

Thermal expansion coefficient of hydrogenated amorphous carbon

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The coefficient of thermal expansion (CTE) of hydrogenated amorphous carbon (*a*-C:H) was investigated as a function of the concentration of *sp*² hybridization. The CTE, determined using the thermally induced bending technique, depends on the concentration of *sp*² bonded carbon, increasing to the value of graphite as the *sp*² concentration approaches 100%. By using a combination of the thermally induced bending technique and nanohardness measurements, we extract separately the Young's modulus and Poisson's ratio of the *a*-C:H films as function of the *sp*² concentration. © 2003 American Institute of Physics. [DOI: 10.1063/1.1619557]

In spite of a number of technological interests in amorphous carbon there are few reports on its coefficient of thermal expansion (CTE).¹⁻⁵ The main reason for the lack of data in the literature is the high stress of hard amorphous carbon films, which limits the film thickness to below the requirements for measuring the CTE (of the order of a micron). In this letter, we report the dependence of the coefficient of thermal expansion, Young's modulus, and the Poisson's ratio of hydrogenated amorphous carbon (*a*-C:H) as a function of the *sp*² concentration.

Films with different *sp*² concentrations were deposited at the cathode electrode of a glow discharge system by varying the bias voltage from -100 to -1200 V under conditions of room temperature and constant methane (CH₄) gas pressure of 1.0 Pa. The concentrations of the *sp*² bonds were determined by electron energy-loss spectroscopy (EELS) performed on a 100 kV VG scanning transmission electron microscope (STEM), fitted with a McMullan parallel EELS detection system. The *sp*² concentration was determined from the size of the π^* peak in the carbon *K* edge (the *1s*-*2p* transition) which is normalized to the graphite equivalent.^{6,7} The hardness was obtained using a Berkovich diamond tip (NanoTest-100) at a depth of about 20% of the film deposited on silicon substrate, and the results were analyzed using the Oliver and Pharr method.⁸

Equation (1) describes the thermal dependence of the stress ($\Delta\sigma_{th}$) due to mismatch in the CTE of the film (α_f) and that of the substrate (α_s):⁹

$$\Delta\sigma_{th} = E_f / (1 - \nu_f) (\alpha_s - \alpha_f) \Delta T, \quad (1)$$

where *E* and ν are the Young's modulus and Poisson's ratio, respectively, and ΔT is the temperature interval. The subscripts "s" and "f" refer to substrate and film, respectively. The total stress, σ , is given by the modified Stoney equation^{9,10}

$$\sigma = [E_s / (1 - \nu_s)] t_f^2 / 6 f_f (1/R - 1/R_0), \quad (2)$$

where $1/R_0$ and $1/R$ are the curvature before and after the film deposition, respectively, and *t* stands for thickness. The three unknown parameters in Eq. (1) can be reduced to two by defining the biaxial modulus as $E_f / (1 - \nu_f)$; the coefficient of thermal expansion and the biaxial modulus can then be determined from the measured temperature dependence of the stress for the same film deposited onto at least two different substrates.¹¹ The slope $\Delta\sigma/\Delta T$ was measured during the cooling cycle, from 120 °C to room temperature, at a rate of about 1 °C/min. The inset in Fig. 1 displays the result of these measurements performed in one *a*-C:H films deposited on five substrates [*c*-Si (111), 7059 Corning glass,

