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The thermal conductivity of CVD diamond films

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The thermal conductivity of chemical vapour deposition diamond films is controlled by the microstructure, impurity content and carbon double bonds in the films. In high conductivity films, dislocation scattering is dominant at low temperatures, while phonon–phonon scattering limits the conductivity at room temperature. In lower quality films, hydrogen and metal impurities as well as carbon double bonds constrain the conductivity up to room temperature. Significant anisotropies and gradients in the thermal conductivity exist in some films because of their micro structure.

1. Introduction

In the early 20th century, experimental measurements showed that diamond has a high thermal conductivity at both room and liquid nitrogen temperatures. At room temperature, diamond conducts heat better than silver which has the highest thermal conductivity of any metal. Recently, polycrystalline diamond films have been grown by a chemical vapour deposition (CVD) process, that have remarkably high thermal conductivities up to 85 % of those of single-crystal diamond (Morelli *et al.* 1991). Elementary theory shows that the thermal conductivity K of diamond is given by,

$$K = \frac{1}{3} C_v A V, \quad (1)$$

where C_v is the heat capacity of diamond at constant volume and A is the mean free path and V is the velocity of lattice vibrations (phonons) in diamond. The phonon velocity in diamond is higher than any other solid and generates the exceptional thermal conductivity of diamond. Equation (1) can be written in terms of the phonon scattering rate S which is the phonon velocity V divided by the phonon mean free path A to give

$$K = \frac{1}{3} C_v V^2 / S = \beta / S, \quad (2)$$

where β is a constant that is independent of the diamond type since both the heat capacity and sound velocity vary negligibly with the diamond micro structure or isotopic composition (Anthony *et al.* 1992; Morelli *et al.* 1991).

Phonons are scattered in diamond by many different obstacles including vacancies, isotopes, impurities, double and triple carbon bonds (perfect diamond contains only single carbon bonds) dislocations, precipitates, stacking faults, grain boundaries, surfaces and other phonons. These scattering mechanisms can be sorted out into scattering by points S_p , lines S_L , surfaces S_s and intrinsic phonon–phonon scattering S_{ph-ph} . If the presence of one type of scattering mechanism does not affect another, then the total scattering rate S is simply a sum of the scattering rates (Matthiessen's Rule).

$$S = S_p + S_L + S_s + S_{ph-ph}. \quad (3)$$

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2. Point scattering

Rayleigh scattering by isolated impurities, isotopes or point defects is generated by the difference in mass δM and modulus δG of the defect or impurity from the atoms of the host lattice (Ziman 1963).

$$S_p = \alpha q^4 (M/\rho)^2 [(\delta M/M)^2 + 3(\delta G/G)^2], \quad (4)$$

where α is a constant, q is the wave vector of the lattice wave or phonon ($q = 2\pi/\lambda$, where λ is the wavelength of the lattice wave) and ρ is the effective density of the impurity. Lattice distortions from either a contraction inwards in case of a small or an expansion outwards in the case of a large impurity surprisingly cause no scattering of lattice waves in an elastically isotropic solid (Ziman 1963). Diamond has an anisotropy factor of only 1.2 and approximates an elastically isotropic lattice (Kittel 1960).

Only boron, nitrogen and hydrogen dissolve in diamond (Field 1979). Hydrogen occupies a substitutional site in CVD diamond where it forms a sp^3 covalent bond with a neighbouring carbon atom (Baba 1991). Because diamond is a tetravalently bonded solid, the other three carbon atoms around this hydrogen have unsatisfied bonds and will form, respectively, three double bonds with neighbouring carbon atoms. These trigonally bonded carbons will try to force their bonds to be coplanar (Solomons 1980) and will change the local modulus around each hydrogen atom.

