Journal of Ceramic Processing Research. Vol. 6, No. 3, pp. 259~262 (2005)

JOURNAL OF
Ceramic Processing Research

Effects of sequential annealing processes on surface morphology and resistivity of Indium-Tin Oxide (ITO) thin films fabricated by chemical solution deposition

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Indium tin oxide (ITO) thin films were deposited by a chemical solution method from the mixed solutions of Indium (III) acetylacetonate and Tin (IV) iso-propoxide with 2-metoxyethanol as a solvent, and were fired at 500 °C for 30 minutes, then annealed in a temperature range of 400-600 °C for 30 minutes, under two sequential annealing processes; [Vacuum → N_2 → H_2/Ar] and [N_2 → H_2/Ar] and a reducing [H_2/Ar] gas. The effects of the sequential annealing processes and atmosphere on the surface microstructural morphologies and resistivities of the ITO thin films were investigated. The ITO thin film, treated under a [Vacuum → N_2 → H_2/Ar] annealing process at 500 °C, showed a resistivity of approximately 3.3×10^{-3} Ωcm, whose surface grains were larger than those of the samples treated under a [N_2 → H_2/Ar] process and a [H_2/Ar] atmosphere. Therefore it was found that the annealing procedures using several atmospheres have the principal influences over microstructural morphologies and resistivities of the ITO thin films.

Key words: Indium tin oxide (ITO) films, Chemical solution deposition, Resistivity, Sequential annealing process, Surface morphology.

Introduction

Indium tin oxide (ITO) thin film as one of the TCO (transparent conducting oxide) materials shows unique properties of a high visible-light transmittance as well as a high electronic conductivity. Thus, ITO thin films have been extensively utilized in optoelectronic and display devices, anti-static and electromagnetic shields [1, 2]. The preparation of ITO films has been carried out by various techniques such as sputtering [3], chemical vapor deposition [4], spray pyrolysis, electron beam evaporation [5], laser ablation [6] and recently a sol-gel process [7-12]. In particular, ITO films for application in various displays or devices are fabricated mainly by a physical method such as a magnetron sputtering. A chemical solution method such as a sol-gel process has been examined for the preparation of ITO thin films because of several advantages such as a simple and economical process, a stoichiometric ratio of elements in multi-component films.

Basically, the electrical and optical properties of ITO thin films have been controlled by the firing temperature and annealing temperature or atmosphere, which have important influences upon crystallization and densification of thin films. In general, a reduction of resistivity of an ITO film is achieved through an optimization of microstructure and a formation of oxygen vacancies or free electrons in the annealing step [10]. Various reducing atmospheres with single gases or mixed sources of two gases during annealing processes have been introduced to improve the electrical conductivity of ITO thin films.

In this study, ITO thin films on glass substrates were synthesized by a chemical solution deposition method, and treated with the annealing processes; [Vacuum → N_2 → H_2/Ar], [N_2 → H_2/Ar] and a [H_2/Ar] atmosphere. The effects of the annealing conditions on surface morphologies and resistivities of the ITO thin films were examined from atomic force microscopy (AFM) and field emission scanning electron microscopy (FE-SEM) images.

Experimental Procedure

ITO thin film formation

The starting materials for ITO film formation, indium (III) acetylacetonate (99.99+%, Aldrich, USA) and tin (IV) iso-propoxide (99%, Alfa Aesar (USA), A Johnson Matthey Co., UK), were dissolved in 2-metoxyethanol (99.0%, Kanto Chemical Co., Japan). The mixed source with atomic ratio Sn/In of 0.08 was prepared. Soda-lime silicate glass plates (300 × 300 × 1 mm) were used as substrates for the film deposition. The precursor solution containing In and Sn sources was coated on the substrate by spinning and drying cycles (5 times). The solvent in the mixed solution was removed by drying at 150 °C for 10 minutes. The films were fired

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at 500 °C for 30 minutes in air and cooled down to room temperature. An intermittent vacuum treatment was carried out during the firing process. The films were annealed at 400-600 °C for 30 minutes under two sequential atmospheres, [Vacuum → N_2 → H_2/Ar] and [N_2 → H_2/Ar] as well as a [H_2/Ar] gas. In the case of a [Vacuum → N_2 → H_2/Ar] procedure, the intermittent vacuum steps during the annealing process were adopted to promote a thermal decomposition of the films.

