

The effect of solvent on the etching of ITO electrode

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Abstract

In this study, the effect of solvents, HCl and aqua regia at room temperature, on the etching behavior of ITO film was investigated. A higher etching rate was obtained in aqua regia than in HCl. However, via XPS analysis, it was found that there was more surface residual byproduct in aqua regia etchant than in HCl. The surface concentration (ratio of chlorine to indium) was 7.2 and 0.38 in aqua regia and HCl, respectively. It was also observed that the surface residual byproduct reduced the carrier mobility due to the ionized impurity scattering. As seen in the ITO pattern after the etching process, a serious undercut occurred with the aqua regia due to the fast etching rate. Thus, the 9 M HCl solution is more suitable as an etchant for ITO/OLED application.

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1. Introduction

Tin-doped indium oxide (ITO) film is used in various applications, such as organic/polymer light-emitting diodes (O/PLED), solar cells, liquid-crystal displays (LCD) and optical devices. It combines a low electrical resistivity with a good transparency in the visible region. Additional requirements of films for optical device application are that the films must be etchable to enable device patterning via the standard photolithography process. The etching characteristic of ITO thin film, however, is highly dependent upon the process parameter and the process environment due to the different microstructure and crystallinity [1]. Several researchers have reported that the surface roughness, sheet resistance and transmittance of the ITO films directly affect the performance of the O/PLED. This is due to the fact that the ITO film used as the anode provides the hole injection into the O/PLED [2–4]. Either wet etching or dry etching was employed to fabricate a pattern of ITO films. The dry etching, nevertheless, has a lower etching rate and it was difficult to pump out the byproduct. This is attributed to the fact that the byproduct has a low vapor pressure [5]. In contrast to the dry etching, the wet etching has relatively excellent throughput and is easy to transport the byproduct away from the ITO surface. In this investigation, the wet etching

method was used to investigate the etching behavior of ITO films.

It was reported that the ITO can be dissolved in etchants of halogen acids with a concentration of over 4 M [6–8]. Generally, the aqua regia is used to etch the industrial ITO film with high throughput. The etching behavior of ITO was investigated in 8 M HCl solution but the quantity of the residual chlorine in the ITO film was not discussed in detail after the wet etching process [1]. The wet etching behavior of ITO in various HCl and aqua regia solutions was investigated with respect to the concentrations and temperatures in this paper.

2. Experimental procedure

An ITO coated glass, from Corning corporation, was employed in this investigation owing to its low sheet resistance, $9 \Omega \text{ sq}^{-1}$, and high transparency (90%) in the visible region. Before the start of the etching process, the specimen was cleaned sequentially with acetone, methanol, DI water for rinsing and N_2 gas for drying. The etching experiments were carried out with hydrochloric acid (HCl) and aqua regia (the volume ratio of nitric acid to hydrochloric acid is 1:3) in various concentrations and temperatures. The ITO glass was immersed vertically in the etching solution, without stirring during the etching process. After the ITO etching process, the various characterizations were performed.

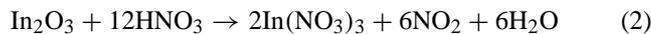
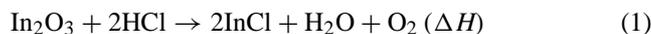
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The surface residual chlorine, carrier concentration, mobility, and surface morphology of the ITO film before/after the etching process were measured by energy dispersion spectroscopy (EDS), Hall measurement and scanning electron microscopy (SEM), respectively. In addition, the X-ray photoelectron spectroscopy (XPS) measurement was employed by a monochromized Al K α (1486.6 eV) X-ray source. All binding energies (BE) reported in this work are referenced to the binding energy of the carbon C 1s peak at 285.3 eV. Furthermore, the thickness of the ITO films before/after etching was monitored by ellipsometer.

