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A Study on an Oxygen Vacancy and Conductivity of Oxide Thin Films Deposited by RF Magnetron Sputtering and Annealed in a Vacuum

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Usually, the oxygen vacancy is an important factor in an oxide semiconductor device because the conductivity is related to the oxygen vacancy, which is formed at the interface between oxide semiconductors and electrodes with an annealing processes. ZTO is made by mixing n-type ZnO and p-type SnO_2. Zink tin oxide (ZTO), zink oxide (ZnO) and tin oxide (SnO_2) thin films deposited by RF magnetron sputtering and annealed, to generate the oxygen vacancy, were analyzed by XPS spectra. The contents of oxygen vacancy were the highest in ZTO annealed at 150°C, ZnO annealed at 200°C and SnO_2 annealed at 100°C. The current was also increased with increasing the oxygen vacancy ions. The highest content of ZTO oxygen vacancies was obtained when annealed at 150 . This is the middle level in compared with those of ZnO annealed at 200°C and SnO_2 annealed at 100°C. The electrical properties of ZTO followed those of SnO_2, which acts a an enhancer in the oxide semiconductor.

Keywords: ZnO, SnO_2, ZTO, XPS, Oxygen vacancy, O 1s spectra

1. INTRODUCTION

Recently, attention has been focused on the zink based oxide (ZnO) semiconductors due to their superior characteristics that include a flexibility and transparency for application to electronic devices [1-6]. One promising candidate material for electronic device oxide semiconductors is a zink tin oxide (ZTO), made by mixing of ZnO : SnO_2=1 : 1. The physical, chemical and electrical properties of ZTO follow the characteristics of n-type ZnO and p-type SnO_2. Indium free ZTO has merit for its low production, low resistivity and high mobility, as well as transparency and flexibility [7-11]. The conductivity of zink based on oxide semiconductors usually changes in accordance with ionized carriers such as Zn interstitials (Zn_i), oxygen vacancies (V_o) and oxygen interstitials (O_i). The oxygen vacancy in an oxygen deficient interlayer acts as an electron trap, controlling the conductivity of oxide semiconductors [12-15]. The oxygen vacancies, as an electron donor, were generated using various methods of annealing, and increased with increasing annealing temperature. Oxygen vacancies act as localized trap barriers, interfere with the drift current, and induce diffusion current. This results from Schottky contact owing to the oxygen deficient layer. The similarity of ZTO, SnO_2 and ZnO films, annealed in an atmosphere condition to increase high conductivity, was researched in previous work [16]. However, the oxygen vacancy content generated by annealing in a vacuum cannot be similar to the result in an air atmosphere. Therefore, the relationship between the conductivity and oxygen vacancy owing to annealing conditions of oxide semiconductors are not clearly understood.

The effect of oxygen vacancy due to annealing in a vacuum, for ZTO, ZnO and SnO_2 oxide semiconductors is researched in this study. The variation of oxygen vacancy was analyzed by the deconvolution of O 1s orbital binding energy. The relationship between annealing temperature in a vacuum and oxygen vacancy content was researched. The conductivity due to diffusion current was observed at an oxygen deficient interlayer in ZTO, ZnO and SnO_2 films prepared on ITO glass. Although oxygen vacancies represent the dominant factor governing the conduction of oxide

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semiconductors, the formation temperature of oxygen vacancies in a vacuum was not clear in the previous works. Therefore, the electrical characteristics of ZTO, ZnO and SnO_2 films are researched at 100°C, 150°C and 200°C annealing temperatures.

2. EXPERIMENTS

ZTO, SnO_2 and ZnO thin films as oxide semiconductors were deposited on ITO glass by a RF magnetron sputtering at a pressure of 0.01 Torr. ZTO, SnO_2 and ZnO targets (99.99% purity) were supplied by LTS Research Laboratories, Inc., U.S.A. The flow rate of the oxygen (99.9999%) was controlled by a mass flow controller (MFC) from 17 sccm for 10 minutes, and the sputtering RF power was 70 W. The base pressure was 4.5×10^{-5} Pa. The chemical analysis of the film was performed using an X-ray photoelectron spectroscopy (ESCALAB 210) at The Center for Research Facilities, Chungbuk University, Cheongju, South Korea. The oxygen vacancy content was verified from the deconvolution of O 1s electron orbital spectra. The electrical properties were researched using MIS (Al metal/oxide semiconductor/ITO glass) structure and a mask pattern with a diameter of 200 μm.

