Thermal conductivity of diamond-like carbon films

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The authors report the thermal conductivity (K) of a variety of carbon films ranging from polymeric hydrogenated amorphous carbons (a-C:H) to tetrahedral amorphous carbon (ta-C). The measurements are performed using the 3ω method. They show that thermal conduction is governed by the amount and structural disorder of the sp^3 phase. If the sp^3 phase is amorphous, K scales linearly with the C–C sp^3 content, density, and elastic constants. Polymeric and graphitic films have the lowest K (0.2–0.3 W/mK), hydrogenated ta-C:H has $K \sim 1$ W/mK, and ta-C has the highest K (3.5 W/mK). If the sp^3 phase orders, even in small grains such as in micro- or nanodiamond, a strong K increase occurs for a given density, Young's modulus, and sp^3 content. © 2006 American Institute of Physics. [DOI: 10.1063/1.2362601]

Diamond-like carbon (DLC) is an amorphous carbon with a significant fraction of C–C sp^3 bonds. Hydrogen-free DLCs with the highest sp^3 content are called tetrahedral amorphous carbons (ta-C). Hydrogenated amorphous carbons (a-C:H) can be classified into four classes:[1] (i) polymer-like a-C:H (PLCH), with ~35–60 at. % H and up to 70% sp^3 bonds; (ii) diamond-like a-C:H (DLCH), with ~20–35% H and sp^3 content between 20% and 60%; (iii) hydrogenated tetrahedral amorphous carbon (ta-C:H), with ~70% sp^3 and ~25–30 at. % H (iv) graphitelike a-C:H (GLCH), with less than 20% sp^3.

Diamond-like carbon is very promising as a protective coating and for microelectromechanical systems.[2,3] The thermal properties and, in particular, the thermal conductivity (K) of DLCs are very important for thermal engineering of microdevices.[2–6] K for different forms of carbon materials, ranging from graphite and diamond to nanocrystalline graphite and nanodiamond (nD), has been reported in literature.[7–11] There are some reports of K in amorphous and diamond-like carbons, but K was estimated with different techniques, and not for a comprehensive set of samples. K of some ta-C, a-C:H and amorphous carbon nitride (a-C:N) was measured by photothermal mirage effect[12–15] and 3ω.[16,17]

Here we measure K for a comprehensive set of carbon films ranging from a-C:H to ta-C:H to ta-C (thickness range: 18.5–100 nm). All our films are directly characterized in terms of density (ρ), Young's modulus (E), and H content, and their structure is further assessed by multiwavelength Raman spectroscopy. All K measurements are performed using the same technique (3ω). We find that K is well described by the evolution of the Raman fit parameters. This allows us to present a general relation between microstructure and thermal properties for every amorphous and diamond-like carbon.

The films were prepared with different deposition systems: PLCH and DLCH were deposited by plasma enhanced chemical vapor deposition;[1] ta-C:H by electron cyclotron wave resonance;[18] GLCH by magnetron sputtering in an Ar/H_2 atmosphere;[1] one ta-C by single bend filtered cathodic vacuum arc (FCVA),[19] another by S-bend FCVA,[20] and one by filtered high current pulsed arc (HCA).[21] All films were deposited on silicon. ρ and H content were determined from nuclear reaction analysis and/or from x-ray reflectivity;[1,22] and E by laser induced acoustic waves and/or by surface Brillouin scattering.[22–24] Visible and UV Raman measurements were performed using Renishaw Raman spectrometers.[1,25] Table I summarizes the details of the films.

K is measured with a home-built 3ω setup. The 3ω technique was initially established for bulk materials[26] and was later extended to thin films and nanostructures.[10,27,28] The measurements are performed by placing a thin conductor directly on the surface of the material of interest. An alternating current at frequency 1ω heats the conductor. This produces a resistance change at frequency 3ω. The amplitude of the temperature oscillation depends on the power per unit length, frequency (f), and physical properties of the material, such as ρ, K, and heat capacity C_p.[29] We use Cr (10 nm)/Au (100 nm) heater-thermometer sensors 5 and 10 μm wide. These are patterned on the top of each film by photolithography. No additional insulating film is deposited between the film and the sensor or under the film, in contrast to previous 3ω DLC studies,[16] in order to improve the accuracy of our measurement. In the case of thin films on a substrate, such as those measured here, the temperature drop

TABLE I. Properties of measured carbon films.

