Zr-Content Dependence of Electrical Properties in Heat-Treated In_2O_3: Zr Thin Films Grown on a Sapphire Substrate by Sputtering

Yuichi Sato*, Minoru Hatakeyama, Yuhei Muraki, Kazuki Sonoda, and Yoshifumi Murakami

Electrical and Electronic Engineering Course, Graduate School of Engineering Science, Akita University, Japan

Abstract: Zirconium-doped indium oxide (In_2O_3:Zr) thin films of various Zr-contens were hetero-epitaxially grown on a sapphire single-crystalline substrate by a magnetron sputtering method. The films were heat-treated in an N_2 atmosphere and the variations of their electrical properties as a function of the Zr-content were investigated. We observed the resistivity decreasing without any deterioration in their crystallinity and optical transmission property after the heat-treatment when the impurity content was within 2 wt.%, and then, the degree of the resistivity-decrease saturated since their mobility started to decrease due to the heavy impurity doping.

Keyword; Sapphire, Multichannel spectroscopes, Nitride semiconductor, Photovoltaic cells, Van der Pauw.

1. INTRODUCTION

Sapphire (α-Al_2O_3) is one of the most utilized single-crystalline substrate materials used for hetero-epitaxial growths of group-III nitride semiconductor thin films [1-7]. It has a high optical transmission property, therefore; for example, it can be applied to fabrications of photovoltaic cells in which the nitride semiconductor thin films are grown on the sapphire substrate as optical absorbing layers. In such cases, a highly transparent and single-crystalline conducting layer is needed between the nitride thin films and the sapphire substrate because sapphire is an insulator. Fortunately, indium oxide (In_2O_3), which is one of the most popular transparent conducting materials, has a hetero-epitaxial-relationship to c-face sapphire. In addition, the nitride semiconductor thin films are able to be grown hetero-epitaxially on a (111)-preferential-oriented In_2O_3 film without deteriorations in crystallinity of the nitride thin films [8].

Resistivity of the In_2O_3 film has to be low enough to apply it to the conducting layer, and the film should be single-crystalline and highly transparent in the wavelength region from near-ultraviolet (N-UV) to near-infrared (N-IR). Generally, resistivity of In_2O_3 can be easily lowered by doping adequate impurities such as tin, however, most of the resistivity-lowered In_2O_3 films are polycrystalline. Moreover, their transparency, especially in the N-IR region, tends to become poor because of existence of excess carriers. Therefore, resistivity of the In_2O_3 films must be lowered with keeping the required crystallinity and transmission properties.

Additional requirement for the In_2O_3 films is that the films should be prepared by conventional methods to the extent possible. There have been several reports on preparations of In_2O_3 films which have high performances [9,10], however, most of them have been prepared by rather highly sophisticated growth methods. On the other hand, sputtering method is considered to be one of the most conventional methods for preparations of thin films in various applications. We have previously investigated about In_2O_3 thin film preparations by the sputtering method from a viewpoint of sputtering conditions as well as heat-treatment conditions of the films [11,12]. The required properties were mostly obtainable by precise optimizing of the sputtering conditions, however; the sputtering conditions were relatively critical. On the other hand, relatively wider margins were seemed to exist in the heat-treatment conditions. That is, resistivity of In_2O_3 thin films can be easily lowered by heat-treatments compared with the case in which sputtering conditions are precisely adjusted to obtain the films with high crystallinity and transparency.

Generally, electron mobility in In_2O_3 thin films is kept high when Zr is chosen as the dopant to decrease the resistivity [10]. Therefore, a slightly Zr-doped In_2O_3 thin film (ZrO_2: 0.5 wt.%) was prepared and heat-treated in the previous work [12] to improve properties of the sputter-grown In_2O_3 thin films. In that case, different gases were successively introduced to an electric furnace as the two-step heat-treatments. In this work, Zr-doped In_2O_3 thin films of various Zr-contents grown on a c-face sapphire single-crystalline substrate by a

*Address correspondence to this author at the Electrical and Electronic Engineering Course, Graduate School of Engineering Science, Akita University, Japan;
E-mail: yusato@gipc.akita-u.ac.jp

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sputtering method were additionally heat-treated by a much simpler one-step method. Variations in electrical properties of the films by the heat-treatment were investigated as a function of the Zr-content.