3. RESULTS AND DISCUSSION

To characterize the oxygen vacancy in oxide semiconductors, the correlation between electrical properties and relative content of oxygen vacancies was researched using XPS spectra. The binding energy of the ZTO O 1s spectra was analyzed.

Figure 1 is the O 1s electron orbital spectra of ZTO deposited and annealed at 150°C, 200°C and 250°C to research the electrical properties of ZTO. The O 1s electron orbital spectra showed various formations according to the increase in oxygen gas flow rates. The reaction of Zn cations and oxygen anions became more polarized under the oxygen rich condition. To observe the effect of oxygen vacancies, the O 1s electron orbital spectra were deconvoluted by three bonds: metal oxygen (O_m), oxygen vacancy (V_o), and OH related bonds.

The ZTO film O 1s binding energy of O 1s of ZTO film changed with rising annealing temperatures, and the metal oxygen (O_m), oxygen vacancy (V_o) and OH related bonds werealso shifted in accordance with annealing temperatures. This can be estimated from the deconvolution of O 1s. The relative contents of the metal oxygen (O_m), oxygen vacancy (V_o^+) and OH bonds depend on the strength of bonding between the oxygen and neighboring atoms [17-20]. The oxygen vacancy as an anion is a carrier that increases current and affects the electrical properties of ZTO.

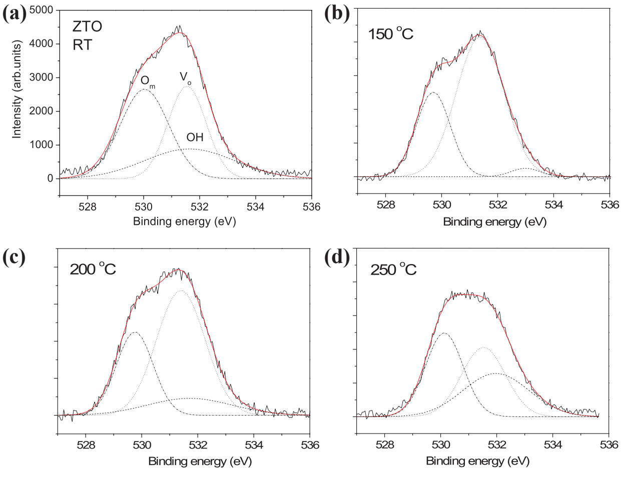

Fig. 1. O 1s electron orbital spectra of ZTO annealed at various temperatures: (a) room temperature, (b) 150°C, (c) 200°C, and (d) 250°C.

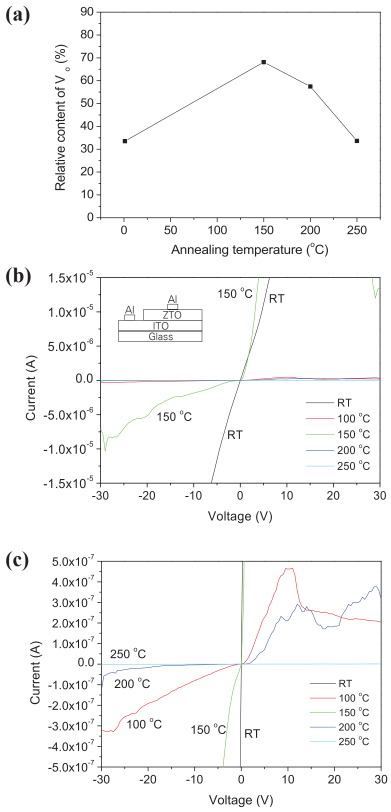

Fig. 2. Relationship between V_o and I-V curves of ZTO films, (a) relative content of oxygen vacancy, (b) electrical properties in a range of $-{\sim}10^{-5}<I<+{\sim}10^{-5}$, and (c) electrical properties in a range of $-{\sim}10^{-7}<I<+{\sim}10^{-7}$.

To research the change in oxygen vacancies due to the annealing effect, the relative oxygen vacancy content was analyzed with increasing annealing temperatures. Figure 2(a) is the relative oxygen vacancy conten (V_o) with increasing annealing temperature and Figs. 2(b) and 2(c) are the I-V curves of ZTO films researched by using the MOI structure (metal/oxide semiconductor/ITO glass). The inset shows the schematic structure. The relative content of oxygen vacancy content was highest in ZTO annealed at 150°C. The current also increased in ZTO annealed at 150°C, anad in samples annealed without the deposited ZTO. The oxygen vacancy decreased at high temperature under 150°C. Figure 2(c) shows the reduction of current at the higher annealing temperatures of 200°C and 250°C. The metal oxygen (O_m) and OH bonds are more polarized than the oxygen vacancy. Therefore, the binding energy of oxygen vacancy has a middle value. It can be suggested that ZTO electrical properties are affected by the bonding structure due to the oxygen vacancy content. The oxygen vacancy is formed by annealing a deposited film. So the change of oxygen vacancy in an annealed film can be considered as the conduction mechanism as a result of I-V curve of oxide semiconductors.

