論 文 内 容 の 要 旨

Chapter 1. Introduction

Overview of metallic oxides based on the typical metal-oxygen (MO) or transition metal-oxygen (TMO) system of compound semiconducting materials. The typical MO semiconduction materials of IV-oxides and III-oxides, TMO semiconduction materials of II-oxides and I-oxides has been reviewed. In addition, the properties of ZnO and ZnO-based heterojunction has been specifically reviewed.

Chapter 2. Fabrication Systems and Characterization Techniques of metallic Oxide Thin Films

The working principles, apparatus structures and parameters, and operation processes of fabrication equipment and characterization devices were introduced.

Chapter 3. Fabrication and characterization of ZnMgO thin film grown by mist CVD

Aiming for optimizing the performance of ZnO-related material devices, the crucial point is to grow high-quality ZnO-based thin films. The studies based on 3rd generation of mist CVD system that can supply the precursors separately for ZnMgO deposition found and verified that setting different Mg carrier gas/dilution gas can precisely control the Mg component ratios, and the increasing of Mg carrier gas flow rate led to higher incorporation of Mg atom in the grown films at 400oC, and the morphology and crystallinity of ZnMgO films were extensively impacted by the Mg content [4]. There are still lots of issues that need to be investigated for the improvement in the characteristics of ZnMgO. Currently, we are investigating the dependence of $[H_2O]/\{[Zn]+[Mg]\}$ supply ratio on the characteristics of ZnMgO. Even though we had already reported on the changes of ZnO characteristics with the supply ratio of $[H_2O]/[Zn]$ [5], after introducing Mg the properties of ZnMgO have changed very much. The results indicate that the H_2O supply amount was influenced by Mg c.g./d.g., and the supply ratio of $[H_2O]/\{[Zn]+[Mg]\}$ has strongly impacted the growth rate and crystal orientations; the optical band gaps of ZnMgO films were widened from 3.22 to 3.8 eV by increasing the H_2O concentration with fixing Mg c.g./d.g. = 1.0/4.0; at the same supply ratio of $[H_2O]/\{[Zn]+[Mg]\}$ after adding the support oxidant O3, the resistivity increased to 2.8×10^9 Ω·cm; Under without O_3, the resistivity decreased to 3.4×10^7 Ω·cm.

Chapter 4. Fabrication and characterization of Ag_xO thin film grown by mist CVD

We report the results of Ag_xO films grown via a mist chemical vapor deposition (mist-CVD) system. It has been found that the mist CVD system has the potential to grow Ag and Ag_xO thin films, the oxidants of O_3 and H_2O have an extensive impact on the Ag_xO properties, and the mist CVD system has been proved to have the potential to be used for the metallic-oxide thin films deposition.

Chapter 5. The Effects of R[O_2] % on the Properties of Ag_xO Thin Films Grown by RFM-Sputtering

In this study, the Ag_xO thin film has been deposited by radio frequency magnetron sputtering (RFM-SPT). While adjusting oxygen flow ratios (R[O_2] %) from 0 % to 30 %, Ag_xO thin film transitioned from metal to semiconductor and/or insulator with different transparent appearances on the surface observed in XRD and transmittance measurement. At high oxygen flow ratios, the Ag_xO film is multi-phased as a mixture of $Ag^{(II)}O$ and $Ag_2^{(III)}O_3$. In addition, the work function (ϕ) of those samples changes from 4.7 eV to 5.6 eV as measured by photoelectron yield spectroscopy (PYS). The compositional and chemical state changes that occur at the Ag_xO surface during the increments of R[O_2] % are evaluated by the relative peak intensities and binding energy shifts in x-ray photoelectron spectroscopy (XPS). With the incorporation of more electrons in chemical bonding, the oxygen-induced band forms. And combining all the results from transmittance (band gaps confirmation), PYS (work function confirmation), and XPS (valence band position confirmation), the estimation band diagrams are given for the oxidation state of Ag_xO with various oxygen flow ratios.

Chapter 6. Fabrication of $Zn_{1-x}Mg_xO/Ag_yO$ Heterojunction Diodes by Mist CVD at Atmospheric Pressure

We report on the preparation of heterojunction based on $Zn_{1-x}Mg_xO$/p-Ag_yO semiconductor heterostructure. A series of multi-layers, containing $Zn_{1-x}Mg_xO$ (ZnMgO) films stacked on InSnO (ITO) films, were prepared using a mist chemical vapor deposition system with different flow rates for the Mg carrier gas/dilution gas (c.g. / d.g.). Ag_yO films then were deposited on the ZnMgO/ITO substrates. It was found that as the flow rate of the Mg c.g. / d.g. increased, the morphology and crystallinity of the ZnMgO films were extensively impacted by the Mg content and the cross-section images of the ZnMgO/Ag_yO HJDs showed spontaneous order of the random alloys and partial inclinations of the multi-layers, the band gaps of ZnMgO broadened from 3.3 to 3.7 eV, and resistivity increased to 1.58×10^8 Ω·cm; the work function of Ag_yO films increased to 5.6 eV at the highest O_2 flow rate (R[O_2] = 30 %) during the sputtering process. Although the energy gap variations caused abrupt interfaces, these

ZnMgO/Ag_yO HJDs demonstrated rectifying behavior with a barrier height of around 0.98 eV, which is comparable to that achieved using similar but more expensive preparation methods.

Chapter 7. Conclusions

The main results have been summarized in this chapter and depending on the understanding of the past work, looking into the future and planning the blueprint.