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Measurement of the elastic constants of nanometer-thick films

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Abstract

Reliable measurement of the elastic constants of films of nanometric thickness is needed for the development of several nanotechnologies, but is still an open issue, especially in the case of hard films. We show that by combining surface Brillouin scattering (SBS) and X-ray reflectivity (XRR) measurements, the elastic constants of nanometric supported films can be obtained. The dispersion relations of surface acoustic waves (SAWs) are measured by SBS. The same dispersion relations are computed as functions of substrate properties, and the film thickness, mass density and elastic constants. The film thickness and density are obtained by X-ray reflectivity measurements; the elastic constants are then derived by fitting the computed SAW dispersion relations to the measured ones. We present results obtained on tetrahedral amorphous carbon films, having thickness below 10 nm, deposited on silicon. We show that the elastic constants can be measured also for these ultrathin films.

Keywords: Elastic constants; Surface acoustic waves; Brillouin scattering; Thin films; Amorphous carbon

1. Introduction

Free-standing thin films of micrometric thickness are a main building block of microsystems. Coated films could also be considered: an example is offered by carbonaceous materials. Silicon is presently the most common material for microsystems, but it has problems, namely, for the construction of sliding parts: it is prone to sticking and its wear resistance is low. These problems prompted the interest for various kinds of diamond-like carbon (DLC) for the construction of microsystems [1]. The possibility can also be considered of a DLC coating on a silicon film. Knowledge of mechanical properties of micrometric free-standing films, possibly coated by nanometric films, is important for the design of microsystems. However, in the case of such films, techniques like indentation are applicable with difficulties, if applicable at all, and mechanical testing methods have to be developed.

The methods that exploit acoustic waves have a significant potential [2]. Acoustic waves involve exclusively reversible elastic strains, and are therefore unable to supply information about any kind of inelastic behaviour of films. However, for this reason, they are the most appropriate tool to explore the elastic properties [3,4]. The behaviour of acoustic waves can be probed by quantitative acoustic microscopy, by laser acoustics [5] and by Brillouin scattering (BS). BS is the scattering of an electromagnetic wave (a photon) by an acoustic wave (a long wavelength acoustic phonon); it exploits thermally activated phonons, and is intrinsically a contactless technique. In laser acoustic measurements, acoustic waves are excited by laser pulses; detection can also be performed by optical means, giving also in this case a contactless technique. Acoustic microscopy measurements require a contact fluid for coupling with the acoustic lens. Laser acoustic measurements require a propagation path of a few millimetres, while BS only needs the area illuminated by the focused laser beam (without a microscope), that is, down to a few tens of microns. Furthermore, BS probes acoustic wavelengths down to a quarter of a micron, shorter (by one or two orders of magnitude) than those probed by other techniques. It has therefore the best potential for achieving a high spatial resolution, although measurements are time consuming and the presently achieved precision is lower than that obtained by other techniques [5]. In transparent materials and in semiopaque materials such as silicon, BS can measure both bulk acoustic waves and surface acoustic waves (SAWs), including the longitudinally polarised

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SAWs or pseudo-SAWs, which cannot be observed by other techniques. In metallic materials, all the techniques probe only the SAWs polarised along the normal to the surface. The experiment directly measures the SAW velocity v_m and, when the velocity depends on wavelength, the SAW dispersion relation. In this work, the potential of surface BS (SBS, i.e. BS by SAWs) is explored by measurement of nanometer-thick amorphous carbon films.

2. Derivation of the elastic constants

The stiffness of an amorphous, and therefore mechanically isotropic, film is fully characterised by two independent parameters, which are typically taken among Young's modulus E, shear modulus G, bulk modulus B, Poisson's ratio ν or among the elements C_{ij} of the elastic tensor. Any two of them determine all the others. For crystalline materials, a higher number of independent parameters is needed, more than the three needed for cubic materials. Since the velocities of both bulk acoustic waves and SAWs can be accurately computed as functions of the elastic moduli, the mass density ρ and the layer thickness (in layered structures), their measurement provides an access to the elastic properties. In particular, in the case of a single isotropic layer on an anisotropic substrate, the elastic constants of films have been measured, for film thickness ranging from hundreds to tens of nanometers [6,7]. This work explores even thinner layers.

More precisely, here we consider the Rayleigh wave modified by the presence of the film [modified Rayleigh wave (MRW)]. MRW is a general feature for thin films. Its velocity can be computed [8] as mentioned above. It depends on the nondimensional product $q_{\parallel}h$ of the parallel wavevector $q_{\parallel}$ times the film thickness h. It is thus possible to solve the inverse problem, that is, the derivation of the elastic constants from measured SAW velocities [2,9]. The elastic constants and mass density of the anisotropic substrate are known independently. The SAW wavevector is determined by the scattering geometry. X-ray reflectivity (XRR) is used to measure thickness and density of carbon films down to a thickness of less than 2 nm [10,11]. Thus, the acoustic velocities remain functions of only the unknown elastic constants of the film. It has been shown [12] that among the various elastic moduli mentioned above, the (E,G) pair is, for isotropic materials, the most appropriate for the solution of the inverse problem. The velocities $v_c(E,G)$ are computed for each acoustic wavevector at the nodes of a rectangular mesh. The couple $(E,G)_{film}$ is obtained by a least squares fit of the computed velocities v_c to the measured ones v_m:

$$R = \sum_i \left(\frac{v_c^i(E,G) - v_m^i}{\sigma_e^{\,i}} \right)^2 = \min,$$

where $\sigma_e^{\,i}$ are the variances of the corresponding v_m^i due to the various uncertainties connected to the measurement. The (E,G) couple that minimises R is the most probable solution of the inverse problem, and the regions corresponding to any fixed confidence level are also obtained.

