

Organic Acid Mixing to Improve ITO Film Etching in Flat Panel Display Manufacturing

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This study examines how oxalic acid mixed with tartaric acid affect indium tin oxide (ITO) etching. When the ITO films were etched with the mixed solutions of oxalic acid and tartaric acid, the dissociation of tartaric acid impeded the formation of oxalate ion and decreased the etching rate of ITO films. Furthermore, the potential–pH diagrams for indium and tin in oxalic acid and tartaric acid systems reveal that indium oxide could be dissolved to form $In(C_2O_4)_2^-$ in oxalic acid etchants, and that indium oxide and tin oxide were both soluble in the mixed etchants of oxalic acid and tartaric acid. Additionally, the X-ray photoelectron spectroscopy results demonstrate that the removal rate of SnO_2 was slower than that of In_2O_3 in oxalic acid etchants, which induced many residues after the etching process. However, adding tartaric acid to oxalic acid increased the dissolution rate of tin oxide and decreased the level of residues. Consequently, the ITO etching by oxalic acid with tartaric acid shows a more uniform pattern than that by only oxalic acid.

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Manuscript submitted May 22, 2005; revised manuscript received September 21, 2005. Available electronically December 6, 2005.

Flat panel displays, such as liquid crystal displays (LCDs) and organic light-emitting diodes (OLEDs), are extensively found in daily use. Flat panel displays require a transparent and conductive material to operate each pixel. Indium tin oxide (ITO) is widely employed as a pixel electrode in flat panel displays due to its ability to provide both excellent optical transmittance and good electrical conductivity. In addition to the operation of each pixel, the resistance-type touch panel also comprises the ITO films in its structure. The touch panel has been widely applied for the portable electronics, such as personal digital assistants, digital cameras, and car navigators. For patterning ITO films, either dry etching or wet etching can be adopted to produce the fine patterns. Wet etching is a simpler process than dry etching and has a high throughput and low cost. Therefore, wet etching is often used to pattern ITO films in the panel industry.

The wet etching processes, however, might cause problems of selective grain-boundary etching and isotropic etching, and the ITO deposition methods also tend to generate different ITO etching rates. Such nonuniform etching phenomena worsen the electrical properties of the ITO electrode and might lead to serious undercut phenomena. Therefore, the ITO etching process must be studied to optimize the process for mass production of flat panel displays or touch panels.

Different ITO films may require different wet etching solutions. Because the wet etching characteristics of ITO are highly dependent on the microstructure and microcrystallinity of the film itself, small variations in the films could leave residues after etching and also could cause the sidewall consumption of ITO films.^{3,4} Conventional etchants are generally composed of strong acids, such as halogen acid, ^{5,7} and aqua regia.² For the widely used top-ITO structures in LCD, the corrosion of the underlayer metal is serious during patterning ITO films using strong acids, ⁸ and the residual halide also degrades devices.² Therefore, weak acid etchants are increasingly used for ITO films instead of strong acids, and oxalic acid is the most frequently applied weak acid. However, the mechanisms of ITO etching using weak organic acids have seldom been investigated.

In this study, authors investigate the oxalic acid-based solutions applied to etch ITO films. Potential–pH diagrams and open-circuit potentials (OCPs) were used to examine the etching behaviors of ITO in oxalic acid systems. Additionally, another organic acid was also employed to compare with the etching behaviors of oxalic acid on ITO surfaces. Tartaric acid herein was chosen because of its ability to chelate the indium ion (In³⁺) and stannous ion (Sn²⁺). As

indicated in Table I, the stability constants of tartaric acid with In³⁺ and Sn²⁺ are close to those of oxalic acid, but those of other common organic acids such as formic acid, acetic acid, maleic acid, glycolic acid, and EDTA show greater difference.^{9,10} The etching experiments were done using oxalic acid, tartaric acid, and the mixed acids to examine their effects on patterning ITO films.

Experimental

Chemicals and materials.— ITO thin films, with a thickness of 1000 Å on the glass, were employed in these experiments. Before the etching process, the ITO samples were diced in the size of 1×1 cm and immersed in 150 ppm Triton X-100 solution for 3 min with an ultrasonic bath to remove the surface impurities. The samples were then rinsed in deionized (DI) water and dried by nitrogen gas.

