学　位　論　文　内　容　の　要　旨

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学　位　論　文　題　名

Study on the Heat and Electron Transport Properties of Tungsten Oxide Films with Various Atomic Arrangements
（様々な原子配列を有する酸化タングステン薄膜の熱・電子輸送特性に関する研究）

Nowadays, waste heat has attracted attention as a renewable energy resource. Waste heat is heat that is dumped outward in the process of harnessing energy, less than 50 % of energy is used, more than 50 % of the remaining energy is dumped as waste heat. In the prior technology, the heat sink and Peltier device are used because the heat generated in the nanometer-scale ultra-small area with the ultra-miniaturization and ultra-high integration of electronic devices causes the malfunction and failure of the device. Thus, the heat is thrown away without use. On the other hand, if such heat can be effectively reused as energy by using, for example, a thermoelectric conversion technique, it is possible to reduce energy loss. Because the thermoelectric energy conversion technology covert the waste heat into usable electricity. [1,2] Despite this advantage, thermoelectric devices have not yet been actively commercialized. The reason is that the technology related to thermoelectric devices has not yet been sufficiently developed.

In order to develop thermoelectric devices, it is important that understanding the heat and electron transport properties in media. Because, the performance of thermoelectric material is evaluated by $ZT = S^2 \cdot \sigma \cdot T \cdot \kappa^{-1}$, where Z, T, S, σ, and κ are figure of merit, absolute temperature, thermopower (= Seebeck coefficient), electrical conductivity and thermal conductivity, respectively. To improve the performance of thermoelectric devices, the material should have large σ, S and low κ. Generally, Electron and heat transports in media are associated with σ, and κ, respectively. σ is a product of the carrier (electron) concentration and mobility. In the case of a crystalline material, quantized lattice vibration (phonon) carries heat. In general, electron propagation is suppressed by phonons, impurities, atomic vacancies, and boundaries, and phonon propagation is suppressed by impurities, atomic vacancies, and boundaries. Because both σ and κ are increased/suppressed simultaneously by reducing/introducing impurities, atomic vacancies, and boundaries, it is considerably difficult to solely control the σ or κ. Therefore, there is a strong necessity for discovering the versatile thermoelectric material showing unusual electron and heat conduction such as the coexistence of high electron conduction and low heat conduction are required to realize efficient thermal management systems.

Based on this background, I selected tungsten oxide (WO_x) as a material system. WO_x is attracting attention as an active material for many other useful applications such as material for an electrochromic device [3], electrode of Li-ion batteries [4], gas sensors [5]. Nevertheless, research on the fundamental physical properties of WO_x, especially epitaxial film, is still lacking. There are three reasons for the selection of WO_x as the research topic material. First, it is easy to create oxygen vacancies. In other words, it is easy to generate carrier electrons, so that electrical conductivity can increase. Second, WO_x has various crystalline phases. Reduction of monoclinic WO_3, leads to the formation of a unique structure called the Magnéli phase (x = 2.9, 2.82, and 2.72). There is also metastable hexagonal WO_3, which has a quite unique crystal structure with empty hexagonal and trigonal tunnels. Lastly, because of widespread tungsten 5d orbitals, it can be kept high σ even when the bond angle has fluctuated. This is the reason why oxygen deficient amorphous WO_x has quite high σ. Therefore, WO_x is an ideal material to clarify the relationship between atomic arrangement and heat and electron transport properties through controlling oxygen vacancies.

The aim of this thesis is that understanding of heat and electron transport properties of WO_x films with various atomic arrangements. There are three interesting topics on amorphous WO_x, 1D defect tunnel stabilized WO_x epitaxial film, and hexagonal WO_x epitaxial film are discussed. In order to achieve our research goal, amorphous WO_x and WO_x epitaxial film are fabricated by using pulsed laser deposition technique and the x of both amorphous and epitaxial WO_x films is systematically changed. Then, I observed atomic arrangements and clarify their electron and heat transport properties. This thesis is mainly composed following sections:

In chapter 1, the background and objective of this research are introduced.

In chapter 2, experimental methodes are introduced.

In chapter 3, I report that the low thermal conductivity of amorphous WO_x films. The electrical, optical, and thermal properties of amorphous WO_x films are systematically clarified. [6] I fabricated amorphous WO_x films with several valence states of +6 (d^0), +5 (d^1), and +4 (d^2) for x ranging from 2.511 to 2.982. Both optical transmissivity and electrical resistivity decreased drastically with an increase in the +5 concentrations, which also slightly enhances the thermal conductivity because heat can be carried by additional conduction electrons. As the +4 state became dominant in the film, the resistivity slightly increased, whereas the low visible transmission was maintained.

In chapter 4, I report the coexistence of low thermal conductivity and high electrical conductivity in WO_x films. [7] WO_x epitaxial films were fabricated on $LaAlO_3$ substrates under a precisely controlled oxygen atmosphere. Crystallographic analyses revealed that one-dimensional (1D) atomic defect tunnels are formed randomly along the rectangular-shaped grains in the in-plane direction. The cross-plane thermal conductivity of the WO_x films dramatically decreased with decreasing x, while the electrical conductivity drastically increased because of an increase of carrier electrons, and high electron conduction and low heat conduction coexist when $x \langle 2.9$.

In chapter 5, I report the anisotropy of electrical conductivity in WO_x films with 1D atomic defect tunnel structure. [8] The crystallographic analyses of the WO_x films revealed that highly dense atomic defect tunnels were aligned one-dimensionally along [001] $LaAlO_3$. The electrical conductivity along the 1D atomic defect tunnels was ~5 times larger than that across the tunnels.

In chapter 6, I report the reversible redox reaction of hexagonal WO_x and heat and electron transport properties are investigated. Hexagonal WO_x epitaxial films were fabricated on (111) YSZ substrate. Crystallographic analyses revealed that hexagonal tunnel aligned along out-of-plane direction. By applying gate voltage on YSZ substrate, hexagonal WO_x was electrochemically oxidized/reduced. Also, by changing hexagonal tunnel direction, anisotropic thermal conductivity was measured.

In chapter 7, the present study is summarized.

My thesis will provide the heat and electron transport properties of tungsten oxide films with various atomic arrangements for developments of WO_x based future applications.

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