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Surface treatment of Indium Tin Oxide (ITO) thin films synthesized by chemical solution deposition

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Indium tin oxide (ITO) thin films were synthesized on glass substrates by chemical solution deposition from starting materials of Indium (III) acetylacetonate and Tin (IV) iso-propoxide. The ITO films were fired in a temperature range of 400 °C to 600 °C and annealed under N_2 gas at 500 °C. The effects of surface chemical treatment on the sheet resistance of ITO films were investigated with AFM surface morphology and sheet resistance. The spin-coated ITO thin films, which was etched with KOH solution for 20 seconds, exhibited a sheet resistance value of approximately 352 Ω/square. The AFM surface morphologies of ITO thin films revealed a difference of surface roughness and morphology between the as-received films and the etched films. Also, ITO thin films showed an optical transmittance of about 90% in the range of 800 nm.

Key words: Indium tin oxide (ITO) thin films, Chemical solution deposition, Sheet resistance, Surface treatment.

Introduction

Indium tin oxide (ITO) thin films have been applied to conductive transparent films for optoelectronic devices, since they have high electrical conductivity and transmittance in the range of visible light [1, 2]. Presently, ITO films have become one of the essential materials in flat panel displays (FPD). Generally, ITO films have been fabricated by such diverse techniques as sputtering [3], chemical vapor deposition [4] and a sol-gel process [5-7]. Mostly a magnetron sputtering method is selected as a commercial fabrication process, although a sol-gel method [5] has several advantages of a simple and low cost process and film preparation of large areas. Because ITO thin films, which were prepared through a chemical solution method show rather low conductivity compared to those obtained by physical processes, their practical use as the transparent conducting materials is limited [8, 9].

Therefore, there have been persistent attempts to enhance the conductivity of ITO thin films fabricated by various deposition processes. Annealing techniques using reducing atmospheres have been utilized to obtain ITO thin film with low resistivity. These studies were concerned mainly with the optimization of microstructure and the creation of free electrons by oxygen vacancy formation in the thin film. On the other hand, the chemical etching has been used to remove the carbon content or reduce the surface roughness on ITO thin films [10-12]. Generally, the roughness and contaminations in the surface region would deteriorate the conductivity and homogeneity of ITO thin films, thus it is required to minimize the influences of these obstacles for the conduction behavior and device operation through such additional treatments as chemical etching.

In the present study, ITO thin films were prepared by a chemical solution deposition method, an XRD pattern of the ITO thin film was taken and optical transmittance of the film was measured in the region of visible light. Then, surface treatment of the ITO thin film after annealing was carried out by chemical etching with KOH solution. The sheet resistance and AFM morphologies of the as-received film and the etched film were examined.

Experimental

Indium (III) acetylacetonate (99.99+%, Aldrich, USA), Tin (IV) iso-propoxide (98%, Alfa Aesar (USA), A Johnson Matthey Co., UK) and 2-metoxyethanol (99.0 %, Kanto Chemical Co., Japan) were used as starting materials. The Sn/In ratio of the solutions used was fixed at 8 wt.%. Cleaned soda-lime silicate glass plates ($200 \times 200 \times 1$ mm) were used as a substrate for 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: 10s and 2000 rpm: 20s) and drying process. The solvent in the mixed solution was removed by drying at 150 °C for 10 minutes. The ITO thin films were fired at 400-600 °C for 30 minutes in air and cooled down to room temperature, and annealed at 500 °C for 30 minutes under N_2 gas. Also, the annealed ITO thin films were etched with KOH solution (15%) for 20s to 80s. The crystal structure of the ITO films was examined by X-

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ray diffraction (RAX-10, Rigaku, Japan). Surface micro-structural morphologies of ITO thin films were observed by FE-SEM (JSM-6430F. JEOL, Japan) and AFM (AP-1090, Park Scientific Ins., USA). The sheet resistance of ITO films was measured by a four-point probe method (Jandel Eng. Ltd., England). The optical transmittance of ITO thin films in the wavelength range of 300 nm to 800 nm was examined with an UV/vis spectrometer (Lambda 25, Perkin-Elmer Ins. Co. Ltd., USA).

Results and Discussion

Indium tin oxide (ITO) thin films with 8 wt% Sn were prepared on glass substrates by a sol-gel spin coating technique and subsequently firing & annealing processes. The thin films exhibited a typical XRD pattern of cubic bixbyite structure (Fig. 1), whose largest (222) peak indicates a (111) preferred orientation of the ITO phase. A (111) preferred orientation for ITO thin films has been reported in other cases using several fabrication processes such as a sputtering method [3] and an evaporation method [13].

