Crystal-grain size, phonon and carrier mean free paths in the basal plane, and carrier density of graphite films prepared from aromatic polyimide films

Yoshihiro Hishiyamaa), Akira Yoshidab) and Yutaka Kaburagic),*

The electrical and thermal conductivities in the basal plane of graphite films prepared from aromatic polyimide films were evaluated with reference to previously measured electrical and thermal conductivities along their longitudinal directions at room temperature with the aid of magnetoresistance anisotropy measurement at 77 K. The average crystal-grain size of each graphite film was obtained from the relation between thermal conductivity and grain size originally derived by Klemens and Pedraza. It was found that at room temperature the crystal-grain boundary scattering of phonons could dominantly occur for crystal-grains with sizes smaller than ~520 nm or the average \( d_{002} \) value of grains larger than ~0.3357 nm. When the grain size exceeds the intrinsic phonon mean free path in a single graphite crystal, i.e. ~1760 nm, or the average \( d_{002} \) value of the crystal-grains is less than ~0.3357 nm, the three phonon process in thermal conduction becomes dominant. The mean free paths of carriers were found to be much shorter than those of phonons and it was shown that at 77 K grain sizes smaller than ~220 nm could cause boundary scattering of carriers. The total carrier density at 77 K evaluated from the magnetoresistance and electrical conductivity data shows a decrease from the value of a single crystal of graphite as the crystallinity of the graphite film is reduced.

KEYWORDS: Graphite films, Thermal conductivity, Electrical conductivity, Crystal-grain size, Mean free path

1. Introduction

Around room temperature and above, the heat conduction of graphite can only be related to heat transport by lattice waves, i.e. phonons, because the density of electrons and holes in graphite crystal is extremely low. Because of the high bonding strength of the \( sp^2 \) hybrid orbital in the hexagonal layer of graphite crystal the phonon thermal conductivity is very high. On the other hand, graphite shows a high basal plane electrical conductivity even at room temperature irrespective of low densities of electrons and holes. The high electrical conductivity is due to the very high mobilities of electrons and holes in the basal plane. Therefore, at room temperature, graphite is a unique material in which heat is transported by phonons and small numbers of electrons and holes are responsible for electrical conduction. However, for practical application, to obtain the relationship between thermal conductivity and electrical conductivity for graphite materials is important, especially for highly crystallized materials. In the previous study, we prepared highly-crystalized graphite films using carbonized films derived from commercially available aromatic polyimide films and using rectangular samples of these graphite films, commercially available graphite films and sheets, and a thin-cleaved commercially available pyrolytic graphite plate. Thermal conductivities and also electrical conductivities along directions parallel to the film surface are the same and we are able to process equivalent rectangular samples chosen arbitrarily. For brevity, all of these graphite films, sheets and thin-cleaved pyrolytic graphite, we express hereafter as graphite films. As indicators of crystallinity of graphite films, the resistivity ratio \( \rho_{RT}/\rho_{77K} \) (\( \rho_{RT} \); the resistivity measured at room temperature, \( \rho_{77K} \); the resistivity measured at liquid nitrogen temperature (77 K))

* Corresponding Author, E-mail: ykabura@tcu.ac.jp

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and the maximum transverse magnetoresistance at 77 K in a magnetic field of 1 T, \((\Delta \rho/\rho)_{\text{max}}\), were employed\(^{1}\). The findings follow:

1) Good correlation between thermal conductivity and electrical conductivity with a rapid increase and trend toward saturation of thermal conductivity for increasing electrical conductivity.

2) Good correlation between thermal conductivity and \(\rho_{\text{RT}}/\rho_{77\text{K}}\), with a rapid increase of thermal conductivity against \(\rho_{\text{RT}}/\rho_{77\text{K}}\) at first and reducing to a gradual increase at \(\rho_{\text{RT}}/\rho_{77\text{K}} \sim 0.88\).

3) Good correlation between thermal conductivity and \([(\Delta \rho/\rho)_{\text{max}}]\)^{1/2} at 77 K and in a field of 1 T, i.e. the approximate geometric mean mobility at 77 K, with rapid increase of thermal conductivity at first and a trend of final saturation against mean mobility.

The previously obtained thermal conductivities were the averaged thermal conductivity along a longitudinal direction weighted by an orientation function for preferred orientation of constituent crystallites or crystal-grains. Thermal conductivity in the basal plane can be obtained with the aid of anisotropy measurement of magnetoresistance for the films at 77 K\(^2\). The magnetoresistance measurement in the previous study was extended to the anisotropy measurement in the present study. The thermal conductivity in the basal plane for the graphite films thus obtained can be related to the crystal-grain model developed by Klemens and Pedraza\(^3\) and this expression was extended to the anisotropy measurement of magnetoresistance.

The carrier mean free path in the basal plane at 77 K can be obtained from the previously measured electrical conductivity at room temperature and \(\rho_{\text{RT}}/\rho_{77\text{K}}\). Similar to the evaluation of the thermal conductivity in the basal plane, the electrical conductivity in the basal plane at 77 K was obtained. The carrier mean free path in the basal plane at 77 K can be evaluated from the electrical conductivity and magnetoresistance in the basal plane at 77 K. We note that the carrier mean free path at 77 K for graphite film gives indirect information on crystalline defects in the basal plane at 77 K.

