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# Study of wet etching thin films of indium tin oxide in oxalic acid by monitoring the resistance

Suelene S. Mammana [a,*], Alessandra Greatti [a], Francis H. Luiz [a], Francisca I. da Costa [a], Alaide P. Mammana [a], Guilherme A. Calligaris [b], Lisandro P. Cardoso [b], Carlos I.Z. Mammana [a], Daniel den Engelsen [a]

[a] Brazilian Association for Informatics - ABINFO, Rua Deusdete Martins Gomes 163, CEP 13084-723, Campinas, SP, Brazil
[b] Institute of Physics Gleb Wataghin, State University of Campinas-UNICAMP, CEP 13083-859, Campinas, SP, Brazil

## ARTICLE INFO

## ABSTRACT

We describe a study on wet etching of thin films of indium tin oxide (ITO) using a simple method by monitoring the resistance of the thin film in aqueous solutions of oxalic acid and hydrochloric acid. Generally three different regimes can be distinguished during etching ITO in acids: (1) initial etching, which is slow, (2) a fast etching phase and (3) slow etching stage at the end. These regimes are explained in terms of a porosity–roughness model. This porosity model has been confirmed largely by X-ray reflection measurements at grazing incidence, roughness measurements and scanning electron microscopy (SEM).

A reliable method for monitoring the resistance during etching has been developed. This method is based on a 2-strips measuring jig with a very low series contact resistance.

The activation energy of the etch rate of ITO films was found to be $80 \pm 5$ kJ/mol for oxalic acid and $56 \pm 5$ kJ/mol for HCl. SEM analyses in the final stage of the etching process indicate an enrichment of Sn in the residual film material. These observations are explained in terms of preferential etching of $In_2O_3$. X-ray analyses showed that the density of the ITO film decreased by etching. By adding ferric chloride to the oxalic acid solution we could accelerate the etch rate substantially.

## 1. Introduction

Transparent conductors continue to be of extreme importance for several applications such as displays, touch screens, photovoltaic devices and flexible electronics. Many of these devices employ one or more layers of a transparent conductive material. The high electrical conductivity and optical transparency of thin films of indium tin oxide (ITO) make them the most widely used transparent conductors for these devices.

The impressive growth of the area of the substrates coated with ITO and the increasingly smaller dimensions of the devices built on them are requiring higher control of the processes for both depositing and patterning the ITO films. Furthermore, besides the high cost of ITO, its deposition and patterning processes represent a reasonable percentage of the final cost of the devices, reason why less costly processes continue to be searched as alternatives. At the same time, environmental responsibility is driving the search for processes that are less harmful to the environment as well as less aggressive to people enrolled in the processing.

Patterning of thin films of ITO is usually done by lithography, which includes an etching step that is mostly wet etching since it requires less investment in equipment than others, for instance plasma etching or laser ablation.

Hydrochloric acid (HCl) and HCl with additional nitric acid ($HNO_3$) or ferric chloride ($FeCl_3$) are often used as wet etchants at slightly elevated temperature for ITO films [1–4]. Etch rates of poly crystalline ITO films in these etchants vary between 5 and 50 nm/min, depending on temperature and concentration. It should be stressed that amorphous ITO films show about a factor of 100 larger etch rates [5–7], indicating that the structure of the ITO film is a paramount parameter for the etch rate. Device makers for displays etc. often prefer to apply amorphous ITO films, because of the high etch rate.

HCl-based etchants have some drawbacks such as: uncontrolled under or lateral etching, attack of the metal layers beneath the ITO-top film, corrosion of equipment and fume exhaust facilities. Organic acids such as oxalic acid, acetic acid, formic acid, citric acid and tartaric acid are less corrosive and generally do not attack the metallization of a backplane with thin film transistors. For that reason, these acids are now being investigated for wet etching of ITO and other transparent conductive oxides such as indium zinc oxide and indium gallium zinc oxide [6,8–11].

ITO typically consists of 90% $In_2O_3$ and 10% $SnO_2$; its crystal structure is bixbyite (cubic structure), which is identical to the crystal structure of $In_2O_3$ [12]. In ITO, $Sn^{4+}$ ions sit on $In^{3+}$ lattice sites: therefore ITO is sometimes indicated as Sn-doped $In_2O_3$. Since $In_2O_3$ is well dissolving

in acids whereas $SnO_2$ is not, it is a priori not clear how the etching of a thin ITO film in an acidic solution will proceed. So, the following question is relevant: is $In_2O_3$ dissolving preferentially from the thin film of ITO? To answer this question one needs to study the kinetics of the etching process of ITO in detail.

The purpose of our work is twofold:

(1) Presenting a simple and cost effective method to study the kinetics of etching thin films of ITO in acidic solutions;
(2) Illustrating the usefulness of our method for studying the etching process with etchants consisting of oxalic acid and mixtures of oxalic acid and oxidizing or reducing agents.

Some preliminary results of our study have been presented in the Proceedings of LatinDisplay 2012/IDRC 2012 [13,14].

In studies on wet etching of ITO, the procedure to evaluate the etch rate is very often not explicitly mentioned [1,3,4,6–10]. Since the focus in those studies is on overall etch rates, it is likely that the etch rate is evaluated by dividing the film thickness by the total etch time. However, it is not mentioned how the total etch time is determined. The underlying assumption for the evaluation of the etch rate in those studies is that it is constant during the etching process. Kinetic studies of the etching process of thin films of ITO and other transparent conductive materials such as $SnO_2$ and ZnO require measuring the thickness of the film or the mass removed during the process.