3. Experiments

Tetrahedral amorphous carbon (ta-C) films were deposited using an S-bend filtered cathodic vacuum arc (FCVA) with an integrated off plane double bend (S-bend) magnetic filter. The deposition chamber was evacuated to 10^{-8} Torr using a turbomolecular pump. ta-C films with particle area coverage of less than 0.01% and uniform cross section are consistently deposited with this system [13]. A series of ultrathin films was grown; thickness density and layering of these ultrathin samples were derived by XRR [10,11]. Here we focus on two films, having the same mass density, 2.8 g/cm^3, and thickness of 8 and 4.5 nm; a bare substrate is also considered for reference. Amorphous carbon films can have a density gradient in proximity of the outer surface and the film–substrate interface [10,11]. The structure of these ultrathin S-bend FCVA films resembles that of thicker S-bend films, with a scaling of the bulk layer thickness, but not of the surface and interface layers (which are in the subnanometer range both in thick and thin films). To avoid exceeding complexities, the films are modelled as a single homogeneous equivalent film, with a sharp interface with the substrate. The properties of the Si substrate are known: $C_{11} = 166$ GPa, $C_{12} = 63.9$ GPa, $C_{44} = 79.6$ GPa, $\rho = 2.33$ g/cm^3.

SAW velocities of all the samples were measured by SBS: the specimen is illuminated by laser light and the spectrum of the scattered light is analysed. Besides the strong peak of the elastically reflected light at frequency Ω, the spectrum contains the doublet at frequencies $\Omega \pm \omega$,

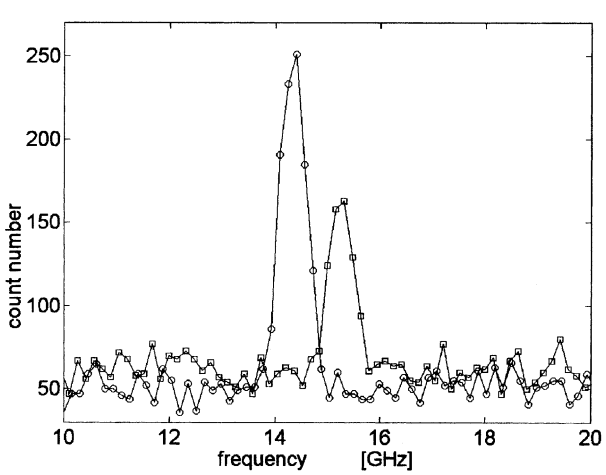

Fig. 1. Portions of Brillouin spectra at 50° incidence showing the peak due to modified Rayleigh wave, measured under identical conditions on bare silicon (○) and on silicon covered by an 8-nm ta-C film (□).

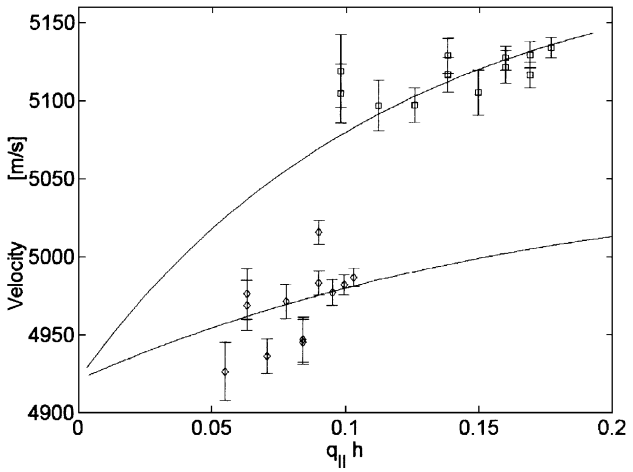

Fig. 2. Measured velocities for the 4.5-nm film (◇) and the 8-nm film (□); dispersion relations computed with the film elastic moduli obtained from the best fit procedure and with accepted values of silicon properties. The limit at null $q_{\parallel} h$ is the Rayleigh velocity of a bare silicon substrate.

shifted by the SAW frequency ω. The SAW wavevector $q_{\parallel}$ is selected by the scattering geometry (in backscattering, at incidence angle θ, $q_{\parallel} = 2(2\pi/\lambda) \sin \theta$, where λ is the laser wavelength) and the SAW velocity $v = \omega/q_{\parallel}$ is directly obtained. Measurements were performed with SAW propagation along the [100] direction on the (001) face of the Si substrate, at room temperature, in backscattering, with incidence angle θ from 30° to 70°. The incident light is p-polarised; the scattered light is collected without polarisation analysis, and analysed by a tandem 3 + 3-pass high-contrast interferometer of the Sandercock type. The light source was an Argon ion laser operating at $\lambda = 514.5$ nm. The incident power on the specimen was around 100 mW, focused into a spot of the order of 10^3 μm^2. Irradiation did not induce film modifications. Fig. 1 shows portions of the spectra measured on the bare substrate and on the 8-nm film, showing that the modification due to such a film is well measurable.