Film	Density (g/cm^3)	H (at. %)	E (GPa)	K (W/mK) at RT	θ_D (K)
PLCH	1.55	36	16	0.277	310
DLCH	1.76	28	95	0.69	584
DLCH	1.86	30	150	0.566	550
GLCH	1.8	18	⋯	0.374	412
GLCH	2	24	⋯	0.248	379
ta-C:H	2.2	30	250	0.77	⋯
ta-C:H	2.4	28	300	1.3	⋯
ta-C HCA	2.59	0	396.8	1.41	1217
ta-C single	3	0	700	2.7	⋯
ta-C Sbend	3	0	700	2.2	⋯
ta-C Sbend	3.26	0	760	3.5	⋯

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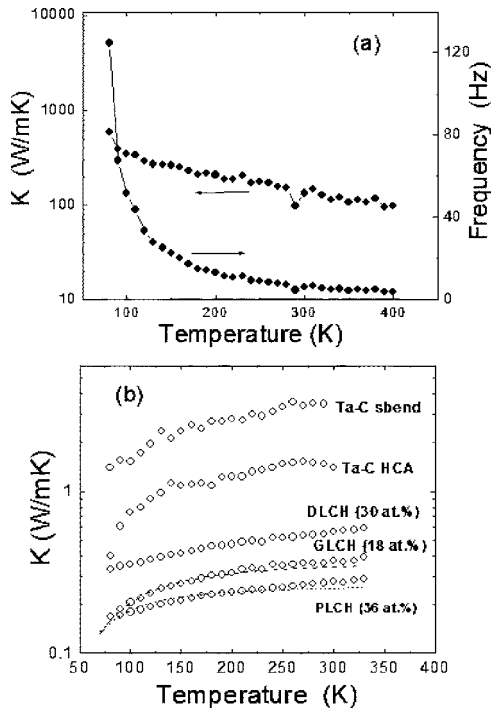
FIG. 1. (a) Measured K of Si substrate from 80 to 400 K (left axis) and the corresponding frequencies at which the thermal diffusion length reaches the substrate bottom. (b) Measured K vs T for representative samples.

FIG. 2. (a) K at RT as a function of ρ. (b) K as a function of FWHM(G).

over the film needs to be separated from that over the Si substrate. This can be done by ensuring that the modulated thermal diffusion length $\Lambda_{th} \approx [K/(2\pi f C_p)]^{1/2}$ is much smaller than the substrate thickness. We check this by determining K for the Si substrate [Fig. 1(a), left axis]. The results are in good agreement with the tabulated Si values [K at 298 K is 142.2 W/mK (Ref. 30)]. The corresponding frequencies at which Λ_{th} reaches the bottom of the substrate are indicated on the right axis of the same plot. This sets the lower frequency for the analysis of our carbon films on Si for a given temperature (T). The frequency range is thus between 500 Hz and 2 kHz, depending on thickness and T.

Figure 1(b) shows the measured K temperature dependence for different types of DLCs: one PLCH, one GLCH, one DLCH, one ta-C:H, and two ta-C's of different densities. K increases with T, which is typical of amorphous materials.[29] Since the film thickness is small, the contribution of the Kapitza thermal boundary resistance[31] to the overall thermal resistance of the structure could be substantial.

Figure 1(b) also shows (lines) the result of the K calculation for two samples using the "minimum thermal conductivity" approach. It is based on the assumption of random walks between localized excitations in an amorphous material with K given as[29]

$$K = (\pi/6)^{1/3} k_B (n_A)^{2/3} \sum_i v_i (T/\theta_i)^2 \int_0^{\theta_i/T} x^3 e^x (e^x - 1)^{-2} dx. \quad (1)$$