The etchants were prepared using oxalic acid and tartaric acid. A heating circulator supplies water to maintain the temperature of the water jacket used to keep the etching reactor at a specified temperature.

Open-circuit potential measurements.— The open-circuit potentials (OCPs) of ITO films in various etchants were measured by the Autolab PGSTAT30 potentiostat with respect to an Ag/AgCl electrode. Dilute potassium hydroxide solution was added into the etchants to alter the pH values. The stable OCP can then be obtained in a period of about 50 s. All potentials in this study were reported with respect to a standard hydrogen electrode (SHE).

Etching rate measurements.— In the etching of metal film, the change in optical reflectivity between the etched film and its underlayer usually denotes the end-point. However, the ITO film is transparent and not suitable for optical method. Thus, the etching rate reported herein was determined by the change in the measured resistance of ITO films. ¹¹ The samples were immersed in the etchants to record the resistance changes with time until the resistance increased suddenly. Then the etching duration was determined from the sudden change in resistance. The etching rate was calculated by dividing the thickness of ITO films by the etching duration.

Surface observation and analysis.— The surface images of ITO films with patterns after etching with oxalic acid or with the mixed etchants were studied using an optical microscope (OM) and a scanning electron microscope (SEM). The ratios of indium oxide to tin oxide before or after etching were examined by X-ray photoelectron spectroscopy (XPS). In order to avoid the contamination of the ITO surface before detection, the sample was immersed in 150 ppm Tri-

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Table I. Stability constants (β) of indium and tin complexes at 25°C and 1 atm (from Ref. 9 and 10).

	Ligands (L)	Metal ion (M)	Stability constants $(\beta_{ML_n} \text{ or } \beta_{MHL})^a$				
Chelating agents			$log \; \beta_{ML}$	$\log \beta_{ML_2}$	$log \beta_{ML_3}$	$log \; \beta_{ML_4}$	$log \; \beta_{MHL}$
Oxalic acid	$C_2O_4^{2-}$	In ³⁺	5.3	10.52			3.08
		Sn ²⁺	6.8	12.2			
Formic acid	CHO ₂	In ³⁺	2.74	4.72	5.7	6.7	
Acetic acid	$C_2H_3O_2^-$	In^{3+}	3.5	5.95	7.9	9.08	
		Sn ²⁺	3.3	6.0	7.3		
Glycolic acid	$C_2H_3O_3^-$	In^{3+}	2.93	5.52	7.3	7.95	
Maleic acid	$C_4H_2O_4^{2-}$	In^{3+}	5.0	7.1	6.2		
Tartaric acid	$C_4H_4O_6^{2-}$	In ³⁺	4.44	8.46			
	. 4 0	Sn ²⁺	5.2	9.91			

^a $\beta_{ML_n} = [ML_n]/([M][L]^n)$ and $\beta_{MHL} = [MHL]/([M][H^+][L])$ where M is the metal ion, L is the ligand, H⁺ is the hydrogen ion, ML_n is the complex of metal ion, and MHL is the proton-complex of metal ion.

ton X-100 solution for 3 min with an ultrasonic bath to remove the surface impurities. Then the samples were rinsed in an ultrasonic deionized water bath and dried by nitrogen gas.

potential-pH Construction of potential-pH diagrams.— The diagrams of indium-oxalic acid-water, tin-oxalic acid-water, indium-tartaric acid-water, and tin-tartaric acid-water systems were constructed, respectively, by thermodynamic data collected from the literature. ^{9,10,12,13} Table II lists the considered species of indium and tin in oxalic and tartaric acid solutions and their standard free energies of formation, which were obtained from the literature. 12,13 However, the standard free energy of formation of tartaric acid was not available in the literature and so was estimated by the group contribution method, which combines the broken functional groups of the compound. 14 By this method, the free energy of doubly charged tartrate ion was estimated as -224.53 kcal/mol. To examine the accuracy of the used group contribution method, the free energy of the doubly charged oxalate ion was estimated as -160.84 kcal/mol, which is similar to the value in the literature, -159.40 kcal/mol. All of the free energy values used herein are presented in Table II. Thus, the chemical or electrochemical reaction can be obtained from these data, enabling the potential-pH diagram to be constructed.