The first aim of the present study is to discuss the change of dominant scattering mechanism of phonons at room temperature against crystal-grain size in the graphite films. To evaluate carrier mean free paths at 77 K in graphite films and to discuss them with crystallinity are other aims. The final objective is to relate the total carrier density at 77 K in the graphite films to crystallinity.

2. Background of Evaluation

2.1 Thermal conductivity of graphite crystal-grain in the basal plane

The thermal-conductivity ellipsoid of a single crystal of graphite is

![Fig. 1 Schematic of single graphite crystal specimen for thermal conductivity measurement, where \(j\) is heat current, \(a\) and \(c\) are crystal axes (\(\angle a, c = \pi/2\)) and \(\theta\) is angle between \(j\) and \(c\) axis.](image-url)
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\[ T_{\min}(\theta) \]

Fig. 2 Spherical coordinates of point P on a sphere of radius \( r \) and solid angle \( d\omega \) respect to origin \( O \) of area \( dS \) surrounding point \( P \).

\[
\kappa_{\alpha} = \frac{\int_0^{\pi/2} \int_0^{\pi/2} \kappa_x I(\phi) \sin \phi \, d\phi \, d\psi}{\int_0^{\pi/2} \int_0^{\pi/2} I(\phi) \, d\phi \, d\psi}
\]

We assume that each crystal-grain in the graphite film obeys the square law dependence of the magnetic field magnitude of the magnetoresistance at 77 K. We achieve this condition when the magnetic field \( B \) is applied at an inclination angle \( \theta \) from the symmetry axis as

\[
(\Delta \rho/\rho_0)_{\theta} = \bar{\mu}^2 B^2 \left[ \frac{1}{2} I_3 + \left( \frac{3}{2} I_1 \right) \cos^2 \theta \right]
\]

where \( (\Delta \rho/\rho_0)_{\theta} \) is the value of the magnetoresistance averaged over the crystal-grains when \( B \) is inclined at an angle \( \theta \) with respect to the \( Z \) axis (symmetry axis), and \( \bar{\mu} \) is the geometric mean of the motilities of electrons and holes.\(^3\)

In order to adapt Eq. (7) to the magnetoresistance measurement for graphite films following magnetic rotation schemes, a TL rotation scheme and T rotation scheme, were introduced. The two rotation schemes are illustrated in Fig. 3. In both rotation schemes, the maximum magnetoresistance \( (\Delta \rho/\rho_0)_{\max} \) is measured when the magnetic field is applied parallel to the symmetry axis; in the TL rotation scheme the magnetic field is rotated in the plane including the symmetry axis and an axis along the electric current direction, while in the T rotation scheme the magnetic field is rotated in the plane perpendicular to the current direction. We measure the minimum magnetoresistance in both schemes when the inclination angle of the magnetic field to the \( Z \) axis, for the magnetic field direction for \( (\Delta \rho/\rho_0)_{\max} \) is \( \pi/2 \). We denote the minimum values as \( (\Delta \rho/\rho_0)_{TL\min} \) in the TL rotation scheme and \( (\Delta \rho/\rho_0)_{T\min} \) in the T rotation scheme. If the symmetry axis exists, \( (\Delta \rho/\rho_0)_{TL\min} = (\Delta \rho/\rho_0)_{T\min} \). Usually \( (\Delta \rho/\rho_0)_{TL\min} \sim (\Delta \rho/\rho_0)_{T\min} \), because the \( Z \) axis is the approximate symmetry axis. We obtain the following relations\(^3\),

\[
(\Delta \rho/\rho_0)_{\alpha} = (\Delta \rho/\rho_0)_{\max} (1 + 2r_{\text{mean}}) = \bar{\mu}^2 B^2 ,
\]

\[
I_3 = \frac{2r_{\text{max}}}{1 + 2r_{\text{min}}} ,
\]

\[
r_{\text{max}} = r_{TL} + r_T ,
\]

\[
r_{TL} (\Delta \rho/\rho_0)_{TL\min} , \quad r_T = (\Delta \rho/\rho_0)_{T\min} / (\Delta \rho/\rho_0)_{\max}
\]

In Eq. (8), \( (\Delta \rho/\rho_0)_{\alpha} \) can be defined as average crystal-grain layer plane transverse magnetoresistance and a parameter for crystallinity.\(^8\)
2.2 Phonon thermal conductivity and crystal-grain size in the basal plane

A theoretical expression for the phonon thermal conductivity of single crystal graphite in the basal plane at room temperature was derived by Klemens and Pedraza with their two-dimensional phonon-gas model\(^1\). Using this model, the following describes first the thermal conductivity of single crystal graphite and further those for graphite materials consisting of crystal-grains with finite mean grain size \(L_g\).

2.2.1 Two-dimensional phonon gas model and phonon angular frequency range for a single graphite crystal

Since the interlayer spacing \(d_{002}\) is large and the binding forces between the basal planes (graphene layers) are weak, the phonon dispersion curves of graphite have an almost two-dimensional character. Klemens and Pedraza regarded the graphite crystal as a simple stacking of graphene layers with a spacing of \(d_{002}\), because of the weak binding forces between the graphene layers\(^1\). They replaced the graphite Brillouin zone of hexagonal prism with a circular cylinder zone, of which the base area is equal to that of the hexagonal Brillouin zone as shown in Fig. 4. The radius of the base circle of the circular Brillouin zone \(q_m\) becomes

\[
q_m = \frac{2}{\omega_0} \left( \frac{2\pi}{\sqrt{3}} \right)^{1/2} = 1.55 \times 10^{10} \text{ m}^{-1} \ (\omega_0 = 0.246 \times 10^{-9} \text{ m}),
\]

where \(\omega_0\) is the lattice constant.

