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Phonon Scattering and Thermal Resistance Due to Grain Boundaries[1]

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The thermal conductivity of polycrystalline dielectric solids is reduced because the phonon mean free path is limited by the size of crystallites or grains. This reduces the contribution to the conductivity of low-frequency modes. Quantitative expressions for this reduction have been obtained in terms of a mean free path L, of the order of the average grain diameter, but there has been no good understanding of what influences the back-scattering probability at the grain boundary, which enters as a factor in $1/L$. It is proposed here that there are two contributions to the backscattering. One, which is independent of frequency, depends for large-angle boundaries on the mean square variation of the phonon velocity v, as a function of direction, about its average value. Low-angle boundaries scatter as the square of the tilt angle. This contribution is small. The second contribution is due to a layer of disorder between grains. This varies as the square of the frequency at low frequencies and saturates at a value of one-half at higher frequencies. The theory is compared to measurements of the thermal conductivity at low temperatures of chemically vapor deposited diamond films.

KEY WORDS: diamond films; grain boundaries; phonon scattering; polycrystalline solids; thermal conductivity.

1. INTRODUCTION

In dielectric solids at low and moderately high temperatures, heat is conducted by phonons. In polycrystalline materials phonons are scattered by grain boundaries; this reduces the mean free path of at least some of the normal modes and reduces the thermal conductivity. Since the intrinsic

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mean free path of all modes increases with decreasing temperature, the reduction of the thermal conductivity is most pronounced at low temperatures. The first low-temperature measurements of the thermal conductivity λ of polycrystalline dielectric solids (alumina and berylia) were made by Berman [1]. In alumina the conductivity could be compared to single crystal values. Writing

$$\lambda = (1/3)\, C(T)\, vl \tag{1}$$

where $C(T)$ is the specific heat per unit volume and v the phonon speed, the apparent mean free path l was found to be comparable to the size of the larger grains and to increase slowly with decreasing temperature. In single crystals l is determined by the shortest linear dimensions of the crystal and is constant, so that at lowest temperatures $\lambda \propto C(T)$.

At ordinary and high temperatures one has to consider the variation of the intrinsic mean free path l_i with (angular) frequency ω. Since $l_i(\omega) \propto \omega^{-2}$, grain boundary scattering, limiting the mean free path to a constant value L, makes $l = Ll_i(\omega)/[L + l_i(\omega)]$ and l is affected by grain boundaries only at the lowest frequencies. There is a reduction in conductivity even if the average mean free path is well below L; this reduction is given by [2, 3]

$$\delta\lambda_B = \lambda_i(\omega_B/\omega_D) \arctan(\omega_D/\omega_B) \tag{2}$$

where ω_D is the Debye frequency and ω_B is the frequency at which

$$l_i(\omega_B) = L \tag{3}$$

For example, in the case of UO_2, $l_i(\omega_D) = 1.5 \times 10^{-7}$ cm at 600 K. From Eq. (3),

$$\omega_B/\omega_D = (1.5 \times 10^{-7}/L)^{1/2} (600/T)^{1/2} \tag{4}$$

If $T = 600$ K and the grain size is $L = 3 \times 10^{-4}$ cm, $\omega_B/\omega_D = 2.0 \times 10^{-2}$ and $\delta\lambda_B/\lambda_i = 3.1 \times 10^{-2}$. A 3-$\mu$m grain size should reduce the conductivity below its intrinsic value by about 3%. At room temperature, the reduction would be about 4.5%.

Here it has been tacitly assumed that phonons are randomly scattered at each grain boundary, so that L can be identified with an average grain diameter. It is, however, not obvious that this should be the case. Estimates of the scattering probability of a tilt boundary give values which, while independent of frequency, are at least on order of magnitude smaller. Such an estimate is given below.