Results and Discussion

Figure 1 shows the etching rates of ITO films with different concentrations of oxalic acid at different temperatures, indicating that ITO films were not etched without oxalic acid. When oxalic acid was added, the etching rate of ITO films increased with the concentration of oxalic acid. When the concentration exceeded 3 wt %, the etching rate started to increase slightly. Additionally, the etch-

ing rate of ITO films rose with the temperature. The similar effects of the concentration and temperature on ITO films could also be found using tartaric acid etchants. The etching rate of ITO films increased with the concentration of tartaric acid and temperature as shown in Fig. 2. After the concentration of tartaric acid reached 1 wt %, the etching rate started to increase slightly. However, the etching rate of ITO films was slow in tartaric acid. Even at 65°C, the ITO etching rate in 7 wt % tartaric acid was less than 30 nm/min. Unlike this, the etching rate rose drastically when tartaric acid solutions were mixed with 3 wt % oxalic acid at 25 or 35°C. The etching rate of ITO films in 3 wt % oxalic acid with 1 wt % tartaric acid at 35°C was clearly higher than that in 7 wt % tartaric acid at 65°C. Moreover, the etching rate in the mixed solution fell with increasing tartaric acid concentrations, as shown in Fig. 2, because the added tartaric acid impeded the dissociation of oxalic acid via the common ion effect, lowering the reaction rate between the oxalate ion and ITO films.

The logarithm of etching rate vs reciprocal temperature for each sample in various etchants is plotted in Fig. 3. The linear plot demonstrates that the Arrhenius relationship was obeyed in these reactions. The activation energy was then calculated from the slopes of these plots. It was found that the average activation energy of etching ITO films with oxalic acid was 66.75 kJ/mol and that with tartaric acid was 115.99 kJ/mol. These findings show that the high etching rate of ITO films in oxalic acid solutions was caused by the low activation energy. When 3 wt % oxalic acid was mixed with 1 wt % tartaric acid, the activation energy rose to 69.92 kJ/mol, revealing that the added tartaric acid not only impeded oxalate ion formation by the common ion effect but also increased the energy barrier of etching ITO films.

Table II. Standard Gibbs free energies of formation ($\Delta G_{\rm f}^{\rm o}$) of species in indium/tin-water-oxalic acid and indium/tin-water-tartaric acid systems at 25°C and 1 atm.

Species	$\Delta G_{ m f}^{ m o}$ (kcal/mol)	Species	$\Delta G_{ m f}^{ m o}$ (kcal/mol)	Species	$\Delta G_{ m f}^{ m o}$ (kcal/mol)	Species	$\Delta G_{ m f}^{ m o}$ (kcal/mol)	
	In-H ₂ O ^a		Sn-H ₂ O ^a		In/Sn-C ₂ H ₂ O ₄ ^b		$In/Sn-C_4H_6O_6^c$	
H_2O	-56.69	H_2O	-56.69	$H_2C_2O_4$	-166.80	$H_2C_4H_4O_6$	-234.62	
In	0	Sn ²⁺	-6.275	$HC_2O_4^-$	-165.12	$HC_4H_4O_6^-$	-230.48	
In^+	-3.20	Sn^{4+}	0.65	$C_2O_4^{2-}$	-159.40	$C_4H_4O_6^{2-}$	-224.53	
In^{2+}	-12.40	SnO	-61.50	$InC_2O_4^+$	-190.46	$InC_4H_4O_6^+$	-254.28	
In ³⁺	-23.70	SnO_2	-123.2	$In(C_2O_4)_2^-$	-356.84	$In(C_4H_4O_6)_2^{-}$	-484.29	
InO_2^-	-104.0	$HSnO_2^-$	-98.00	$InHC_2O_4^{2+}$	-193.02	$SnC_4H_4O_6$	-237.89	
In_2O_3	-196.4	SnO_3^{2-}	-137.42	SnC_2O_4	-175.63	$Sn(C_4H_4O_6)_2^{2-}$	-468.85	
InH	45.00	SnH_4	99.00	$Sn(C_2O_4)_2^{2-}$	-341.71			

^a The data are from Ref. 12.

 $^{^{\}rm b}$ The $\Delta G_{\rm f}^{\rm o}$ value of oxalic acid is from Ref. 13, and the others were calculated using stability constants.

^c The $\Delta G_{\rm f}^{\rm o}$ value of tartrate ion was estimated by the group contribution method, and the others were calculated using stability constants.