Characterization of ITO thin films

The crystal structures were examined by X-ray diffraction (RINT-2500V, Rigaku Co). The resistivity of the ITO films was measured by a 4-point probe method (Jandel Eng. Ltd., England). The optical transmittance of the films was measured by an UV-VIS spectrometer (Shimadzu UV-1201, Japan) in a wavelength range of 200-1200 nm. Surface morphologies of the ITO films were observed by FE-SEM (JSM-6430F, JEOL, Japan) and AFM (Nanoscope IIIa, Digital Instrument, USA).

Results and Discussion

XRD pattern of ITO thin film

Figure 1 shows X-ray diffraction patterns of the ITO films. The ITO film, annealed under a [Vacuum → N_2 → H_2/Ar] process showed the peak of a (222) plane and weak peaks of a (400) plane and a (440) plane. The XRD pattern of the ITO film annealed with a [H_2/Ar] atmosphere gave just the peak of a (222) plane. It is well known that a large (222) peak in the XRD pattern indicates that the ITO film has a (111) preferred orientation [13].

Resistivity and microstructure of ITO thin films

The measurement of resistivity of the ITO thin films

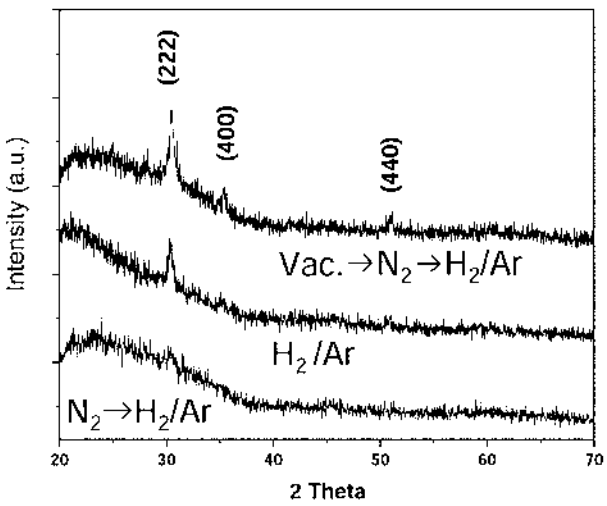

Fig. 1. XRD patterns of ITO thin films fired at 500°C and annealed 500°C.

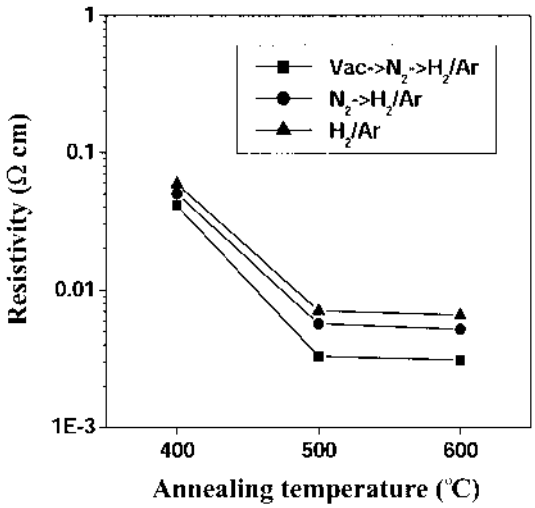

Fig. 2. Resistivities of ITO thin films fabricated under different annealing conditions.

was carried out several times for different points on the film surface. The relations of the annealing processes and annealing temperature on resistivities of the ITO thin films are shown in Fig. 2. The resistivity of the ITO films decreased with an increase of the annealing temperature from 400 °C to 500 °C (Fig. 2). The ITO film with a relatively low resistivity (3.3×10^{-3} Ωcm) could be fabricated through the firing process including the intermittent vacuum treatment at 500 °C (30 minutes) and subsequently the sequential annealing process of a [Vacuum → N_2 → H_2/Ar] atmosphere at 500 °C (30 minutes). In this study, the definite reasons for this result are not clear yet; it could be presumed that the differences of resistivities of the ITO films are related directly to microstructural morphologies such as grain size as well as shape to be controlled according to the annealing procedures.

