学　位　論　文　内　容　の　要　旨

博士の専攻分野の名称　　博士（情報科学）　　氏名　張　雨橋

学　位　論　文　題　名

Study on the Thermoelectric Properties of $SrTiO_3$ – $SrNbO_3$ Solid Solutions using the Epitaxial Thin Films and the Artificial Superlattices

（エピタキシャル薄膜と人工超格子を用いた $SrTiO_3$ – $SrNbO_3$ 固溶体の熱電特性に関する研究）

Nowadays, approximately 60 % of energy resources are discharged as waste heat into the environment without applications. Hence thermoelectric energy conversion technology attracts great attention to convert the waste heat into electricity.[1, 2] The principle of thermoelectric energy conversion was first discovered by T.J. Seebeck in 1821 that a voltage is generated between two ends of a metal bar by introducing a temperature difference. Thus, when electric loads are connected at both ends of the metal bar, electric current can be obtained.[3] This phenomenon is so called Seebeck effect.

Generally, the performance of thermoelectric materials is evaluated in terms of a dimensionless figure of merit, $ZT = S^2 \cdot \sigma \cdot T \cdot \kappa^{-1}$, where Z, T, S, σ and κ are a figure of merit, absolute temperature, thermopower (= Seebeck coefficient), electrical conductivity and thermal conductivity, respectively. The ZT values of practical thermoelectric materials such as Bi_2Te_3 and PbTe are about 1, which is so called lowest requirement for practical applications.[4, 5] Even though a number of heavy metal based thermoelectrical materials with high ZT have been developed, these materials are not so attractive due to the low stability at high temperature and high toxicity.

Based on this background, metal oxide thermoelectric materials recently are attracting increasing attentions. And materials with promising performance have been reported one after another, such as $CaMnO_3$ [6], Al-doped ZnO [7], Na_xCoO_2 [8] and electron doped $SrTiO_3$ [9-11]. Especially, crystalline electron doped $SrTiO_3$ shows comparable power factor (PF = $S^2 \cdot \sigma$) to the commercial Bi_2Te_3. However, similar with other metal oxides, due to the high κ the ZT value of crystalline electron doped $SrTiO_3$ is only 0.2~0.35 at 1000 K, which is still far from the applicable level ($ZT \geq 1$). In 1993, Hicks and Dresselhaus theoretically predicted that two-dimensional thermoelectric figure of merit, $Z_{2D}T$ of quantum well for thermoelectric semiconductors can dramatically be enhanced by using superlattices because only S value increases with the density of states (DOS) of the quantum well and enhancement effect is inversely proportional to quantum well thickness / de Broglie wavelength (λ_D) ratio in a 2D quantum well system.[12, 13] And using this effect, Ohta *et al.* realized significant enhancement of ZT to 2.4 at 300 K in quantum wells of $SrTi_{0.8}Nb_{0.2}O_3|SrTiO_3$ superlattices. However, if thick insulating $SrTiO_3$ barrier layers are also considered into calculation, the ZT is only 0.24. After that although many researches were focused on Nb doped $SrTiO_3$ system, none of them could get desirable improvements, mainly ascribed to the lack of high quality $Sr(Ti, Nb)O_3$ single crystals due to the low solubility of Nb into $SrTiO_3$ lattice. Rare report could reach to Nb doping over 30%.[14]

To fully understand thermoelectric transport properties in $SrTiO_3 - SrNbO_3$ solid solutions system, in this study we fabricated high quality $SrTi_{1-x}Nb_xO_3$ ($0 \leq x \leq 1$) epitaxial films and artificial superlattices by pulsed laser deposition (PLD). And my research is mainly composed of two sections:

1. Thermoelectric phase diagram of $SrTiO_3 - SrNbO_3$ full range solid solutions.[15]

In this study $SrTi_{1-x}Nb_xO_3$ ($0.05 \leq x \leq 1$) solid solution thin films were epitaxially grown on (001) $LaAlO_3$ substrates. And a thermoelectric phase diagram for $SrTi_{1-x}Nb_xO_3$ ($0 \leq x \leq 1$) solid solution system was presented. We observed two thermoelectric phase boundary in the system, which originate from the step-like decrease in carrier effective mass at $x \sim 0.3$ and from a local minimum in carrier relaxation time at $x \sim 0.5$. These phase boundaries are considered to be related to isovalent/heterovalent B-site substitution: parabolic Ti 3d orbitals dominate electron conduction for compositions with $x < 0.3$, whereas the Nb 4d orbital dominates when $x > 0.3$. At $x \sim 0.5$, a tetragonal distortion of the lattice, in which the B-site is composed of Ti 3d and Nb 4d ions, leads to the formation of tail-like impurity bands, which maximizes the electron scattering. These results provide a foundation for further research into improving the thermoelectric performance of $SrTi_{1-x}Nb_xO_3$.

2. Double thermoelectric power factor of a 2D electron system (2DES).[16]

Based on Section 1, we found two different λ_D in $SrTiO_3 - SrNbO_3$ full range solid solution system, which are due to the conduction band transition at $x = 0.3$: ($x > 0.3$: λ_D~5.3 nm; $x < 0.3$: λ_D~4.1 nm).Therefore $SrTi_{1-x}Nb_xO_3$ is an ideal system to clarify the effectiveness of an enhanced two-dimensionality to enhance thermoelectric PF in superlattice structures. By fabricating superlattices of [N unit cell $SrTi_{1-x}Nb_xO_3$|11 unit cell $SrTiO_3$]$_{10}$ ($0.1 \leq x \leq 0.9$), we successfully enhanced the effective PF to ~5 mW m^{-1} K^{-2}, which doubles the value of optimized bulk $SrTi_{1-x}Nb_xO_3$. The present 2DES approach—use of longer λ_D—is epoch-making and is fruitful to design good thermoelectric materials showing high PF.

My study will provide not only accordance for the further developments in $SrTiO_3$ based thermoelectric materials, but also direct experimental evidence for the effectiveness of 2D quantum wells in enhancing thermoelectric performance.

Reference

[1] D. M. Rowe, *CRC Handbook of Thermoelectrics*, CRC Press, 1995.
[2] H. J. Goldsmid, *Introduction to Thermoelectricity*, Springer, 2010.
[3] T. J. Seebeck, *Abh. K. Akad. Wiss.* 1823, 265.
[4] T. M. Tritt *et al.*, *MRS Bull.* 2006, 31, 188-194.
[5] G. J. Snyder *et al.*, *Nature Mater.* 2008, 7, 105-114.

[6] M. Ohtaki *et al*., *J. Solid State Chem*. 1995, 120, 105-111.
[7] M. Ohtaki *et al*., *J. Appl. Phys*. 1996, 79, 1816-1818.
[8] I. Terasaki *et al*., *Phys. Rev. B* 1997, 56, 12685-12687.
[9] T. Okuda *et al*., *Phys. Rev. B* 2001, 63, 113104.
[10] S. Ohta *et al*., *J. Appl. Phys*. 2005, 97, 034106.
[11] S. Ohta *et al*., *Appl. Phys. Lett*. 2005, 87, 092108.
[12] L. D. Hicks *et al*., *Phys. Rev. B* 1993, 47, 12727-12731.
[13] N. T. Hung *et al*., *Phys. Rev. Lett*. 2016, 117, 036602.
[14] C. Rodenbucher *et al*., *Sci. Rep*. 2016, 6, 32250.
[15] Y. Zhang *et al*., *J. Appl. Phys*. 2017, 121, 185102.
[16] Y. Zhang *et al*., *Nature Commun*. 2018, 9, 2224.