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Characterization of indium tin oxide (ITO) thin films prepared by a sol–gel spin coating process

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Abstract

Indium tin oxide (ITO) thin films were prepared by a sol–gel spin coating method, fired, and then annealed in the temperature range of 450–600°. The XRD patterns of the thin films indicated the main peak of the (2 2 2) plane and showed a higher degree of crystallinity with an increase in the annealing temperature. Upon annealing the films at 500 and 600°, two binding energy levels of Sn^{4+} ion of 486.9 eV and 486.6 eV, respectively, were measured in the XPS spectra. The ITO film that was annealed at 600° contained two oxidation states of Sn, Sn^{2+} and Sn^{4+}, and it had a higher sheet resistance based on a rather low doping concentration of Sn^{4+}. The film that was annealed at 500° and subsequently treated with 0.1 N HCl solution for 40 s showed a sheet resistance of 225 Ω/square. The surface treatment by the acidic solution diminished the RMS (root mean square) roughness value and the residual carbon content (XPS peak intensity of carbon) of the ITO films. It seems that the acid-cleaning of the ITO thin films led to a decrease of the surface roughness and sheet resistance.

Keywords: A. Sol–gel process; Indium tin oxide films; Surface treatment; Sheet resistance; X-ray photoelectron spectroscopy

1. Introduction

Indium tin oxide (ITO, $SnIn_2O_3$) is a transparent conducting oxide material frequently applied in the fields of optoelectronics, electroluminescence and flat panel displays [1–3]. Also, tin-doped indium oxide has a high electrical conductivity and an optical transmittance in the range of visible light; thus, it has been extensively utilized as a transparent conductor for optoelectronic devices, several display panels and electrochromic devices [4]. ITO films can be fabricated by sputtering, chemical vapor reaction and sol–gel processing [5–7]. Generally, a magnetron sputtering method is used for the commercial processing of ITO. A sol–gel method has several advantages, including simplicity, low cost, easily controlled doping levels and feasible preparation of large area films.

The electrical and optical properties of ITO films can be controlled by changing either the firing temperature and the annealing temperature or the atmosphere, in which the annealing is performed; this affects the crystallization and densification of the ITO green films. In general, a reduction in the resistivity of an ITO film is achieved through the optimization of the microstructure and a formation of oxygen vacancies or free electrons in the annealing step [5]. Annealing processes that employ reducing atmospheres have been used to obtain ITO thin films with a low resistivity due to these effects. These studies were concerned mainly with the optimization of microstructure and the creation of free electrons by oxygen vacancy formation in thin films.

However, chemical etching has been used to remove the carbon content or reduce the surface roughness of ITO thin films [8–10]. Generally, the roughness and contamination in the surface region tend to deteriorate the conductivity and homogeneity of the ITO thin films; thus, to minimize the influences of these obstacles on the conductive behavior and device operation, additional treatments, such as chemical etching, are required. If an ITO film is either exposed to contamination or synthesized through an insufficient annealing procedure after sol–gel processing, its XPS (X-ray photoelectron spectroscopy) results will reveal the presence of carbon or

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hydrocarbons [11]. To improve the physical properties of the ITO films, the carbon content or contaminants on the ITO film surface should be removed by surface treatments, such as a simple chemical etching, plasma etching, and additional annealing processes.

In the present study, ITO thin films were prepared by a sol–gel spin coating method, and the crystal phases of the thin film was identified by XRD. Surface treatment of the ITO thin film after annealing was carried out by chemical etching with an HCl solution. The sheet resistance and AFM morphologies of both the fired film and the ITO film treated with solution were examined. The XPS spectra from before and after the acidic treatment of the ITO thin films were compared.

