I. Introduction

Several nitride insulators showing good thermal conductivities are important for heat sink materials used at elevated temperatures. Wurtzite-type w-AlN, which has an Adamantine (diamond-like) crystal structure, was noted by Slack et al.~\cite{slack} as exhibiting a large thermal conductivity of over 100 WK-1m-1. Si3N4 has been more recently recognized as one of the good thermally conductive insulators. Remarkable advances in technologies related to the densification of the ceramic body and microstructural control have pushed the thermal conductivities of Si3N4 ceramics up to 177 WK-1m-1.~\cite{zhou,hirao,watari,hirosaki} Since Si3N4 ceramics also exhibit high mechanical strength at elevated temperatures, they are regarded as ideal for use in various applications, such as engine components, gas turbines, and heat sink substrates of power semiconductor devices.

At atmospheric pressure, Si3N4 exists in one of two phases, α and β, both in the hexagonal lattice system, which are generally considered to be low- and high-temperature phases, respectively.~\cite{zhou,hirosaki,riley} Their crystal structures are commonly formed by stacking of basal layers of SiN4 tetrahedra. The stacking manners in α and β-Si3N4 are as ABCDABCD.. and ABAB.., respectively. In Fig. 1, this difference is depicted from the principal axis direction. The CD layers are related to AB by the c glide operation.~\cite{hampshire}} The unit cell periodicity of the α phase is approximately two times longer than that of the β phase, with lattice constants of c = 5.62~\cite{yashima} and 2.91~\cite{boulay} Å, respectively. In addition to the α and β phases, the cubic spinel γ-Si3N4 can be obtained upon compression and in-situ heating.~\cite{zerr,zhang} The reported transition pressures were scattered from 10 to 36 GPa depending on the experimental conditions. The produced γ phase can be experimentally quenched to atmospheric pressure and room temperature.

By using high-resolution thermoreflectance microscopy, Li {\it et al.}~\cite{li} reported the thermal conductivities of individual rod-shaped β-Si3N4 grains in a ceramic to be 69 and 180 WK-1m-1 along the a and c axes, respectively, and thus revealed the large anisotropy in thermal conductivity. Takahashi et al. ~\cite{takahashi} recently developed a technique whereby β-Si3N4 grains are coated with graphene of relatively high magnetic susceptibility, enabling them to align their c axes along the external magnetic field. Based on this large anisotropy in thermal conductivity, it was proposed that the textural structure of rod-shaped β-Si3N4 grains would increase their thermal conductivity to a level matching or exceeding that of w-AlN.

Although the fabrication of millimeter-sized β-Si3N4 single crystals has been reported~\cite{yamamoto}, the thermal conductivity of no isolated single crystal of any Si3N4 phase has yet been experimentally determined. It was proposed~\cite{watari-trans} that the anisotropy in the thermal conductivity of β-Si3N4 phase grains may not stem from the intrinsic crystal properties, but rather, from the selective removal of crystal defects along the c axis of the grains. Theoretically, Hirosaki et al. ~\cite{hirosaki-md} estimated the room-temperature lattice thermal conductivities (LTCs) κ*xx* and κ*zz* of α-Si3N4 to be 105 and 225 WK-1m-1 , and κ*xx* and κ*zz* of β-Si3N4 to be 170 and 450 WK-1m-1, respectively, by applying the Green-Kubo formulation to the molecular dynamics method with the interatomic potentials proposed by Vashishta et al. The ratio of the LTCs in the β phase along the a and c axes agreed well with the experimental results obtained by Li et al.; however, the absolute values were more than two times larger than the experimental results. The MD results suggest that the difference in the stacking orders in α and β-Si3N4 affects much their LTC, although the recent calculation of the LTC in many polymorphs of the zincblende and wurtzite structures showed that their stacking orders does not.[Togo] The LTC of the γ phase has not been experimentally reported. It has been estimated only by the Slack model.~\cite{morelli}} While the thermal conductivity of polycrystalline β-Si3N4 has been significantly improved~\cite{zhou,hirao,watari,hirosaki}, our basic knowledge of, for example, the thermal conductivity tensors of the different crystal phases remains insufficient.