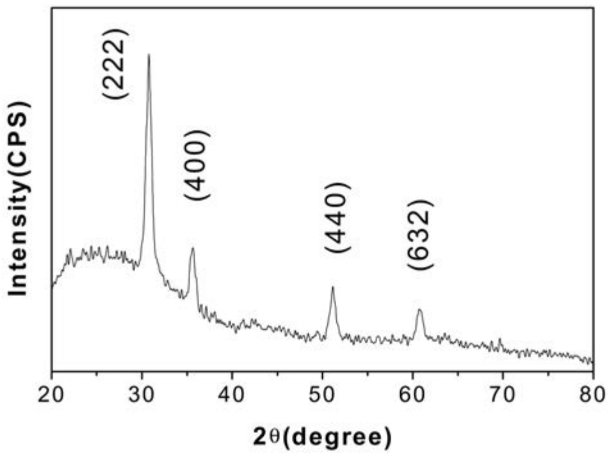

Fig. 1. XRD pattern of ITO thin film fired (500 °C) and annealed (500 °C) in a N_2 atmosphere.

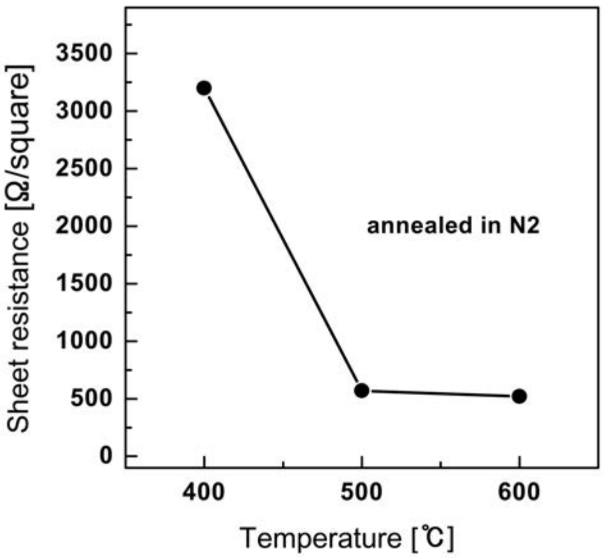

Fig. 2. Sheet resistane of the ITO films with firing temperature. (Annealed at 500 °C in a N_2 atmosphere).

The variation of sheet resistance of ITO thin films according to the firing temperature is shown in Fig. 2. ITO thin films exhibited a noticeable decline in sheet resistance by increasing the firing temperature from 400 °C to 500 °C. The sheet resistance of ITO thin film, which was fired at 500 °C and annealed at 500 °C under a N_2 atmosphere, was approximately 570 Ω/square. Thus, it was suggested that the relation between sheet resistance and firing temperature is connected with the crystallization behavior, namely the organic thermal decomposition of the starting materials in the deposited films. Meanwhile, the difference of crystallization behavior according to the firing temperature would have influenced densification behavior during the annealing process, which is a major factor for sheet resistance of ITO film

On the other hand, ITO thin film, which was etched for 20 s with KOH solution, showed a relatively low sheet resistance value (352 Ω/square) compared to that of the as-received film (Fig. 3) and a marked change in AFM surface morphologies (Fig. 4). Also, the average surface roughness of the ITO thin film decreased through the surface treatment (Fig. 5). But the ITO thin film after chemical etching for 40 s showed an increase of sheet resistance (407 Ω/square), which was considered to be due to the surface damage on the thin film. Actually, ITO thin film, which was etched for 80 s, showed excessive damage in surface morphology as well as a higher surface roughness in the central region of the thin film. As a result, the surface chemical etching for 20 s brought down the sheet resistance of the ITO thin film through modification of the surface roughness and morphology. Concerning the surface treatment of ITO thin films and their electrical properties,

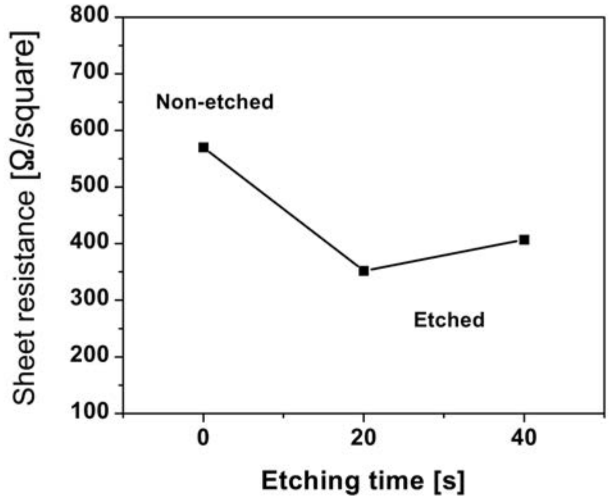

Fig. 3. Sheet resistance of the etched ITO thin films. (Firing at 500 °C, annealing at 500 °C in a N_2 atmosphere).

