

Elastic constants of tetrahedral amorphous carbon films by surface Brillouin scattering

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The elastic constants of tetrahedral amorphous carbon (ta-C) and hydrogenated tetrahedral amorphous carbon (ta-C:H) thin films were determined nondestructively by surface Brillouin scattering. Besides the usual Rayleigh surface mode, we also observe a new pseudosurface acoustic mode of longitudinal polarization, which is a modified version of the longitudinal guided mode usually found in slow-on-fast supported films. The Young's modulus E of a ta-C with 88% sp^3 is 757 GPa, and the shear modulus G is 337 GPa. The moduli of ta-C:H with 70% sp^3 and 30 at. % H are lower, $E = 300$ GPa and $G = 115$ GPa. © 1999 American Institute of Physics.

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The determination of the elastic constants of films thinner than $1 \mu\text{m}$ poses serious experimental problems. Various approaches have been previously used, such as nanoindentation,¹⁻⁴ and laser spectroscopic methods using surface acoustic waves (SAW) such as surface Brillouin scattering (SBS) (Refs. 4-6) and laser-induced SAW (LISAW).⁷ Nanoindentation measures the hardness, but the reduced Young's modulus $E' = E/(1 - \nu^2)$ can be derived from the indentation curve,^{1,2} so that E itself can be found if a value for the Poisson's ratio ν is assumed. Nanoindentation needs an indentation depth less than 10% of the film thickness and it is high sensitive to the substrate for hard films on soft substrates. Nevertheless, nanoindentation has been widely used to derive the E' of various diamond-like carbon (DLC) films, such as amorphous hydrogenated carbon ($a\text{-C:H}$),⁴ tetrahedral amorphous carbon (ta-C),¹⁻³ and hydrogenated ta-C (ta-C:H).⁸ The difficulties of this method are clear in that while the hardness values of ta-C vary between 60 GPa (Refs. 1 and 2) and 90 GPa,³ the E' values vary more widely, from 400 GPa (Refs. 1 and 2) to 1100 GPa.³

SAW-based methods allow nondestructive measurements of the elastic constants of films. In general, SBS is capable of higher accuracy for thin films because the SAW penetration depth decreases with increasing frequency and SBS works in the 10-100 GHz range while LISAW works in the 0.1-0.2 GHz range. However, LISAW could be faster as the laser pulse enhances the phonon population, while SBS only uses the smaller thermal phonon population.

SBS is, in principle, the best method to measure elastic constants of films. First, it can give the two independent elastic constants of an isotropic film. Second, there is no disadvantage to measure a fast film on a slower substrate, in contrast with nanoindentation, where the yield of the soft substrate greatly affects measurements on a hard overlayer. Indeed, we will show that SBS has the unique ability to measure hard carbon layers with thickness less than 10 nm.

SBS already derived the elastic constants for thick carbon films, sometimes in combination with nanoindentation.⁹⁻¹³ Bottani *et al.*¹³ used only SBS to get the elastic constants of thin (~ 100 nm), very soft, cluster-beam deposited $a\text{-C}$ films on Si.

Here, we use SBS to measure the elastic constants of ta-C and ta-C:H thin films. The ta-C was deposited using an S-bend filtered cathodic vacuum arc (FCVA) on Si(100) wafers at ion energy of 100 eV.¹⁴ An sp^3 content of 88% was obtained from the electron energy-loss spectrum (EELS) and a density of 3.26 g/cm^3 was derived from x-ray reflectivity (XRR).¹⁵ The stress was ~ 10 GPa. The ta-C:H films were deposited on Si(100) from acetylene using an electron cyclotron wave resonance plasma source,¹⁶ with an sp^3 content of 70%, a density of 2.35 g/cm^3 , and a hydrogen content of $\sim 30\%$.¹⁶ The stress was ~ 6 GPa. This ta-C:H is more dense than an $a\text{-C:H}$ of comparable sp^3 content because of its lower H content. The thicknesses were 76 and 70 nm, respectively, by XRR. We assume that these amorphous films are elastically isotropic.

SBS is the inelastic scattering of laser photons by thermally excited SAW by the dynamical modulation of the dielectric function of the medium (the elasto-optic effect) and/or dynamic corrugation of the surface (the surface ripple).¹⁷ The scattering angle θ^i is used to probe different SAW wave vectors $q_{\parallel} = (4\pi \sin \theta^i)/\lambda$. The frequency shifts ω of the spectral peaks directly give the experimental SAW velocities $v_e = \omega/q_{\parallel}$.