3. Results and discussion

In this investigation, HCl and aqua regia were used as the etching solution. The etching reactions are



where the ΔH in Eq. (1) is the enthalpy of reaction. Its algebraic sign indicates whether the reaction is endothermic or exothermic. When the sign of ΔH is positive the reaction is endothermic. The etching rate versus etching solutions is shown in Fig. 1. It is quite evident that the etching rate increases with the increase of both the HCl and of the aqua regia concentration. The etching rate of aqua regia is greater than that of HCl due to the fact that it contains nitric acid. The significant turning point of the etching rate occurs at the 5 and 7 M in aqua regia and HCl, respectively. This behavior is the result of less activity of dissociation acid in aqueous solutions [9]. The etching temperature has a profound effect on the etching rate of the ITO film, as shown in Fig. 2. The fact that the etching rate increases with the increase of the etching temperature is a result of the acceleration of the reaction among the chlorine (Cl), indium (In) and tin (Sn) by heat energy. The etching process was performed from 5 to 45 °C. For obtaining the optimum con-

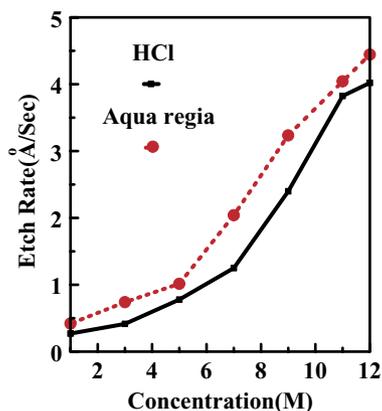


Fig. 1. The etching rate vs. the concentration of etchant at room temperature.

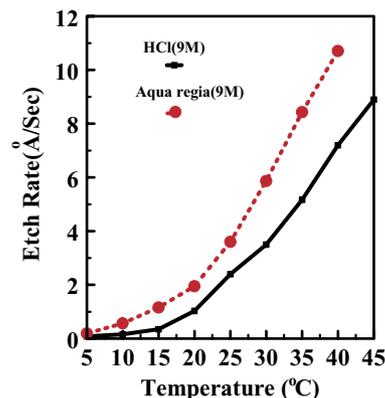


Fig. 2. The etching rate vs. temperature at 9 M HCl and 9 M aqua regia.

trol point, the etching temperature was limited at 40 and 45 °C in aqua regia and HCl, respectively. This was done because the etching rate, 642 Å min⁻¹, is too fast to control at 40 and 45 °C, respectively. The results of Figs. 1 and 2 indicate that the etching rate of aqua regia is higher than that of HCl in all conditions investigated. That is because aqua regia can supply more chlorine and therefore promote the production of the chloride compounds, such as InCl_x and SnCl_x [5]. Besides, the nitric acid also enhanced the etching rate. The etching rate is about 194 Å min⁻¹ at 9 M aqua regia, which is generally favorable for the industrial process. The concern is that the residual chlorine on the ITO surface could diffuse into the ITO films with the increase in the reaction temperature. For operation purpose the etching temperature was kept at room temperature.

The carrier mobility, as a function of the etchant at a fixed time period, is demonstrated in Fig. 3. The carrier mobility of ITO films changes significantly with the etchant concentration at 1 and 3 M in aqua regia and HCl, respectively. The raise in carrier mobility is due to the fact that the amount of carbon (C) contamination at the ITO surface is decreased

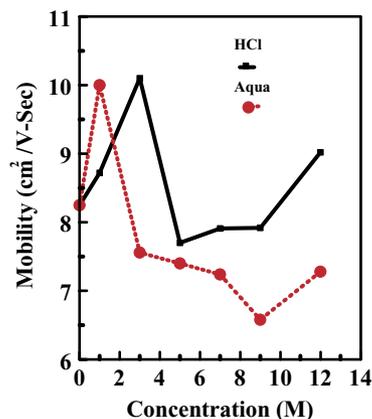


Fig. 3. The carrier mobility vs. concentrations etchant at room temperature.

with the increase of the etchant concentration under low concentration [10]. In the range of high concentration, the carrier mobility rapidly reduces with the increase in etchant concentration. The decrease in mobility can be presumed to be because the Sn atom diffuses out from the interstitial states or grain boundary, and is considered as the scattering center. It is well known that the carrier mobility is depending upon lattice and impurity scattering [11], as shown below:

$$\frac{1}{\mu_{\text{total}}} = \frac{1}{\mu_{\text{lattice}}} + \frac{1}{\mu_{\text{impurity}}} \quad (3)$$

Generally the effect of lattice scattering is unchangeable when the film has grown. Frank and Köstlin also reports that the impurity scattering mechanism dominates the scattering phenomena in the ITO films [12]. This means that the major scattering center is possibly the impurity scattering center, which is perhaps due to the ionized impurity scattering or the residual byproduct on the ITO surface [10,13]. The greater chlorine content in the aqua regia than in HCl may reasonably explain why the carrier mobility in aqua regia is lower than that in HCl.