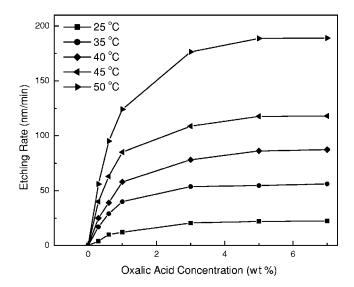


Figure 1. Etching rate of ITO films vs oxalic acid concentration at various temperatures.

Figure 4a and b illustrates the potential-pH diagrams of indium and tin, respectively, in a 3 wt % oxalic acid aqueous system. Calculations were performed for two different activities of indium and tin, 10^{-4} and 10^{-6} . For indium, the favorable oxidized species were found to be In⁺ and In³⁺ in strongly acidic solutions, and InC₂O₄⁺ and $In(C_2O_4)_2^-$ in weakly acidic solutions. In other words, indium tends to dissolve in acidic solutions with oxalate ions. In neutral and weakly basic conditions, In₂O₃ is thermodynamically stable. At high pH values, In₂O₃ may be dissolved to generate InO₂. For tin, the Sn^{2+} , Sn^{4+} , SnO_2 , SnC_2O_4 , and $Sn(C_2O_4)_2^{2-}$ are stable at low pH values, while SnO_2 , $HSnO_2^-$, and SnO_3^{2-} are stable at high pH values. Therefore, ITO films might not dissolve completely in acidic etchants with oxalate ions due to the insoluble SnO₂ or SnC₂O₄. These insoluble species could still be removed by stripping during the In₂O₃ dissolution, but many solid residues would be formed after etching. The points in Fig. 4 show the measured OCPs of ITO films in 3 wt % oxalic acid with different pH values. These points illustrate that ITO films formed $In(C_2O_4)_2^-$ and SnC_2O_4 in only oxalic acid solution and dissolved to $Sn(C_2O_4)_2^{2-}$ with increased pH.

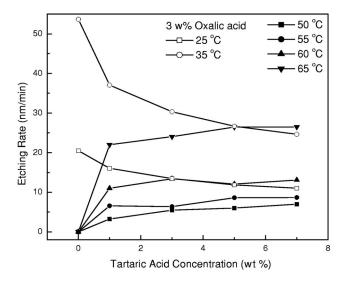


Figure 2. Etching rate of ITO films vs tartaric acid concentration with and without 3 wt % oxalic acid at various temperatures.

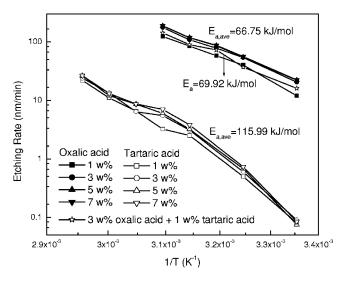


Figure 3. Etching rate of ITO films vs reciprocal temperature in various solutions. The calculated results of activation energies are also shown.

Figure 4 also shows the OCP of ITO films in 3 wt % oxalic acid with tartaric acid, clearly indicating that the OCP decreased with the addition of tartaric acid, and no transition across two different thermodynamically stable areas occurred with the addition of tartaric acid. This finding demonstrates that etching of ITO films in the mixed solution of oxalic acid and tartaric acid would occur through the complexation of indium and tin but that tartaric acid impeded the formation of oxalate ions and lowered the concentration of $In(C_2O_4)_2^{-1}$.