SBS spectra (Fig. 1) were recorded in backscattering geometry, with θ^i from 20° to 70° , to give the experimental velocities v_e^i (Fig. 2), using an Ar-ion laser at 514.5 nm. With respect to the Si(001) substrate, the [001] surface phonon propagation was explored. The scattered light was analyzed by a tandem 3+3 pass Sandercock interferometer,¹⁸ with a finesse of about 100. The power on the sample was ~ 100 mW on $\sim 10^{-3} \text{ mm}^2$. No sample damage was observed.

The theoretical SAW velocities v_e^i are computed for

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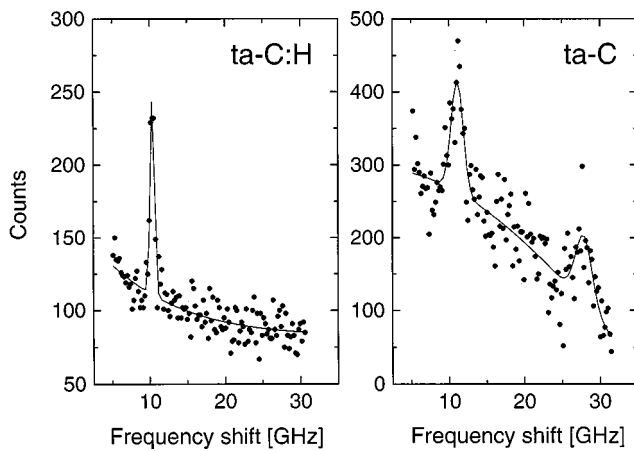


FIG. 1. Experimental Brillouin spectra of ta-C:H and a ta-C. In ta-C:H only the Rayleigh wave peak is visible, while in ta-C also a second peak, at ~ 28 GHz, associated with a pseudosurface wave, can be seen. Both spectra are taken at 30° .

each q_{\parallel}^i by solving the elastodynamics equations with appropriate boundary conditions using a Green function method.⁶ v_c^i depend on the density and elastic constants of the substrate and on the thickness, density, and elastic constants of the film. The density and elastic constants of the Si substrate are well known and film thickness and density were measured independently. Thus, the calculated SAW velocities at each q_{\parallel} depend only on the two independent elastic constants of the film, which we take as E and shear modulus G . E and G are found by fitting the calculated velocities to the experimental ones to minimize the residual R :

$$R = \sum_i \left[\frac{v_c^i(E, G) - v_e^i}{\sigma_e^i} \right]^2, \quad (1)$$

where σ_e^i (~ 30 m/s) are the errors at each v_e^i .

The ta-C sample showed two branches of the SAW dispersion curve, the modified Rayleigh wave, and a pseudosurface wave (PSW) of longitudinal polarization. This mode is a modified version of the longitudinal guided mode (LGM) usually found in slow-on-fast supported films, but here it has been detected for a fast film on a soft substrate.^{17,19} The dispersion of the Rayleigh wave itself allows a precise determination of E and G , however, it is less sensitive to the bulk modulus, B , and Poisson's ratio, ν , due to error propagation

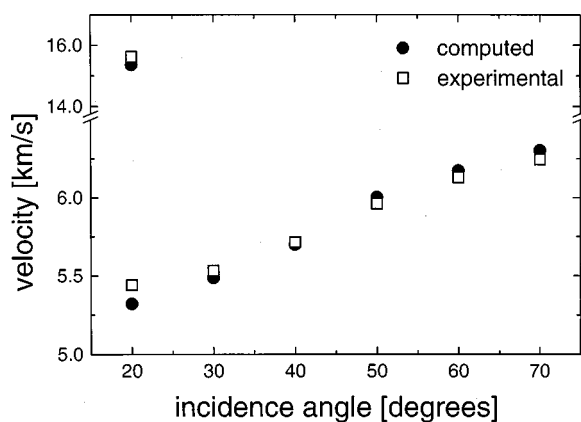


FIG. 2. Dispersion of surface waves for uniform ta-C. The lower branch is the Rayleigh wave. The upper one, consisting of only one point (due to cross-section problems) is the longitudinal guided mode.

