EUROPHYSICS LETTERS 15 May 1998

Europhys. Lett., **42** (4), pp. 431-436 (1998)

Mesoscopic elastic properties of cluster-assembled carbon films

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(received 26 January 1998; accepted in final form 26 March 1998)

PACS. 61.46+w – Clusters, nanoparticles, and nanocrystalline materials.
PACS. 68.60Bs – Mechanical and acoustical properties.
PACS. 78.35+c – Brillouin and Rayleigh scattering; other light scattering.

Abstract. – The mesoscopic elastic response of cluster-assembled carbon films was measured by Brillouin light scattering. The values of bulk modulus and shear modulus were estimated from the shifts of both surface and bulk phonon peaks. The most basic mechanical properties of these new materials were so investigated down to the scale of a few hundreds of nanometers. The shear modulus is found in the range of that of crystalline graphite, whereas the bulk modulus and Poisson's ratio are significantly different. The results agree with the mainly sp^2 coordinated granular structure shown by Raman spectroscopy.

Recently the use of carbon clusters and nanotubes as building blocks for the synthesis of nanocrystalline and composite materials with unusual elastic properties has been suggested [1]-[3] and several experiments to identify possible synthetic routes have been reported [4], [2], [5]. In particular several authors have suggested that the assembling of carbon clusters could be used to produce an entire new class of porous materials with interesting structural and functional properties [4]-[7]. Cluster beam deposition has been proposed to deposit nanocrystalline carbon thin films where the sp^2-sp^3 content could be controlled by the choice of the precursor clusters [4], [5]. The nano- and meso-porosity resulting from cluster stacking with reduced fragmentation could give origin to a material with interesting mechanical, acoustic, thermal and electronic properties.

Experimental characterization and theoretical modellization of cluster-assembled materials have to face the problem of cluster coalescence and of their organization in structures spanning length scales from the nanometer up to the micrometer. The different structures in which the precursor clusters are organized need experimental probes sensitive to the different length scales typical of intra-cluster and inter-cluster interactions. For carbon-based materials, Raman

spectroscopy can be used to characterize the sp^2-sp^3 presence on a nanometer scale [8]. In order to study the organization of clusters on a scale of hundreds of nanometers, which is the typical scale of thermally excited long-wavelength acoustic phonons, Brillouin light scattering can be used [9]. Films of graphite [10], polycrystalline diamond [11], diamond-like a-C:H [12], C_{60} (fullerite) [13], and phototransformed C_{60} [14] have already been studied by Brillouin scattering.

In general the elastic properties of thin films, with a thickness less than 1 μm, cannot be measured using macroscopic external probes either with conventional techniques or even with more sophisticated ones, like nanoindentation (which gives only the hardness) and acoustic microscopy [9]. The only possible method utilizes the scattering of laser light off surface acoustic phonons (surface Brillouin scattering). Normally this spectroscopic technique is applied to homogeneous compact films with perfect (atomically flat) surfaces and buried interfaces. Particularly challenging is instead the attempt of getting and interpreting Brillouin spectra of films with a rough surface and/or a granular or porous structure [15]. The extraction of the elastic properties of these systems from the spectroscopic data can be based only partially on what is known in the case of *good* films and a complete theory is still lacking.

Here we present a characterization of the mesoscopic elastic properties of cluster-assembled carbon thin films by Brillouin scattering. Bulk and surface Brillouin scattering signals have been obtained from films characterized by a complex structure from the atomic to the hundreds of nanometers level, showing that this technique can be used also for nanostructured materials with irregular surfaces. Bulk and shear modulus of the material have been determined giving information on the acoustic properties on a mesoscopic scale. This allows to infer the nature of the bonding between the carbon aggregates.

