論文の内容の要旨

論文題目

Development of Tin-Based Transparent Conductive Oxides with High Carrier Mobility

（高キャリア移動度スズ系透明導電性酸化物の開発）

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Transparent conductive oxides (TCOs), exhibiting excellent transparency and conductivity simultaneously, are of increasing importance for optoelectronic applications such as electrodes in solar cells and flat panel displays. Generally, conductivity increases as carrier Hall mobility (μ_H) and carrier density (n_e) increase, whereas too high n_e results in the loss of transparency due to plasma absorption. Thus, a key to practical TCOs is to achieve high Hall mobility in degenerately-doped regime ($n_e \sim 10^{20}$ cm^{-3}), which can increase electrical conductivity without sacrificing optical transparency. A main strategy to attain high μ_H is to design carrier conduction pathway consisting of spatially-extended s-orbital of cation, such as Sn^{4+}, In^{3+}, and Zn^{2+} for electron-transporting (n-type) TCO and Sn^{2+}, Pb^{2+}, and Bi^{3+} for hole-transporting (p-type) TCO. Sn-based TCOs are a unique class of materials exhibiting both high electron mobility and high hole mobility, depending on the valence of Sn.

In my Ph. D study, I aimed to develop Sn-based TCOs with high-μ_H. I first investigated the electron transport properties of doped SnO_2. Although doped SnO_2 is practically important TCO, the highest μ_H value reported for SnO_2 films is significantly lower than those in bulk single crystals. Therefore, it is highly desirable to determine the upper limit of experimentally accessible μ_H in SnO_2 films and to develop guiding principles to achieve such high μ_H. From this point of view, I investigated electron transport properties of Ta-doped SnO_2 (TTO) epitaxial films, focusing on the growth orientation and n_e dependence of μ_H. As a result, I found that (001)-oriented growth is essentially favorable for achieving high-μ_H because of the suppressed propagation of {101} CSPs. The (001)-oriented TTO films exhibited maximum μ_H of 130 $cm^2V^{-1}s^{-1}$ at $n_e \sim 1\times10^{20}$ cm^{-3}, which almost

reached the intrinsic limit of μ_H determined by phonon and ionized impurity scatterings. Subsequently, the transport properties for (001)-oriented W-doped SnO_2 epitaxial films were investigated. Although the WTO films have been known to be a high-μ_H TCO, the detailed carrier generation mechanism remains to be known. As a result, the n_e values for the WTO films lay on the ideal n_e assuming $1e^-/W^{5+}$, indicating that each W^{5+} ion generated one carrier electron. Moreover, the μ_H values for the obtained WTO films (~ 136 $cm^2V^{-1}s^{-1}$) were as high as that of the TTO films, agreeing well with the intrinsic limit of μ_H on the assumption of W^{5+}. These results suggested that W^{5+} ions in SnO_2 act as singly charged donors without impairing high-μ_H of SnO_2.

Then I explored another dopant for SnO_2, P, which has recently been suggested as a promising dopant for SnO_2 by the first principles calculation [1]. As a result, the doping efficiency approached to 100% as the phosphorus amount decreased. This behavior is consistent with the prediction by theoretical calculation. The epitaxial P-doped SnO_2 (PTO) films on TiO_2 exhibited relatively high μ_H (40 $cm^2V^{-1}s^{-1}$). Use of a seed-layer might be effective to improve the mobility of PTO films on glass towards practical applications of PTO.

Next, I tried to fabricate SnO_2 films in a practical manner toward an application to solar cells. I proposed the fabrication of textured transparent conductive SnO_2 films by processing substrates with a bottom-up technique. I used self-assembled nanospheres of SnO_2 as nanostructured templates. This template approach is potentially more productive and scalable than alternative methods because the template can be fabricated in the same sputtering chamber used to deposit TCO layers.

I also attempted to fabricate novel p-type Sn-based TCOs based on $Sn_5O_2(PO_4)_2$. A recent theoretical calculation predicted that $Sn_5O_2(PO_4)_2$ can be a host material for p-type TCO with high μ_H [2]. I successfully fabricated phase-pure $Sn_5O_2(PO_4)_2$ thin films with 001-orientation by using Y_2O_3 buffered glass. The obtained $Sn_5O_2(PO_4)_2$ film showed a high transparency in the visible and near-infrared spectral regions with a large bandgap of 3.87 eV. In addition, the film was an intrinsic semiconductor without intentional doping, which is suitable for studying the fundamental physics of the material.

In conclusion, I investigated the optoelectronic properties of Sn-based TCO thin films with n-type and possible p-type conductivity toward high-μ_H. In the study of impurity-doped SnO_2 films, the results revealed that (001)-orientation is essentially favorable to high- μ_H due to the suppression of {101} CSPs propagation. Then I explored other promising dopants for SnO_2, W and P. The WTO epitaxial films showed high-μ_H comparable to that of TTO films approaching the intrinsic limit. The PTO films showed high doping efficiency with high-μ_H, indicating the P ions behave as good dopant in SnO_2. In addition, from the viewpoint of the application of SnO_2, I proposed the fabrication of textured transparent conductive SnO_2 films by processing substrates with a bottom-up technique. In the study of $Sn_5O_2(PO_4)_2$, which is predicted to be a p-type TCO with high μ_H, 001-oriented thin films were successfully fabricated on glass substrates buffered by (111)-textured Y_2O_3. The obtained

$Sn_5O_2(PO_4)_2$ film showed high transparency in the visible light region and a wide bandgap of 3.87 eV which agreed well with theoretical calculation. The $Sn_5O_2(PO_4)_2$ film showed highly insulating behavior, and intentional doping was needed for future investigation of fundamental electrical properties of $Sn_5O_2(PO_4)_2$. These results opened up a novel avenue of search for high-μ_H Sn-based TCOs.

References

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