THERMAL CONDUCTION IN TITANIUM OXIDE NATURAL SUPERLATTICE WITH AN ORDERED ARRANGEMENT OF PLANAR FAULTS WITH PICO-SCALE STRUCTURAL PERFECTION

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1. INTRODUCTION

Coherent control of phonons by nanoscale periodic structures is of great interest for the advanced thermal management which differs from the diffusive picture that follows Fourier’s law¹. Coherent thermal conduction in nanostructures has investigated by phononic crystals²,³, artificial superlattice thin films⁴,⁵ or other nanostructured materials⁶. Although phononic crystals successfully demonstrated the control of low frequency phonons as well as heat conduction at liquid helium temperature, it is necessary for the heat control especially above room temperature to achieve atomic scale periodic structure with pico-scale structural perfection. Artificial superlattices are the ideal system to investigate the coherent heat conduction. However, the imperfection of interfaces in artificial superlattice hinders the coherent heat conduction and the heat conduction through artificial superlattices was revealed to be mainly incoherent⁷. Although interfaces with high structural perfection were reported to be achieved in the artificial superlattices, the realization of coherent interfaces for thermal phonons is still challenging. In order to obtain nanostructure with coherent interfaces, we focused on the titanium oxides natural superlattice with crystallographic shear (CS) structures⁸. In our previous study, we have reported that the interfaces in the titanium oxide natural superlattices have pico-scale structural perfection, and the interfaces are expected to behave as coherent for almost all phonons in rutile TiO₂⁹,¹⁰. In the present study, we investigated the thermal conduction in the titanium oxide natural superlattices depending on the period of the coherent interfaces.

2. EXPERIMENTAL

Three crystals were used for the measurement of thermal conductivity. One was a rutile TiO₂ single crystal grown by the Verneuil method. Another was a reduced rutile crystal, which was prepared from a rutile TiO₂ single crystal by annealing at 1573 K for 24 h in vacuo (<1×10⁻⁴ Pa). The other was a titanium-chromium oxide grown by the optical floating zone (FZ) method with the nominal composition of Ti:Cr = 3:1. The atomic structure was examined by high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM). The thermal conductivity of the crystals was measured by a time-domain thermoreflectance (TDTR).

3. RESULTS AND DISCUSSION

Figure 1 shows HADDF-STEM images taken from the reduced rutile and titanium-chromium oxide natural superlattices. In the HAADF-STEM images, cation (Ti⁴⁺, Ti³⁺ and/or Cr³⁺) columns are imaged as bright spots, while anion (O²⁻) columns are not imaged individually. The arrangement of the cation columns deviates on the (132)rutile and (121)rutile CS planes for the reduced rutile and the titanium-chromium oxide, respectively. From the HAADF-STEM observations, the interplanar spacings of the CS planes can be evaluated as 2.7 and 0.9 nm.

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respectively. Furthermore, atomic structure of the interfaces (CS planes) seems not to be disturbed and it is expected that the interfaces behave as coherent interfaces. Figure 2 shows the thermal conductivity depending on the interface density. The thermal conductivity has clear minimum especially at low temperatures (below room temperatures) indicating a crossover from incoherent to coherent thermal conduction. In the high temperature range (above room temperatures), the interface density dependence of thermal conductivity is very small, which indicates the phonon mean free path is smaller than the interval of the interfaces. Actually, the value of the phonon mean free path in rutile TiO₂ estimated from phonon gas model at room temperature (2.1 nm), which is a transition temperature for these dependency of interface density, is almost corresponding to the interface density for thermal conductivity minimum.

4. CONCLUSIONS
We have prepared titanium oxides natural superlattice crystals with the different interspacing of CS plane having smooth interfaces and investigated their thermal conduction. The thermal conductivity has clear minimum especially at low temperatures, indicating coherent thermal conduction become apparent. Considering the tunability of the periodicity and the structural perfection, titanium oxide natural superlattices are an ideal system for the investigation of the details of coherent thermal conduction in nanoscale periodic structures.

REFERENCES