Substitutional hydrogen thus will scatter phonons and decrease the thermal conductivity as has been observed (Baba *et al.* 1991). The hydrogen content C_H of CVD diamond increases exponentially with increasing hydrocarbon concentration in the CVD gas mixture (Baba *et al.* 1991). The hydrocarbon concentration is a proxy for the diamond growth rate G because the diamond growth rate is a linear function of the hydrocarbon concentration in the gas. Hence,

$$C_H = C_{H0} \exp[\gamma G], \quad (5)$$

where C_{H0} is a constant and γ is a parameter dependent on atomic hydrogen concentration in the gas. Diamond grows by hydrocarbon radicals attaching to the diamond surface. Atomic hydrogen then abstracts away the hydrogen on the radical leaving behind pure diamond. If the diamond growth rate is high, not all of the hydrogen is removed and hydrogen becomes incorporated into the diamond. For processes such as the hot-filament CVD process, the atomic hydrogen concentration is low and γ is large. In high-temperature plasma processes, the concentration of atomic hydrogen is high and γ is small. Additions of oxygen can also lower γ .

Atomic hydrogen also stabilizes sp^3 bonds on the growth surface and prevents surface reconstruction. Low concentrations of atomic hydrogen and high growth rates may result in partial surface reconstruction and incorporation of the associated sp^2 bonds into the diamond bulk. sp^2 bonding decreases the thermal conductivity (Ono *et al.* 1986). The concentration C_{sp^2} of these sp^2 bonds will follow a relation similar to equation (5). The total scattering is

$$S_p \propto C_H + C_{sp^2} \propto \eta \exp[\gamma G], \quad (6)$$

where η is a constant. In diamond when sp^2 bonds and hydrogen are the dominant scatterers, equations (2) and (6) yield the thermal conductivity K as a function of the diamond growth rate G ,

$$K = \beta/S_p = (\beta/\eta) \exp[-\gamma G]. \quad (7)$$

Equations (2) and (5) predict a hyperbolic relation between the thermal conductivity and the hydrogen content of the diamond. This is the type of relationship observed by Baba *et al.* (1991). Equation (7) indicates that films with the highest thermal conductivity are grown at the lowest diamond growth rate G in agreement with experiment (Graebner *et al.* 1992*a*). In addition, films with the highest thermal conductivity are grown with the most atomic hydrogen or with oxygen additions, i.e. low γ .

The second most prevalent 'impurity' in CVD diamond is the isotope ^{13}C at a concentration of 1.1 % in a matrix of 98.9 % ^{12}C . The ^{13}C atom is slightly smaller than the ^{12}C atom because the heavier isotope has a lower zero-point energy (Holloway *et al.* 1991). As discussed above, this size difference will not scatter phonons. Since the moduli are equal, only the mass difference causes phonon scattering. Pomeranchuk (1942) first predicted that isotopically pure dielectrics would conduct heat better than the same substances containing their natural abundance of isotopes. Recently, isotopically pure single-crystal diamond was found to have a thermal conductivity 50 % higher than that of natural isotopic abundance diamond at room temperature (Anthony *et al.* 1990). This large enhancement has been theoretically explained in different ways (Berman *et al.* 1976; Nepsha *et al.* 1991; Bray *et al.* 1991; Hass *et al.* 1992; Berman 1992). The thermal conductivity of diamond has been measured across the entire ^{12}C – ^{13}C binary diagram (Anthony *et al.* 1992) and at high and low temperatures (Onn *et al.* 1992).

The first attempt to see an isotope effect in a CVD diamond film failed because other mechanisms dominated isotope scattering (Anthony *et al.* 1991). High-quality CVD diamond films with thermal conductivities of $17 \text{ W cm}^{-1} \text{ K}^{-1}$ (Morelli *et al.* 1991) would have a thermal conductivity of $25 \text{ W cm}^{-1} \text{ K}^{-1}$ if they were isotopically pure (Anthony *et al.* 1992).

Other common impurities in CVD diamond films are metals that are contaminants from hot filaments or electrodes. In addition to causing phonon scattering, these metals can also induce the formation of sp^2 bonds in diamond similar to the case of hydrogen. The rate of incorporation I_{M} of metal in diamond from a hot filament increases exponentially with the filament temperature (Hinneberg 1992),

$$I_{\text{M}} = I_0 \exp(-H/kT), \quad (8)$$

where I_0 and H are constants that depend on the filament. Because the concentration of carbon atoms is much greater than metal atoms, the concentration per unit volume C_{M} of metal in a diamond film growing at a rate of G is

$$C_{\text{M}} = I_{\text{M}}/G. \quad (9)$$

If both hydrogen and metal dominate phonon scattering in the growing diamond film, the scattering rate S_{p} is

