Thermal conductivity of ultrathin tetrahedral amorphous carbon films

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We investigate the thermal conductivity of ultrathin tetrahedral amorphous carbon (*ta*-C) films on silicon, down to subnanometer thickness. For films with an initial sp^3 content of 60%, the thermal conductivity reduces from 1.42 to 0.09 W/mK near room temperature as the thickness decreases from 18.5 to $\sim$1 nm. The variation in *ta*-C film thickness is accompanied by changes in Young's modulus, density, and sp^3 content. The thermal resistance of the finite-thickness interface layer, which forms between *ta*-C and silicon, is $\sim 10^{-8}$ m^2 K/W near room temperature, thus producing a noticeable effect on thermal transport in ultrathin *ta*-C films. © *2008 American Institute of Physics.*
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The problems of size-scaling limit and heat dissipation, which are currently challenging the future progress of conventional Si complementary metal-oxide-semiconductor technology, stimulate the search for new materials.[1] Carbon has a variety of allotropes, including graphene, carbon nanotubes, diamond, and diamondlike carbons (DLC). These have very different properties, depending on structure and hybridization. For example, diamond has thermal conductivity above 2000 W/mK at room temperature[2] (RT), while hydrogenated DLC has less than 1 W/mK.[3] Carbon films have been recently used in the deep-trench dynamic random access memory designed for the 40 nm technology node.[4] Hydrogen-free DLC with the highest density and sp^3 content, tetrahedral amorphous carbon (*ta*-C), is ideal as protective coating for ultrahigh density data storage[5,6] and as low stiction material for microelectromechanical systems.[7] The data storage technology requires the use of ultrathin films with thickness well below 3 nm.[5,6] Understanding thermal transport in thin *ta*-C films is thus essential for material processing and applications.

We previously investigated the relation between thermal conduction in DLC and its structure.[3] We have shown that its thermal conductivity, *K*, is related to the ordering and amount of the sp^3 phase. When the sp^3 phase is amorphous, *K* scales with the sp^3 content, density, and elastic constants; *ta*-C films with $\sim$90% sp^3 have the highest *K* ($\sim$3 W/mK) among DLCs.[3] The incorporation of H increases the topological disorder while not strongly affecting the structural disorder. Thus, hydrogenated-amorphous carbons show thermal conductivity below 1 W/mK. We derived an empirical relation between thermal conductivity and density, ρ (for $\rho > 1.6$ g/cm^3)[3]: K_C(W/mK) $= 1.77\rho$[g/cm^3] $- 2.82$. For *ta*-C the relation between density and Young's modulus, *E*, is given by[5,8]: ρ(g/cm^3) $= 1.37 + [E$(GPa)$]^{2/3}/44.65$. Combining these two equations, we get an empirical relation between the thermal conductivity and Young's modulus for thick *ta*-C samples:

$$K_C(\text{W/mK}) = 0.04[E(\text{GPa})]^{2/3} - 0.4. \qquad (1)$$

Previous studies focused on *ta*-C films at least 20 nm thick[3,9–11] and neglected the contribution of the thermal boundary resistance (TBR) to the overall thermal resistance.[3] However, ultrathin films with thickness in the nanometer range are particularly interesting. Apart from practical applications, at this length scale one can expect "size effects" on thermal transport as observed in regular crystalline solids.[12,13] These are, e.g., phonon-boundary scattering or phonon spectrum modifications. To the best of our knowledge, they have not been studied yet in nanoscale films made of disordered, or partially disordered, materials such as DLCs. By measuring a set of DLC films with thickness down to subnanometer, and comparing their *K* trend with that expected for bulk samples, we can probe the size effects. This allows us to clarify the role of the finite-width interface layer between *ta*-C and Si[8,14] on the thermal resistance of *ta*-C films.