In order to explain the grain boundary resistance both at high and at low temperatures, it is suggested that scattering at grain boundaries is due to a layer of material between the grains, which is highly disordered and perhaps less dense. Turk et al. [4] developed a theory of phonon scattering by thin plates, to treat nitrogen platelets in diamond. For large but thin plates, scattering varies as ω^2 at low frequencies. It increases with frequency, but cannot exceed a saturation value with a scattering probability near 0.5. Frequency-dependent scattering of phonons by grain boundaries, and a consequent increase in the average mean free path with decreasing temperature, was already noted by Berman. It was seen recently by Morelli et al. [5] in polycrystalline vapor-deposited diamond films. The theory is compared with their observations.

2. SCATTERING OF PHONONS BY TILT BOUNDARIES

A tilt boundary can be regarded as two half-spaces, separated by the plane $z = 0$, such that the velocity of a phonon of wave-vector $\mathbf{q}$ changes from $v + \Delta v/2$ to $v - \Delta v/2$ at the interface. Assume for simplicity that the temperature gradient is parallel to the z-direction. The tilt boundary causes a fraction of the incident energy to be back-scattered from mode $\mathbf{q}$ into $\mathbf{q}'$, such that $\omega = \omega'$ and the wave-vector components normal to the z-direction are also equal. Thus $\mathbf{q}' - \mathbf{q} = \mathbf{Q}$, where $\mathbf{Q}$ is parallel to z.

Let the instantaneous displacement due to mode $\mathbf{q}$ be $\mathbf{u}(\mathbf{r}) = V^{-1\,2} a(\mathbf{q}) \boldsymbol{\varepsilon} \exp(i\mathbf{q} \cdot \mathbf{r})$, where V is the volume of the crystal containing one tilt boundary. The relaxation rate due to back-scattering of mode $\mathbf{q}$ can be written in the form [4]

$$\frac{1}{\tau(\mathbf{q})} = \frac{V}{(2\pi)^3} \rho^{-2} \omega^{-2} \sum_{j'} \oint v_g^{-1} 2 \, |c_2(\mathbf{q}, \mathbf{q}')|^2 \, dS' \tag{5}$$

where ρ is the density, and the perturbation Hamiltonian linking $\mathbf{q}$ and $\mathbf{q}'$ is $c_2(\mathbf{q}, \mathbf{q}') \, a^*(\mathbf{q}') \, a(\mathbf{q})$, which in this problem has the form

$$c_2(q, q') = V^{-1} 2 \rho \omega^2 \int d\mathbf{r} \, \delta v(\mathbf{r}) \, e^{i\mathbf{Q} \cdot \mathbf{r}} (\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}') \tag{6}$$

Here v_g is the group velocity of mode q' and dS' is a surface element in $\mathbf{q}'$-space of the contour $\omega' = \omega$. Also j' refers to the three polarizations of the mode $\mathbf{q}'$, and $\boldsymbol{\varepsilon}$ and $\boldsymbol{\varepsilon}'$ are unit vectors in their polarization direction. We assume, for simplicity, that $\sum_{j'} (\boldsymbol{\varepsilon} \cdot \boldsymbol{\varepsilon}')^2 = 1$. Because of the conservation of the tangential wave vector, c_2 vanishes except for one normal mode, for which $dS' = (2\pi)^2/V^{2/3}$. If L_z is the dimension of the solid in the z-direction,

$$\int_0^{L_z/2} e^{iQz}\,dz = -(iQ)^{-1}\,[1 - e^{iQL_z/2}] \tag{7}$$

Since the phonon velocity in a crystal is anisotropic, $QL_z/2$ is not an integral multiple of 2π, the expression does not vanish, and the second term in the square bracket can be disregarded, being oscillatory in L_z. Therefore,

$$c_2 = 2(\Delta v/v)\,iQ^{-1}\rho\omega^2(\boldsymbol{\varepsilon}\cdot\boldsymbol{\varepsilon}') \tag{8}$$

Writing $q_z^2 = \omega^2/3v^2$, one finally obtains

$$\frac{1}{\tau} = \frac{2}{3}\,(v/L_z)(\Delta v/v)^2 \tag{9}$$

making the reflection probability R

$$R = \tfrac{1}{3}(\Delta v/v)^2 \tag{10}$$

Now $\Delta v/v$, averaged over all directions, is typically of magnitude 0.1 to 0.3, depending on the velocity anisotropy of a crystal, so that even for fairly anisotropic crystals the tilt boundary reflectivity R is around 0.03. Thus the orientational misfit at grain boundaries makes only a minor contribution to phonon scattering.