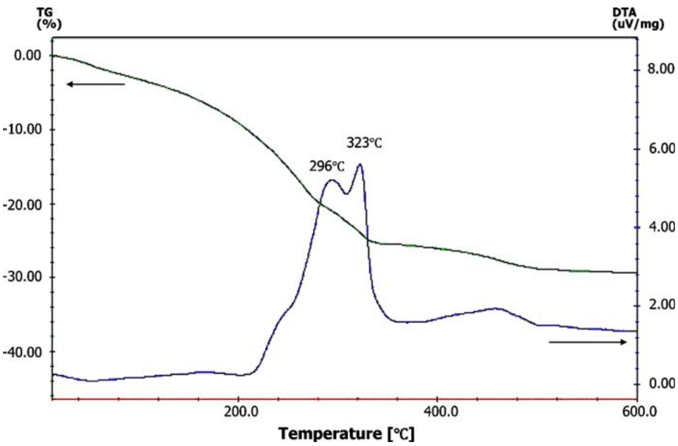

Fig. 1. TG-DTA profiles of a mixture of In and Sn materials.

2. Experimental procedure

Indium (III) acetylacetonate (99.99+%, Aldrich, USA), tin (IV) isopropoxide (98%, Alfa Aesar (USA), A Johnson Matthey Co., UK) and 2-methoxyethanol (99.0%, Kanto Chemical Co., Japan) were used as starting materials. The Sn/In ratio was fixed at 8 wt%. The weight loss and exothermic reaction behavior of the precursor solution containing the In and Sn sources was obtained by TG-DTA (thermogravimetric-differential thermal analysis, TG-DTA 2000, MAC Science Co., Ltd., Japan) analysis. Cleaned soda-lime silicate glass plates (200 mm × 200 mm × 1 mm) were used as substrates for the film deposition. The precursor solution containing In and Sn sources was coated on the substrate by the repetition (5 times) of the spinning (500 rpm: 10 s and 2000 rpm: 20 s) and drying process. The solvent in the mixed solution was removed by drying at 150 °C for 10 min. The ITO thin films were fired at 450–600 °C for 30 min in air, cooled down to room temperature and annealed at 500–600 °C for 30 min under an Ar atmosphere. Also, the annealed ITO thin films were etched with 0.1 N HCl for 5–60 s. The crystal structure of the ITO films was examined by X-ray diffraction (RAX-10, Rigaku, Japan). Surface microstructural morphologies of the ITO thin films were observed by FE-SEM (field emission-scanning electron microscopy JSM-6430F. JEOL, Japan) and AFM (Digital instruments, USA). The sheet resistance of the ITO films was measured by a four-point probe method (Jandel Eng. Ltd., England). The XPS spectra (ESCALAB 220i, VG Scientific, UK) of the ITO films were compared before and after a simple chemical treatment.

3. Results and discussion

Fig. 1 shows the TG-DTA data of the mixture of In and Sn sources. The thermal decomposition and exothermic reaction behavior of the mixture were investigated. The exothermic peaks at 296 °C and 323 °C were found on the DTA curve. A conspicuous weight loss, observed in the temperature range of 200–350 °C, is based on the burn-out of organic compounds included in the mixture, and a weak, broad exothermic peak at 450 °C is considered to be due to the crystallization process of the ITO film [12].

Fig. 2 shows the X-ray diffraction patterns of the ITO films as a function of annealing temperature. The ITO film, annealed in an Ar atmosphere showed a sharp peak from the (2 2 2) plane and weak peaks from the (4 0 0) to (4 4 0) planes. Basically, the pure In_2O_3 phase has a preferred orientation in the [1 0 0] direction. Such a sharp (2 2 2) peak in the XRD pattern indicates a (1 1 1) preferred orientation of the ITO film, which was reported previously using a sputtering method and an evaporation method [5,13]. Therefore, the (1 1 1) preferred orientation implies that the tin source replaces indium substitutionally in the bcc lattice. With an increase in the annealing temperature, the peak intensity of the (2 2 2) plane of the ITO film increased, which can be explained as the increase in either the crystallite size or the degree of crystallinity.