$$S_{\text{p}} \propto C_{\text{H}} + \phi C_{\text{M}} = C_{\text{H}0} \exp[\gamma G] + \phi[I_{\text{M}}]/G, \quad (10)$$

where ϕ is the phonon scattering ratio of a heavy metal relative to a hydrogen atom. Equation (10) can be differentiated with respect to G to find a minimum in phonon scattering ratio as a function of the diamond growth rate. At high growth rates, hydrogen incorporation dominates and causes high rates of phonon scattering. At low diamond growth rates, metal incorporation prevails and also causes high rates of phonon scattering. At intermediate diamond growth rates, the scattering reaches a minimum and the thermal conductivity attains its maximum value.

Vacant sites also decrease the thermal conductivity because a vacancy has a large modulus change ($\delta G = G$) and a large mass change ($\delta M = M$). The equilibrium concentration of vacancies is small because of the high energy of formation of vacancies in diamond. Even so, in highly perfect isotopically pure diamonds, effects of vacancies on the thermal conductivity of diamonds may be seen (Onn *et al.* 1992). In CVD diamond processes, high concentrations of vacancies may be grown into the crystal because of lack of atomic mobility. High diamond growth rates may aggravate this situation.

3. Line scattering

Phonons can be scattered by dislocations by three mechanisms. First, the long-range asymmetric strain field around a dislocation scatters phonons. This effect dominates the second mechanism, namely, scattering by the core of the dislocation. The third scattering mechanism is a dynamic one in which mobile dislocations ‘flutter’ in the phonon breeze and is not important in diamond at room temperature. The phonon scattering S_{dis} for a dislocation density of N_d perpendicular to the phonon propagation direction is

$$S_{\text{dis}} \propto N_d \Gamma b^2 q, \quad (11)$$

where Γ is Gruneisen’s constant, b is the Burgess vector of the dislocation and q is the wave vector of the phonon (Ziman 1963).

Most dislocations in diamonds lie parallel to the crystal growth direction (Wilks *et al.* 1991). Hence, dislocations in CVD films are oriented in a direction perpendicular to the substrate. Dislocations parallel to the direction of phonon motion scatter phonons weakly while dislocations perpendicular to the direction of phonon motion scatter phonons strongly (Klemens 1958; Ziman 1963). Consequently, the thermal conductivity of CVD films parallel to the surface is less than the thermal conductivity perpendicular to the surface. This type of behaviour has been observed in various diamond films (Graebner *et al.* 1992a).

Competitive growth between adjacent grains develops a cone-like columnar grain structure perpendicular to the substrate in CVD diamond films (Wild *et al.* 1989, 1990). Certain favourably oriented grains dominate and grow larger so that the average grain size increases monotonically from the substrate to the growth side of the film. Dislocations within each grain fan out as the grains grow in cross sectional area (Wilks *et al.* 1991) so that the dislocation density N_d decreases as the inverse square of the distance Z from the substrate side of the film,

$$N_d = N_0/Z^2, \quad (12)$$

where N_0 is the dislocation density near the substrate surface. A second scattering mechanism will eventually dominate when the dislocation density falls below a critical value. Addition of this second phonon scattering mechanism and combination of equations (2), (11) and (12) show that the thermal conductivity $K(Z)$ in the film increases from the substrate to the growth surface where it approaches a constant value as

$$K(Z) \propto (C_1 Z^2)/(Z^2 + C_2), \quad (13)$$

where C_1 and C_2 are constants. This qualitative type of behaviour has been observed by Graebner *et al.* (1992b) in some CVD films.

4. Surface scattering

If CVD films are extremely thin or at low temperatures, phonon scattering by external surfaces may affect the thermal conductivity of the films by effectively limiting the mean free path λ to the film thickness Z_0 . Substitution into equation (1) gives (Klemens 1958):

$$K = \frac{1}{3} C_v V Z_0. \quad (14)$$

Almost all CVD films are polycrystalline films with a cone-like columnar structure with the grain size increasing from the substrate to the growth surface. The phonon scattering power of simple grain boundaries in diamonds should not be large because of the destructive interference of long range strain fields by the multiple dislocations at boundaries. Scattering comes only from dislocation cores which are ineffective scatterers of the type of long wavelength (1500 atom spacings) phonons that are dominant in diamond at room temperature. Consequently, phonons impinging on boundaries at normal incidence are only weakly scattered. Only phonons impinging on boundaries at glancing angles will be strongly scattered (Ziman 1963). However, such glancing collisions make up only a minority of the phonon–boundary collisions.