The XPS investigation was performed to further explore the etching behavior. The XPS analysis of the etched ITO film in 9 M aqua regia and 9 M HCl at room temperature is shown in Fig. 4. According to the XPS analysis, it is well known that the following equation is employed to calculate the surface concentration of ITO films [14]:

$$\frac{P_n}{P_m} = \left(\frac{I_n}{I_m} \right) \left(\frac{K_m}{K_n} \right) \quad (4)$$

where n and m are the analysis element, P the concentration, I the intensity and K the relative sensitivity factors (RSF). The K value in this study is 14.8, 13.32 and 1.69 for Sn, In and Cl, respectively. From Eq. (4), the surface concentration ratio of Cl to Sn is 2.1 and 0.014 in aqua regia and HCl, respectively. Similarly the value of the surface concentration ratio of Cl to In is 7.2 and 0.38 in aqua regia and HCl, respectively. It is clear that the value of the surface concentration ratio in aqua regia is higher than that in HCl. Fig. 4(b) and (c) shows the spectra of indium and tin before/after etching process, respectively. There is no significant variation in the binding energy for the spectrum of Sn after the etching process. Besides, there is a slight shift to the higher energetic position after etching process in the In spectrum. This phenomenon is presumed to be because the ITO surface after etching process becomes more oxidized, indicating that the valence electron is removed from the ITO film due to the lower electronegativity ($\text{In} = 1.78$). Eq. (1) indicates that the reaction byproduct is chloride, which causes a reduction of the electrical property on the ITO surface. This explains why the mobility of aqua regia is always smaller than that of HCl. The degradation mechanism of OLED is attributed to the mobile ion diffusion from the ITO surface, because the ITO surfaces roughen and crystallize organic material [15–17]. It is reasonably to say that the surface residual

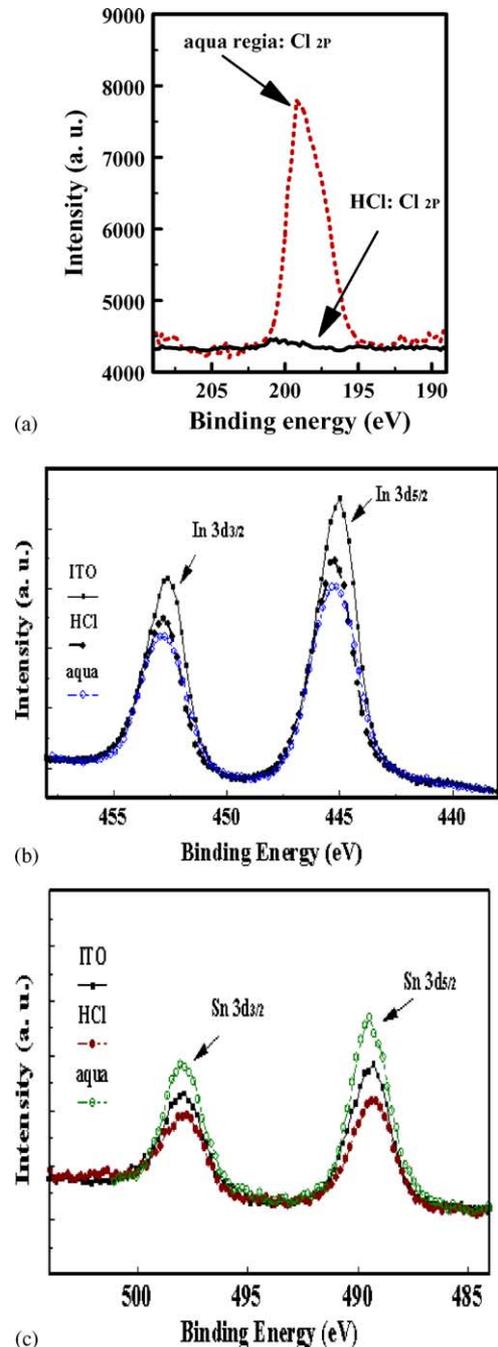


Fig. 4. The XPS spectrum of: (a) Cl after the etching process; (b) In before/after the etching process by HCl and aqua regia; (c) Sn before/after the etching process by HCl and aqua regia.

byproduct gave rise to surface contamination and resulted in degradation of OLED.