A similar result had been obtained by this author [6], treating the tilt boundary as an array of dislocations. The scattering thus derived was even lower by a factor of about 10, but mainly because that theory considered only screw dislocation scattering, underestimating scattering by a single dislocation by a similar factor.

3. SCATTERING BY INTERGRAIN REGIONS

Since disorientation between neighboring grains is not a significant source of scattering, one must look to the disorder of the region between the grains. This region may be regarded as a sheet, of thickness t and of large area, in which the phonon velocity v is changed by Δv. Since the intergrain region is less compact than the crystal, one expects Δv to be negative, so that $|\Delta v| < v$.

Using the result of Ref. 4, Eq. (19), the relaxation rate for normal incidence becomes

$$1/\tau = 8t^2/L_z(\Delta v/v)^2\,\omega^2/v \tag{11}$$

provided $\omega t/v$ is small. For a grain boundary of random orientation, $1/\tau$ is reduced by a factor 3. The reflection probability R becomes

$$R = \frac{2\omega^2 t^2}{3v^2} (\Delta v/v)^2 \tag{12}$$

As $\omega t/v$ increases, the two boundaries of the sheet loose scattering coherence and each scatters as a tilt boundary according to Eq. (10), so that

$$R \simeq \tfrac{2}{3}(\Delta v/v)^2 \tag{13}$$

where now Δv is no longer the change in v due to a change in orientation, but due to the changed composition (lack of compactness) in the intergranular region. Since $(\Delta v/v)$ is expected to be larger than for changes in orientation, the value of R is appropriately larger, and the boundary mean free path $L = L_z/2R$ is reduced. However, $|\Delta v/v|$ cannot exceed 1, so that

$$1/L < 3/4L_z \tag{14}$$

where L_z is the average distance between grain boundaries.

Thus the scattering by grain boundaries is independent of frequency above a critical frequency,

$$\omega_c \simeq v/t \tag{15}$$

where t is the thickness of the intergranular regions. At frequencies well below ω_c, scattering varies as ω^2.

An alternative derivation of Eq. (11), which is useful when phonon wavelength and thickness are comparable, can be obtained by treating the intergrain film as two boundaries of opposite velocity change Δv. Then c_2 of Eq. (8) becomes

$$c_2 = 2(\Delta v/v)\, i/Q[1 - e^{iQt}](\varepsilon \cdot \varepsilon') \tag{16}$$

since the second boundary is displaced by a distance t and has a relative phase factor $-\exp(iQt)$. Therefore,

$$|c_2|^2 = \tfrac{4}{3}(\Delta v/v)^2\, \rho\omega^2 Q^{-2} 2(1 - \cos Qt) \tag{17}$$

In the limit $Qt \ll 1$, $2Q^{-2}(1 - \cos Qt) = t^2$, so that Eq. (11) is obtained. More generally, for normal incidence, Eq. (17) becomes

$$1/\tau = 16L_z^{-1}(\Delta v/v)^2\, \omega^2 v^{-1} Q^{-2}(1 - \cos Qt) \tag{18}$$

For random directions, Eq. (13) is generalized to

$$R = \tfrac{4}{3} (\Delta v/v)^2 \omega^2 v^{-2} Q^{-2} (1 - \cos Qt) \tag{19}$$

where $Q = 2\omega/v$. When Qt is large, $R = (1/3)(\Delta v/v)^2$. This differs from Eq. (13) because there is coherence between the two boundaries. If Qt is large but t is not quite constant, which is probably a more realistic model, the two boundaries scatter incoherently and Eq. (13) is more appropriate.