Here the sum is over three phonon polarization branches ($i=L$ for longitudinal and $i=T_1$ and $i=T_2$ for transverse), k_B is the Boltzmann constant, $n_A = N_A \rho / M$ is the number of atoms per unit volume (N_A is Avogadro's number and M is the atomic mass), v_i is the phonon group velocity of the ith branch, and θ_i is the cutoff temperature of ith branch. Distinguishing separate θ_i for the polarization branches is not very well justified for our disordered material system. How-
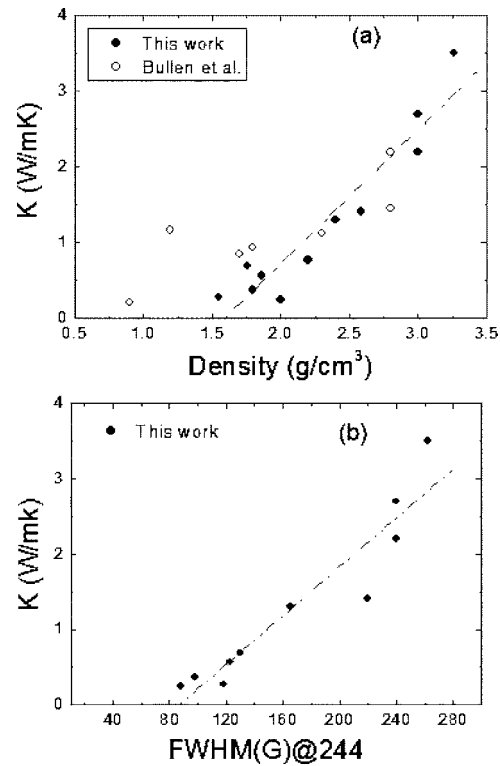
ever, since E and Poisson's ratio ν are known,[23] in our calculations we consider separate phonon group velocities given by $v_L = (E/\rho)^{1/2}$ and $(v_T/v_L)^2 = 2(1-\nu)/(1-2\nu)$. $\nu = 0.12$ for ta-C and ~0.3 for a-C:H.[23] As reported in Ref. 32 there is no well-defined procedure for computing the Debye temperature (θ_D) in disordered solids. The heterogeneous nature of the material, with sp^2 clusters and sp^3 regions, makes it even more challenging to define (θ_D)theoretically. Thus, we consider θ_D to be an adjustable parameter and use it instead of separate θ_i.

The calculated dependence, shown in Fig. 1(b), reproduces the measured T dependence of K very well. The extracted values for the effective θ_D are between 310 and 1300 K, depending on the film structure (Table I). In particular, θ_D scales with ρ. Indeed, a linear extrapolation gives $\theta_D \sim 1900$ K for $\rho = 3.5$ g/cm^3, very close to that of diamond (~1880 K).[33] For comparison, the planar θ_D in graphite is ~2280 K,[7] while the perpendicular θ_D is ~760 K;[7] the extrapolated θ_D of SiO$_2$ is 342 K,[32] while other amorphous solids, such as B$_2$O$_3$ and CuZr, have θ_D as low as 150 K.[32] Since our θ_D extraction is based on fitting Eq. (1) the method has limitations and cannot be extended to ta-C films with high E and ρ.

Figure 2(a) plots K measured at room temperature (RT), as a function of ρ. 3ω data from literature are also included.[16] Figure 2(a) shows that K scales linearly with ρ and that the H content *per se* plays a minor role. For $\rho > 1.6$ g/cm^3, a linear fit to our data gives

$$K[\text{W/mK}] = 1.77\rho[\text{g/cm}^3] - 2.82. \quad (2)$$

Since in amorphous and diamond-like carbons ρ scales with C–C sp^3 content,[22] Fig. 2(a) implies that K scales in the same way. Indeed, amongst hydrogenated carbon films, ta-C:H has the highest K because it has the highest C–C sp^3 content. The highest thermal conductivity amongst all DLCs is
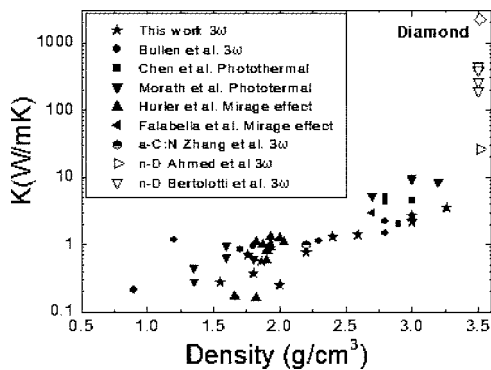
FIG. 3. *K* at RT measured by 3ω here and other literature data as a function of ρ for a variety of DLC, nD and diamond.