In the phonon dispersion curves, there are two branches that make the major contribution to the heat current: the longitudinal branch with wave velocity \(v_L=2.36 \times 10^3 \text{ m s}^{-1}\) and the fast transverse branch with a velocity \(v_T=1.59 \times 10^4 \text{ m s}^{-1}\). The Debye velocity for this two-dimensional phonon gas was defined by Klemens and Pedraza\(^3\) as

\[
\frac{2}{\langle v \rangle} = \frac{1}{\langle v_L \rangle} + \frac{1}{\langle v_T \rangle}.
\]

So that \(\langle v \rangle = 1.86 \times 10^4 \text{ m s}^{-1}\), and the maximum angular frequency of phonons becomes \(\omega_m = \langle v \rangle q_m = 2.88 \times 10^{14} \text{ s}^{-1}\). On the other hand, it is known that heat propagation along the \(c\)-axis direction occurs only for modes of angular frequency \(\omega\) below \(\omega_c = 2.5 \times 10^{13} \text{ s}^{-1}\). Considering the phonon dispersion curves of graphite, Klemens and Pedraza presented a model of the thermal conductivity in terms of a two-dimensional phonon gas in the angular frequency \(\omega\) range from \(\omega_c\) to a Debye-like cut off frequency \(\omega_m\) in which the \(\omega\)-contours in \(q\)-space are cylindrical surfaces parallel to the \(q_z\)-direction\(^5\). The angular frequency range is defined as \(\omega_c \leq \omega \leq \omega_m\).

2.2.2 Relaxation rate for phonon propagation in a single graphite crystal

The relaxation rate \(1/\tau\) for phonon propagation arises from anharmonic three-phonon processes. The rate process is that a phonon \(q\) combines with a phonon \(q'\) to form a phonon \(q''\). Given \(q', q''\), \(q'\) is determined by a wave vector selection rule

\[
q' + q'' - q = g
\]

where \(g\) is a reciprocal lattice vector. Klemens and Pedraza derived the relaxation rate of the processes as

\[
\frac{1}{\tau} = \frac{2\gamma}{kT} \frac{\omega^2}{Mv}\frac{\omega}{\omega_m}
\]

where \(\gamma\) is the Grüneisen parameter and according to Klemens and Pedraza \(\gamma^2 = 4\), \(M\) is the mass of carbon atom, \(k\) is the Boltzmann constant, \(T\) is the temperature and \(v^2 = \langle v^2 \rangle^2\).

2.2.3 Intrinsic thermal conductivity of a single graphite crystal

The thermal conductivity can be written in the form

\[
\kappa_a = \int \kappa_a(\omega) d\omega \approx \int C(\omega) \omega^d r(\omega) d\omega \quad \text{(11)}
\]

where \(C(\omega) d\omega\) is the spectral contribution to the specific heat per unit volume from modes in the angular frequency interval \(d\omega\). \(\theta\) is the angle between a wave vector and the temperature gradient and \(\langle \cos^2 \theta \rangle\) is the average over all directions of \(q\). \(\langle \cos^2 \theta \rangle\) becomes 1/2 in two dimensions. Applying the classical equipartition law to the integral of \(C(\omega)\) in Eq. (11), \(C(\omega)\) can be obtained analogous to that derived by Klemens and Pedraza as

\[
C(\omega) = \frac{16k}{V_c} \frac{\omega}{\omega_m}
\]

where \(V_c\) is the unit cell volume of a single graphite crystal\(^3\).

Substituting Eq. (12) into Eq. (11) and using Eq. (10), we obtain

\[
\kappa_a = \frac{4M}{V_c^2} \frac{v^4}{\omega_m T} \int \frac{d\omega}{\omega^d} \frac{d\omega}{\omega} \approx \frac{\rho}{\omega_m^d} \frac{v^4}{\omega_m^2 T} \ln \frac{\omega_m}{\omega_c}
\]

where \(4M/V_c = \rho\) is the density of graphite crystal; \(\rho = 2.26 \times 10^3 \text{ kg m}^{-3}\). Setting \(v = 1.86 \times 10^4 \text{ ms}^{-1}\), \(\omega_m = 2.88 \times 10^{14} \text{ s}^{-1}\), \(\omega_c = 2.51 \times 10^{13} \text{ s}^{-1}\), and \(\gamma^2 = 4\), \(\kappa_a\) of a single graphite crystal at 300 K is obtained as

Fig. 4 Bases of hexagonal-prism Brillouin zone and circular-cylinder Brillouin zone for graphite.
\( \kappa_{s} = 1910 \text{ W} \cdot (\text{m} \cdot \text{K})^{-1} \).

This value agrees well with the observed value of 1950 W m\(^{-1}\) K\(^{-1}\) for highly oriented pyrolytic graphite (HOPG) at 300 K\(^9\). According to Klemens and Pedraza, Eq. (13) expresses the intrinsic thermal conductivity in the basal plane\(^3\). We denote hereafter \( \kappa_{s} \), the left side of Eq. (13), as \( \kappa_{s,i} \).