The present study aims to qualitatively understand the LTC tensors among the three Si3N4 phases by means of the first principles approach. After the methodology section, we examine the validity of the present LTC results first. Then the harmonic phonon states and phonon linewidths are examined to find what microscopic property determines the characteristics in the LTC.

II. Computational procedures

A. Lattice thermal conductivity calculation

The LTCs were calculated by solving the linearized Boltzmann transport equation (LBTE) within the single-mode RTA. We also tried the direct-solution of LBTE~\cite{chaput-direct} and shortly leave its calculated LTC values in the following section. However the difference of LTCs between by the single-mode RTA and by the direct solution was found minor for our discussion. Therefore we limited our research based on the single-mode RTA to take advantage of the intuitive closed form of LTCs with the single-mode RTA.

In the following sections, we denote a phonon mode by λ = (**q**, *p*) by the set of the phonon wave vector **q** and band index *p*. The relaxation time due to phonon-phonon scattering was obtained as reciprocal of linewidth, τλ,ph-ph = (2Γλ )-1, where the linewidth that we employed in this study is as follows:

Equation of linewidth (1).

Here ωλ is the harmonic phonon frequency of the phonon mode λ, *n*λ = [exp(*ħ*ωλ/kB*T*) - 1]-1 shows the Bose-Einstein distribution at temperature *T*, and Φ-λλ’λ’’ denotes the three-phonon-scattering strength. Φ-λλ’λ’’ was obtained by usual coordinate transformation of third-order force constants from direct space to phonon space.~\cite{phono3py} The second- and third-order real-space force constants were obtained from the *ab-initio* calculation, whose details are written in the next section.

In order to compare the more realistic results of the calculated LTC with the experimental data, the isotopic scattering effect due to the natural isotope distribution was taken into account according to the second-order perturbation theory.~\cite{tamura} With the relaxation times of the phonon-phonon scattering and isotropic scattering, τλ,ph-ph and τλ,iso, the total relaxation time for a phonon mode was assumed to be 1/τλ = 1/τλ,ph-ph + 1/τλ,iso, according to Matthiessen's rule.

These LTCs were calculated with the phonon-phonon interaction calculation code PHONO3PY~\cite{phono3py}, while the harmonic phonon states were analyzed with the phonon calculation code PHONOPY~\cite{phonopy}. These codes have been developed and maintained by the authors in this study.

The available experimental thermal conductivity data of the Si3N4 system have been measured on the polycrystalline samples and not measured from any single crystals. In order to consider the effect of various lattice defects in the polycrystalline samples, such as grain boundaries, impurities, and vacancies, we crudely took them into account by a relaxation time τλ,bs = *L*/|**v**λ| of a phonon boundary scattering model, where **v**λ = ∇**q**ωλ is the group velocity and *L* a parameter regarding to the boundary mean free path. We consider τλ,bs as a variable parameter and included it to LTCs according to Matthiessen's rule.

The closed form of the LTC tensors within RTA were obtained via

equation of LTC (2)

where *N***q** is the number of **q**-points, Ω is the unit cell volume, and cλ is the mode heat capacity. To analyze the LTC in detail, we calculate the cumulative thermal conductivity:

equation of cumulative thermal conductivity (3)

B. Computational details

The force constants were calculated using the first-principles projector augmented wave method~\cite{paw} (VASP code~\cite{vasp-1996,vasp-1995, vasp-1999}). The generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof~\cite{pbe} was used for the exchange correlation potential. A plane wave energy cutoff of 500 eV was employed. The crystal structures were optimized until the convergence in the residual forces acting on the constituent atoms were less than 10-6 eV/Å. The structural optimization was firstly performed for a temperature of 0 K and 0 GPa. Here the temperature and pressure were considered only for the electronic system and the zero point lattice vibration was not taken into account. The calculated lattice parameters were a=7.808 Å and c=5.659 Å for the α phase, a=7.660 Å and c=2.925 Å for the β phase, and a=7.787 Å the γ phase, which agree with the experimental data~\cite{yashima,boulay,paszkowicz-gSi3N4} within +0.7 % errors The lattice volume optimized at 0 K and 0 GPa within the local density approximation (LDA)~\cite{lda} for the exchange correlation potential was 143.8 Å3 for β-Si3N4, being 3 \% smaller than the volume with GGA, which is a typical volume contraction of LDA. In our test using β-Si3N4 at 0 K and 0 GPa, the LTC calculated with LDA was larger by 2.6 \% than that with GGA. For our discussion, this difference is enough small, therefore the impact of choice of exchange correlation potential is considered to be minor in our study.

