

# A Dependence of Crystallinity of $\text{In}_2\text{O}_3$ Thin Films by a Two-Step Heat Treatment of Indium Films on the Heating Atmosphere

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## Abstract

A difference in crystallinity of  $\text{In}_2\text{O}_3$  thin films on sapphire substrates by heat treatment of indium films was reported. Indium films were heated in an inert atmosphere or in air until they reached a specified temperature and then oxidized in air at much higher temperatures. Crystallinity of the  $\text{In}_2\text{O}_3$  thin film which was heat-treated in air from room temperature was quite poor. On the other hand, narrow X-ray rocking curves of the  $\text{In}_2\text{O}_3$  films were obtained when the temperature was increased in an inert atmosphere to a specified temperature.

**Keywords:** Solid Phase Epitaxy, Oxides, Sapphire, Semiconducting Materials

## 1. Introduction

Recently, single-crystal sapphire wafers have been used widely as substrates for heteroepitaxial growth of semiconductor thin films such as gallium nitride (GaN) [1]. Sapphire is a transparent material, therefore, practical applications of it to such as transparent substrates for single-crystalline thin film photovoltaic cells have been also expected. However, it is relatively difficult to collect electric currents effectively in the thickness direction of the semiconductor thin films because sapphire is also an insulating material. Therefore, to allow electric currents to flow effectively to the thickness direction of the semiconductor thin film some conductive layers should be formed between the sapphire substrate and the semiconductor thin film.

Indium oxide ( $\text{In}_2\text{O}_3$ ), which is a wide band gap material, is widely used as a transparent conducting film. It is usually prepared by sputtering techniques [2] and heteroepitaxy of  $\text{In}_2\text{O}_3$  on sapphire substrates have been also investigated by using various techniques such as atomic layer deposition [3], pulsed laser deposition [4] and reactive magnetron sputtering [5] methods. As  $\text{In}_2\text{O}_3$  has a cubic crystal structure [6], it can have a heteroepitaxial relationship between [111]  $\text{In}_2\text{O}_3$  and [0001] sapphire. In such case,  $\text{In}_2\text{O}_3$  film will grow epitaxially on the sapphire substrate. In addition, another semiconductor thin

film which will be formed on the  $\text{In}_2\text{O}_3$  film will also grow epitaxially on it if the semiconductor has a heteroepitaxial relationship to  $\text{In}_2\text{O}_3$ . Therefore, the semiconductor thin film will have better properties than films grown on polycrystalline or amorphous underlayers. As an example for it, we have epitaxially grown  $\text{In}_2\text{O}_3$  thin films on sapphire substrates by a sputtering method and grown Cadmium Telluride (CdTe) thin films on the underlayers [7]. In the experiment, the CdTe thin films could be epitaxially grown on the  $\text{In}_2\text{O}_3$  thin films without deterioration compared with CdTe thin films grown directly on sapphire substrates.

Metal indium thin films can be quite easily deposited using simple and inexpensive vacuum evaporation techniques. In addition, indium can be readily oxidized by heating at a low temperature in an atmosphere containing oxygen. Therefore, it may be possible to easily produce indium oxide thin films using simple evaporation and oxidization processes. Furthermore, performing this processing by laser radiation heating will permit local oxidization of indium thin films, enabling the transparency and conductivity of the films to be locally controlled. From the easiness and possibility for expansion of the process utility, we have considered that it is worth to develop this processing method.

The ultimate goal of our research is to obtain heteroepitaxially grown  $\text{In}_2\text{O}_3$  thin films on single-crystal

sapphire substrates by using the above-mentioned simple techniques. In the pursuit of this goal, we observed different crystallinities of  $\text{In}_2\text{O}_3$  thin films that had been heat treated by a two-step heat treatment. This difference depended on the atmosphere used in the two-step heat treatment. In this paper, we report the effect of the heat-treatment atmosphere on the crystallinity of  $\text{In}_2\text{O}_3$  thin films obtained by the two-step heat treatment of metal indium thin films.