Using Eq. (10), the mean free path \( l \) for the phonon with angular frequency \( \omega \) can be written

\[
    l = v_{f} \frac{1}{2} \frac{M_{0}^{3}}{kT} \frac{\omega_{m}}{\omega^{2}}.
\]

Since \( \omega_{c} \leq \omega \leq \omega_{m} \), the longest mean free path \( l \) can be obtained setting \( \omega = \omega_{c} \), as

\[
    l = \frac{1}{2} \frac{M_{0}^{3}}{kT} \frac{\omega_{m}}{\omega_{c}^{2}} = B
\]

\[
    B = \frac{1}{2} \frac{M_{0}^{3}}{kT} \frac{\omega_{m}}{\omega_{c}}
\]

\[
    (14.1)
\]

\[
    (14.2)
\]

\( l \) is the phonon mean free path in a single graphite crystal, i.e. the intrinsic phonon mean free path in a single graphite crystal, so we attached a suffix \( j \) under \( l \). At 300 K we obtain \( l = 1760 \text{ nm} \).

### 2.2.4 Thermal conductivity of graphite limited by crystal-grain size

For graphite material consisting of crystal-grains with c-axes in parallel, the thermal conductivity becomes insensitive to grain size if the grain size exceeds \( l \). In the previous study, we found that the thermal conductivity along the longitudinal direction of the graphite films \( \kappa_{s} \) decreases with reduction of crystallinity. We determine the decrease of the conductivity relative to the decrease of the crystal-grain size in the basal plane, and we calculate the conductivity as a function of grain size.

We denote the mean grain size in the graphite film as \( \bar{L}_{G} \) and the related thermal conductivity in the basal plane, i.e. the experimentally obtained conductivity in the basal plane, as \( \bar{\kappa}_{G} \). We specify hereafter the quantity averaged over crystal grains with the suffix \( G \). \( \bar{\kappa}_{G} \) can be written according to Eq. (11) as

\[
    \bar{\kappa}_{G} = \frac{1}{2} \int \left[ C(\omega) \chi(\omega) \right] d\omega = \frac{v}{2} \int C(\omega) \chi(\omega) \omega d\omega \quad \text{..........}(15)
\]

with \( \chi(\omega) \)

\[
    l(\omega) = \frac{1}{l_{1} + \frac{L_{G}}{L_{G}}}, \quad \text{..........}(16)
\]

where \( L_{G} = B / \bar{\kappa}_{G} \). Using Eqs. (12) and (14), \( C(\omega) \chi(\omega) \) becomes

\[
    C(\omega) \chi(\omega) = \frac{16k_{B}}{V_{c}} \frac{B}{\omega_{c}^{2}} \frac{\omega}{\omega^{2} + \omega_{c}^{2}}\quad \text{..........}(17)
\]

Substituting Eq. (17) into Eq. (15) and integrating, using Eq. (14) we obtain \( \bar{\kappa}_{G} \) as

\[
    \bar{\kappa}_{G} = \frac{1}{2} \ln \left( \frac{\omega_{m}^{3} + \omega_{c}^{3}}{\omega_{c}^{3} + \omega_{m}^{3}} \right) \kappa_{s,i}
\]

\[
    i.e.
\]

\[
    \frac{\omega_{m}}{\omega_{c}} = \exp \left( \frac{2}{\gamma} \bar{\kappa}_{G} \ln \left( \frac{\omega_{m}}{\omega_{c}} \right) \left( \frac{\omega_{m}}{\omega_{c}} \right)^{2} - 1 \right) \quad \text{..........}(18)
\]

and

\[
    \bar{L}_{G} = B / \bar{\kappa}_{G} = \frac{1}{2} \frac{M_{0}^{3}}{kT\omega_{m}} \frac{1}{\left( \omega_{m} / \omega_{c} \right)^{2}} \quad \text{..........}(19)
\]

With the experimentally obtained \( \bar{\kappa}_{G}/ \kappa_{s,i} \) we can obtain \( \bar{\kappa}_{G}/ \omega_{m} \) by Eq. (18) and \( \bar{L}_{G} \) by Eq. (19). At 300 K, \( (1/2)^{2} (M_{0}^{3} / kT\omega_{m}) \) becomes 13.4 nm. In Eq. (18), for \( \kappa_{s,i} \), we use the value of thermal conductivity for one of the highest quality HOPGs, 1950 W · (m · K)\(^{-1}\)\(^9\). For this HOPG, because \( \bar{\kappa}_{G}/ \kappa_{s,i} = 1 \) and \( \omega_{m}/\omega_{c} = 11.5 \), Eq. (18) gives \( \omega_{m}/\omega_{c} = 0.00119 \), and we evaluate \( \bar{L}_{G} = 9.5 \text{ mm} \) from Eq. (19). On the other hand, Klemens and Pedraza list observed conductivity values for other HOPGs as 1660 and 1850 W · (m · K)\(^{-1}\)\(^3\). Equations (18) and (19) gives \( \bar{L}_{G} \) values of 1.13 and 9.10 \mu m, respectively, for these HOPGs. The present authors AY and YH evaluated \( \bar{L}_{G} \) values for different HOPG samples with residual resistivity ratios, \( \rho_{RT}/\rho_{4.2 K} \), 6.8 and 8.1, respectively, by observation of electron channeling contrast (ECC) images\(^3\). The former sample is denoted as HOPG 7 and the latter as HOPG 8. The ratio \( \rho_{RT}/\rho_{4.2 K} \) is an indicator for crystallinity of graphite materials\(^1\), where \( \rho_{RT} \) and \( \rho_{4.2 K} \) are the electrical resistivities at room temperature and 4.2 K, respectively. Their ECC images revealed \( \bar{L}_{G} \) values of 55.5 \mu m for HOPG 7 and 58.7 \mu m for HOPG 8.