2. EXPERIMENTAL

The Zr-doped In_2O_3 thin films were prepared by the radio-frequency (RF, 13.56 MHz) magnetron sputtering method. The substrate used was a c-face sapphire single-crystalline wafer. Zirconium oxide (ZrO_2)-mixed In_2O_3 powders were used as the sputtering target, and O_2-Ar mixed gas was used as the sputtering gas. The O_2 mixing ratio was fixed to 0.2, while the RF power and the substrate temperature were fixed to 100 W and 500 ℃, respectively. Thicknesses of the obtained films were around 300 nm. Then, the sputter-grown thin films were heat-treated for 1 h at 900 ℃ in N_2 atmosphere. Crystallinities of the films were evaluated by the X-ray diffraction (XRD) method. Optical transmission spectra of the films were measured in the wavelength region between 350 and 2000 nm by multichannel spectroscopes. Electrical properties of them were measured by the van der Pauw method.

3. RESULTS AND DISCUSSION

The indispensable properties for the transparent conducting layers, for example in the single-crystalline nitride semiconductor photovoltaic cells, are high crystallinity and high transmittance in the wide wavelength region from N-UV to N-IR. Therefore, the crystallinity and the transparency of the In_2O_3 films have to be kept high enough even after the heat-treatments. Typical XRD patterns and transmission spectra of the as-grown and the heat-treated In_2O_3 thin film (ZrO_2 0.7wt.%) are shown in Figures **1** and **2**, respectively. The c-face sapphire can be considered as a hexagonal crystal system; therefore, the In_2O_3 thin film, which is a material of the cubic crystal system, might hetero-epitaxially grow on the substrate at least with the (111) preferential orientation. Figures **1** (**a**) and (**b**) indicate the results, and the preferential orientation state is well kept even after the heat-treatment. The optical transmission property of the films is also important. The as-grown In_2O_3 film showed high transmittance in the wide wavelength region from the N-UV to N-IR, and the high transmittance was kept even after the heat-treatment as shown in Figures **2** (**a**) and (**b**).

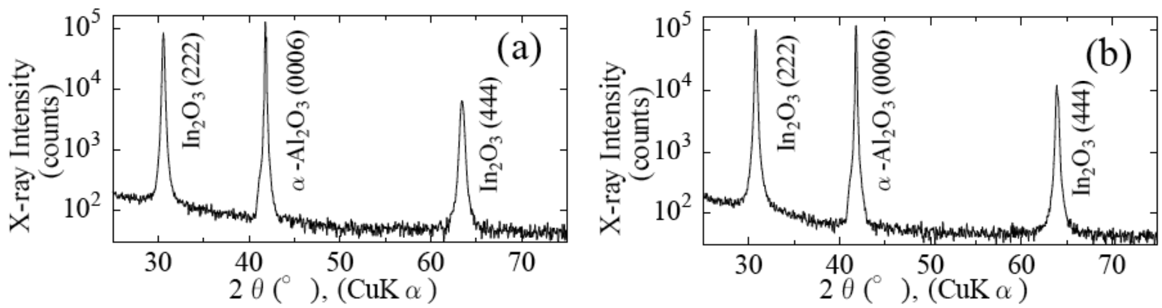

Figure 1: XRD patterns of the typical (**a**) as-grown and (**b**) heat-treated In_2O_3 (ZrO_2 0.7wt.%) thin films. The as-grown thin film was heat-treated at 900 ℃, 1 h, and N_2 atmosphere.

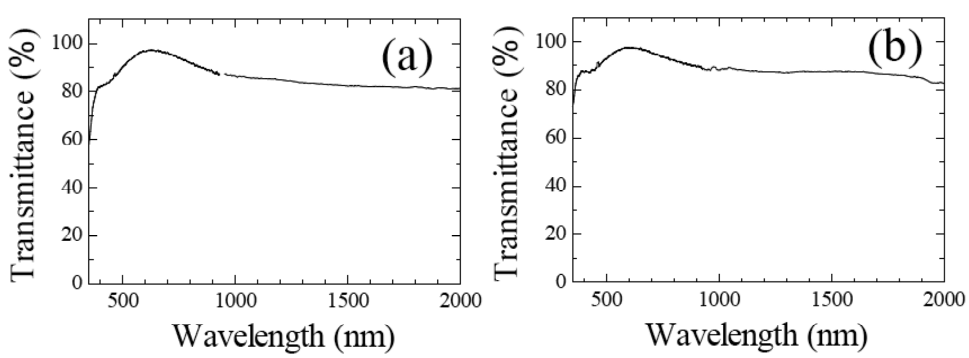

Figure 2: Optical transmission spectra of the typical (**a**) as-grown and (**b**) heat-treated In_2O_3 (ZrO_2 0.7wt.%) thin films. The as-grown thin film was heat-treated at 900 ℃, 1 h, and N_2 atmosphere.

