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Author(s)	魏, 冕
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博士の専攻分野の名称 博士（工学） 氏名 魏 冕

学 位 論 文 題 名

Study on the Optoelectronic Properties of Transparent Oxide Semiconductor ASnO_3 ($A = \text{Ba}, \text{Sr}, \text{and Ca}$) Epitaxial Thin Films

(透明酸化物半導体 ASnO_3 ($A = \text{Ba}, \text{Sr}, \text{Ca}$) エピタキシャル薄膜の光・電子特性に関する研究)

Transparent thin film transistors (TFTs) are considered to be the fundamental of new optoelectronic devices. As the key parameter of transparent TFT, the transparent oxide semiconductor (TOS) with unique properties of optical transparency in the visible range and controllable electrical conductivity has been widely used in various optoelectronic devices. There are several well-known TOSs such as In_2O_3 : Sn (ITO, bandgap E_g 3.50~3.65 eV, $\sim 10000 \text{ S cm}^{-1}$) [1, 2], α -IGZO ($E_g \sim 3 \text{ eV}$, $\sim 400 \text{ S cm}^{-1}$) [3], SnO_2 ($E_g \sim 3.6 \text{ eV}$) [4], Al-doped and Ga-doped ZnO thin films shows conductivity $\sim 5000 \text{ S cm}^{-1}$. However, ITO and IGZO require an element with low abundance, the sensitivity to temperature and humidity limits practical application of SnO_2 , and controlling the Zn is more difficult than others due to its more active than Sn and In under oxygen atmosphere. Furthermore, deep-ultraviolet (DUV, 200-300 nm in wavelength) TOSs with high carrier mobility are promising candidates as the active layer of TFTs for next generation optoelectronics such as biosensors and bio transistors. Well-known DUV-TOSs such as β - Ga_2O_3 ($E_g \sim 4.9 \text{ eV}$, $\sim 1 \text{ S cm}^{-1}$) [5-6], electron-doped calcium aluminate (C12A7:e-, $\sim 4 \text{ eV}$, $\sim 800 \text{ S cm}^{-1}$) [7-9], and Mg-substituted ZnO ($E_g \sim 4.4 \text{ eV}$, $\sim 1000 \text{ S cm}^{-1}$) [10] show relatively low electron mobility, and the TFTs based on these materials exhibit poor performances. In order to meet the growing requirement of high-speed DUV-TFTs, we need to balance two opposite physical characteristics: bandgap and electrical conductivity.

Recently, La-doped ASnO_3 ($A = \text{Ba}, \text{Sr}, \text{and Ca}$) have attracted rising attention as the active channel of transparent TFTs, owing to their wide bandgap and high electrical properties. La-doped BaSnO_3 (LBSO, $E_g \sim 3.1 \text{ eV}$) single crystals with cubic perovskite structure ($a = 4.115 \text{ \AA}$) exhibited an extraordinary high mobility of $320 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. [11, 12] When a smaller Sr atom is substituted in the A-site, La-doped SrSnO_3 (LSSO) shows a wider bandgap, allowing SrSnO_3 -based TFTs to transmit DUV light, which exhibit great potential in DNA-sensing in biology.[13] Following this trend, if Ca, an even smaller alkaline element, occupies the A-site, further widening of the E_g value can be expected. However, the observed mobility of LBSO epitaxial films has been low compared to that of single crystals, [14-17] and the origin of the limited electron mobility in LBSO thin films have not been clearly explained. Besides, due to difficulties in growing high-quality LSSO films, their electron transport properties have not been extensively studied compared to the optical properties and electronic structures. Additionally, the reported theoretical and experimental bandgap values of CaSnO_3 scattered from 1.95 to 5.38 eV. [18-20] Briefly speaking, although this ASnO_3 system can be considered as an excellent solution for finding a good balance of optoelectronic properties, the perfor-

mance of ASnO_3 need to be further optimized, and the effect of *A*-site substitution on the optoelectronic properties of ASnO_3 has not been clarified in detail due to the lack of a systematic study.

The aims of this research are development of high-performance TOSs and DUV-TOSs, ASnO_3 . In order to achieve this target, three objectives were given as follows: firstly, heteroepitaxial growth of LBSO and clarify the origin of mobility suppress in the thin films; then, fabrication of high-quality LSSO films with good performance; lastly, clarify the optoelectronic properties of ASnO_3 ($A = \text{Ba}, \text{Sr}, \text{and Ca}$). This thesis is mainly composed of the following sections:

In chapter 1, the background and purpose of the above research are clarified.

In chapter 2, I report that the carrier mobility of 2 % LBSO films on (001) SrTiO_3 and (001) MgO substrates strongly depends on the thickness whereas it is unrelated to the film/substrate lattice mismatch (+5.4 % for SrTiO_3 , -2.3 % for MgO). The mobility dependences on the film thickness in both cases were almost the same, saturating at $\sim 100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ while the charge carrier densities approached the nominal carrier concentration ($= [2 \% \text{ La}^{3+}]$).

In chapter 3, I show that the electron mobility of LBSO films can be improved without inserting any buffer layers if the films are grown under highly oxidative ozone (O_3) atmospheres. The resultant O_3 -LBSO films showed improved mobility values up to $115 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is among the highest in LBSO films on SrTiO_3 substrates and comparable to LBSO films with buffer layers.

In chapter 4, I report that high electrically conducting (exceeding 3000 S cm^{-1}) LSSO thin films with an energy bandgap of $\sim 4.6 \text{ eV}$ can be fabricated by pulsed laser deposition (PLD) on MgO substrate followed by simple annealing in vacuum. We found that lateral grain growth occurred during the annealing, which improved the activation rate of La ion, leading to a significant improvement of carrier concentration ($3.26 \times 10^{20} \text{ cm}^{-3}$) and Hall mobility ($55.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).

In chapter 5, I show that the optoelectronic properties of ASnO_3 can be tuned systematically by changing the average size of *A*-site ions. We fabricated ASnO_3 films heteroepitaxially on (001) LaAlO_3 substrate and measured the optical absorption spectra and the electron transport properties of the resultant films. The lattice parameter almost linearly increased from 3.95 to 4.14 Å with increasing the average ionic radii of the *A*-site ion from 1.34 (Ca^{2+}) to 1.61 Å (Ba^{2+}). The optical bandgap gradually decreased from ~ 4.6 to $\sim 3.6 \text{ eV}$ with small positive bowing. The electrical conductivity gradually increased from $\sim 10^0$ to $\sim 10^3 \text{ S cm}^{-1}$ due to gradual increase of both carrier concentration and mobility with increasing the lattice parameter.

In chapter 6, the present study is summarized.

In short, the present results in my study are of significant importance for designing ASnO_3 -based

transparent electronic devices.

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