The conductivity values could be evaluated as 1937.6 W · (m · K)\(^{-1}\)\(^9\) for HOPG 7 and 1938.3 W · (m · K)\(^{-1}\)\(^3\) for HOPG 8 by Eqs. (18) and (19). These considerations could reveal the plausibility of evaluation of \( \bar{L}_{G} \) with Eqs. (18) and (19) using thermal conductivity data.

For graphite films with \( \bar{L}_{G} > l \), the three-phonon process is predominant. For the case of \( l \geq l_{1} > \bar{L}_{G} \) thermal conduction in the basal plane is limited by grain size, i.e. phonons are scattered by grain boundaries.

### 3. Experimental

The X-ray diffraction measurements for the graphite films were made in addition to the measurements in the previous study for crystallographic characterization of the graphite films. Magnetoresistance measurements at 77 K for the graphite films were also conducted to evaluate the integral ratio \( l_{1}/l_{2} \) directly through the measurements.
3.1 X-ray diffraction

The X-ray diffraction measurements were conducted using CuKα radiation in reflection. Film samples were used, setting them on a specially designed sample holder for films. The 004 diffraction profiles were measured for the samples and the interlayer spacing \(d_{002}\) for each sample was determined from the profile corrected for Lorentz-polarization and atomic scattering factors, with reference to the 004 line of a thin HOPG specimen with a flat cleaved surface \((d_{002} = 0.3354 \text{ nm})\) and also to the 311 line of high purity Si powder. We did not correct the profiles by absorption factor because the samples were sufficiently thin.

3.2 Magnetoresistance measurements

The magnetoresistance measurements for the graphite films in the previous study, made in liquid nitrogen and in magnetic fields of 1 T, were extended to measurements with the magnetic field rotation schemes for the TL and T rotations. The values of \((\Delta \rho / \rho_0)_{\text{max}}, (\Delta \rho / \rho_0)_{\text{TLmax}},\) and \((\Delta \rho / \rho_0)_{\text{min}}\) were determined for each sample.

4. Results and Discussion

4.1 General aspects of thermal conductivity in the basal plane of graphite films

In Table 1, the values of the interlayer spacing \(d_{002}\), resistivity ratio \(\rho_{\text{RT}}/\rho_{77\text{ K}}\) and the magnetoresistance data at 77 K and in a magnetic field of 1 T for the graphite films are displayed. The magnetoresistance data listed are \((\Delta \rho / \rho_0)_{\text{max}}, (\Delta \rho / \rho_0)_{\text{TL}},\) and the geometric mean of the mobilities of electrons and holes \(\mu_{77\text{ K,LT}}\). The values of the interlayer spacing \(d_{002}\), ratio of electrical resistivity at room temperature to that at 77 K, \(\rho_{\text{RT}}/\rho_{77\text{ K}}\) for the samples obtained in the previous study and magnetoresistance data for the samples at 77 K and in field of 1 T; \((\Delta \rho / \rho_0)_{\text{max}},\) \(I_S/I_T\), \((\Delta \rho / \rho_0)_{\text{TL}},\) and \(\mu_{77\text{ K,LT}}\). The values of the interlayer spacing \(d_{002}\), ratio of electrical resistivity at room temperature to that at 77 K, \(\rho_{\text{RT}}/\rho_{77\text{ K}}\) for the samples obtained in the previous study and magnetoresistance data for the samples at 77 K and in field of 1 T; \((\Delta \rho / \rho_0)_{\text{max}}, I_S/I_T, (\Delta \rho / \rho_0)_{\text{TL}},\) and \(\mu_{77\text{ K,LT}}\). The values of the interlayer spacing \(d_{002}\), ratio of electrical resistivity at room temperature to that at 77 K, \(\rho_{\text{RT}}/\rho_{77\text{ K}}\) for the samples obtained in the previous study and magnetoresistance data for the samples at 77 K and in field of 1 T; \((\Delta \rho / \rho_0)_{\text{max}}, I_S/I_T, (\Delta \rho / \rho_0)_{\text{TL}},\) and \(\mu_{77\text{ K,LT}}\). The values of the interlayer spacing \(d_{002}\), ratio of electrical resistivity at room temperature to that at 77 K, \(\rho_{\text{RT}}/\rho_{77\text{ K}}\) for the samples obtained in the previous study and magnetoresistance data for the samples at 77 K and in field of 1 T; \((\Delta \rho / \rho_0)_{\text{max}}, I_S/I_T, (\Delta \rho / \rho_0)_{\text{TL}},\) and \(\mu_{77\text{ K,LT}}\).
Fig. 5 Interlayer spacing $d_{002}$ plotted as a function of resistivity ratio $\rho_{RT}/\rho_{77K}$. $\rho_{RT}$ and $\rho_{77K}$ are resistivities measured at room temperature and 77 K, respectively.