Our films are produced by a high current vacuum arc (HCA) with a 120 macroparticle filter.[15] They are deposited on Si substrates at room temperature. The thickness is between 0.9 and 20 nm, as determined by x-ray reflectivity (XRR).[16] The Si substrate cleaning and predeposition preparation are discussed in detail elsewhere.[5,6,8,16–20] The Young's modulus is derived by a combination of surface Brillouin scattering and laser induced surface acoustic waves.[17–19] The evolution of the structure with decreasing thickness is further investigated by Raman spectroscopy.[20] The thickest film measured here (20 nm) has a Young's modulus of $\sim$400 GPa, and density of $\sim$2.6 g/cm^3.[5,16,20] This corresponds to a sp^3 content of $\sim$60%. A structural change happens below 10 nm: the sp^3 content, density, and Young's modulus decrease. Indeed a $\sim$1 nm thick HCA *ta*-C film has Young's modulus of $\sim$50 GPa.[16,18,20] This trend can be understood if we consider the cross sectional structure of *ta*-C films.[5,8] The top layer is low density and more graphitic. Underneath there is the bulk tetrahedral matrix, which is sp^3 rich. Between the "bulk" layer and the substrate an interface layer is formed. Since the deposition conditions are kept con-

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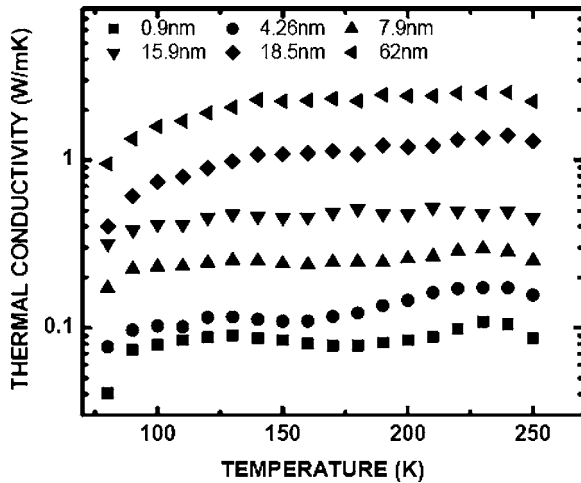d)Current address: Physics Department, Free University, D-14195 Berlin, Germany.

FIG. 1. Measured thermal conductivity as a function of temperature in a set of ultrathin *ta*-C films with thickness down to ~1 nm. For comparison the data for a 62 nm film, from Ref. 3, is also shown.
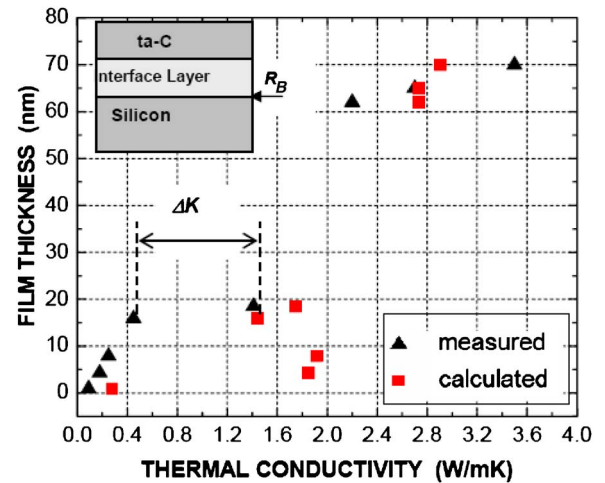

FIG. 2. (Color online) Correlation of thermal conductivity with film thickness. The triangles are the measured values of thermal conductivity, K_M, while the red rectangles are the calculated values of the thermal conductivity, K_C, from Eq. (1), which the films would have due to the material parameters variation even in the absence of any size effects. The inset shows the a schematic film cross section. The uncertainty in the thickness measurements is ~0.1 nm, while in E is ± 50 GPa; the standard error in thermal conductivity measurements is estimated to be around 5%–10%.

