Change in thermal conductivity of natural superlattice oxides accommodating with oxygen deficiency

S. Harada[1,2], Y. Yuge[2], A. Nakamura[2], M. Tagawa[1,2], T. Ujihara[1,2,3]

[1]Center for Integrated Research of Future Electronics (CIRFE), Institute of Materials and Systems for Sustainability (IMaSS), Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan
[2]Department of Materials Science and Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan
[3]GaN Advanced Device Open Innovation Laboratory, National Institute of Advanced Industrial Science and Technology, Furo-cho, Chikusa-ku, Nagoya, Japan

Active control of heat conduction has attracted great attention due to the thermal management. Recently, the modulation of heat conduction by the metal-insulator transition of VO_2 was reported [1]. The thermal conductivity of thin film VO_2 increases by as much as 60% in the metallic phase across the metal-insulator transition around 340 K [1]. For the modulation of thermal conductivity, we focus on the change in the crystal structure of natural superlattice oxides accommodating with oxygen deficiency. Recently, we revealed that the thermal conductivity of the homologous series of natural superlattice titanium oxides (T_nO_{2n-1}) with crystallographic shear (CS) structure containing dense periodic planar faults decreases with increasing density of the planar faults [2]. So far, we have successively control the interval of planar faults in natural superlattice titanium oxides ranging from 0.7 nm to 3.3 nm. In the present study, in order to largely change the thermal conductivity, we focus on tungsten oxides. Tungsten oxides exhibit many types of crystal structure according to the oxygen deficiency from WO_3: WO_3 with deformed-ReO_3 type, the homologous series of W_nO_{3n-2} and W_nO_{3n-1} with CS structure, pentagonal column (PC) structure of $W_{18}O_{49}$ and $W_{24}O_{68}$, and WO_2 with deformed-rutile type [3]. Furthermore, the electrical conductivity of tungsten oxides was reported to largely change from metallic to semiconducting. In the present study, we investigated the change in the thermal conductivity of natural superlattice tungsten oxides with the different oxygen deficiency. We demonstrated that the reversible control of thermal conductivity by oxidation and reduction reaction by successive annealing.

The values of thermal conductivity for tungsten oxides (WO_{3-x}) change depending on the oxygen deficiency x. In the composition range from $WO_{3.00}$ to $WO_{2.00}$, thermal conductivity of polycrystalline specimens prepared by spark plasma sintering exhibits 425% change from $WO_{2.95}$ (2.79 W/mK) with CS structure to $WO_{2.00}$ (17.5 W/mK) with deformed rutile structure of WO_2 at a maximum. Change in the thermal conductivity of tungsten oxides accommodating with the oxygen deficiency results from the combination of both electrical and lattice contribution to thermal conductivity. The electrical contribution to the thermal conductivity increases with increasing oxygen deficiency x up to 0.28. The lattice contribution to the thermal conductivity of tungsten oxides including the natural superlattice of CS and PC structures having complicated crystal structures with large unit cell size, is lower than that of WO_3 and WO_2 having relatively simple crystal structure with small unit cell size.

Furthermore, we controlled the oxygen deficiency by annealing in reduction and oxidization atmospheres. Finally, we have demonstrated 280% reversible change in thermal conductivity of a tungsten oxides pellet by repeatedly changing in the phases from WO_3 to PC structure of $W_{18}O_{49}$.

References

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