Fig. 6 Plots of room temperature electrical and thermal conductivities $\bar{\sigma}_{G,RT}$ and $\bar{\kappa}_{G}$ against $d_{002}$ for graphite films, including virtual graphite material HQG, $\bar{\sigma}_{G,RT}$ (a) and $\bar{\kappa}_{G}$ (b). The curve in (a) and the straight line in (b) are guides for variations.

Fig. 7 Plots of $\bar{\kappa}_{G}$ as a function of $\bar{\sigma}_{G,RT}$ for graphite films, including virtual graphite material HQG. The straight lines in the figure are regression lines.

Fig. 8 Plots of room temperature electrical and thermal conductivities $\bar{\sigma}_{G,RT}$ and $\bar{\kappa}_{G}$ against $\rho_{RT}/\rho_{77K}$ for graphite films, including virtual graphite material HQG, $\bar{\sigma}_{G,RT}$ (a) and $\bar{\kappa}_{G}$ (b). The curves in the figures are guides for variations.
ues of $\overline{(\Delta \rho / \rho_0)}_{\text{max}}$ are those obtained in the previous study$^1)$, while the values of $I_l/I_1$, $\overline{(\Delta \rho / \rho_0)}_{\text{RT}}$ and $\overline{g_{\gamma K,1T}}$ are those calculated with Eq. (8). $\overline{\rho}$ and $\overline{\kappa}$ measured at room temperature are listed in Table 2 for convenience. The electrical and thermal conductivities in the basal plane $\overline{\sigma}_{\text{GRT}}$ and $\overline{\kappa}_{\text{G}}$ calculated from $\sigma_\parallel$ and $\kappa_\parallel$ with Eq. (8) using the values of $I_l/I_1$ in Table 1 are shown in Table 2, where the suffix RT is attached after the suffix G of $\overline{\sigma}_{\text{G}}$ to clarify the room temperature value. In Tables 1 and 2, the sample HQG (high quality graphite) is a virtual graphite material characterized by the lowest limit value of $d_{022}$, and highest limit values of $\rho_{\text{RT}}/\rho_{77 K}$ ($\overline{(\Delta \rho / \rho_0)}_{\text{max}}$ $\overline{\sigma}_{\text{GRT}}$ and $\overline{\kappa}_{\text{G}}$ for HOPG, single graphite crystal, and Kish graphite with $I_l/I_1=0$ from refs. 1, 13 and 14.

The interlayer spacing $d_{022}$ is plotted against $\rho_{\text{RT}}/\rho_{77 K}$, a parameter for crystallinity, in Fig. 5. Since the $d_{022}$ values scattered so much, the detail of the variation of $d_{022}$ against resistivity ratio could not be derived without a trend against $d_{022}$ to decrease with improvement of crystallinity. The curve in the figure is a guide for the trend.

The plots of $\overline{\sigma}_{\text{GRT}}$ and $\overline{\kappa}_{\text{G}}$ are shown as a function of $d_{022}$ in Fig. 6. Both plots are scattered but show trends to decrease with increasing $d_{022}$. The curve in Fig. 6(a) and the straight line in Fig. 6(b) are guides for variations by least squares fits.

Figure 7 shows plots of $\overline{\kappa}_{\text{G}}$ as a function of $\overline{\sigma}_{\text{GRT}}$. A discontinuous change for $\overline{\kappa}_{\text{G}}$ vs. $\overline{\sigma}_{\text{GRT}}$ relation appears at $\overline{\sigma}_{\text{GRT}} \sim 1.0 \times 10^6$ S·m$^{-1}$. This relation corresponds to finding 1 in the previous study described in the Introduction$^1)$. The discontinuity could mainly be due to the dependence of $\overline{\kappa}_{\text{G}}$ on crystallinity as shown in Fig. 8. In Fig. 8(a) and (b), $\overline{\sigma}_{\text{GRT}}$ and $\overline{\kappa}_{\text{G}}$ are shown as separate plots as a function of $\rho_{\text{RT}}/\rho_{77 K}$. The curve in each figure is a guide for variation. In Fig. 8(a) $\overline{\sigma}_{\text{GRT}}$ increases almost monotonically with $\rho_{\text{RT}}/\rho_{77 K}$, while in Fig. 8(b) $\overline{\kappa}_{\text{G}}$ increases rapidly with $\rho_{\text{RT}}/\rho_{77 K}$ at first, shows an inflection at $\rho_{\text{RT}}/\rho_{77 K} \sim 0.88$ as displayed by the guide curve and then levels off. Behavior in Fig. 8(b) is similar to the plots of $\kappa_{\text{core}}$ against $\rho_{\text{RT}}/\rho_{77 K}$ in the previous study, i.e. finding 2 in the previous study$^1)$. The discontinuity at $\overline{\sigma}_{\text{GRT}} \sim 1.0 \times 10^6$ S·m$^{-1}$ in $\overline{\kappa}_{\text{G}}$ vs. $\overline{\sigma}_{\text{GRT}}$ plots and also the inflection at $\rho_{\text{RT}}/\rho_{77 K} \sim 0.88$ in $\overline{\kappa}_{\text{G}}$ vs. $\rho_{\text{RT}}/\rho_{77 K}$ plots correspond to the same $d_{022}$ values of $\sim 0.3357$ nm.