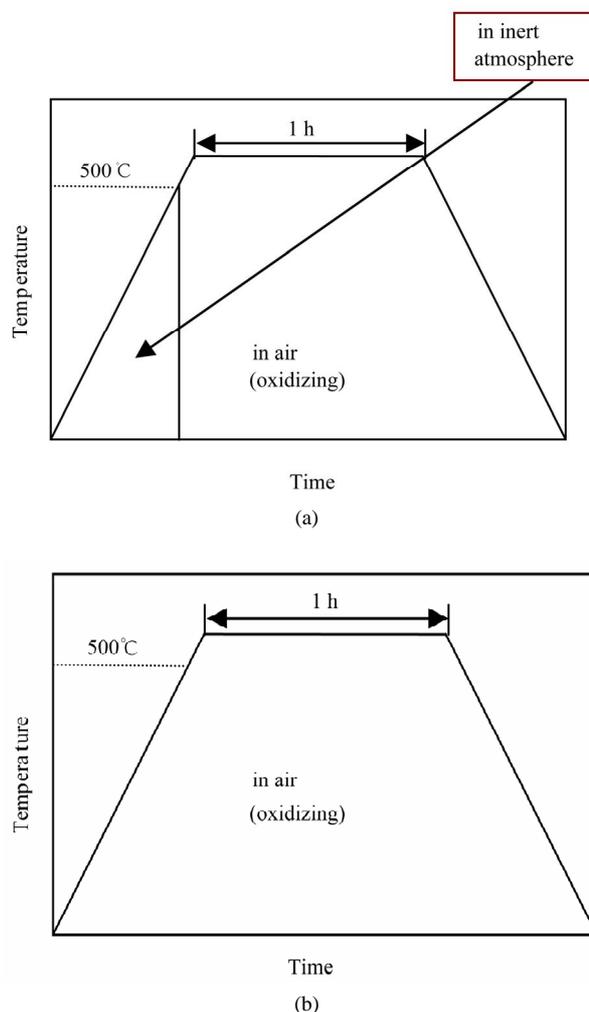
## 2. Experiments

Indium thin films were deposited by using a vacuum evaporation system with a resistive heater for evaporating indium shots (6 N). Sapphire (0001) single-crystal wafers and synthetic quartz glass plates for comparison were used as substrates. The indium thin films were about 100 nm thick. After deposition, the indium thin films were heat treated in an infrared heating furnace and oxidized to form  $\text{In}_2\text{O}_3$  thin films. The heat treatment patterns are schematically shown in **Figure 1**. In the first step of the heat treatment, the temperature was increased from room temperature to  $500^\circ\text{C}$  in an inert  $\text{N}_2$  atmosphere or air. In the second step, the inert atmosphere was replaced with air when the temperature reached to  $500^\circ\text{C}$ , then the temperature was increased to  $900^\circ\text{C}$  and maintained for 1 h. Crystallinities of the obtained thin films were evaluated by X-ray diffraction (XRD).

## 3. Results and Discussion

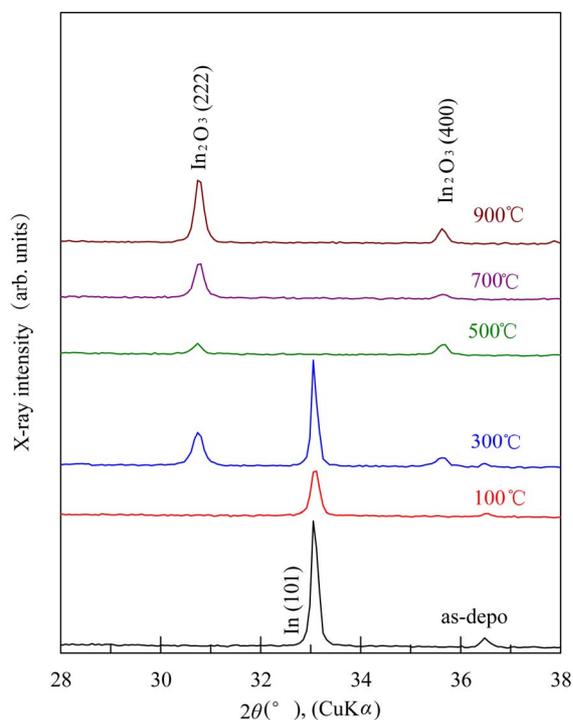
First, indium thin films that had been deposited on quartz glass substrates were conventionally heat treated in air for 1 h at various temperatures. **Figure 2** shows the XRD patterns of the obtained thin films. In this case, the temperature was increased from room temperature in air (*i.e.*, not in an inert atmosphere). The indium thin films gradually become oxidized with increasing heat-treatment temperature. The diffraction peaks for metal indium are not visible when the heat-treatment temperature exceeds  $500^\circ\text{C}$ . Thus,  $\text{In}_2\text{O}_3$  thin films are obtained when the heat-treatment temperature exceeds  $500^\circ\text{C}$ . In addition, it is considered that crystallization of the  $\text{In}_2\text{O}_3$  thin films progresses with increasing heat-treatment temperature as the X-ray intensity of  $\text{In}_2\text{O}_3$  increases by increasing the temperature.