4. GRAIN BOUNDARY RESISTANCE AT HIGH TEMPERATURES

Since Eq. (2) assumes grain boundary scattering independent of frequency, while the scattering by intergrain regions decreases with frequency at frequencies below ω_c, this equation overestimates $\delta\lambda_B$ when ω_c approaches ω_B. It is completely inapplicable if $\omega_c > \omega_B$, i.e., when the intergrain region is thin. For common grain sizes of order 1 μm, $\omega_B/\omega_D \sim 0.02$ to 0.04; with v typically around 3×10^5 cm $\cdot$ s^{-1}, $\omega_D \sim 3 \times 10^{13}$ s^{-1}, ω_c/ω_D will be less than 0.01 provided $t > 10^{-6}$ cm. For smaller grains, for which ω_B is larger, the condition $\omega_c < \omega_B$ is satisfied for even smaller t.

Nevertheless, it is still difficult in general to explain observed reductions of conductivity by grain boundaries. One should therefore remember that the intergrain regions are not likely to be of uniform thickness, since grains have irregular shapes. The factor $\omega^2 t^2/v^2$ in Eq. (12) arises from a distructive interference between two plane parallel surfaces. In reality this is an inadequate model, so that Eq. (12) underestimates scattering, since the destructive interference is not complete. The ω^2 dependence of Eq. (12) may hold fully only at very low frequencies, so that it would show up only in the conductivity at low temperatures. The results of Ref. 5 are thus of interest.

5. GRAIN BOUNDARY RESISTANCE AT LOW TEMPERATURES

At low temperatures Eq. (1) holds, provided the mean free path does not depend strongly on frequency. More generally

$$\lambda = \tfrac{1}{3} \int C(T, \omega)\, vl(\omega)\, d\omega \tag{19}$$

where $C(T, \omega) \propto \omega^2 x^2 e^x/(e^x - 1)^2$ is the spectral contribution to the specific heat and $x = \hbar\omega/kT$. Since $\omega^2\, d\omega \propto T^3 x^2\, dx$, the specific heat varies as T^3 at low temperatures. If $l(\omega) \propto \omega^{-n}$, $\lambda \propto T^{3-n}$, provided $n < 3$, as it must be to prevent a low-frequency divergence. For scattering by thin sheets, as discussed above, $n = 2$ and $\lambda \propto T$.

The polycrystalline diamond specimens of Ref. 5 were vapor-deposited films, about half a millimeter thick (L_{ext}), by either the hot filament (H) or the microwave (M) method. The grains were columnar across the films, with grain sizes from 25 to 50 and from 40 to 70 μm, respectively. Conductivities were measured along the films. At low temperatures where intrinsic processes are negligible, the average mean free path l is given by

$$1/l = (1/L_{\mathrm{ext}}) + (1/L_{\mathrm{grain}}) \tag{20}$$

so that l, increasing with decreasing T, saturates at L_{ext}.

The microwave-assisted CVD film (M) has a mean free path varying as T^{-1} from 1 to 20 K, the hot filament-grown film (H) varies as T^{-2} below 20 K but saturates near 3 K. To account for the $l \propto T^{-1}$ variation around 3 K for M, one requires $Qt \simeq \pi/2$ or $tq_z = \pi/4$, since scattering varies as $1 - \cos Qt$, where t is the intergrain film thickness. Now the dominant thermal frequency is $4kT/h$, so that $\omega_c = v/t = 12k/h$. This makes $\omega_c = \omega_D/200$. Since $\omega_D = (6\pi^2)^{1/3}\, v/a$, where a^3 is the atomic volume, $t \simeq 50$a or somewhat less than 100 Å. To fit the data for the M specimen, one needs the intergranular regions to be of that thickness. The T^{-2} regime is not attained at lower temperature, because of the finite thickness of the deposited films.

In the H specimen, where $l \propto T^{-2}$, film thickness saturation is reached at higher temperatures (ca. 8 K), but the intergranular regions seem to be thinner. Indeed, l is larger in the H specimen over a small temperature range below 20 K.

This interpretation is subject to uncertainties. It is, however, likely that similar studies of the thermal conductivity of polycrystalline materials at low temperatures may provide useful information on the nature of the region between the grains. Such information could perhaps be related to the strength and the effective moduli of polycrystalline aggregates.

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