4.2 Crystal-grain size along the basal plane in graphite films

Values of $\overline{\kappa}_{\text{G}}$ for the samples in Table 2 and also in Fig. 6 are principally modified thermal conductivities of the intrinsic conductivity of single graphite crystal at room temperature by reduction of crystal-grain size. Similarly, $\overline{\sigma}_{\text{GRT}}$ is the electrical conductivity at room temperature modified by crystal-grain size reduction. Graphite materials including partially graphitized materials generally show crystallinity improvement accompanying crystal-grain size increase, and vice versa. Therefore, the behavior in Fig. 8(b) could be related to the mean crystal-grain size in the basal plane $\overline{L}_G$. We calculated $\overline{L}_G$ for the samples by Eqs. (18) and (19), using the values of $\overline{\kappa}_{\text{G}}$ in Table 2, and displayed in Table 2.

Figure 9 depicts $\overline{L}_G$ vs. $\overline{\kappa}_{\text{G}}$ plots for graphite films, showing each plot on a smooth curve. In Fig. 10, $\overline{L}_G$ is plotted against $\rho_{\text{RT}}/\rho_{77 K}$ with $\overline{L}_G$ on a logarithmic scale. A discontinuous change in $\overline{L}_G$ appears at $\rho_{\text{RT}}/\rho_{77 K} \sim 0.88$, with a small width of $\rho_{\text{RT}}/\rho_{77 K}$ about 0.03. The discontinuity is more clearly seen in the inset of the figure, where $\overline{L}_G$
is scaled antilogarithmically. Dashed horizontal lines in the figures indicate the intrinsic mean free path of phonons in single graphite crystals at room temperature, \( l_i \), i.e. 1760 nm. The discontinuity divides the \( \tilde{L}_G \) vs. \( \rho_{RT}/\rho_{77K} \) plots into two classes according to \( G_l < l \); or \( G_l > l \). For the first class, phonons could be scattered predominantly at the crystal-grain boundaries, while for the second class phonons conduct prevailingly with a three-phonon process irrespective of crystal-grain size, i.e. the phonon mean free paths are equal to \( l \) and independent of \( \tilde{L}_G \). The maximum value of \( \rho_{RT}/\rho_{77K} \) for grain boundary scattering could be \( \sim 0.88 \) which corresponds to the \( d_{002} \) and \( \tilde{L}_G \) values of \( \sim 0.3357 \) nm and \( \sim 520 \) nm, respectively. This \( \tilde{L}_G \) value corresponds to \( \kappa_G \) value of \( \sim 1370 \) W·(m·K)\(^{-1}\). On the other hand, the minimum value of \( \tilde{L}_G \) for three-phonon process could be evaluated to \( \sim 2000 \) nm arising from \( \tilde{L}_G \) value of \( \sim 1700 \) W·(m·K)\(^{-1}\).

The phonon thermal conductivity and geometric mean of mobilities of electrons and holes, i.e. carrier mobilities, are indirectly related quantities. However, there was a good correlation between thermal conductivity and the square root of maximum transverse magnetoresistance at 77 K and in a field of 1 T, as shown in the previous study (finding 3 described in the Introduction\(^3\)). Quite similar and more drastic change appears in \( \tilde{L}_G \) vs. \( \tilde{L}_G \) plots as shown in Fig. 11, indicating a kink for \( \tilde{L}_G \) at \( \tilde{L}_G \sim 1.48 \) m\(^2\)·(V·s\(^{-1}\)). The corresponding value of \( d_{002} \) at the kink is \( \sim 0.3357 \) nm. Since the relation between \( \tilde{L}_G \) and \( \tilde{L}_G \) can be expressed as a smooth curve as shown in Fig. 9. Figure 11 is much easier to understand if we replace \( \tilde{L}_G \) with \( \tilde{L}_G \) as depicted in Fig. 12. In Fig. 12 \( \tilde{L}_G \) is scaled logarithmically and an inset shows plots of \( \tilde{L}_G \) on an antilogarithmic scale for \( \tilde{L}_G (\sim 2.5 \) m\(^2\)·V\(^{-1}\)·s\(^{-1}\)). With increasing \( \tilde{L}_G \), \( \tilde{L}_G \) shows a discontinuous increase at \( \tilde{L}_G \sim 1.48 \) m\(^2\)·(V·s\(^{-1}\)), i.e. a jump, of \( \tilde{L}_G \) from \( \sim 520 \) nm to \( \sim 2000 \) nm. The upper value of \( \tilde{L}_G \) at the jump corresponds to the minimum grain size for disappearance of the crystal-grain boundary scattering of phonons while the lower value of \( \tilde{L}_G \) gives the maximum grain size for the boundary scattering.