**Figure 3** shows X-ray rocking curves (XRCs) of the  $\text{In}_2\text{O}_3$  (222) peaks of films prepared on sapphire and quartz glass substrates. The films were produced by a conventional single-step heat treatment in air at  $900^\circ\text{C}$  for 1 h with no inert atmosphere. The XRC of the  $\text{In}_2\text{O}_3$  thin film obtained on sapphire substrate is broad and almost



**Figure 1.** Heat treatment schematics of (a) the two-step heat treatment using inert atmosphere tried in this work and (b) conventional single-step heat treatment with no inert atmosphere. In the two-step treatment, the temperature was increased in an inert atmosphere to  $500^\circ\text{C}$  and then the inert atmosphere was replaced with air.

same with that obtained on quartz glass substrate, that is, crystallinity of the film is quite poor. There is no difference in the XRCs of the films prepared on the single-crystal sapphire and quartz glass substrates despite  $\text{In}_2\text{O}_3$  having a heteroepitaxial relationship with the sapphire substrate. This implies that there is no epitaxial effect from the single-crystal sapphire substrate to the  $\text{In}_2\text{O}_3$  thin film. This is considered to be because the melting point of indium is about  $157^\circ\text{C}$ , so that indium thin films may be oxidized at this low temperature, which causes their recrystallization temperature to increase abruptly. Therefore, films that have been oxidized at low temperatures are not able to recrystallize when heat treated in an atmosphere containing oxygen. Consequently,  $\text{In}_2\text{O}_3$  films prepared on a single-crystal sap-

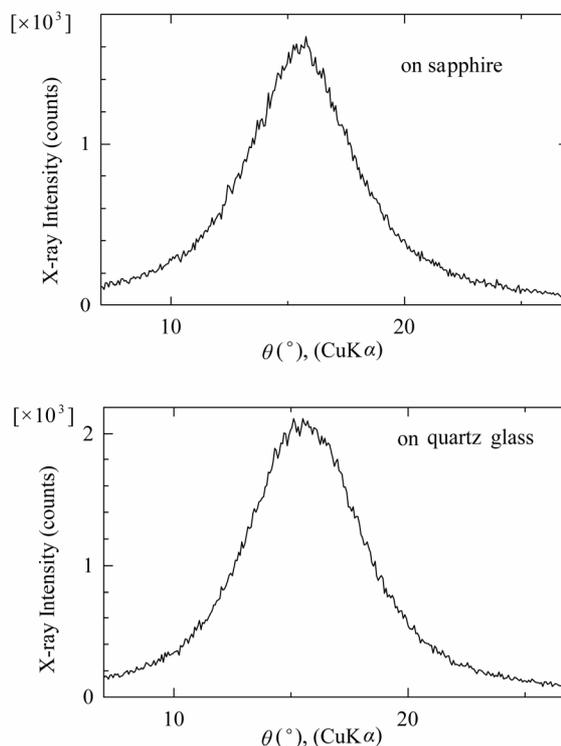


**Figure 2.** XRD patterns of indium thin films deposited on quartz glass substrates that were heated using a conventional single-step heat treatment in air at five different maximum temperatures with no inert atmosphere.

phire substrate have similar poor crystallinities to  $\text{In}_2\text{O}_3$  thin films prepared on amorphous quartz substrates.

Next, we tried heat treatments of indium thin films from room temperature to a specified temperature in an inert atmosphere in the first step. In the second step, the inert atmosphere was replaced with air and the temperature was increased to a specified maximum temperature. In this study,  $\text{N}_2$  gas was used as the inert atmosphere at the low temperatures because  $\text{N}_2$  gas does not react directly with metal indium [8]. Indium thin films that had been deposited on the sapphire and quartz substrates were heat treated in the  $\text{N}_2$  gas atmosphere until the temperature reached  $500^\circ\text{C}$ . The atmosphere was then replaced with air and maximum temperature was maintained for 1 h.