Supercell and finite difference approaches were used to calculate the force constants.~\cite{wei-supercell} The 1×1×2, 1×1×3, and 1×1×1 supercells of the conventional unit cells were adopted for the third-order force constants of the α, β, and γ phases,respectively, while the larger supercells 3×3×4, 3×3×8 and 2×2×2 were adopted for the respective second-order force constants. The constant atomic displacement distance was set to 0.03 Å. Table \ref{table:LTC} shows the calculated LTC values for several different choices of supercell sizes, indicating that our calculated LTCs are reasonably converging with respect to the supercell sizes.

Uniform **k**-point sampling meshes of 4×4×2, 4×4×3, and 3×3×3 were used for the

third-order force constants of the α, β, and γ phases. For the former two phases the center of the a\*-b\* plane were sampled though the off-center grids along c\*-axis were sampled. For the γ phase, non-Γ center mesh was used. For the second-order force constants, the Γ-point was only sampled for the α and β phase supercells and the only one **k**=(0.5, 0.5, 0.5) point was sampled for the γ phase supercell. The **q**-point sampling meshes of 14×14×16, 14×14×32, and 22×22×22 direct solutionに合わせるwere used to calculate the LTCs in Eq.~(\ref{eq:kappa}) for the α, β, and γ phases. LTC convergence wrt num of q points.

To compare the calculated LTC with the experimental data measured at

finite temperatures, the experimentally measured lattice parameters may

be preferred in case that they are known. We examined LTC of

$\beta$-Si$\_3$N$\_4$ at the equilibrium volumes ($V\_\text{eq}(T)$) within the

quasi-harmonic approximation (QHA).~\cite{dove-p76} Except for this, the LTC values

were calculated with the equilibrium volume at 0 K ($V\_\text{eq}(T=0)$).

We calculated volumetric thermal expansion coefficients and compared

them with the reported experimental values so as to check the validity

of the present calculation, because the thermal expansion is originated

from the anharmonicity of the interatomic potential as well as lattice

thermal conduction. The calculated values are 4.31 and 4.19 ($10^{-6}$

K$^{-1}$) at 300 K for the $\alpha$ and $\beta$ phases, while the

experimental values were 3.75 and 3.55 ($10^{-6}$ K$^{-1}$)~\cite{minikayev-alpha}. The present

calculation reproduced the experimental tendency where the $\alpha$

phase has a slightly larger thermal expansion coefficient than the

$\beta$ phase, supporting that the present calculations enable us to

qualitatively compare the LTC values of the Si$\_3$N$\_4$ phases.

The microscopic phonon properties we have seen are located in specific paths or planes in the Brillouin zone. In order to more rigorously inspect the lattice thermal conductivities, we examine phonon properties taken over the Brillouin zone. As such properties, in Fig. x are shown phonon densities of states (DOS), cumulative thermal conductivities and their frequency derivatives, weighted DOS with the squares of the group velocity components (vλ,x and vλ,z), and finally, frequency distributions of Γλ．

Firstly, we relate DOS (Fig. x-a) with the cumulative thermal conductivity (Fig. x-b). In α- and γ-Si3N4, the phonons contributing to the lattice thermal conductivities are mainly located below the 1st peaks indicted by an arrow in Fig. x-a, indicating that the main heat carriers are the phonons on the acoustic branches. In contrast, more than a half of the contributions to the zz component of lattice thermal conductivity in β-Si3N4 are derived from the phonons above the 1st DOS peak, indicating that the low frequency optical phonons contribute to this component exceptionally largely.