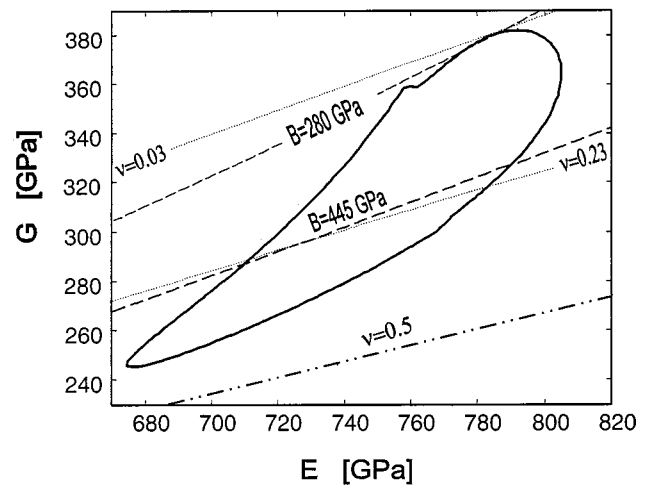


FIG. 3. E, G confidence plot for uniform ta-C film. The solid contour line defines the 95% confidence region. The dashed lines and dotted lines define the corresponding intervals for B and ν . The zone above the lowest dotted line is the region of thermodynamic stability.

problems. The LGM gives a precise estimate of $C_{11} = B + (4/3)G$,¹⁷ and thus of B (and ν), once G is known. Figure 3 shows that the 95% confidence region corresponding to a bulk modulus lower than that of diamond for the (E, G) pair is $E = 710\text{--}805$ GPa and $G = 290\text{--}385$ GPa. This selects wider intervals for (B, ν) : $B = 280\text{--}445$ GPa and $\nu = 0.03\text{--}0.23$. The average $E = 757.5$ GPa and $G = 337.5$ GPa give $B = 334$ GPa and $\nu = 0.12$, for an sp^3 fraction of 0.88 (Table I).

For the ta-C:H sample, we detected only the modified Rayleigh wave. The 95% confidence region corresponding to a bulk modulus lower than diamond covers the range $E = 291\text{--}304$ GPa and $G = 105\text{--}116$ GPa. This corresponds to a much wider range of values, $\nu = 0.3\text{--}0.39$ and $B = 248\text{--}445$ GPa, compared to E and G . This does not allow to take the average E and G as the physically meaningful values and would imply that B is essentially undetermined, in that the computed $v_c^i(E, G)$ are sensitive to E and G and almost insensitive to B . Physically, noting that ta-C:H has a density of 66% of diamond and 30 at. % hydrogen, we can assume the minimum of B for ta-C:H, of 248 GPa, by scaling from the B of diamond. This sets the Poisson's ratio to 0.3.

The ta-C and ta-C:H films studied in these two experiments were homogeneous. Another ta-C film (85% sp^3) deposited with a single-bend FCVA was found to have a layered microstructure,¹⁵ with a surface layer about 7 nm thick

TABLE I. Elastic constants of our films, compared to the isotropic (Voigt–Reuss–Hill) average for diamond.

	ta-C:H	ta-C	diamond
Thickness (nm)	70	76	
Density (g/cm ³)	2.35	3.26	3.515
H (at. %)	30		
sp^3 (%)	70	88	100
E (GPa)	300_{-9}^{+4}	757.5 ± 47.5	1144.6
G (GPa)	115_{-10}^{+1}	337.5 ± 47.5	534.3
B (GPa)	248_{-0}^{+197}	334_{-54}^{+111}	444.8
ν	$0.3_{-0}^{+0.09}$	$0.12_{-0.09}^{+0.11}$	0.07

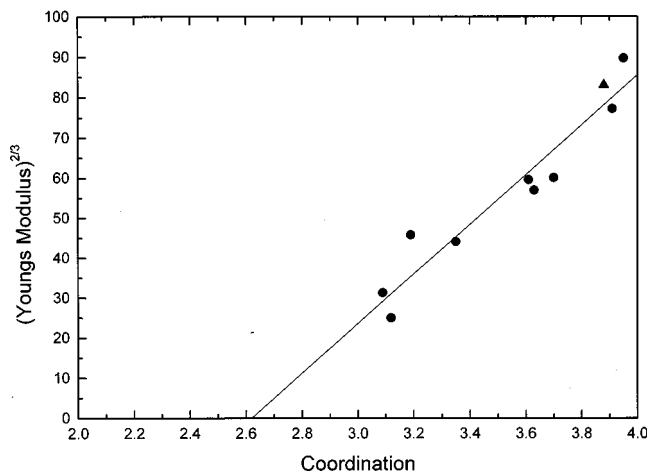


FIG. 4. $E^{2/3}$ vs sp^3 fraction for various *a*-C films: present result (▲) and data from Schultrich (●) (Ref. 21).