stant for all films, the interface and surface layers are roughly independent from the overall thickness.[8] Thus, the thickness reduction results in a reduction in the bulk, mainly sp^3, phase.[5,14,20] When the thickness of the bulk layer becomes comparable or smaller than that of the surface or interface layers, a strong decrease in the Young's modulus is observed.[5,20] Thus, since K scales with sp^3 content and density, we expect K to decrease with thickness for ultrathin films. However, the TBR, associated with the interface layer between film and silicon substrate, induces an even faster K decrease, as we show here. All examined samples were stable in air and very robust; their properties have not changed over years of examinations.[3,5,6,8,16–20]

The thermal conductivity is measured using a home-built 3ω setup following the methodology developed by Cahill.[21] This technique has been previously successfully applied to various bulk, thin films, and nanostructured materials.[3,9,10,21–23] It is based on driving an ac current through a metal heater line at frequency 1ω, which results in heating, measurable as a resistance change at the frequency of 3ω.[21] Cr (100 Å)/Au (1000 Å) heater-thermometer sensors with widths of 5 and 10 μm are patterned on the top surface of each film by photolithography and fabricated by e-beam evaporation followed by lift-off. The 3ω measurements are conducted inside a vacuum cryostat in the 80–250 K range.

Figure 1 shows the measured K as a function of temperature for *ta*-C films with different thicknesses. K weakly increases as T varies from 80 to ~150 K. For higher T, K is nearly constant or increases very slowly. Such temperature dependence is typical of amorphous and disordered materials.[22] The measured K near RT for the thickest 20 nm *ta*-C is ~1.4 W/mK. The thermal conductivity for *ta*-C has been reported to be up to ~3 W/mK.[3] However the *ta*-C films produced by HCA for hard disk coating have a smaller sp^3 content and density, compared with those by *S*-bend cathodic vacuum arc.[5,16,20,24] The thickest *ta*-C measured here has a density of ~2.6 g/cm^3.[5,16,20] This would correspond from Eq. (1) to K~1.8 W/mK, which is in excellent agreement with our measurements.

One can also see from Fig. 1 that K decreases with thickness; the thinnest film shows K ~0.09 W/mK near RT. This

is an extremely small value for any carbon-based material, which suggests a possible application as a thermal insulating coating. The best thermal insulators, such as foam glass and plastic, have a near-RT K~0.045 W/mK and 0.03 W/mK, while that of air is 0.025 W/mK.[25] If the film structure would not change with thickness, then the observed K dependence on thickness would be entirely assigned to size effects, such as acoustic phonon-rough boundary scattering.[26] Indeed, in crystalline materials, the thermal conductivity limited by phonon-boundary scattering can be approximated as $K \approx (1/3)C_V V_G L$ (here C_V is the heat capacitance per unit volume, V_G is the average phonon group velocity, and L is the film thickness). This approximation is obtained from the expression $K \approx (1/3)C_V V_G \Lambda$, by replacing the phonon mean free path (MFP) Λ with the film thickness, when L becomes smaller than Λ.[2,12] However, since the properties of *ta*-C vary with thickness, we need to separate the K dependence on material structure from size effects.

In Fig. 2 we plot the thermal conductivity as a function of thickness. The triangles mark the experimental values of K (=K_M) measured directly in this work together with those for thicker *S*-Bend bulk *ta*-C films from Ref. 3. The rectangles represent the expected variation of thermal conductivity with thickness, as predicted from Eq. (1). This calculated value, denoted as K_C, does not include any nanoscale size effects. In this sense it can be viewed as the bulk reference value for a given *ta*-C film. Figure 2 shows that, apart from the thinnest film, the measured K_M for the ultrathin films is much smaller than what we would expect from Eq. (1). Another very important observation is that the difference ΔK =K_C-K_M does not manifest any apparent scaling with the thickness. It changes from sample to sample.