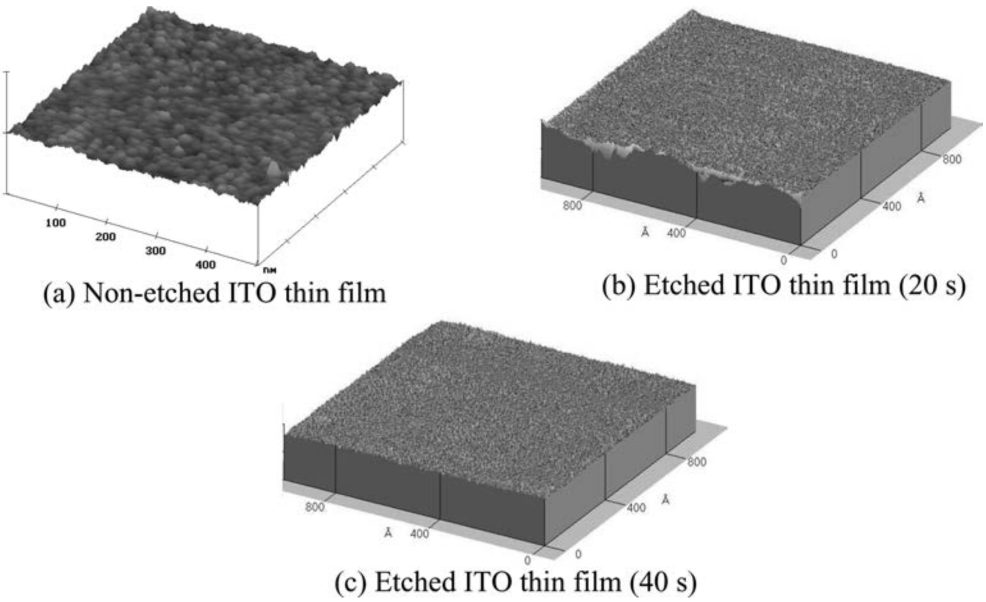

Fig. 4. AFM images of the non-etched film and the etched ITO thin films. (Firing at 500 ^oC, annealing at 500 ^oC in a N_2 atmosphere).

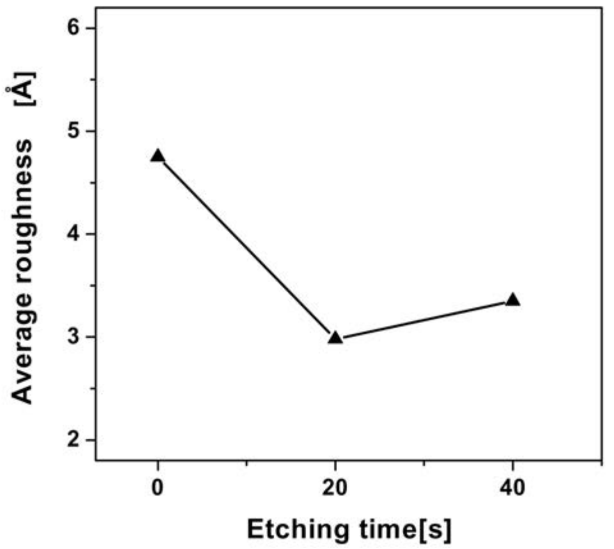

Fig. 5. Average surface roughness of ITO thin films with etching time. (Firing at 500 ^oC, annealing at 500 ^oC in a N_2 atmosphere).

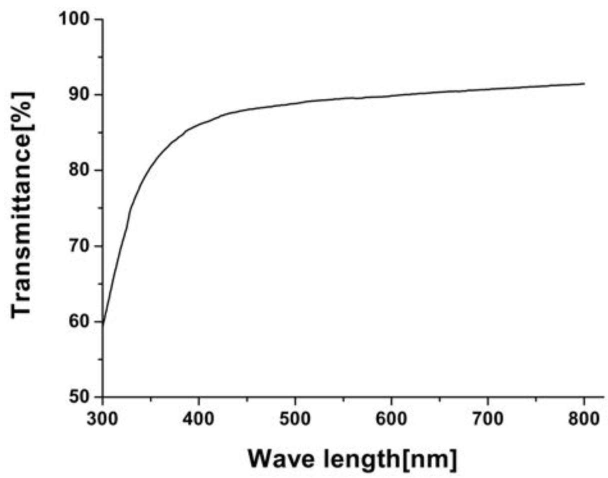

Fig. 6. Optical transmittance of ITO thin film. (Firing at 500 ^oC, annealing at 500 ^oC in a N_2 atmosphere).

it has already been reported that the removal of carbon from the ITO film surface through chemical etching could increase the carrier mobility [12]. In conclusion, it was thought that the decrease of sheet resistance of ITO thin films after chemical etching was accomplished through either the carbon removal or a reduction in surface roughness of the ITO thin film. Also, it was inferred for etching over 40 s that the sheet resistance increased by the creation of surface damage and an enhancement of roughness on the over-etched thin film (Fig. 4).

The optical transmittance of the ITO thin films between 300 nm to 800 nm is shown in Fig. 6. The optical transmittance of ITO film was about 90% at 800 nm, which is a sufficiently high value for application in transparent conduction devices.

Conclusions

Transparent conductive indium tin oxide (ITO) thin films were deposited on soda-lime silicate glass substrates by a sol-gel process using a spin-coating method. The crystal structure of thin film showed a typical XRD pattern of the cubic bixbyite structure. It was known that the sheet resistance of ITO thin film was controlled by the firing temperature. ITO thin films etched with KOH solution showed a rather low sheet resistance and smaller average roughness of the thin films as compared with the as-received ITO films. In conclusion, the modification of the surface morphology and roughness through such a simple chemical treatment could decrease somewhat the sheet resistance of ITO thin films prepared by a sol-gel spin coating process.

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