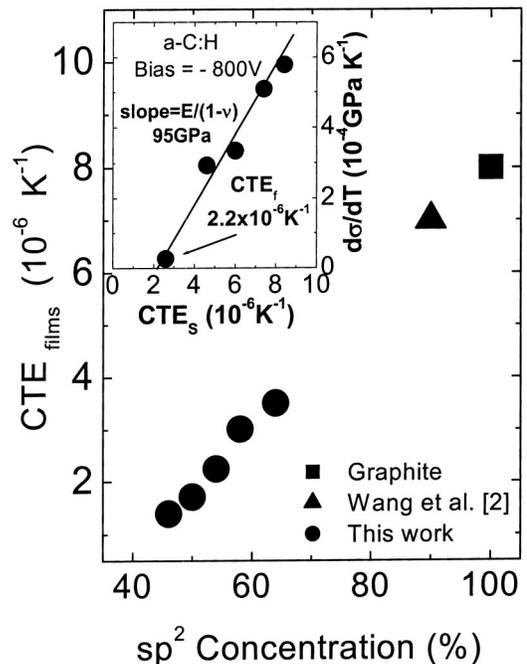


FIG. 1. Coefficient of thermal expansion of *a*-C:H films as a function of the *sp*² concentration. The inset displays the slope of the stress vs temperature measurements, $\Delta\sigma/\Delta T$, as a function of the CTE of five different substrates, α_s [$\alpha_{Si(111)} = 2.6 \times 10^{-6} \text{ C}^{-1}$, $\alpha_{7059} = 4.6 \times 10^{-6} \text{ C}^{-1}$; $\alpha_{Ge(111)} = 6 \times 10^{-6} \text{ C}^{-1}$, $\alpha_{0211} = 7.4 \times 10^{-6} \text{ C}^{-1}$, and $\alpha_{Sapphire} = 7.5 \times 10^{-6} \text{ C}^{-1}$], for an *a*-C:H film.

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TABLE I. Thermal expansion coefficient of amorphous carbon films and other carbon structures.

Structure	CTE ($\times 10^{-6} \text{ C}^{-1}$)	References
Hard <i>a</i> -C:H	1.5–7.0	[This work, 1–5]
<i>ta</i> -C and <i>ta</i> -C:H	Not available	...
Diamond	1.0	13
CVD Diamond	0.7	12
Graphite		
—Perpendicular to the basal plane	27	14
—Parallel to the basal plane	–1.5	
—Average	8	

c-Ge(111), 0211 Precision glass, and sapphire], and illustrates the technique for obtaining the CTE and the elastic modulus. The solid curve represents a linear fit whose slope is the biaxial modulus, $E_f/(1-\nu_f)$, and whose intercept with the α_s axis is the CTE of the film,⁵ according to Eq. (1).

The above procedure was used to determine the CTE of *a*-C:H films as a function of the sp^2 -bond concentration (Fig. 1). The CTE increases with the amount of sp^2 -bonded carbon from $2 \times 10^{-6} \text{ C}^{-1}$ to $\sim 7 \times 10^{-6} \text{ C}^{-1}$, comparable to the average CTE of graphite (see Table I). Demichelis *et al.*³ determined the behavior of the thermal expansion of *a*-C films, and observed a qualitative reduction in the CTE as the percentage of sp^3 bonds increases, but their data was obtained only at low temperature (10–200 K). Using a photothermal reflection technique, Lee *et al.*¹ determined the CTE of *a*-C:H as a function of the hydrogen concentration and found out that it increases slightly, from 2.02 – $2.41 \times 10^{-6} \text{ K}^{-1}$, as the hydrogen concentration increases from 15% to 50%. The hydrogen concentration of the samples of Fig. 1, determined by elastic recoil detection analysis, is in the 0% to 25% range, but the CTE varies from $1.3 \times 10^{-6} \text{ K}^{-1}$ to $7.0 \times 10^{-6} \text{ K}^{-1}$. These two completely different results could be explained if hydrogen has little influence on CTE. In fact, hydrogen has only one bond and so it is a terminal bond that provides the “catalyst” for a void-like structure, which will have little influence on the thermal expansion properties. On the other hand, sp^2 and sp^3 bonds contribute to the skeletal structure of the carbon network, which is ultimately responsible for the thermal expansion.

Table I shows a summary of data for different forms of carbon structures. The CTE of amorphous carbon is between those of diamond and graphite (if one adopts an average-CTE for graphite). Chemical vapor deposited diamond (CVD diamond) has a CTE very close to that of natural diamond.¹² The CTE of *a*-C:H approaches that of diamond as the sp^3 concentration increases, therefore we can also expect that the CTEs of *ta*-C and *ta*-C:H to be close to that of diamond.

The increase of the CTE of *a*-C:H with increasing concentration of sp^2 sites indicates that clusters of piled aromatic layers are being formed. This assumption is supported by the anisotropic characteristics of the CTE in graphite, which is very high ($27 \times 10^{-6} \text{ C}^{-1}$) in the direction perpendicular to the basal planes of aromatic rings, but negative in plane (see Table I). Basal planes are bonded by van der Waals forces, resulting in high thermal expansion coefficients, as for the majority of metals, whilst the in-plane bonding is due to the strong σ bonds. On the other hand, the CTE is negative in plane, which is characteristic of strong σ