reached for ta-C ($\sim$3.5 W/mK). Raman spectroscopy further confirms the correlation between film structure and thermal properties. Figure 2(b) plots the *G* peak full width at half maximum measured at 244 nm excitation [FWHM(*G*) @244] as a function of *K*. Since FWHM(*G*) is proportional to the structural disorder, and this increases for increasing sp^3 content for as deposited samples,[1,25] Fig. 2(b) confirms that *K* is linked to the sp^3 C–C content for as-deposited samples. We can also get a simple relation between FWHM(*G*) @244 nm and *K* for FWHM(*G*) @244 $>$80 cm^{-1},

$$K[\text{W/mK}] = -1.397 + 0.0168 \text{FWHM}(G) \ @ 244[\text{cm}^{-1}]. \tag{3}$$

Note that if we just scale *K* of *a*-Si (Ref. 34) to that of an ideal fully sp^3 bonded amorphous carbon film[23,35] we would get $K \sim 3$ W/mK. On the other hand, the minimum thermal conductivity[29] of such an ideal material can be estimated to be $\sim$1.5 W/mK. These simple estimates are in excellent agreement with our measured *K* for the highest sp^3 ta-C, which sets the upper limit for *K*. On the other hand, some literature reports show much higher values. Reference 13 has *K* for ta-C of 4–5 W/mK and Ref. 12 between 8 and 10 W/mK. They both used photothermal techniques, which require assumptions on the heat capacitance. We thus believe these values to be overestimated.

Note as well that *K* of diamond[9] is much higher than the maximum extrapolated for a fully amorphous sp^3 material. This means that *K* is also extremely sensitive to the *ordering* of the sp^3 phase, unlike any of the other common structural parameters used to characterize carbon films (ρ, E, etc.), which depend on the *amount* of sp^3, but not in any significant way on this being amorphous or (nano)-crystalline. This is demonstrated in Fig. 3, which plots *K* as a function of ρ for all DLCs reported in literature and for diamond and nanodiamond. In some cases ρ was not reported in previous studies, only H, sp^3 content, or optical gap. In these cases we estimated ρ by using the general relations of Refs. 1 and 22. Figure 3 shows that *K* of nD, which has sp^3 content and E just marginally higher than ta-C, is significantly bigger than that of ta-C. This is due to the presence of a crystalline, rather than amorphous, sp^3 phase. Similarly, for very low sp^2 contents, the ordering of the sp^2 phase in graphitic regions would significantly increase *K*.[7]

In conclusion, we have shown that the thermal conduction in amorphous and diamond-like carbons is related to the amount and structural disorder of the sp^3 phase. If the sp^3 phase is amorphous, *K* scales linearly with C–C sp^3 content, density, and elastic constants. In this case, FWHM(*G*) can be used as a simple measure of *K*. If the sp^3 phase orders, even in small grains such as in nD, a strong *K* increase occurs for a given density, Young's modulus, and sp^3 content.