Secondly, in Figs. x-b and c, the directional differences in the derivatives of the cumulative thermal conductivities in α and β phases are qualitatively well consistent with the directional differences in the weighted DOS. The relatively larger intensities in the weighted DOS with vλ,z in β-Si3N4 critically causes the large anisotropy in its lattice thermal conductivities.

Fig.x-d shows significantly similar Γλ distributions between the α and β phases, which let the group velocities alone play a decisive role on the different degrees of the anisotropy in the lattice thermal conductivities. Since it might be curious that Γλ are similar although group velocities have marked differences, we investigate this similarity further. Recently Togo et al. Showed that peaks in imaginary part of self energy, Γ(ω), which gives Γλ at ω= ωλ, are mainly brought about by the three phonon selection rules [Togo]. In Eq. (1) of Γλ, the three-phonon interaction strength Φ-λλ’λ’’ contains the selection rule for the momentum conservation[Togo], while the selection rule for the energy conservation is expressed by the δ function in Eq. (1). We separately examine the impacts of Φ-λλ’λ’’ on Γλ and those of the selection rules, although both of them are not isolated from each other. In Table. xx, Φ-λλ’λ’’ are compared as the averages over the ωλ frequency ranges between 0 and 15 THz and 0 and 35 THz. The values of the α and β phases are very close to each other, indicating that the Φ-λλ’λ’’ have similar impacts on Γλ of the α and β phases .

In order to analyze the impacts of the selection rules on Γλ, we employ the joint density of states (JDOS),

(JDOS eq.)

Fig.xx shows the JDOS at three different q points. Although Eq. (1) includes Bose-Einstein functions for the involved phonon modes and JDOS can be weighted with these functions, as in ref. Togo and Scirep, they are omitted for simplicity. With the weights, the absolute values are affected but the weighted JDOS of the α and β phases are still similar. At the low frequency region responsible for the lattice thermal conductivities, among the two terms D(1) and D(2) in (JDOS eq.), dominant is D(2) which corresponds to the half part (ω>= 0) of the auto-correlation function of DOS. The DOS of the α and β phases in Fig. x-a commonly show the frequency gap. The auto-correlation functions, D(2), reflect this DOS feature, dropping suddenly around 0 THz and showing a small shoulder around 7 THz, which corresponds to the width of the gap. Moreover D(2) shows a broad peak around 18 THz, which corresponds to the frequency shift to make the largest correlation between the higher and lower portions of DOS across the gap. Because the gap is basically originated from the differences in vibrations of the planer NSi3 commonly existing in the α and β phases [Kuwabara], the major shapes of D(2), reflecting this DOS feature, are similar in these phases. With the same origin, the JDOS of D(1) are also similar in these phases. With these similar impacts of Φ-λλ’λ’’ and JDOS on Γλ, Γλ in Fig. xx-d are similar in the α and β phases.

As a small difference in Γλ between these phases, Γλ below 5 THz in the β phase are scattered onto two different lines, while those in the α phase are aligned on a smooth line. We investigate the characters of the phonon modes responsible for this differnece. In Fig.xxx-a, Γλ are classified using colors according to the sums of the squares of the eigenvector components along q; the sum is 1 for perfectly longitudinal waves. However, these sums have no clear contrast to distinguish the two branches in the β phase. Fig.xxx-b shows the same plot as Fig.xxx-a, but with colors according to the sums of the squares of the eigenvector components along the ab plane, which has 1 when the eigenvectors on the ab plane. There is a tendency in the β phase that Γλ are large for the vibrations along the ab plane. Therefore, for the phonon modes below 5 THz, all of which belong to the acoustic phonon branches, the vibration modes along the ab plane are more easily scattered in the β phase, no matter whether they are longitudinal or transverse. In Fig. xxxx-b-2 a straight line is drawn to divide the phonon modes into two groups. The numbers of the phonon modes in the upper and lower parts are 357 and 126, which are reasonable as the numbers of the vibration modes along the ab plane and out of the ab plane.