AFM and FE-SEM surface morphologies of the ITO films, treated with two sequential annealing processes and the non-oxidizing gas, are shown in Fig. 3 and Fig. 4. Surface morphologies of the ITO films represent the effects of the sequential annealing processes and reducing gas. The grains of the ITO film surface, annealed via the sequential treatment of a [Vacuum → N_2 → H_2/Ar] atmosphere, were larger than those of the specimens treated with a [N_2 → H_2/Ar] atmosphere and a reducing [H_2/Ar] gas. It is suggested that the sequential annealing processes including a short-term vacuum step stimulated a thermal decomposition or microstructural changes such as densification and grain growth in the ITO thin film.

In the AFM images (Fig. 4), the ITO films, which were fabricated under a [Vacuum → N_2 → H_2/Ar] annealing step, showed rather a low RMS (root-mean-square) value (~20 Å) compared to those (40 Å, 50 Å) of the films prepared by a [N_2 → H_2/Ar] process and a reducing [H_2/Ar] gas. In Fig. 4(b), the ITO film shows

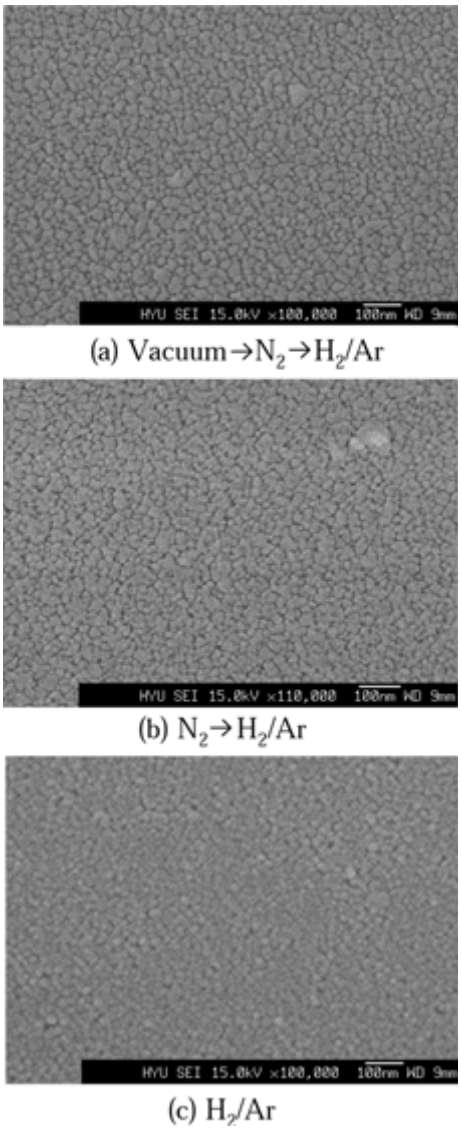

Fig. 3. FE-SEM surface morphologies of ITO thin films fabricated under different annealing conditions.

rectangular grains, sporadically grown in the AFM surface morphology. Surface morphologies of the ITO thin films, which were annealed through a [Vacuum → N_2 → H_2/Ar] process, showed remarkable differences compared with those of the ITO films treated with a [N_2 → H_2/Ar] process and a [H_2/Ar] gas.