When the firing temperature was above 500 °C, the ITO films, annealed from 450 °C to 600 °C, showed a higher sheet resistance. It was inferred that a high firing temperature, above 500 °C, induces an overall densification behavior within the films and deteriorates the removal of oxygen or the formation of oxygen vacancies (creating free electrons) in the films. The sheet resistance of the ITO films was changed with an increase of the annealing temperature from 450 °C to 600 °C. The ITO film, fired at 500 °C and annealed at 500 °C under an Ar atmosphere, showed a relatively low sheet resistance of

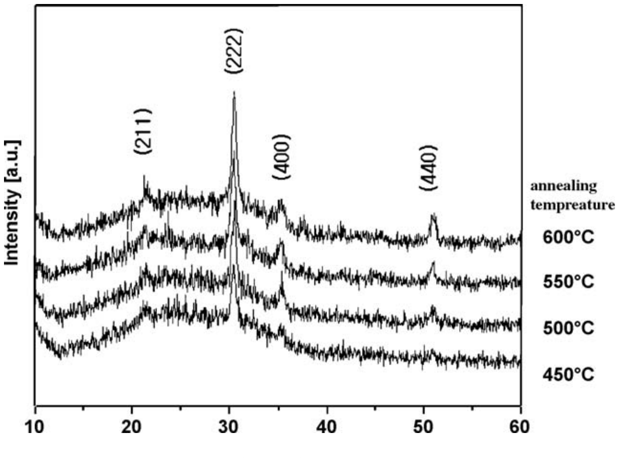

Fig. 2. XRD patterns of ITO films with annealing temperature.

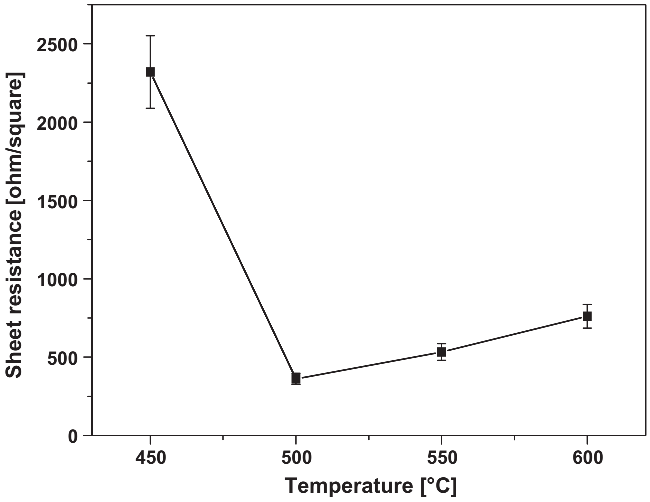

Fig. 3. Sheet resistance of ITO films with annealing temperature.

Table 1
RMS roughness variation of ITO films with acidic treatment time.

	Non-etched	20 s	40 s	60 s
RMS roughness (nm)	3.120	.325	1.256	3.614

approximately 361 Ω/square (Fig. 3). Upon increasing the annealing temperature above 500 °C, the ITO film showed a higher sheet resistance (533 Ω/square at 550 °C).

The cross-sectional morphologies of the ITO films were observed by FE-SEM (Fig. 4). The ITO films that were fired and annealed at 500 °C showed a surface microstructure of grains of approximately 20–30 nm in size. The higher annealing temperature (600 °C) induced some microcracks as observed in the FE-SEM image in Fig. 4(c). It was inferred that the microcracks increased the sheet resistance of the ITO thin films.

Also, the ITO thin film that was etched for 40 s with 0.1 N HCl solution showed a relatively low sheet resistance (225 Ω/square) compared to that of the fired film. Increasing the treatment time above 40 s increased the ITO film sheet resistance. This is likely the result of damage to the surface morphology caused by excessive etching. The RMS roughness variations of the ITO films treated with 0.1 N HCl solution are shown in Table 1. The ITO films revealed the lowest roughness value when the acid treatment was administered for 40 s.

