論 文 内 容 の 要 旨

The structural, electrical, optical, and transport properties of Ga-doped ZnO (GZO) thin film prepared by radio frequency magnetron sputtering have been investigated in this dissertation. This dissertation is consists of eight chapters.

First chapter is “Introduction”. In this chapter, purpose of the study covering all topics in this dissertation, and outline of this dissertation are summarized.

Second chapter is “Fundamentals”. In this chapter, general properties of zinc oxide (ZnO) as a semiconductor, crystal structure of ZnO, polarity of ZnO, defects in ZnO, scattering mechanism of charge carriers in ZnO, principles of magnetron sputtering, and background of gas sensors based on metal oxide semiconductors are briefly introduced.

Third chapter is “Research Methodology”. In this chapter, methodology of thin film deposition, characterization techniques employed in this dissertation, and analytical evaluations are described.

Next four chapters are main part of this dissertation consists of four topics published (or to be published) in refereed journals. The each chapter is consists of introduction of the topics, experimental method in details, results and discussion, and conclusion.

Fourth chapter is “Control of microstructure by using self-buffer layer and its effects on the properties of Ga-doped ZnO thin films”. In this chapter, the influence of microstructure on the properties of GZO films deposited by radio frequency magnetron sputtering was investigated by a combination of microstructural control and post-deposition annealing. GZO films deposited on bare glass substrates at room temperature (RT) showed poor *c*-axis orientation; however, insertion of a thin GZO layer deposited at 200 °C as a self-buffer layer resulted in high *c*-axis orientation. Regardless of the microstructure, the carrier concentration, Hall mobility, and optical transmittance of the GZO film deposited at RT were lower than those of the GZO film deposited at a higher substrate temperature of 200 °C, because of the presence of defects in the former film. The carrier concentration and optical transmittance of both the GZO film with the self-buffer layer and the GZO film without the self-buffer layer increased after the post-deposition annealing. However, a significant improvement of the Hall mobility was observed only for the highly *c*-axis oriented GZO films deposited on the self-buffer layer. Evaluation of the contribution of grain boundary scattering to the Hall mobility by employing optical mobility as the measure demonstrated that the contribution of grain boundary scattering clearly existed in the case of the GZO films without the self-buffer layer but it was almost negligible in the case of well-oriented GZO films deposited on the self-buffer layer.

Fifth chapter is “Change of scattering mechanism and annealing out of defects on Ga-doped ZnO films”. This chapter examines the change of carrier scattering mechanism and defects states in GZO thin films deposited by RF magnetron sputtering as a function of the substrate temperature (Ts) during deposition. The GZO films deposited at room temperature exhibited a high defect density that resulted in a lower carrier concentration, lower Hall mobility, and optical absorption in visible wavelength range. Such defects were created by ion bombardment and were eliminated by increasing the Ts. The defects related to the optical absorption disappeared at a Ts of 125 °C. The defects responsible for the suppression of the carrier concentration gradually decreased with increasing Ts up to 200 °C. As the results, the carrier concentration and in-grain carrier mobility gradually increased. The Hall mobility was also influenced by film structural properties depending on the Ts. In addition to the c-axis preferred orientation, other oriented grains such as the (10-11) plane parallel to the substrate surface appeared below 150 °C. This orientation of the (10-11) plane significantly reduced the Hall mobility via grain boundary scattering. The films deposited at a Ts higher than 175 °C exhibited perfect c-axis orientation and grain boundary scattering was thus negligible in these films. The appearance of the (10-11) peak in x-ray diffraction profile was correlated with the contribution of grain boundary scattering in heavily doped GZO films.

Sixth chapter is “The significant effects of polarity inversion on the electrical properties of Ga-doped ZnO thin films”. This chapter investigates how polarity inversion influences the relationship between the electrical properties of heavily GZO films deposited by RF magnetron sputtering and their thickness. The electrical properties observed in very thin films are correlated with a change of polarity from O-polar to Zn-polar face upon increasing the film thickness based on results of valence band spectra measured by X-ray photoelectron spectroscopy. It is found that the electrical properties of very thin GZO films deposited on Zn-polar ZnO templates are significantly improved compared to those deposited on O-polar face. A low resistivity of 2.62×10^{-4} Ωcm, high Hall mobility of 26.9 cm^2/Vs, and high carrier concentration of 8.87×10^{20} cm^{-3} being achieved with 30 nm-thick GZO films using Zn-polar ZnO templates on a glass substrate. In contrast, the resistivity of 30 nm-thick GZO films on bare glass that shows more likely O-polar is poor about 1.44 x 10^{-3} Ωcm with Hall mobility and carrier concentration are only 11.9 cm^2/Vs and 3.64×10^{20} cm^{-3}, respectively. It is therefore proposed that polarity inversion plays an important role in determining the electrical properties of extremely thin GZO films.

Seventh chapter is "Hydrogen gas sensor based Ga-doped ZnO thin films". This chapter is related to hydrogen gas sensor based on GZO thin films deposited by RF magnetron sputtering. The effects of the microstructural properties, i.e., grain size and *c*-axis orientation on sensitivity for hydrogen gas have been investigated in order to elucidate the main factor to determine sensitivity of hydrogen gas sensors based on GZO thin films. In the case of GZO films deposited on bare glass substrates, the 100 nm thick film showed better c-axis orientation with larger grain size compared to the 30 nm thick film that showed poor c-axis orientation and smaller grain size. We found that the 30 nm thick film showed the higher sensitivity compared to the 100 nm thick film. On the other hand, in the case of 30 nm thick-GZO films deposited on the ZnO template, the c-axis orientation was very well oriented similar to the 100 nm thick GZO film on bare glass and nearly comparable each other, while the grain size obviously increased with increasing the thickness of ZnO templates. However, the sensitivity of these films on ZnO template was nearly identical. And it was also comparable with that of the 100 nm thick film on bare glass. In contrast, the 30 nm thick GZO films deposited on bare glass showed the highest sensitivity compare to all of other samples. It is therefore proposed that c-axis orientation plays an important role on the sensitivity of hydrogen gas.

The last part of this dissertation is “Concluding Remarks”. This chapter concludes findings and achievement thorough this study and some concluding remarks are given.