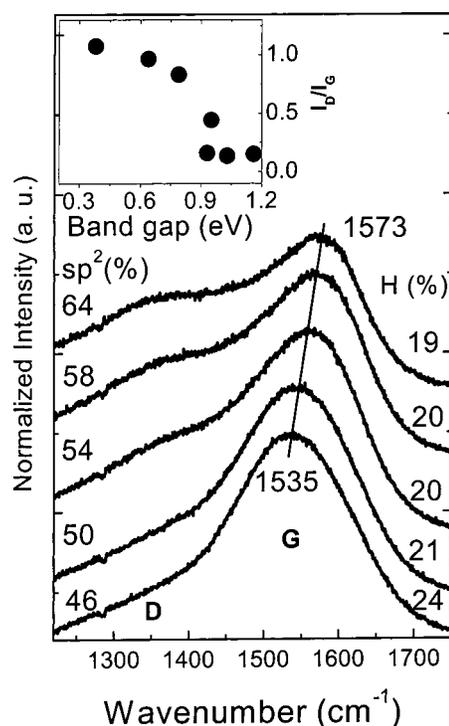


FIG. 2. Raman scattering of the *a*-C:H films displayed in Fig. 1, showing the shift of both *D* and *G* bands as the sp^2 concentration increases. The inset displays the behavior of the I_D/I_G ratio, where I_D and I_G represent the integrated area of the *D* and *G* bands, respectively.

bonds. This interpretation is also supported by Raman scattering, Fig. 2, where the shift on the *G* band indicates an increase in the formation of clusters with the increase of the sp^2 content. Also, the relation I_D/I_G versus band gap (see, inset in Fig. 2) has been used to point towards an increase of the cluster size.¹⁵ Thus, if *a*-C:H films are prepared with a high concentration of randomly dispersed sp^2 sites or another structure with small concentration of clusters of aromatic planes, we would expect a small thermal expansion coefficient. This may explain the results obtained by Lee *et al.*¹

The elastic constants ν and E usually appear mixed in most equations, making it difficult to determine each one separately. Using the thermally induced bending (TIB) technique, for instance, one obtains the $E/(1-\nu)$ ratio,¹¹ while nanohardness measurements give the $E/(1-\nu^2)$ ratio (using the Oliver and Pharr model).⁸ However, one can extract E and ν if both measurements are performed on the same sample. In Fig. 3 we show the use of this approach. Figure 3(a) displays both elastic modulus, and Figs. 3(b) and 3(c) display E and ν , respectively, as derived from the data of Fig. 3(a). The Young's modulus decreases as the sp^2 concentration increases. This behavior is little influenced by Poisson's ratio, since it remains constant, within experimental error, and of the order of 0.3 in the range of sp^2 concentrations investigated. A different approach has been used by Jiang *et al.* to extract both E and ν ¹⁶ of *a*-C films, using a combination of Brillouin scattering and nanohardness measurements. Their data for the Poisson's ratio is also displayed in Fig. 3(c), and is comparable to the results obtained in the present work. Similar results have also been found for a *ta*-C:H film [with a higher Young's modulus ($\sim 300 \text{ GPa}$)

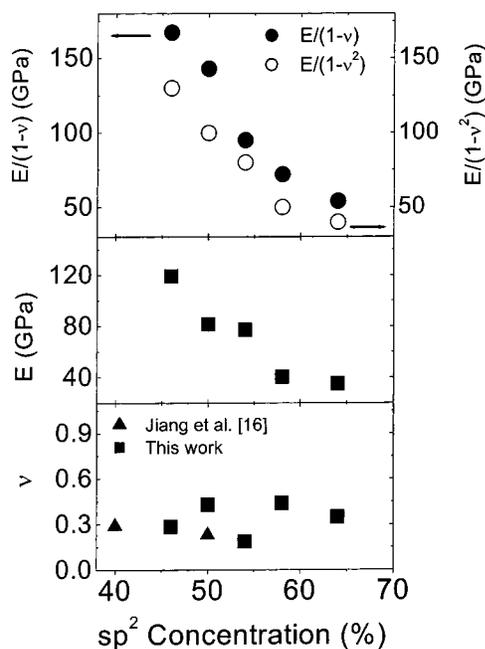


FIG. 3. (a) Composite elastic constant obtained by the TIB, $E/(1-\nu)$, and by nanohardness measurements, $E/(1-\nu^2)$; (b) Young's modulus, E , and (c) Poisson's ratio, ν .

due to the higher sp^3 c -C concentration] by Ferrari *et al.*¹⁷ using Brillouin scattering.

In conclusion, the coefficient of thermal expansion of hydrogenated amorphous carbon films was found to depend on the clustering of aromatic planes. The Young's modulus and Poisson's ratio of these films could also be extracted separately from the composite elastic modulus obtained from nanohardness measurements and from the thermally induced bending technique.

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