It has already been reported that the removal of carbon from the ITO film surface through chemical etching can increase the charge carrier mobility [10]. It was thought that the decrease in the sheet resistance of the ITO film after chemical etching was accomplished through the removal of carbon or hydroxyl radicals from the film surface.

Surface morphologies of the ITO films that were treated with the acidic solution were observed as a function of treatment time by AFM (Fig. 5). With an increase in the etching time, the surface morphologies of the films seem to change into a smoother pattern. Such smooth morphologies of the films were observed up to the treatment time of 40 s, but above 40 s, a surface damage was observed in the AFM image (Fig. 5(c)). It was inferred that such rough surface morphologies are caused by over-etching with the HCl solution.

Fig. 6 shows a wide XPS spectrum of the ITO film annealed at 500 °C. The spectrum revealed the presence of impurity, such as carbon, as well as the constituent elements of indium and tin.

It was already well known that the electronic and optical properties of the transparent conductor tin-doped indium oxide (ITO) are critically dependent on the presence and distribution of the Sn^{4+} electron donors [14]. Thus, it was presumed that the high sheet resistance of the ITO films annealed above 600 °C is based on the change in the oxidation state of the Sn^{4+} ion. The

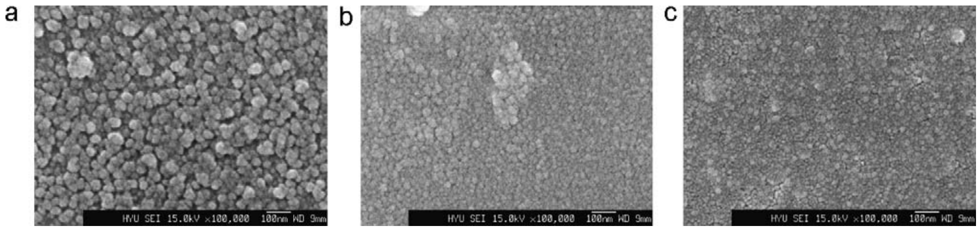

Fig. 4. FE-SEM images of ITO films annealed with temperature. (a) 450 °C, (b) 500 °C, (c) 600 °C in Ar atmosphere.

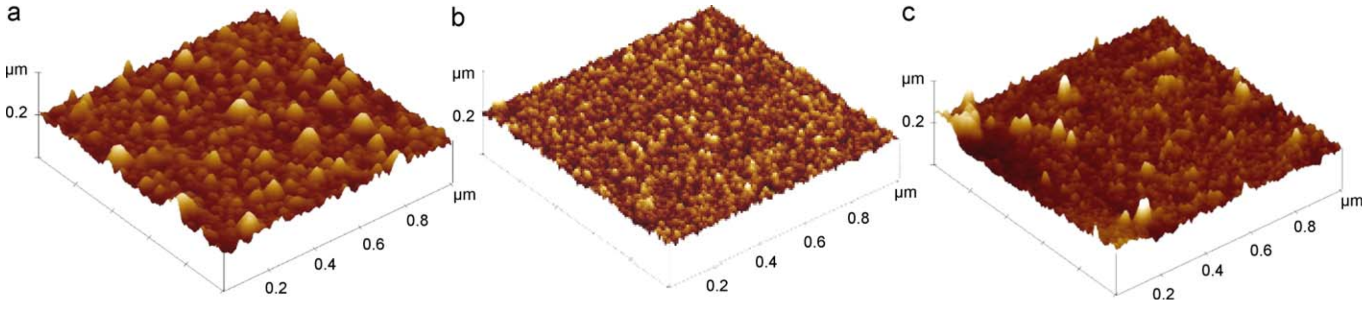

Fig. 5. AFM images of ITO thin films etched by 0.1 N HCl solution. Etching time: (a) 0 s, (b) 40 s, (c) 60 s.