Furthermore, electrical properties of the obtained thin films were investigated. Figures **3** show the electrical properties of the thin films of various impurity-contents before and after the heat-treatment. Concerning with the as-grown films, the carrier density increases with the increase of the impurity-content, therefore; the resistivity of the films decreases with the increase of the carrier density. However, the carrier density saturates at the order of 10^{19} cm^{-3}, therefore; the decrease of the resistivity also saturate at the order of 10^{-2} Ω. cm. On the other hand, the carrier density of the films increases to the order of 10^{20} cm^{-3} after the heat-treatment. Therefore, the resistivity decreases with the increase of the carrier density, and the value decreases to about 1×10^{-3} Ω. cm.

If carrier density in the film can be increased much larger than the value beyond 10^{20} cm^{-3} range, the resistivity will decrease much lower than the value obtained in this experiment. However, in that case, the optical transmittance especially at the longer wavelength will drastically decrease, and it cannot be utilized as the transparent conducting layers. The crystallinity will also deteriorate by increasing the carrier density because the increase of the carrier density to the degenerate level in In_2O_3 mainly owes to its relatively large deviations from the stoichiometry in addition to existence of the excess impurities.

Another way to reduce the resistivity is increase of the mobility. Generally, the mobility increases by the heat-treatment as shown in Figure **3**. However, the mobility in the heavily doped films rather decreases with the increase of the impurity-contents probably due to carrier scattering by the excess impurities. As a result, the value of the resistivity saturated as described above when the impurity-content was 2 wt.%.

CONCLUSION

The obtained Zr-doped In_2O_3 thin films showed high transparency in the wide wavelength region and highly (111)-oriented structures. Resistivities of the films decreased to about 1×10^{-3} Ω. cm after the heat-treatment. Carrier densities of the films increased to the order of 10^{20} cm^{-3}. The mobilities increased after the heat-treatment compared with those of the as-grown films, respectively. However, the value started to decrease when the impurity content was too high.

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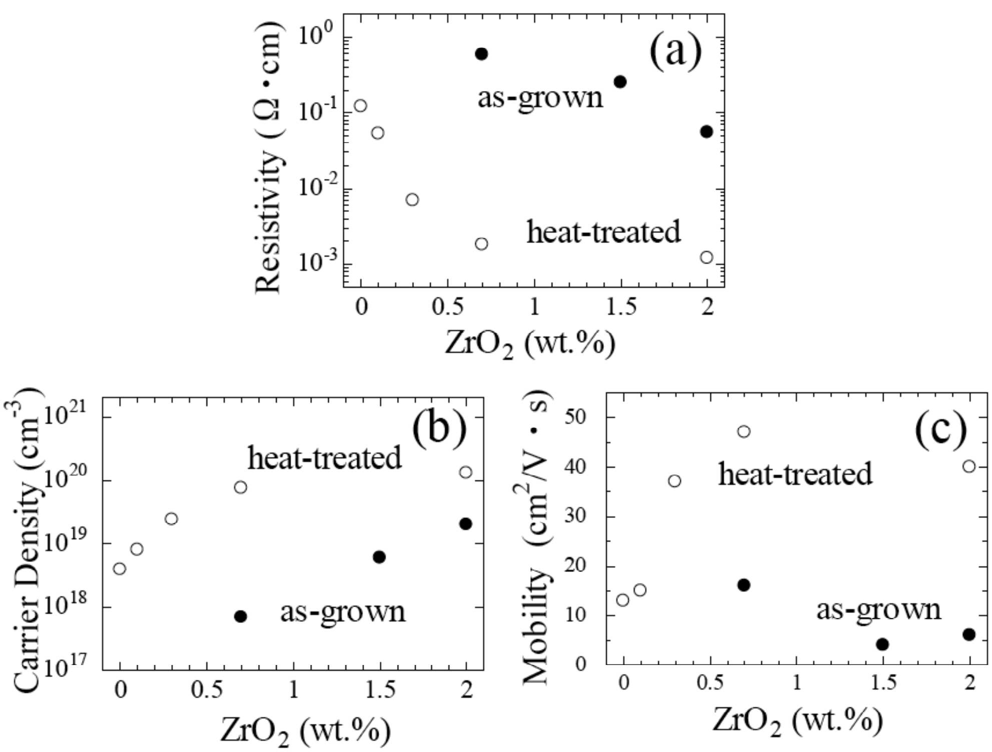

Figure 3: (**a**) Resistivity, (**b**) carrier density, and (**c**) mobility of the Zr-doped In_2O_3 thin films as a function of the impurity-content.

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