It is possible that the width of grain boundaries and thus the degree of boundary phonon scattering in CVD films exceeds the normal boundary parameters because of hydrogen segregation or dislocations clustering near grain boundaries. Then, the thermal conductivity for CVD diamond with a grain size of D would be (Klemens 1958):

$$K = \begin{cases} C_v V A_i, & A_i < D, \\ C_v V D, & A_i > D, \end{cases} \quad (15a)$$

$$(15b)$$

where A_i is the intrinsic mean free path of phonons in the diamond found within the CVD grain. For high quality diamond with a thermal conductivity of $22 \text{ W cm}^{-1} \text{ K}^{-1}$ at room temperature, $A_i = 0.2 \mu\text{m}$. Most CVD diamond films 300–500 μm thick have an average grain size $\langle D \rangle$ of at least 20 μm which is 100 times greater than the intrinsic mean free path of phonons A_i . This condition $A_i \ll D$ implies that grain boundaries in these CVD films should not cause anisotropies or gradients in thermal conductivities of the type observed by Graebner *et al.* (1992a–c).

For polycrystalline CVD films with a much smaller columnar grain size, gradients and anisotropy in the thermal conductivity are possible. In this case, a derivation similar to equation (13) shows that $K(Z)$ varies as,

$$K(Z) \propto (C_3 Z)/(Z + C_4), \quad A_i > D. \quad (16)$$

5. Temperature dependence

The temperature dependence $K(T)$ of the thermal conductivity of CVD diamond films (Morelli *et al.* 1988, 1991b; Anthony *et al.* 1991) is similar to previous work on diamond gem stones (Berman *et al.* 1976). Both the temperature dependence of the specific heat $C_v(T)$ and the dependence of the scattering factor S on the phonon wavevector $q(T)$ which varies with temperature affects $K(T)$. Up to room temperature, $C_v(T)$ follows a T^3 dependence (Kittel 1960).

The peak in the phonon energy content at a temperature T occurs at a phonon frequency equivalent to $4T$ (Klemens 1981). Scattering of these phonons has the most effect on the thermal conductivity. The wave vector q of these phonons is

$q(T) = 8\pi kT/(hV)$, where k is the Boltzmann and h is the Planck constant. For point, line and surface phonon scattering, $K(T)$ is from equations (2), (4), (11) and (15) (Klemens 1958):

$$K(T) \propto C_v(T)/S(T) \propto \begin{cases} T^3/T^4 = 1/T, & \text{point scattering,} \\ T^3/T^1 = T^2, & \text{line scattering,} \\ T^3/T^0 = T^3, & \text{surface scattering.} \end{cases} \quad \begin{matrix} (20a) \\ (20b) \\ (20c) \end{matrix}$$

Morelli *et al.* (1988, 1991*b*) and Anthony *et al.* (1991) have seen a $T^{1.9-2.2}$ dependence of the thermal conductivity at low temperatures suggesting that dislocations are the dominant scatterer.

For high conductivity films, non-conservative phonon–phonon scattering (Umklapp processes) dominate at temperatures above the conductivity maximum at 150–170 K. Umklapp processes that involve very energetic phonons degrade the thermal conductivity because they do not conserve momentum. The energy of Umklapp phonons is approximately $\frac{1}{2}k\Theta$, where Θ is the Debye temperature (1840 K). The number of these phonons is given by the Boltzmann factor, $\exp(-\Theta/2T)$. The scattering factor $S_{\text{ph-ph}}$ is proportional to the square of the number of these energetic phonons. Combination of equations (2) and (3) yields $K(T)$ of diamond above conductivity maximum:

$$K(T) \propto T^3 \exp(\Theta/T), \quad \text{phonon–phonon scattering.} \quad (21)$$

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