of lower density, according to electron microscopy and XRR.^{15,20} For this ta-C film, a second branch, corresponding to the pseudomode, was also seen at some incidence angles. The film was modeled as two homogeneous layers: a *surface layer* 7 nm thick with density of 2.7 g/cm³ and a *bulk layer* 63.5 nm thick with density of 3.24 g/cm³.¹⁵ The dispersion relations depend on the elastic constants of both the outer layer (E, G)^{surf} and the inner layer (E, G)^{bulk}. Our final values, corresponding to $B < 450$ GPa, are $E^{\text{bulk}} = 750\text{--}790$ GPa, $G^{\text{bulk}} = 300\text{--}395$ GPa, $E^{\text{surf}} = 200\text{--}300$ GPa, and $G^{\text{surf}} = 70\text{--}150$ GPa. This procedure shows that the Young's modulus of a 7-nm-thick overlayer can be obtained by SBS. Such ultrathin carbon layers cannot be probed by conventional nanoindentation.

We now compare our results to previous studies. Our E values confirm the values of Schneider and co-workers^{7,21} and Morath *et al.*²² on films of similar density. This is because SAW-based methods are highly sensitive to Young's modulus,²³ so they obtain good values even using less film-probing methods, such as LISAW. The SAW are less sensitive to the Poisson's ratio, thus explaining our lower accuracy for ν . On the other hand, nanoindentation is seen to underestimate E for ta-C, giving values of 400–500 GPa.^{1–3} Knapp and co-workers^{3,24} proposed a finite-element model to overcome the limitations of the Oliver–Pharr^{1,2} analysis of the indentation curve, but this now seems to overestimate E at 1020–1100 GPa. Our data indicate that the E of ta-C:H, 300 GPa, is much lower than in ta-C, in this case similar to that found previously in thick ta-C:H films by nanoindentation.⁸ Clearly, the hydrogen content of ta-C:H has strongly reduced its network rigidity.

Figure 4 plots the $E^{2/3}$ of as-deposited *a*-C films measured by SBS here, or by laser-induced SAW,²³ against their sp^3 fraction. The density has been converted to an sp^3 fraction, using correlations derived from EELS and XRR.¹⁵ The constraint-counting theory of the elastic properties of random covalent networks²⁵ predicts that the Young's modulus should depend on mean-atomic coordination Z as

$$E = E_0(Z - 2.4)^{1.5}, \quad (2)$$

where $Z_0 = 2.4$ is the critical coordination, below which the networks have zero rigidity. *a*-C networks with mixed sp^2

and sp^3 bonding provide a good chance to test this theory, as the mean coordination Z varies with sp^3 fraction x_{sp^3} as $Z = 3 + x_{sp^3}$. Figure 4 shows that this correlation (2) gives a reasonable straight line for pure carbon networks. The intercept at $E = 0$ corresponds to $Z_0 = 2.6$, close to the theoretical value of 2.4.

The extrapolation of Fig. 4 to $Z = 4$ gives $E \sim 800$ GPa. This value is less than the isotropic average E of diamond, 1144 GPa. It is closer to the modulus found in a molecular dynamics simulation of a 100% sp^3 *a*-C (823 GPa).²⁶ This suggests that random networks are softer than the isotropically averaged crystals. Table I shows that $\nu = 0.12$ for ta-C, similar to diamond, while $\nu \sim 0.3$ for ta-C:H.

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¹G. M. Pharr, D. L. Callahan, S. D. McAdams, T. Y. Tsui, S. Anders, A. Anders, J. W. Ager, I. G. Brown, C. S. Bhatia, S. R. P. Silva, and J. Robertson, *Appl. Phys. Lett.* **68**, 779 (1996).

