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Characterization of ITO etching by spontaneously evaporated fume of hydrogen chloride

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ABSTRACT

A simple etching process for indium tin oxide (ITO) film was investigated with atmospheric fume of hydrochloric acid (HCl), which was spontaneously evaporated from HCl solution. The fume etching provided many advantages including simpler process, less extents of undercut, and smaller defects on ITO surface than wet etching. A high etching rate of 50–70 nm/min for ITO film on thermal oxide, glass, and flexible polyethyleneterephthalate substrate was obtained. Surface analyses including X-ray photoelectron spectroscopy and Fourier transform infrared (FTIR) spectroscopy suggested that the spontaneously evaporated HCl molecules chemically reacted with ITO and formed water dissolvable etch products. Since the chemical reaction was postulated as a sole source for the etching mechanism, the fume etching would be a suitable process for next-generation flexible electronic applications without any physical damages on substrate.

1. Introduction

Indium tin oxide (ITO) is one of the most primarily used materials as electrode in many electronic applications, especially, including informational displays. In order to have fine feature patterns of micro-scale electrodes, the ITO etching process has been carefully developed for the fabrication of display devices, such as thin film transistors (TFTs) [1,2]. The ITO etching process has been represented as wet etching and dry etching, so far. Before the development of the efficient dry etching, wet etching of ITO has dominantly used [1,2]. However, in the wet etching, it is disadvantageous that the ITO electrode is fully isotropically over-etched at the rim of the photoresist (PR) pattern, which is formed by the lithography process, due to erosion of fluidic etchant [3]. In a word, an undercut, which is the lateral extent of the etching under the PR pattern, is typically severe with the wet etching. Therefore, an etch bias should be considered for the wet etching [3]. In addition, particulate contaminations in etching solution often generate defects on ITO surface even under the PR coverage [3,4]. Or, a conductive residue remains due to occurrence of the PR scumming after the wet etching [3,4]. Furthermore, reverse-sloped profiles, which are originated from inhomogeneous morphology in the film, can be also observed [4]. Therefore, dry ITO etching processes have been successfully developed to overcome the various problems invoked by the wet etching.

For the chemistry of the wet etching mechanism, it has been reported that addition of an oxidizing agent (e.g. HNO_3) would enhance the etch rate, and give sharper features, as compared with pure HCl etching [1]. Additionally, undissociated halogen acid(H–Cl) was the active agent for the etching mechanism. It indicates that halogen acid such as HCl will etch ITO, but that is the non-dissociated HCl molecule rather than H^+ or Cl^- [1,2]. Particularly, it was investigated that In–O bonds in the ITO film were attacked by the undissociated HCl molecules. Sequentially, the In–O and the H–Cl bonds were broken and new In–Cl and O–H bonds were formed. Finally, it was emerged that the products of $InCl_3$ and O–H were formed. In addition, wet etching will be greatly influenced by mass transport for reactant of HCl and etch products. Moreover, the reaction is known to be exothermic to generate heat at the surface of ITO in liquid phase of the wet etching process.

So far, etching properties of ITO films have received much less attentions since the dry etching methods for ITO had been successfully developed and performed due to its anisotropic etching features [4–6]. For the reactive gases of the ITO dry etching, methane (CH_4) and HCl gases have been adopted and reported with plasma application [5,6]. In other word, the reactive ion etching (RIE) process has been widely used in the ITO etching, which is advantageous over the wet etching. However, there can be some disadvantages even with the dry etching in the aspect of difficulty

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to determine etch-stop point or ending point for the process, which is originated from decreased etch selectivity due to ion bombardment during the plasma process [3]. Particularly, for flexible ITO substrate such as polymer substrate, the plasma etching portion can be a source of physical damage on the polymer substrate without an appropriate etch stopping. Typically, the plasma etching consists of both physical effect and chemical reaction. Therefore, if there is any method, a process based on a completely chemical etching mechanism would be more appropriate for the flexible ITO substrate than the physical etching mechanism. In addition, the dry etching usually needs a complicated equipment to have high vacuum system and high energy source of the plasma power.

In general, the surface reaction related to the ITO dry etching was reported to be sensitive even to the PR pattern or geometry [4]. Additionally, in a condition of high CH_4 concentration, plasma could generate undesired hydrocarbon polymer film on the etched ITO surface [5].

The HCl is a colorless gas at room temperature, which frequently forms white fumes upon contact with atmospheric humidity. In other word, HCl itself can be spontaneously a gas phase, not merely a liquid phase. Generally, fume etching has been known as undesirable corrosion phenomena on metal surface for the manufacturing of equipment to be used with strong acids, such as hydrogen fluoride (HF) and HCl. Otherwise, the HF fumes were applied to react with silicon oxide or silicon nitride as a vapor decomposition method, which could remove metal contamination on silicon wafer [7]. For the case of HF fumes, the fumes were spontaneously generated in atmospheric pressure at room temperature.

In this study, we introduce and investigate the HCl fume etching, which has less isotropic etching profile for the ITO than wet etching. The process could be performed with simplified setup in atmospheric pressure at room temperature. In addition, the etching rate of 50–70 nm/min was very high even compared with the wet etching. The chemical mechanism of the fume etching was investigated compared with the wet etching method through analysis of X-ray photoelectron (XPS) spectroscopy and Fourier transform infrared (FTIR) spectroscopy.