The surface morphology of the ITO after etching by 9 M HCl and 9 M aqua regia at room temperature is illustrated in Fig. 5(a) and (b), respectively. Fig. 5 shows that the ITO can be better etched by the HCl than by aqua regia.

The pattern of ITO etched by 9 M HCl at room temperature is shown in Fig. 6(a). Additionally, the pattern

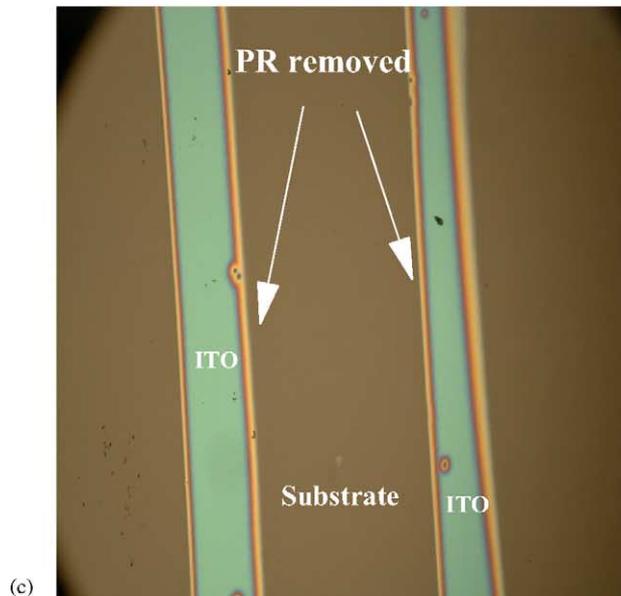
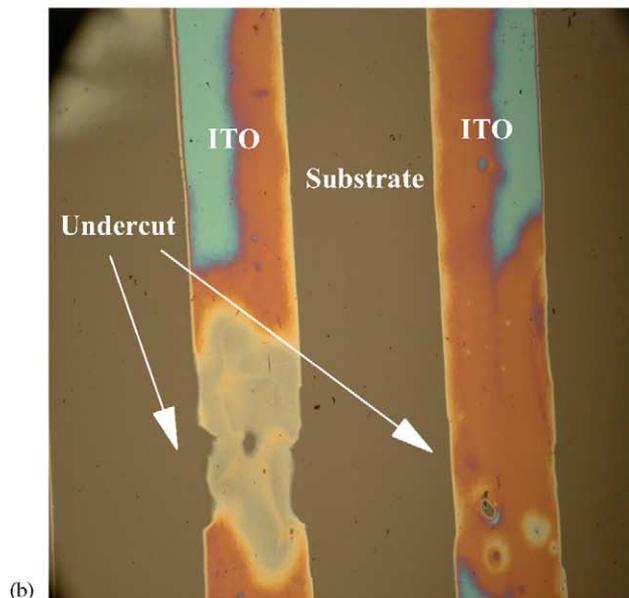
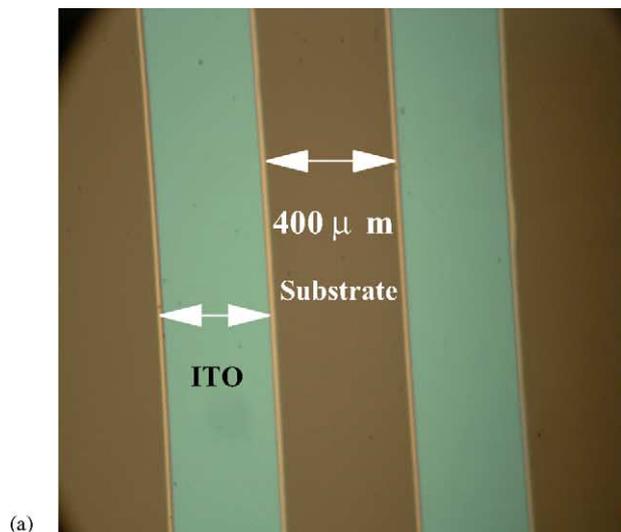
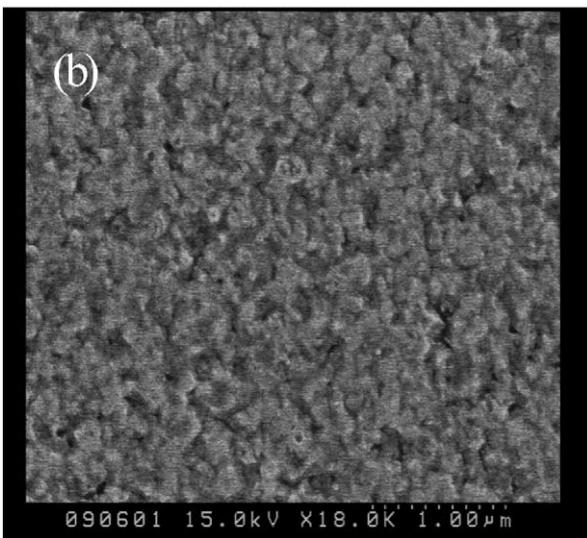
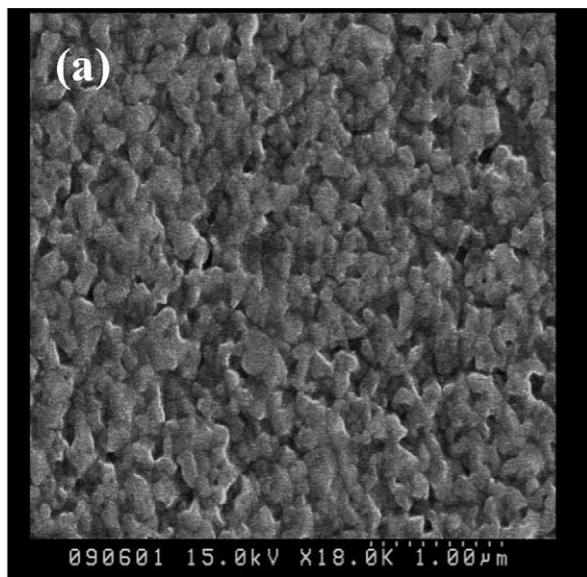