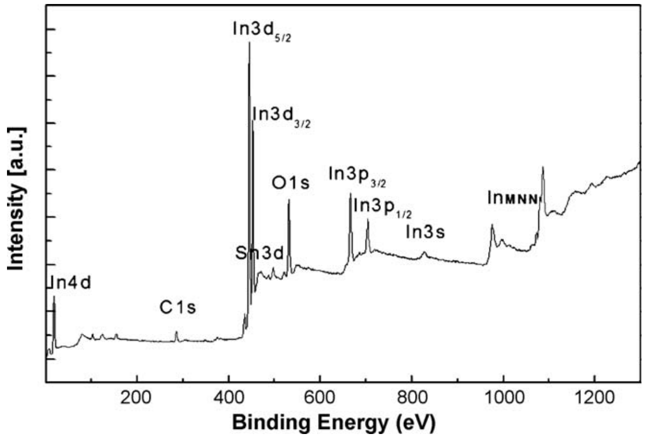

Fig. 6. XPS wide spectrum of ITO film annealed at 500 °C in Ar.

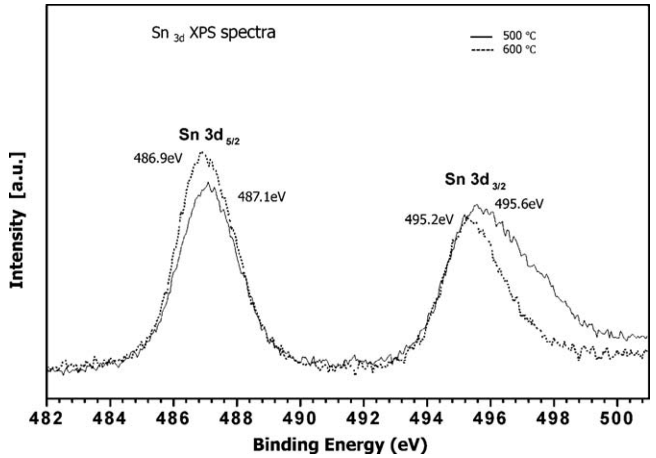

Fig. 7. XPS wide spectrum of ITO film annealed at 500 °C and 600 °C in Ar.

XPS spectra of the Sn element are shown in Fig. 7. In the XPS narrow scan of Sn, the binding energies of Sn $3d_{5/2}$ and Sn $3d_{3/2}$ were measured as 486.9 eV (487.1 eV) and 495.2 eV (495.6 eV) at 500 °C (and 600 °C), respectively. Therefore, it was confirmed that the ITO film annealed at 600 °C was connected with the overlapping region of the binding energies. Practically, tin shows two oxidation states, Sn^{2+} and Sn^{4+}, at 600 °C. The ITO film annealed at 600 °C contained a rather low doping concentration of Sn^{4+}. It seems that the low doping concentration increases the sheet resistance value of the ITO film.

Fig. 8 shows the XPS narrow spectrum results of the fired film and the ITO film treated with the HCl solution, respectively. The XPS narrow scan spectra (O 1s and C 1s) of the residual carbon and oxygen were identified for the film surface before and after chemical cleaning. Removing the impurities on the ITO film surface can reduce the electrical resistance. On the other hand, either base cleaning or O_2 plasma cleaning would generate a significant number of OH^- species on the ITO film surface [11]. After chemical cleaning, the O 1s spectrum did not show the binding energy shift of the core level, as shown in Fig. 8(a). For the O 1s spectrum, a slight decrease of peak intensity (at 531.3 eV) was reported, which, along with the intensity change of the peak shoulder at approximately 534 eV, is connected to the termination of the hydroxyl radical [11]. The ITO surface generally exhibits two O 1s features in the XPS spectrum, a strong peak at 530.5 eV and a second weaker shoulder at about 531.5 eV. The stronger peak is attributable to inorganic lattice oxide, while the weaker shoulder is often taken as evidence of the ITO hydroxyl termination, but this assignment may be problematic [11,12]. Also, a weak peak at 532 eV in the O 1s spectrum is considered to be due to the chemisorbed oxygen on the film [15].

