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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

In this thesis, fundamental technologies for thermoelectric generator composed of transition metal dichalcogenide (TMDC) films are investigated. Thermoelectric generators can directly convert heat energy into electricity by the Seebeck effect, in which a thermo-electromotive voltage proportional to temperature difference across a thermoelectric material is induced, and have been attracting attention as a potential energy harvesting technology. To evaluate conversion efficiency of thermoelectric materials, a dimensionless figure of merit ZT is given by $ZT = (S^2\sigma/\kappa)T = (\mathrm{PF}/\kappa)T$, where S, σ, κ and T is the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. In addition, the power factor PF (= $S^2\sigma$) is also used which is related to the maximum power of the device. To enhance ZT and PF values, high S, high σ and low κ are required. However, there is a trade-off between these parameters with respect to carrier density, where σ and κ increase and S decreases with an increase in a carrier density. Meanwhile, TMDC films have been investigated as thermoelectric materials with high mobility at atomically thin thickness and relatively low κ value. In order to apply TMDC films to thermoelectric generators in industrial applications, chemical vapor deposition (CVD) and atomic layer deposition (ALD) methods have been investigated. Although wafer-scale TMDC films have been produced using these methods, contaminations such as precursor residues remain a concern. Furthermore, a transfer process to another substrate is occasionally required for device fabrication. Therefore, ultra-high vacuum (UHV) radio frequency (RF) magnetron sputtering as a physical vapor deposition (PVD) method has been selected, which has the advantage of suppressing the contamination and thickness controllability. To simultaneously increase the conversion efficiency of p- and n-type materials in the generator and take the advantage of the compatibility of film formation including compensation methods of sulfur (S) atoms in the films, tungsten disulfide (WS_2) and molybdenum disulfide (MoS_2) films are selected. For fabrication of the efficient TMDC-based thermoelectric generator, they are required for the above films that 1. TMDC film with a moderately large grain size for enhancement of carrier mobility and low thermal conductivity, 2. establishment of an accurate and stable evaluation method for thermoelectric properties of PVD-grown 2D TMDC films, and 3. control of carrier density in TMDC films for modulation of thermoelectric characteristics. Therefore, the author approached the above requirement in advance of

fabrication of the TMDC-based thermoelectric generator.

A WS_2 atomic-layer film is synthesized by UHV RF magnetron sputtering as a function of sputtering power. A layered structure parallel to a SiO_2/Si substrate is confirmed from the transmission electron microscopy and X-ray diffraction spectra. The grain size increases with a decrease in the sputtering power. Accordingly, the resistivity and activation energy also increase. However, the PVD-WS_2 film has low S/W ratio up to 1.5 due to a lot of S vacancies, which cause a mobility degradation and an unexpected high carrier density in the film. Therefore, sulfur compensation of PVD-WS_2 film using sulfur vapor annealing (SVA) is performed. The S/W composition ratio in the PVD-WS_2 film increased from 1.60 to 1.94 because of the SVA. Moreover, the Raman peak intensities are significantly enhanced because of successful compensation of S vacancies in the film. In order to measure a mobility, a WS_2 *p*MISFET array is successfully demonstrated by TiN/HfO_2 top-gate stack, TiN contact and UTBB technologies. The maximum field effect mobility of 1.5×10^{-2} $cm^2V^{-1}s^{-1}$ and the log-normal distribution for 50 devices are obtained.

Next, thermoelectric characteristics in PVD-TMDC films are investigated using an on-chip thermoelectric device. Although the PVD-WS_2 film without SVA has a low PF value due to their low σ value, a high S value of 1.17×10^3 μV/K is achieved, which is more than twice as large as those of TMDC films in other papers. Here, the low σ values are attributed to both low carrier density and low mobility in the film. Therefore, the thermoelectric performance is expected to be further enhanced with the appropriate doping level of the TMDC films and enlargement of the grain size.

Finally, a doping method to the TMDC film using a combination of chlorine (Cl_2) plasma and SVA is investigated using PVD-MoS_2 film to optimize the conversion efficiency in the thermoelectric materials. It is achieved that a sheet resistance in the film with Cl_2 plasma treatment is approximately ten times smaller than that without the treatment. From the depth profiles in the time-of-flight secondary ion mass spectroscopy (TOF-SIMS), a Cl ion peak is clearly observed in the MoS_2 film located near the surface. In addition, the Fermi level shift to the conduction band minimum is confirmed from the results in XPS spectra. Therefore, the PVD-MoS_2 film is successfully doped in *n*-type with Cl dopants.