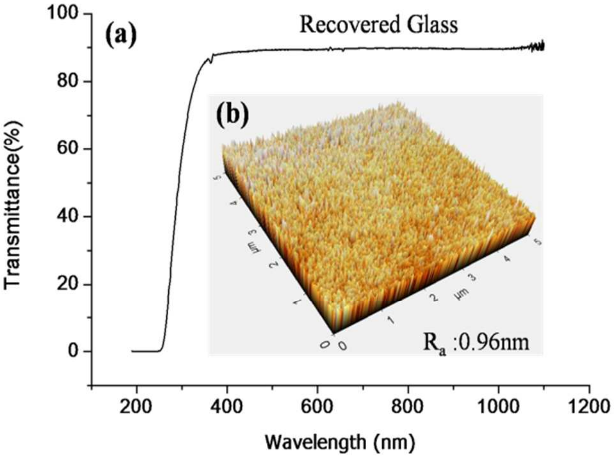


Figure 6. (a) Optical transmittance of recovered glass substrate and (b) surface morphology of the recovered glass.

on the TFT-LCD upper plate. To remove the remaining colour filter, the TFT-LCD upper plate was immersed in sulphuric acid. After 5min, the CF was totally removed, and only BM remained as shown in Figure 5 (c). The composition of the black matrix (BM) was uniform. It depended on the producing company, but the main components are Cr or Cr/CrO_x.[33] We prepared a HCl: H_2O_2 (3:1) mixed solution to remove the BM. After removal of the CF, the TFT-LCD upper plate was immersed in the mixed solution for 5min. As shown in Figure 5 (d), the BM was totally removed, and we recovered free glass substrate. Generally, the TFT-LCD glass substrate should show at least 90% transmittance in the visible region to allow reuse. The possibility of reuse of the recovered glass was confirmed by optical transmission. Figure 6 (a) shows that the optical transmittance of the recovered glass substrate has 90% transmittance in the visible region. These results are quite comparable to other works.[16] In general, a decrease in optical transmittance is generally attributed to rough surface morphology.[34] From this result, we assumed that the recovered glass was not rough because it has a high optical transmittance. Surface roughness of the recovered glass was measured by using non-contact mode AFM (Figure 6 (b)). According to the other work[16], the average roughness (Ra) value of newly produced glass and re-used glass are 0.399 nm and 1.135 nm, respectively. However, in this work herein, the Ra value of recovered glass was 0.96 nm. According to these results, we obtained excellent optical properties and good roughness of the recovered glass so that it could be reused.

Conclusions

ITO and the glass plate were successfully recovered from discarded TFT-LCD by using an electrochemical method followed by acid treatment. The TFT-LCD separated into two parts, an upper layer and a lower layer. We used the upper layer because the amount of ITO in TFT-LCD was more than the lower layer. According to the electrochemical behaviours of ITO, the anodic condition did not show a redox reaction except for oxygen and hydrogen evolutions. However, for the cathodic condition, In or Sn was reduced to metal or metal hydroxide that was deposited on the ITO surface. When we applied an anodic current, the ITO film was removed from the TFT-LCD upper plate selectively. ITO was recovered at 75% from discarded TFT-LCD pieces (4 × 1cm2). However, the quality of the recovered ITO was not good enough to reuse directly, because In/Sn ratio had been changed. For this reason, we are going to use this product with Sn addition treatment for electrode applications. The optical transmittance of the recovered glass substrate was about 90% in the visible region. Also, its Ra was about 0.96 nm. From these results, recovered ITO and glass substrate can be recovered, and the WEEE can be recycled.

Acknowledgement

This work was supported by the Energy & Resource Recycling of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry, & Energy (No.2010501010002B)

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Graphical Abstract

Recovery of indium tin oxide (ITO) and glass plate from discarded TFT-LCD panel using an electrochemical method and acid treatments

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ITO and glass substrate were recovered from discarded TFT-LCD upper layer