2. Materials and methods

The fume etching experiments were performed with DC sputtered ITO films on silicon oxide (100 nm thick ITO) and Corning glass substrate (150 nm thick ITO) with 50 μm or 100 μm wide pattern features by photolithography process with AZ 1512 PR. For flexible substrate, ITO (150 nm thick) coated polyethyleneterephthalate (PET) film (EMI-ito15, Optical filters, UK) was purchased and patterned with the lithography process. The fume was spontaneously generated from HCl or HCl/HNO_3 (3/1 vol.) mixture solution reservoir, where was placed beneath the PR patterned ITO substrate. The etch product of the fume etching was easily dissolved and removed by DI water rinsing. Elemental analysis of 1 min fume etched ITO films was performed by X-ray photoelectron spectroscopy (XPS: ESCA2000, VG Microtech). The FTIR analysis was performed by FTIR (FT/IR 460, JASCO, Japan). The ITO films were prepared on a silicon substrate and the FTIR measurements were performed in the absorbance mode with a beam penetrating the silicon substrate.

3. Results and discussions

Fig. 1 shows a schematic diagram of the HCl fume system for the ITO etching. No vacuum apparatus or pre-treatment was required to perform the fume etching. The ITO surface with the PR pattern was exposed to the HCl fume and the surface was etched by the chemical reaction at room temperature. To reduce aperture opening effects by the HCl gas or byproduct of water droplet during the fume etching, the ITO surface with the PR pattern was faced down to the HCl fume. In addition, no agitations and stirrings were required in the solution to enhance the fume generation. However, the etching behavior was closely related to the relative humidity in air. No significant change in etching rate was not detected within a range of the relative humidity (50–70%). However, if the relative humidity was less than 30%, the etching rate was decreased to less than 20 nm/min. The HCl and HNO_3 mixture for the fume generating could be sustained for several months without losing the fume etching efficiency. Therefore, it was found to be advantageous that no large volume of chemical waste was accompanied with the fume etching process.

Fig. 2 shows SEM images of HCl etched ITO patterns (a) by wet etching and (b) by fume etching. As shown in Fig. 2b, small undercut, which was not noticeable less than 1 μm (0.615 μm), was detected by the fume etching with the etching surface down. Since the etching mechanism can be assumed to be similar to the wet etching, the mechanism for overall reaction can be proposed as follows:

$$In_2O_3 + 6HCl \rightarrow 2In^{3+} + 6Cl^- + 3H_2O$$

As indicated in the chemical reaction, it is estimated that the formation of byproduct of H_2O during the ITO etching resulted in formation of liquid-phase droplet. For the mechanism of the undercut formation, it can be a source of lateral aperture opening under the PR. Therefore, additional treatment such as substrate heating to evaporate the water droplets would be more efficient to reduce the isotropic aspect of ITO etching profile. In this experiment, in order to remove the etch byproduct, rinsing with DI water and subsequent complete removal of moisture by air-gun was adopted during at an interim of the etching process. It was more efficient to have less ragged sidewall of etched ITO layer than without the interim rinsing and drying.

Additionally, the result of conventional wet etching as shown in an inlet image of Fig. 2a, many outward defects were found on the surface of ITO after removal of PR. It is assumed to be originated from particulates contamination of the wet etchant [1,2]. Otherwise, the defects on the ITO surface after the wet etching could be from pinholes in the PR layer. However, no defects with the fume etching were clearly detected on the ITO surface as shown in an inlet image of Fig. 2b. In addition, the sidewall of ITO pattern has differences between Fig. 2a and b. Fig. 2b shows more uniform sidewall than that of the fume etching, which is from less-isotropic etching aspect of the wet etching. Fig. 2a shows that wet-etching has an undercut of 1.42 μm due to In_2O_3 reactions with the HCl and HNO_3 etching solution. As a result, H_2O erode into the ITO layer under the PR. However, Fig. 2b shows that fume has etching undercut of 615 nm since H_2O does not erode into the ITO film under the PR.

Fig. 3 shows FTIR spectra of etch product during the HCl fume etching. The peak at 1625 cm^{-1} and broad peaks around 3100–3400 cm^{-1} represent for the vibrational peaks of etch products, e.g., In–Cl and H_2O. The low hill peaks around 3100–3400 cm^{-1} are expected to be water molecules, which are hydrated with the byproduct salts having In–Cl bonds [8]. Scholten explained the wet etching mechanism by showing that strong oxidizers could delocalize the In–OH intermediate [1]. In some cases, they could remove an electron, resulting in radical OH [1,2]. The In site would retain a positive charge. Therefore, it could react with a Cl^-ion, resulting in an In–Cl bond [1,2]. However, with or without the oxidizers, the In–OH intermediate can move with a certain surface mobility to hop to neighboring molecules [1,2]. As shown in Fig. 3, no apparent FTIR peaks for In–OH intermediate were detected. It indicates that the intermediate could be converted into the In–Cl without the oxidizers.