[1]C. Casiraghi, A. C. Ferrari, and J. Robertson, Phys. Rev. B **72**, 085401 (2005).
[2]J. P. Sulllivan, T. A. Friedmann, and K. Hjort, MRS Bull. **26**, 309 (2001).
[3]J. K. Luo, A. J. Flewitt, S. M. Spearing, N. A. Fleck, and W. I. Milne, Appl. Phys. Lett. **85**, 5748 (2004).
[4]E. Marotta, N. Bakhru, A. Grill, V. Patel, and B. Meyerson, Thin Solid Films **206**, 188 (1991).
[5]C. D. Wright, M. Armand, and M. M. Aziz, IEEE Trans. Nanotechnol. **5**, 50 (2006).
[6]D. A. Czaplewski, J. P. Sullivan, T. A. Friedmann, and J. R. Wendt, Diamond Relat. Mater. **15**, 309 (2006).
[7]B. T. Kelly, *Physics of Graphite* (Applied Science, London, 1981).
[8]S. Mizushima, Phys. Rev. **86**, 1040 (1952).
[9]D. T. Morelli, T. A. Perry, J. W. Vandersande, and C. Uher, Phys. Rev. B **48**, 3037 (1993).
[10]S. Ahmed, R. Liske, T. Wunderer, M. Leonhardt, R. Ziervogel, C. Fansler, T. Grotjohn, J. Asmussen, and T. Schuelke, Diamond Relat. Mater. **15**, 389 (2006).
[11]M. Bertolotti, G. L. Liakhou, A. Ferrari, V. G. Ralchenko, A. A. Smolin, E. Obraztsova, K. G. Korotoushenko, S. M. Pimenov, and V. I. Konov, J. Appl. Phys. **75**, 7795 (1994).
[12]C. J. Morath, H. J. Maris, J. J. Cuomo, D. L. Pappas, A. Grill, V. V. Patel, J. P. Doyle, and K. L. Saenger, J. Appl. Phys. **76**, 2636 (1994).
[13]G. Chen, P. Hui, and S. Xu, Thin Solid Films **366**, 95 (2000).
[14]W. Hurler, M. Pietralla, and A. Hammerschmidt, Diamond Relat. Mater. **4**, 954 (1995).
[15]S. Falabella, D. B. Boercker, and D. M. Sanders, Thin Solid Films **236**, 82 (1993).
[16]A. J. Bullen, K. E. O'Hara, D. G. Cahill, O. Monteiro, and A. von Keudell, J. Appl. Phys. **88**, 6317 (2000).
[17]Z. J. Zhang, S. Fan, J. Huang, and C. M. Lieber, Appl. Phys. Lett. **68**, 2639 (1996).
[18]N. A. Morrison, S. E. Rodil, A. C. Ferrari, J. Robertson, and W. I. Milne, Thin Solid Films **337**, 71 (1999).
[19]B. Kleinsorge, A. C. Ferrari, J. Robertson, and W. I. Milne, J. Appl. Phys. **88**, 1149 (2000).
[20]K. B. K. Teo, S. E. Rodil, J. T. H. Tsai, A. C. Ferrari, J. Robertson, and W. I. Milne, J. Appl. Phys. **89**, 3706 (2001).
[21]T. Witke and P. Siemroth, IEEE Trans. Plasma Sci. **27**, 1039 (1999).
[22]A. C. Ferrari, A. Libassi, B. K. Tanner, V. Stolojan, J. Yuan, L. M. Brown, S. E. Rodil, B. Kleinsorge, and J. Robertson, Phys. Rev. B **62**, 11089 (2000).
[23]A. C. Ferrari, J. Robertson, M. G. Beghi, C. E. Bottani, R. Ferulano, and R. Pastorelli, Appl. Phys. Lett. **75**, 1893 (1999).
[24]D. Schneider, P. Siemroth, T. Schülke, J. Berthold, B. Schultrich, H. Schneider, R. Ohr, B. Petereit, and H. Hillgers, Surf. Coat. Technol. **153**, 252 (2002).
[25]A. C. Ferrari and J. Robertson, Phys. Rev. B **61**, 14095 (2000); **64**, 075414 (2001).
[26]D. G. Cahill, Rev. Sci. Instrum. **61**, 802 (1990).
[27]W. L. Liu and A. A. Balandin, Appl. Phys. Lett. **85**, 5230 (2004); J. Appl. Phys. **97**, 073710 (2005).
[28]M. Shamsa, W. L. Liu, A. A. Balandin, and J. L. Liu, Appl. Phys. Lett. **87**, 202105 (2005).
[29]D. G. Cahill and R. O. Pohl, Solid State Commun. **70**, 927 (1989).
[30]*The TPRC Data Series*, Thermophysical Properties of Matter Vol. 1, edited by Y. S. Touloukion (Plenum, New York, 1970).
[31]E. T. Swartz and R. O. Pohl, Rev. Mod. Phys. **61**, 605 (1989).
[32]J. J. Freeman and A. C. Anderson, Phys. Rev. B **34**, 5684 (1986).
[33]A. C. Victor, J. Chem. Phys. **36**, 1903 (1962).
[34]J. L. Feldman and M. D. Kluge, Phys. Rev. B **48**, 12589 (1993).
[35]P. C. Kelires, Phys. Rev. Lett. **73**, 2460 (1994).