The large value of ΔK and the absence of scaling with L can be explained by assuming that ΔK does not result from acoustic phonon-rough boundary scattering,[2,12,26] or acoustic phonon confinement,[13] but rather from the variation of TBR values among the measured samples. Indeed, if ΔK were mostly due to phonon-rough boundary scattering, it would be

TABLE I. Thermal boundary resistance of *ta*-C films on silicon.

Thickness L (nm)	0.9	4.26	7.9	15.9	18.5	62.0
E (GPa)	70	427	445	316	397	760
R_B^*, $\times 10^{-8}$(cm^2 K/W)	1.0	2.2	2.8	2.4	0.4	0.6

increasing with decreasing *ta*-C thickness, i.e., $\Delta K \sim C_V V_G(\Lambda\text{-}L)$. In this approach, if one neglects TBR, ΔK should approach zero in "thick" films, when MFP is no longer limited by the thickness. Thus, the apparent similarity of the thickness scaling of the measured thermal conductivity of the ultrathin *ta*-Cs (seen in Fig. 1) with that observed in crystalline thin films[13,26] is misleading. On the contrary, the thickness dependence of thermal conductivity in ultrathin *ta*-C films is a result of the material parameters dependence on L, and the variation in the TBR value.

The large value of ΔK and its variation over a substantial range can be explained by the existence of the well known interface layer of finite thickness L_I (0.5 nm $\leq L_I \leq$ 1 nm) between the bulk of *ta*-C film and Si substrate.[8,14] This carbidic interface layer is different in its microstructure from the rest of the *ta*-C film and presents a mixture of Si–C bonds, oxygen, and $c-c$ sp^2 bonds.[8,14] Thus, in addition to the standard TBR, R_B, which appears due to the phonon density of states (PDOS) mismatch between two materials, there will be an addition thermal resistance R_I ($=L_I/K_I$) due to this interface layer. The total TBR can be written as $R_B^*=R_B+L_I/K_I$ with R_B varying over a wide range due to PDOS mismatch and possible boundary defects. In the examined set of samples, we have one with thickness $L_I=0.9$ nm. Owing to its subnanometer thickness, we assume it to consist entirely of the interface layer as defined in Refs. 8 and 14. The "lumped" TBR of this layer is $R_B^*=L/K_M \approx 10^{-8}$ m^2 K/W ($L=L_I$). The variation in L_I may give rise to additional changes in R_B^*, leading to a wider ΔK range. Table I summarizes R_B^* for *ta*-C films on Si using the expression $L/K_M=(L-L_I)/K_C+R_B^*$. The determined R_B^* values are of the same order of magnitude as those for the interface between crystalline interfaces.[2,26]

Unlike most other materials, ultrathin *ta*-C films are characterized by atomic scale smoothness.[27] It is interesting to estimate how the extracted value of TBR compares with the thermal Kapitza resistance, R_K,[28] at the single *ta*-C/Si interface. The Kapitza resistance appears even if the interface is atomically smooth due to the mismatch of the acoustic properties of the adjacent materials.[29] Its value can be estimated from the PDOS difference in the framework of the well-known diffuse mismatch model, which expresses R_K though the sound velocities in the adjacent materials.[29,30] In our calculations we use the longitudinal sound velocity $c_L=8430$ m/s and transverse sound velocity $c_T=5840$ m/s for Si[13], and 5200 and 8500 m/s for the 0.9 nm film, respectively.[18] The calculated near-RT Kapitza resistance is $R_K \approx 0.14 \times 10^{-8}$ m^2 K/W. This is much smaller than the extracted TBR at the *ta*-C/Si interface, as expected. An important observation for coating and thermal management applications of ultrathin *ta*-C is that for 1 nm films the thermal resistance due to the film itself, $L/K \approx 10^{-8}$ m^2/KW, is comparable or smaller than the TBR, and equal to the thermal resistance of the interface layer R_I. This means that the thermal resistance of the interface, which is often neglected in thermal balance calculations, has to be carefully taken into account when dealing with such nanoscale coatings.

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