Generally, it was reported that chemical modification of ITO is related to the carbon overlayers and not to the metal oxide. After a chemical cleaning, the C 1s XPS spectrum showed a conspicuous intensity reduction and change in the profile of the core level, which was considered to be due to a striking decrease in the residual carbon concentration (Fig. 8(b)). Therefore, it was concluded that the reduction of the hydroxyl radical and the carbon source after chemical termination influenced the decrease of the sheet resistance of the ITO films [12].

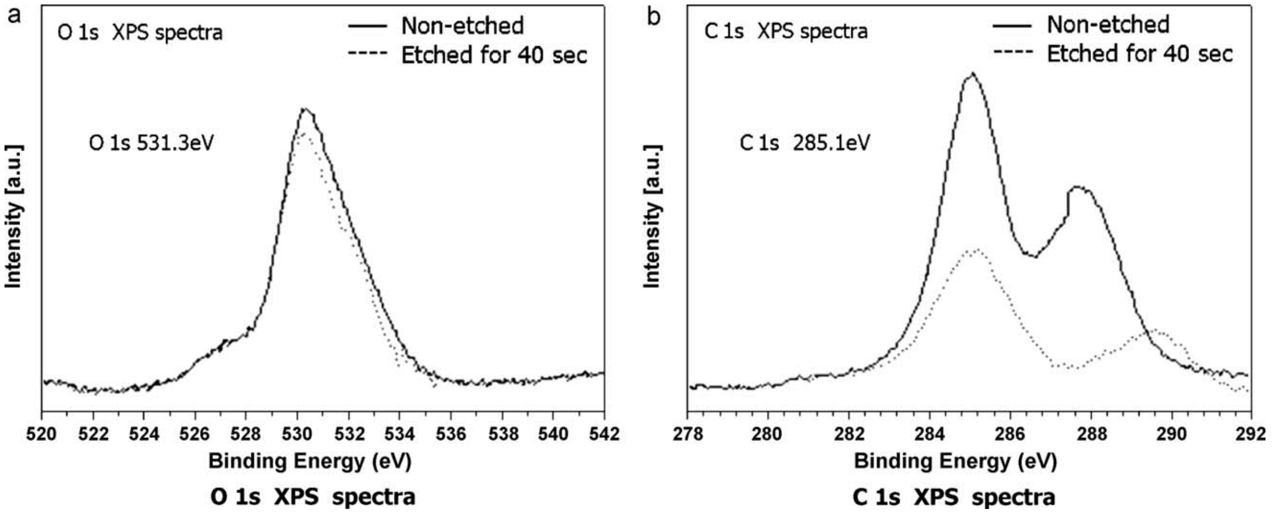

Fig. 8. O-1s, C-1s XPS spectra of ITO film etched by 0.1 N HCl solution.

4. Conclusion

Conductive ITO films were synthesized on soda-lime silicate glass substrates by a sol–gel process using a spin coating method. The ITO films showed a typical XRD pattern of the cubic bixbyite structure with a (1 1 1) preferred orientation. The ITO film that was fired and annealed at 500 °C had a sheet resistance of 361 Ω/square. The sheet resistance of the ITO films was influenced by the oxidation states of the doped tin ion that was changed with annealing temperature. After chemical etching with the HCl solution, the film showed both a lower sheet resistance (225 Ω/square) and a smaller average roughness, as compared with the specimens obtained after firing. It was confirmed that the decrease in the sheet resistance is related to the removal of residual carbon, as identified in the XPS spectrum. In conclusion, the surface modification through such a simple chemical treatment could decrease the sheet resistance of ITO thin films.

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