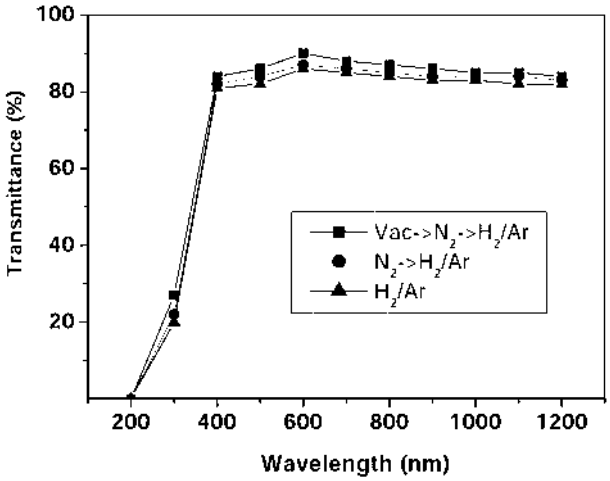

Fig. 5. Optical transmittance of ITO thin films in the region of 200 nm to 1200 nm.

Therefore, it seemed that the differences of resistivities of the ITO thin films was affected by the microstructural features according to the annealing processes. Also, it has been reported that the resistivity of ITO thin film is associated with a grain shape and influenced by a carrier movement to grain boundaries [14]. Therefore, it could be thought that the grain size or the grain shape in the ITO thin films would be the important factors in controlling their resistivities.

Optical transmittance of ITO thin films

The optical transmittance of the ITO films in a wavelength range of 200-1200 nm is shown in Fig. 5. In the case of a [Vacuum → N_2 → H_2/Ar] process, the ITO film showed a high transmittance of approximately 90% at a wavelength of 600 nm. It was thought in the case of sequential annealing processes that this result is due to the effects of the densification and homogeneity in the microstructure of the thin film.

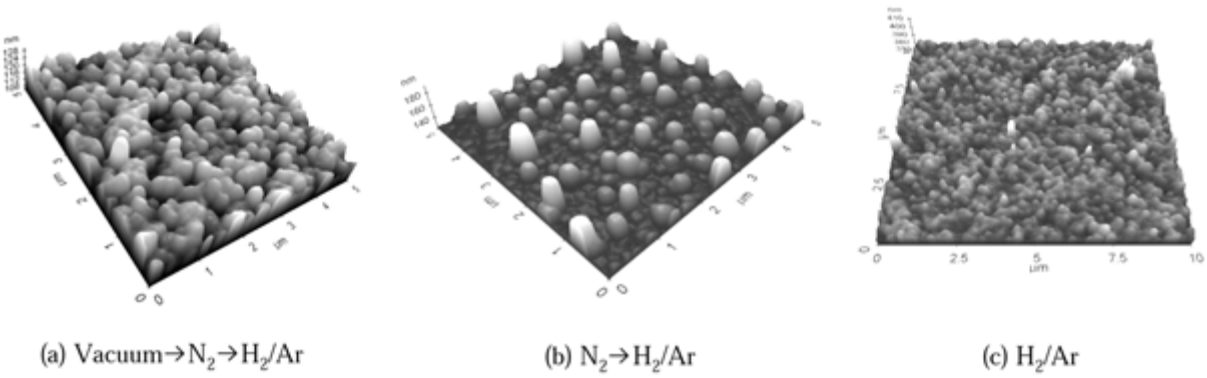

Fig. 4. AFM images of ITO thin films fabricated under different annealing conditions.

Conclusions

The ITO films, which were fabricated by a sol-gel spinning coating procedure, were treated by firing at 500 °C and sequential annealing processes, [Vacuum $\rightarrow N_2 \rightarrow H_2/Ar$] and [$N_2 \rightarrow H_2/Ar$] and a non-oxidizing ($H_2/Ar$) gas in a temperature range of 400 °C to 600 °C. Surface morphologies of the ITO films revealed considerably dissimilar features in the terms of grain size or shape and a surface roughness according to the annealing processes. The ITO films, annealed under a [Vacuum $\rightarrow N_2 \rightarrow H_2/Ar$] atmosphere, showed rather a low resistivity and RMS value as compared with those fabricated by the other annealing processes. It was concluded that the annealing processes and temperature influenced the microstructural features and resistivities of the ITO films.

Acknowledgements

"This work was supported by the Korea Research Foundation Grant." (KRF-2004-050-D00004)

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