Optical methods for monitoring the thickness were used, such as ellipsometry [15], and diffraction on gratings engraved in the film. In the latter method, a lamellar grating built in the film is monitoring the dry etching of very thin layers through the measurement of the depth of the grating grooves. This technique can also be used to precisely detect the end point of the etching process, in situ and in real time, which makes it a powerful tool to control the etching [16–18]. Nevertheless, this method has the disadvantage of requiring the patterning of a diffraction grating on the film.

Jacobs et al. [19] and van den Meerakker et al. [2] employed profilometry to measure the decrease of the thickness of an ITO-film covered with a photoresist pattern with steps. Since this method also requires the patterning of the photoresist, the measurement can be cumbersome for very thin ITO-films because of surface roughness and formation of isolated ITO-residuals on the substrate surface.

For monitoring the etch rate, we propose to measure the electrical resistance of the film as it is a function of the thickness of the film and taking advantage that it does not require photolithographic processes to prepare the samples. Moreover, the electrical conductivity is one of the most important properties of transparent oxide films such as ITO. So, resistance is a convenient parameter to be measured and it is directly related to the electrical properties of the devices obtained by an etching process. Our method is not limited to ITO, but may be applied to study the kinetics of etching of various types of conducting films or to monitor industrial etch processes.

Monitoring the resistance during etching generates information not only on the etch rate but also on the resistivity of the ITO-film as a function of z, being the axis in the direction normal to the substrate. If the resistivity of the film does not change with z, a linear increase of the resistance with time during etching indicates that the etch rate is constant during the process. However, if the resistance does not increase linearly with time, then either the etch rate may vary during the process or the resistivity may change with z.

The difference between surface and bulk properties of ITO films has been described extensively in the literature on thin films of ITO [20–24]. The objective of that work is to increase the work function of the ITO-surface, which facilitates the hole-injection from an ITO-anode into the hole-injection layer of an organic light emitting diode (OLED). King et al. [25] describe that electrons accumulate in the surface area of crystalline pure indium oxide, whereas in the surface zone of ITO they find a depletion of electrons, leading to a higher surface resistance. For ITO this depletion zone is very thin (0.2 nm). The work of King et al. refers to a macroscopic single crystal and it is unknown whether the boundary conditions of their treatment may be applied to the nanocrystals of ITO in thin films during etching.

At the end of the etching process in an industrial ambiance, it is important to know what residues could adhere to the substrate, because these could impair the isolation between tracks or parts of devices produced with etching processes. For this purpose we characterized the ITO-films with respect to topography, crystalline structure, micro-chemical composition before and after different etch times, by using techniques as X-ray reflectivity (XRR), grazing incidence X-ray diffraction (GIXRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and profilometry.

We applied our resistance monitoring method to study the etching process of ITO thin films, employing oxalic acid that is less harmful to people and to the ambient than inorganic acids normally used in laboratories and in the industry. Oxalic acid is a weaker acid than HCl or $HNO_3$; so, it might be expected that etching of ITO films in oxalic acid will be slower.

The effect of adding oxidizing agents to HCl-containing etchants is well documented in the literature [2,19]. Especially $FeCl_3$ enhances the etch rate of ITO in concentrated HCl. The addition of oxidants to oxalic acid etchants has not been studied and we considered it interesting to study whether $FeCl_3$ has an enhancing effect for this etchant as well. Lee [26] found that the addition of a mild reducing compound such as ascorbic acid to an etching bath containing oxalic acid also accelerates the etch rate of ITO films. This observation is not understood, because oxalic acid is also a reducing agent. Nevertheless, we have included the effect of adding another reducing agent, i.e. sodium hypophosphite, to the oxalic acid bath in our research.

## 2. Experiments and characterization

Our samples were cut from soda lime glass plates (1 mm thickness) industrially deposited with thin films of ITO of 25 nm and 175 nm thicknesses and nominal sheet resistances of ~100 and ~10 Ω/square, which correspond to resistivities of ~$2.5 \times 10^{-4}$ Ω.cm and ~$1.8 \times 10^{-4}$ Ω.cm respectively. All samples were highly transparent. The 25 nm ITO film was deposited directly on the soda lime glass, while the substrate glass of the 175 nm ITO film had a thin layer of silicon dioxide ($SiO_2$) as a barrier to prevent diffusion of sodium (Na) ions into the ITO film.

The samples were thoroughly cleaned before etching for 15 min in a solution of 5% Extran® MA02 in an ultrasonic bath, then rinsed with distilled water and, in sequence, with absolute ethyl alcohol, dried with hot air and stored in a dry box. Some samples were also cleaned with a common detergent with anionic surfactants. We did not use aggressive reagents (notably acids) to clean the samples in order to preserve the surface structure of the ITO films.

To study the etch rate as a function of the concentration and of the temperature, the ITO films were etched in solutions of oxalic acid in water. We chose to take concentrations in the range of 0.02 to 1.35 m, in which m stands for molality, while the temperature of the solutions was adjusted to 40, 50 and 60 °C during the etching process. The solubility of oxalic acid in water at room temperature is about 1.3 m, but at the temperatures during etching it is much higher.

Etching was also studied in solutions of oxalic acid containing ascorbic acid and sodium hypophosphite in concentrations of 0.01 to 0.15 m, at temperatures of 40, 50 and 60 °C. Furthermore, etching experiments were done with oxalic acid and iron(III) nitrate in concentrations between 0.08 and 0.5 m at 60 °C as well as with iron(III) chloride in concentrations of 0.3 to 1.0 m, at 60 °C. This study was completed by etching ITO in oxalic acid with potassium chloride. For comparison with oxalic acid, the etching was also done in hydrochloric acid at a concentration of 3.2 M (where M stands for molarity) at 40, 50, 60 and 70 °C.

The etching solutions were prepared with distilled water and high purity (p.a.) reagents. Each etching experiment was done with a freshly