The potential-pH diagrams of indium and tin in tartaric acid solution were also constructed as displayed in Fig. 5a and b, respectively, to determine the thermodynamically favorable species. Both the indium and tin were calculated by two different activities of 10⁻⁴ and 10⁻⁶. In the indium-tartaric acid system, In⁺ and In³⁺ were found to be the favorable oxidized species at pH < 1.5, and $InC_4H_4O_6^+$ and $In(C_4H_4O_6)_2^-$ were found to be stable at pH 1.5–6.5. Moreover, the In₂O₃ is thermodynamically stable in the neutral and weakly basic regions while it is dissolved to InO₂ at high pH values. In the tin-tartaric acid system, $\mathrm{Sn^{2+}}$, $\mathrm{Sn^{4+}}$, and $\mathrm{SnO_2}$ are the favorable oxidized species at pH < 1.6; $\mathrm{SnO_2}$, $\mathrm{SnC_4H_4O_6}$, and $Sn(C_4H_4O_6)_2^{2-}$ are stable at pH 1.6–7.0; and SnO_2 and SnO_3^{2-} are the thermodynamically stable species in the basic region. Figure 5 also shows the measured OCP of ITO films in 1 wt % tartaric acid with and without 3 wt % oxalic acid at different pH values. These points reveal that indium oxide in the ITO films tended to form In³⁺, $InC_4H_4O_6^+$, and $In(C_4H_4O_6)_2^-$ at pH < 6.5 and could not be dissolved at pH 6.5-11. Furthermore, these data also indicate that SnO₂ was stable in tartaric acid solutions without oxalic acid. Hence, indium oxide in ITO films could be etched in tartaric acid etchants, but tin oxide could not. However, when 1 wt % tartaric acid was mixed with 3 wt % oxalic acid, the decreased OCP illustrated the stable species states changed from insoluble SnO₂ to soluble Sn²⁺ or $Sn(C_4H_4O_6)_2^{2-}$. It may be concluded from these diagrams that the tin oxide in ITO films could not dissolve easily in the solutions with only oxalic acid or only tartaric acid, but it could dissolve in their mixed solution.

Figure 6 shows the XPS local spectra of O 1s, In 3d, and Sn 3d peaks on the ITO surface before and after etching in 3 wt % oxalic acid with and without 1 wt % tartaric acid for 1 min at 35°C. This figure clearly reveals that the oxidation states on the ITO surface are the same before and after etching, but the relative composition among O 1s, In 3d, and Sn 3d changed with the etching processes in different solutions. The ITO surface composition after etching in 3 wt % oxalic acid was found to be quite different from that in 3 wt %

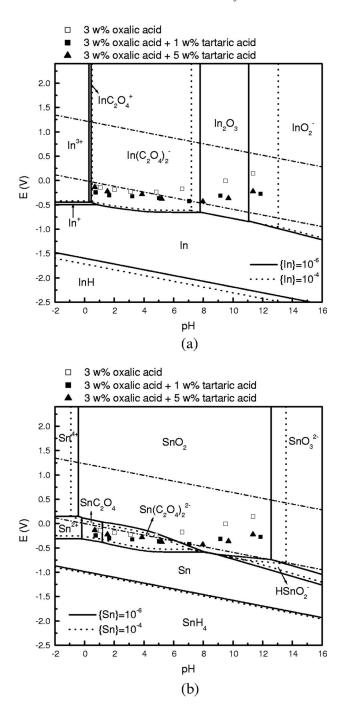
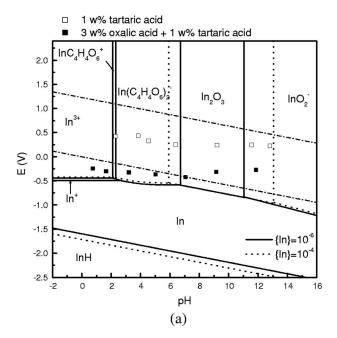


Figure 4. Potential–pH diagrams for (a) indium–oxalic acid– H_2O and (b) tin–oxalic acid– H_2O systems at indium ion or tin ion activities of 10^{-6} and 10^{-4} at 25°C. OCPs of ITO in 3 wt % oxalic acid and in the mixed solutions with various pH values are also indicated.

oxalic acid with 1 wt % tartaric acid. As shown in Fig. 6, the variation in In 3d was larger than that in Sn 3d. Through the quantitative analysis of the XPS spectra, the X value of $\rm In_2O_3 \cdot XSnO_2$ on the ITO surface could be obtained. The X values were 0.193 before etching, 0.326 after 1 min etching in 3 wt % oxalic acid, and 0.187 after 1 min etching in the mixed solution of 3 wt % oxalic acid and 1 wt % tartaric acid. The above data demonstrate that the indium oxide in ITO films was etched faster than tin oxide in oxalic acid, but the tin oxide may still be removed by stripping followed by the dissolution of the indium oxide. However, the addition of tartrate ion could dissolve both indium oxide and tin oxide equally, so the ITO films



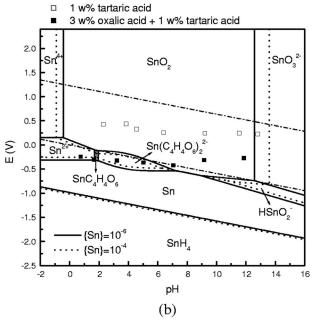


Figure 5. Potential–pH diagrams for (a) indium–tartaric acid– H_2O and (b) tin–tartaric acid– H_2O systems at indium ion or tin ion activities of 10^{-6} and 10^{-4} at 25°C. OCPs of ITO in 1 wt % tartaric acid and in the mixed solutions with various pH values are also indicated.

could be removed more uniformly in the mixed organic acid solution than in only oxalic acid. These chelating characteristics have also been proven by the potential–pH diagrams in Fig. 4 and 5.