Figure 3 shows the O 1s electron orbital spectra of ZnO prepared on ITO glass and annealed at 100°C and 200°C in a vacuum ambient condition. In order to observe the oxygen vacancy content, the O 1s with binding energy of 528 eV~534 eV was deconvoluted. Deposited film has relatively large metal oxygen (O_m), instead of the high OH bonds in annealed films. The feature of oxygen vacancy of deposited film was different in comparison to annealed films.

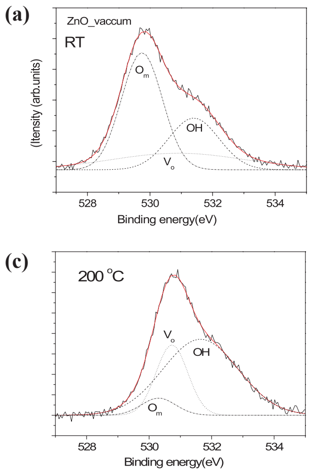

Fig. 3. O 1s electron orbital spectra of ZnO annealed at various temperatures: (a) room temperature, (b) 100°C, and (c) 200°C.

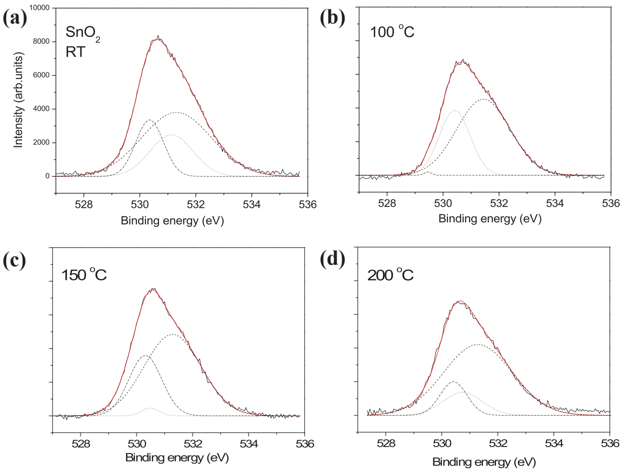

Fig. 5. O 1s electron orbital spectra of SnO_2 annealed at various temperatures: (a) room temperature, (b) 100°C, (c) 150°C, and (d) 200°C.

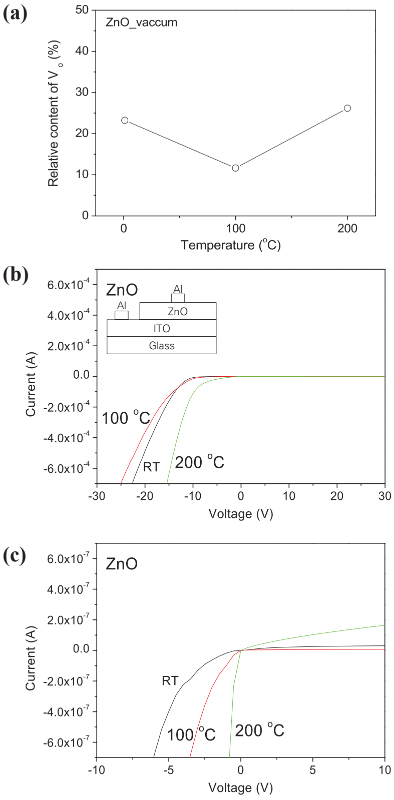

Fig. 4. Relationship between V_o and I-V curves of ZnO films, (a) relative oxygen vacancy content, (b) electrical properties in a range of $-\sim10^{-4}<I<+\sim10^{-4}$, and (c) electrical properties in a range of $-\sim10^{-7}<I<+\sim10^{-7}$.