4. Results

The confidence regions are found in the (E,G) plane. Physical acceptability criteria are also considered: Only the part of the (E,G) plane that corresponds to values of Poisson's ratio ν between 0 and 0.5 and to values of bulk modulus B lower than that of diamond ($B = 445$ GPa) is taken as physically plausible. Considering only the part of the confidence region that falls within this acceptability zone, the following intervals of the elastic moduli are identified. For the 8-nm-thick film, $E = 350 \div 420$ GPa and $G = 130 \div 210$ GPa, while for the 4.5-nm films, $E = 220 \div 260$ GPa and $G = 70 \div 130$ GPa. In both cases, the confidence region encompasses wide ranges of values of ν and B: these moduli remain thus undetermined. This is in agreement with the results of the sensitivity analysis of Ref. [12], which showed that E and G can be determined much better than ν and B. Fig. 2 compares the measured dispersion relations to those computed by best fit parameters. The dispersion relations are shown as functions of the nondimensional parameter $q_{\parallel} h$. If the two films had similar properties, the data from both of them would fall on the same curve. This does not happen, showing that the stiffness of the 4.5-nm film, modelled as a single homogeneous equivalent film, is measurably lower than that of the 8-nm film.

5. Conclusions

It has been shown that the dispersion relations of the modified Rayleigh wave of ultrathin films on Si are measurably different by means of BS down to a few nanometers thickness. The analysis of these dispersion relations allows us to derive the elastic constants of 8- and 4.5-nm-thick ta-C films. These have still good mechanical properties, although the stiffness of the 4.5-nm film is measurably lower than that of the 8-nm-thick film. The two measured films do not give a complete picture of the stiffness vs. thickness relationship, but show that the elastic constants of ultrathin films can be measured.

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References

[1] J.P. Sullivan, T.A. Friedmann, K. Hjort, MRS Bull. 26 (2001) 309.
[2] M.G. Beghi, C.E. Bottani, R. Pastorelli, in: C. Muhlstein, S.B. Brown (Eds.), Mechanical Properties of Structural Films, ASTM STP 1413, American Society for Testing and Materials, West Conshohocken, PA, 2001, in press.
[3] M. Grimsditch, in: M. Levy, et al. (Eds.), Handbook of elastic properties of solids, liquids and gases, vol. 1, Academic Press/Harcourt Publishers, Sidcup, UK, 2000, pp. 331–347.
[4] J.D. Comins, in: M. Levy, et al. (Eds.), Handbook of elastic properties of solids, liquids and gases, vol. 1, Academic Press/Harcourt Publishers, Sidcup, UK, 2000, pp. 349–378.
[5] D. Schneider, Th. Witke, Th. Schwarz, B. Schneich, B. Shultrich, Surf. Coat. Technol. 126 (2000) 136.
[6] P. Zinin, M.H. Manghnani, S. Tlechev, V. Askarpour, O. Lefeuvre, A. Every, Phys. Rev. B 60 (1999) 2844.
[7] A.C. Ferrari, J. Robertson, M.G. Beghi, C.E. Bottani, R. Ferulano, R. Pastorelli, Appl. Phys. Lett. 75 (1999) 1893.
[8] G.W. Farnell, E.L. Adler, in: W.P. Mason, R.N. Thurston (Eds.),

Physical Acoustics, vol. 9, Academic Press, New York, 1972, pp. 35–127.
[9] A.C. Ferrari, J. Robertson, R. Pastorelli, M.G. Beghi, C.E. Bottani, Mater. Res. Soc. Symp. Proc. 594 (2000) 289.
[10] B.K. Tanner, A. Li Bassi, A.C. Ferrari, J. Robertson, Mater. Res. Soc. Symp. Proc. 675 (2001) in press.
[11] A.C. Ferrari, A. Li Bassi, B.K. Tanner, V. Stolojan, J. Yuan, L.M. Brown, S.E. Rodil, B. Kleinsorge, J. Robertson, Phys. Rev. B 61 (2000) 11089.
[12] R. Pastorelli, S. Tarantola, M.G. Beghi, C.E. Bottani, A. Saltelli, Surf. Sci. 468 (2000) 37.
[13] K.B.K. Teo, S.E. Rodil, J.T.H. Tsai, A.C. Ferrari, J. Robertson, W.I. Milne, J. Appl. Phys. 89 (2001) 3706.