The OM and SEM images further demonstrate the phenomena of stripping and the uniformity of etching. Figure 7a and b shows the ITO bars on glass after etching in 3 wt % oxalic acid and in 3 wt % oxalic acid with 1 wt % tartaric acid solutions, respectively, at 35°C. The ITO films in 3 wt % oxalic acid was clearly removed by etching along with stripping, but significant quantities of residual materials were produced and distributed around the ITO bars. Alternatively, the addition of tartaric acid enhanced the removal of residual materials. The OM and SEM images show a decrease in the level of residual materials. Consequently, the mixed organic acid solution improved the etching uniformity.

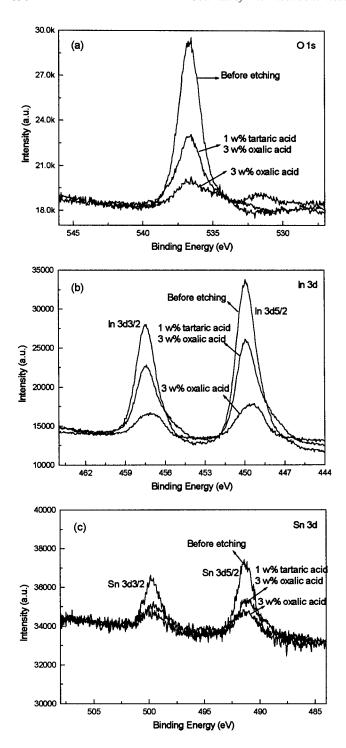


Figure 6. XPS spectra of ITO samples before and after 1 min etching in various solutions at 35°C. (a) O 1s, (b) In 3d, and (c) Sn 3d.

Conclusions

This study has shown that the oxalic acid solution mixed with tartaric acid would improve the uniformity of ITO etching and decrease the amount of residual materials. The results reveal that the etching rate increased with temperature and organic acid concentrations, and appeared to be higher in oxalic acid than in tartaric acid. The etching rate was slower in tartaric acid due to the high activation energy of the ITO etching reaction and the inhibition of the dissociation of oxalic acid. However, the addition of tartaric acid in oxalic acid could help chelate ITO films uniformly. The thermody-

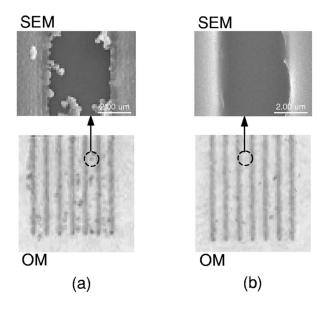


Figure 7. OM and SEM images of ITO bars after the etching process at 35° C with (a) 3 wt % oxalic acid and (b) the mixed solution of 3 wt % oxalic acid, and 1 wt % tartaric acid.

namically favorable species of ITO in oxalic acid or in tartaric acid have been determined using potential—pH diagrams. The experimental data shows that $In(C_2O_4)_2^-$ is the favorable species and that tin oxide might not dissolve easily in oxalic acid solutions. Thus, the insoluble tin species were removed mostly by stripping followed by dissolution in In_2O_3 , and many residues would be formed around ITO bars after etching. However, adding tartaric acid into oxalic acid etchants dissolved tin oxide to form Sn^{2+} or $Sn(C_4H_4O_6)_2^{2-}$, enabling the ITO films to be removed uniformly. Consequently, mixed organic acids, oxalic acid, and tartaric acid are recommended as etchants for ITO patterning, because the reduced stripping behaviors could decrease the level of residual materials around ITO bars and improve the etching uniformity.

Acknowledgment

The authors thank the Northern Taiwan Institute of Science and Technology for supporting this research.

Northern Taiwan Institute of Science and Technology assisted in meeting the publication costs of this article.

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