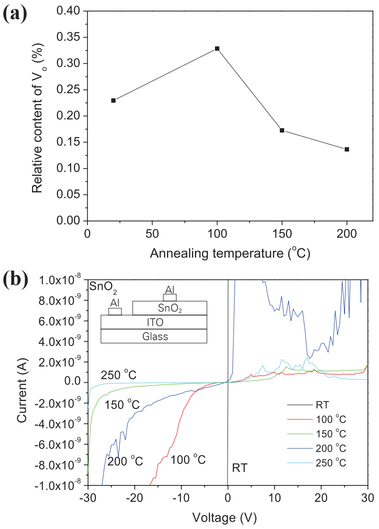

Fig. 6. Relationship between V_o and I-V curves of SnO_2 films, (a) relative oxygen vacancy content and (b) electrical properties in a range of $-\sim10^{-9}<\text{current}<+\sim10^{-9}$.

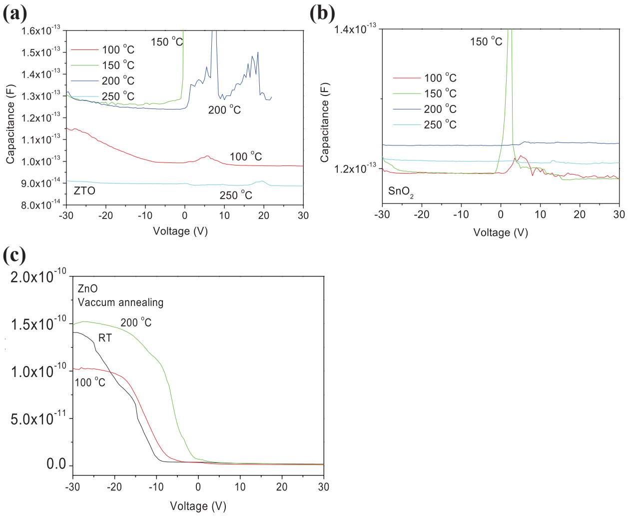

Fig. 7. Capacitance with annealing temperatures, (a) ZTO, (b) SnO_2, and (c) ZnO.

The oxygen vacancy content when annealed at 100°C is less than that at 200°C as shown in Fig. 4(a). The current increased with increasing oxygen vacancy content as shown in Figs. 4(b) and (c).

Figure 5 demonstrates the O 1s electron orbital spectra of SnO_2 prepared on ITO glass and annealed in a vacuum. The intensity of O 1s decreased after annealing processes. Especially, that of SnO_2 annealed at 100°C was lower than other samples. The relative oxygen vacancy content was the largest in SnO_2 annealed at 100°C.

Figure 6 presents that the oxygen vacancy content and electrical properties of SnO_2 at various annealing temperatures. The relative oxygen vacancy content was highest in SnO_2 annealed at 100°C, and as deposited SnO_2 had linearly Ohmic contact as seen in Fig. 6(b). The electrical characteristics of the annealed SnO_2 showed the asymmetric Schottky contact, and the current decreased with increasing annealing temperatures. SnO_2 annealed at 100°C showed high current due to the high oxygen vacancy content as previously mentioned. The trend of electrical properties of ZnO films was similar to the results of ZTO and ZnO. Therefore, we attribute the conductivity in oxide semiconductors to oxygen vacancy.

Figure 7 is the capacitance of ZTO, SnO_2 and ZnO to define the detailed electrical properties. The capacitance of ZTO and SnO_2 had similar trends, such as very low capacitance of about ~10^{-13} F and steep increments at 150°C. On the other hand, the capacitance of ZnO, at about ~10^{-10} F, is higher than that of the ZTO and SnO_2 films. Consequently, it could be confirmed that the electrical characteristic of ZTO is more similar to that of SnO_2.

4. CONCLUSIONS

The correlation between an annealing temperature and oxygen vacancy to enhance the conductivity in an oxide semiconductor was researched in this paper. The formation of oxygen vacancy in an oxygen deficient interlayer was confirmed by analyzing the electrical characteristics of ZTO, SnO_2 and ZnO prepared on ITO glasses. Oxygen vacancies in an oxygen deficient interlayer act as electron traps. The variation of a trap region in an oxygen deficient interlayer contributes to the conduction of oxide semiconductors. This is explained by the model of diffusion currents due to the Schottky contact. The characteristics of ZTO depended on SnO_2 and ZnO, because the ZTO was made by the mixed composition of SnO_2 and ZnO. The oxygen vacancy changed with increasing the annealing temperature and the current increased at high oxygen vacancy content. High SnO_2 conduction was obtained in a film annealed at 100°C with high oxygen content, and ZnO annealed at 200°C with high oxygen content. However, ZTO showed high conduction characteristics when it was annealed at 150°C in the middle range between 100°C and 200°C. This result provides the information to help in understanding the intrinsic nature of oxide semiconductors in a PN junction structure.

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