²S. Xu, D. Flynn, B. K. Tay, S. Praver, K. W. Nugent, S. R. P. Silva, Y. Lifshitz, and W. I. Milne, *Philos. Mag. B* **76**, 351 (1997).

³T. A. Friedmann, J. P. Sullivan, J. A. Knapp, D. R. Tallant, D. M. Follstaedt, D. L. Medlin, and P. B. Mirkarimi, *Appl. Phys. Lett.* **71**, 3820 (1997).

⁴X. Jiang, K. Reichelt, and B. Stritzker, *J. Appl. Phys.* **68**, 1018 (1990).

⁵H. Xia, J. G. Jiang, W. Zhang, K. J. Chen, X. K. Zhang, G. Carlotti, D. Fioretto, and G. Socino, *Solid State Commun.* **84**, 987 (1992).

⁶M. G. Beghi, C. E. Bottani, P. M. Ossi, T. Lafford, and B. K. Tanner, *J. Appl. Phys.* **81**, 672 (1997).

⁷D. Schneider, C. F. Meyer, H. Mai, B. Schöneich, H. Ziegele, H. J. Scheibe, and Y. Lifshitz, *Diamond Relat. Mater.* **7**, 973 (1998).

⁸M. Weiler, S. Sattel, T. Giessen, K. Jung, H. Ehrhardt, and J. Robertson, *Phys. Rev. B* **53**, 1594 (1996).

⁹M. Grimsditch, *J. Phys. C* **16**, L143 (1983).

¹⁰X. Jiang, J. V. Harzer, B. Hillebrands, Ch. Wild, and P. Koidl, *Appl. Phys. Lett.* **59**, 1055 (1991).

¹¹D. Fioretto, G. Carlotti, G. Socino, S. Modesti, C. Cepek, L. Giovannini, O. Donzelli, and F. Nizzoli, *Phys. Rev. B* **52**, R8707 (1995).

¹²X. Jiang, *Phys. Rev. B* **43**, 2372 (1991).

¹³C. E. Bottani, A. C. Ferrari, A. Li Bassi, P. Milani, and P. Piseri, *Europhys. Lett.* **42**, 431 (1998).

¹⁴P. J. Fallon, V. S. Veerasamy, C. A. Davis, J. Robertson, G. A. J. Amaratunga, and W. I. Milne, *Phys. Rev. B* **48**, 4777 (1993).

¹⁵A. Libassi, A. C. Ferrari, V. Stolojan, B. K. Tanner, J. Robertson, and L. M. Brown (unpublished).

¹⁶N. A. Morrison, S. E. Rodil, A. C. Ferrari, J. Robertson, and W. I. Milne, *Thin Solid Films* **337**, 71 (1999).

¹⁷F. Nizzoli and J. R. Sandercock, in *Dynamical Properties of Solids*, edited by G. K. Norton (North-Holland, Amsterdam, 1990), Vol. 6, p. 281.

¹⁸J. R. Sandercock, in *Light Scattering in Solids*, edited by M. Cardona and G. Güntherodt (Springer, Berlin, 1982), Vol. 3.

¹⁹M. G. Beghi, C. E. Bottani, R. Ferulano, P. M. Ossi, R. Pastorelli, L. Giovannini, F. Nizzoli, A. C. Ferrari, and J. Robertson, in *Proceedings of the XVIth International Conference on Raman Spectroscopy*, edited by A. Heyns (Wiley, Chichester, 1998), p. 870.

²⁰M. P. Siegal, J. C. Barbour, P. N. Provencio, D. R. Tallant, T. A. Friedmann, L. J. Martinez Miranda, B. Kleinsorge, and W. I. Milne, *Mater. Res. Soc. Symp. Proc.* (1999).

²¹B. Schultrich, H. J. Scheibe, D. Drescher, and H. Ziegele, *Surf. Coat. Technol.* **98**, 1097 (1998).

²²C. 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).

²³S. Tarantola, R. Pastorelli, M. G. Beghi, and C. E. Bottani (unpublished).

²⁴J. A. Knapp, D. M. Follstaedt, S. M. Myers, J. C. Barbour, and T. A. Friedmann, *J. Appl. Phys.* **85**, 1460 (1999).

²⁵H. He and M. E. Thorpe, *Phys. Rev. Lett.* **54**, 2107 (1985).

²⁶P. C. Kelires, *Phys. Rev. Lett.* **73**, 2460 (1994).