4.3 Mean free paths of electrons and holes along the basal plane in graphite films at 77 K

As described in section 4.2, graphite materials show crystallinity reduction accompanied by crystal-grain size reduction. Crystallinity reduction or improvement can be considered using the geometric mean of mean free paths of electrons and holes at 77 K, \( \tilde{L}_{eh,77K} \) plotted as a function of \( \rho_{RT}/\rho_{77K} \).
where $h$ is the Planck constant divided by $2\pi$, $\bar{k}_{F\text{aw}}$ is the geometric mean radius for the maximum cross sections of the electron and hole Fermi surfaces perpendicular to the $k_x$ axis and $e$ is the elementary charge. Using the areas of the maximum cross sections of the Fermi surfaces for electrons and holes given by Soule et al.\textsuperscript{14}, which yielded $2\bar{k}_{F\text{aw}}/e = 1.73 \times 10^{-7} \text{ V} \cdot \text{s} \cdot \text{m}^{-1}$, and the magnetoresistance data in Table 1, we obtained $\bar{\rho}_{\text{d},77\text{K}}$ as listed in Table 2. The values of $\bar{\rho}_{\text{d},77\text{K}}$ obtained are plotted in Fig. 13, as a function of $\rho_{\text{RT}}/\rho_{77\text{K}}$. $\bar{\rho}_{\text{d},77\text{K}}$ could be related to defects contained in crystal grains and a relation $\bar{\rho}_{\text{d},77\text{K}} > \bar{\rho}_{\text{G}}$ can be seen for graphite films with lower crystallinity. For such graphite films, scattering of carriers by crystal-boundary possibly occurs. Figure 13 shows that at 77 K carriers are possibly scattered at the crystal-boundary for the graphite films with $\rho_{\text{RT}}/\rho_{77\text{K}} = 0.72$ and $\rho_{\text{RT}}/\rho_{77\text{K}} = 0.72$. Referring to Table 1 we could rewrite this condition to $\bar{\rho}_{\text{d},77\text{K}} > \bar{\rho}_{\text{G}}$ as a function of $\bar{\rho}_{\text{d},77\text{K}}$ and $\bar{\rho}_{\text{G}}$ for occurrence of boundary scattering of carriers as 218 nm $\sim \bar{\rho}_{77\text{K}}$ and 218 nm $< \bar{\rho}_{\text{d},77\text{K}}$. This implies that also referring to Table 2 the grain boundary scattering of carriers could be dominant for graphite films with $\bar{\rho}_{\text{G}} \sim 1100 \text{ W} \cdot (\text{m} \cdot \text{K})^{-1}$ and $\bar{\rho}_{\text{G}} < 1100 \text{ W} \cdot (\text{m} \cdot \text{K})^{-1}$.

4.4 Total carrier density in graphite films at 77 K

Total carrier density at 77 K for the graphite film can be evaluated using the data on room temperature electrical resistivity, resistivity ratio $\rho_{\text{RT}}/\rho_{77\text{K}}$ and geometric mean mobility of electrons and holes at 77 K. The total carrier density of the graphite film at 77 K $n_{77\text{K}} + n_{77\text{K}}$ can be written

$$n_{77\text{K}} + n_{77\text{K}} = \frac{\sigma_{\text{G,RT}}}{\sigma_{77\text{K},1T}} \rho_{\text{RT}} = \frac{\rho_{\text{RT}}}{\rho_{77\text{K}}}$$

where $n_{77\text{K}}$ and $n_{77\text{K}}$ are the densities of electrons and holes at 77 K, respectively. Using the values of $\rho_{\text{RT}}/\rho_{77\text{K}}$, $\mu_{77\text{K},1T}$ and $\sigma_{\text{G,RT}}$ in Tables 1 and 2, $n_{77\text{K}} + n_{77\text{K}}$ were calculated. $n_{77\text{K}} + n_{77\text{K}}$ are plotted as a function of $\rho_{\text{RT}}/\rho_{77\text{K}}$ as depicted in Fig. 14. The curve and straight line were drawn by least squares fits.

Figure 14 indicates that $n_{77\text{K}} + n_{77\text{K}}$ decreases from the value for HQG as the crystallinity reduces. $n_{77\text{K}} + n_{77\text{K}}$ shows a kink at $\rho_{\text{RT}}/\rho_{77\text{K}} \sim 0.88$, i.e. at $d_{\text{002}}$ value of $\sim 0.3357 \text{ nm}$ corresponding to the disappearance of boundary scattering of phonons. The decrease of $\bar{\mu}_{77\text{K},1T}$ could be explained by an increase of defects in the basal plane in the crystal-grain. There are two possible explanations for the decrease of $n_{77\text{K}} + n_{77\text{K}}$. The first explanation is that the decrease is due to decrease of Fermi energy from that for HQG with trapping of carriers by defects, as suggested by Mrozowski quite a long time ago\textsuperscript{15}. The second may be ascribed to decrease of $\gamma_2$, the next nearest layer interactions, caused by increase of $d_{\text{002}}$ followed by increase of defects (Fig. 5), since the band overlap between valence and conduction bands is given by $2\gamma_2$.

5. Conclusion

1. The electrical and thermal conductivities in the basal plane for graphite films could be evaluated using previously measured electrical and thermal conductivities.

2. Phonon mean free paths in graphite films could be evaluated with application of the two-dimensional phonon gas model developed by Klemens and Pedraza. Crystal grain size for graphite films decreases from an extraordinarily large size of single crystal graphite with reduction of crystallinity. It was found that in graphite films the boundary scattering in phonon conduction possibly dominates when the mean grain size is below the intrinsic phonon mean free path in single graphite crystal at room temperature, i.e. $\sim 1760 \text{ nm}$. For half the graphite films studied, mean grain sizes were found to be sufficiently large as to be free from boundary scattering, indicating high crystallinity of these graphite films.

3. Analysis of the magnetoresistance data at 77 K showed that the carrier mean free path decreases with reduction of crystallinity, indicating an increase of defects in the grains with reduction of the grain size. The crystal-grain boundary scattering for carriers at 77 K is possibly dominant when the geometric mean of carrier mean free paths exceeds the mean crystal-grain size.

4. The total carrier density for graphite films at 77 K could be found to decrease from the value for single-crystal graphite with reduction of crystallinity.

References

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