**Figure 4** shows the XRC profile about  $\text{In}_2\text{O}_3$  (222) peak for the  $\text{In}_2\text{O}_3$  thin film produced by the two-step heat treatment on sapphire substrate. As a comparison, the XRC profile for the film prepared on same sapphire substrate by the conventional single-step heat-treatment is also shown in it. Both films were heat-treated by same conditions except for the atmosphere until the temperature reached  $500^\circ\text{C}$ . The film prepared by the two-step heat treatment obviously has a narrower XRC profile than that of the film by the single-step heat treatment



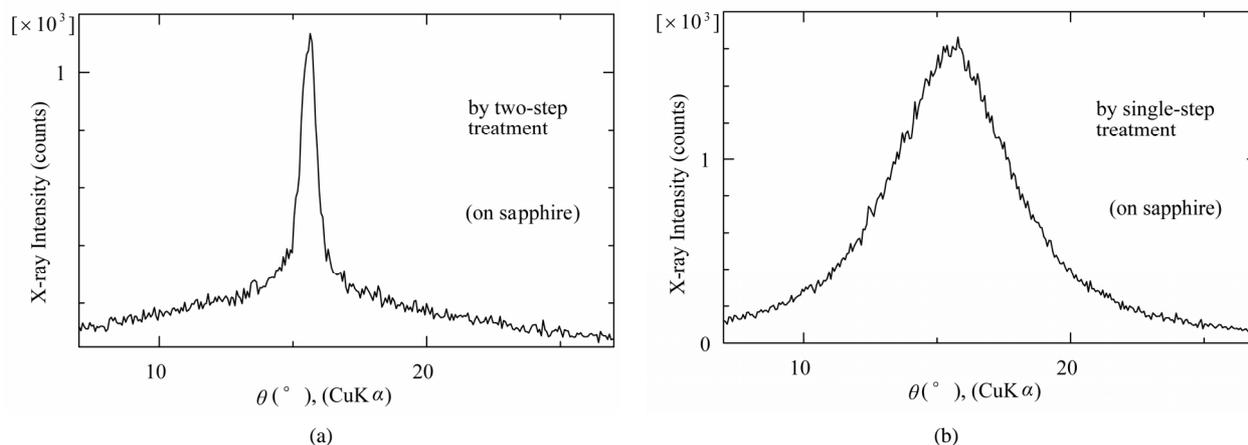
**Figure 3.** XRC profiles showing the  $\text{In}_2\text{O}_3$  (222) peak of  $\text{In}_2\text{O}_3$  thin films produced by conventional single-step heat treatment in air at  $900^\circ\text{C}$  with no inert atmosphere.

with no inert atmosphere. Similar results for the XRC profiles were reproducibly observed even when the heat treatment was performed at various maximum temperatures.

It is considered to be difficult for atoms to migrate in films that had been oxidized at low temperatures when the films are heated from room temperature in an oxygen containing atmosphere. In contrast, atom migration occurs relatively easily in films that had been heat treated in an inert atmosphere at low temperatures and oxidized at higher temperatures. By adjusting the heat-treatment atmosphere, it should be possible to prevent indium thin films from oxidizing at low temperatures at which  $\text{In}_2\text{O}_3$  does not have a high crystallinity. In such cases, indium thin films are oxidized at much higher temperatures, so that the rearrangement and crystallization occur effectively on single-crystal sapphire substrates.

#### 4. Summary

Indium thin films that had been deposited on single-crystal sapphire substrates by vacuum evaporation were heat treated using the two-step method to obtain  $\text{In}_2\text{O}_3$  thin films. Crystallinity of obtained  $\text{In}_2\text{O}_3$  thin films was poor when the heat treatment was not initially



**Figure 4.** XRC profiles about the  $\text{In}_2\text{O}_3$  (222) peak of  $\text{In}_2\text{O}_3$  thin films obtained on sapphire substrates by (a) the two-step heat treatment and (b) conventional single-step treatment. In the two-step treatment, the temperature was increased in an inert atmosphere to  $500^\circ\text{C}$  and then the inert atmosphere was replaced with air.

performed in an inert atmosphere. In contrast, a clear difference and improvement in the crystallinity was observed when the temperature was increased from room temperature to a specified temperature in an inert atmosphere in the first step prior to the second step of the heat treatment in an oxygen-containing atmosphere. Therefore, this kind of two-step heat treatment will become an effective method for producing epitaxially grown  $\text{In}_2\text{O}_3$  thin films easily in the simple oxidation method of metal indium thin films.

## 5. References

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