Fig. 5. The surface morphology of ITO etched by: (a) 9M HCl at room temperature; (b) 9M aqua regia at room temperature.

of ITO etched by 9M aqua regia at room temperature is shown in Fig. 6(b) and Fig. 6(c). As seen in Fig. 6(a), an excellent pattern of ITO is obtained. The opposite condition occurs in the aqua regia etching. A serious undercut phenomenon can be observed in Fig. 6(b), which is due to the strong aqua regia etching or the inadequate thickness of PR to protect the ITO pattern. As can be seen in Fig. 6(c), it is note worthy that aqua regia is too strong as an etchant for S-1813 that resulted in removal of S-1813 from the ITO surface during the etching process. The

Fig. 6. (a) The pattern of ITO etched by 9M HCl at room temperature; (b) the undercut behavior of ITO etched by 9M aqua regia at room temperature; (c) the PR removed pattern of ITO etched by 9M aqua regia at room temperature.

optimal selection, thus, for an ITO etchant is the HCl solution.

4. Conclusions

In summary, we have demonstrated the effect of solvent for producing the ITO patterns. The major effect of the solvent is the residual byproduct on the ITO surface, which was observed by various measurements such as XPS, EDS and SEM. The reduced mobility of ITO films is obviously caused by the residual byproduct, chloride, which plays a role as ionized impurity scattering. From the XPS spectrum, it is easily observed that the amount of surface residual byproduct on ITO film after aqua regia etching is more than that of HCl. As seen in the ITO pattern after the etching process, a serious undercut occurs in the aqua regia due to the fast etching ratio. Various characterizations show that the 9 M HCl solution at room temperature during the ITO etching process is suitable for producing the ITO pattern on OLED.

Acknowledgements

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