The films have been deposited on silicon substrates by a Pulsed Arc Gas Aggregation Cluster Source (PAGACS) [16] and characterized by Scanning Electron Microscopy (SEM), Raman, and optical spectroscopy [5]. Our source is a modified version of a pulsed arc cluster ion source [17]: a description of the source and a detailed cluster beam characterization have been reported elsewhere [5]. Briefly: the beam is characterized by time-of-flight mass spectrometry; deposition is performed by intersecting the beam before the mass spectrometer by the substrate placed on a micromanipulator. The films described in this letter have been deposited using a cluster distribution in the beam with a center of mass of 950 atoms/cluster. The kinetic energy of a medium size aggregate was of 0.3 keV [4], [16]. The presence in the film of multishell polyhedral graphitic particles is also detected by Transmission Electron Microscopy in analogy to what observed in [2].

In fig. 1 we report a SEM micrograph of a film. The granular structure is characterized by particles of several tens of nanometers. Atomic Force Microscopy confirmed the presence of particles of 10–15 nm diameter clumped to form larger aggregates. The granularity of the film is also reflected by the pronounced roughness of the surface.

Brillouin scattering spectra were recorded at room temperature in backscattering at several incidence angles θ in the range 30°–70°. The incident light was p-polarized while no polarization analysis of the scattered light was made due to the low level of the signal. With respect to the Si(001) substrate the [100] surface phonon propagation direction was explored. A tandem six-pass high-contrast interferometer of Sandercock [18] type was used with a finesse of about 100. A free spectral range of 32.59 GHz was adopted. The light source was an argon ion LASER Coherent Innova 300 operating in single frequency at the wavelength $\lambda = 514.5$ nm. The incident power onto the sample surface was 75 mW. No damage of the films was observed at this power. The scattered light was detected by a Hamamatsu bialkali photomultiplier tube, in single-photon counting configuration, with a dark current of 0.7 c.p.s. In the above θ range surface phonons with wave vector $q_{||} = (4\pi/\lambda)\sin\theta$ can be detected. Bulk peaks,

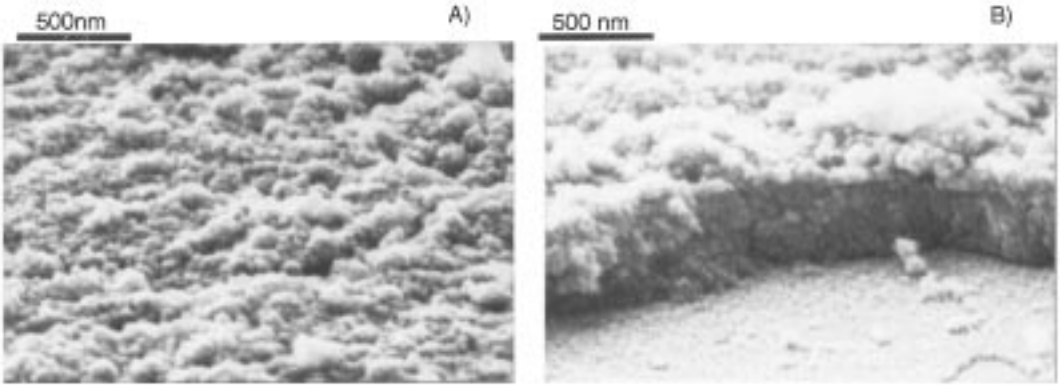

Fig. 1. – SEM micrographs of the surface (A) and the section (B) of a nanocrystalline carbon thin film deposited by cluster beam deposition (see text). The granular structure is visible, characterized by particles of several tens of nanometers in diameter. Note the roughness and irregularity of the surface.

associated with longitudinal or transverse phonons of wave vector $q = (4\pi/\lambda)n$, n being the index of refraction of the film, can also be measured in films with thickness > 0.5 μm. The Brillouin signals were so low as to impede the use of a narrow slit to limit the collection angle. As a consequence no analysis of the width of the peaks, possibly leading to attenuation measurements, was attempted.

We examined thick films (thickness ≥ 0.8 μm) and thin films (thickness $\simeq 0.1$ μm). In thick films we detected only damped bulk acoustic phonons with a typical wavelength λ_{ph} of the order of 170 nm, giving rise to coherent Brillouin scattering of laser light [19]. This indicates that for a length $d \geq \lambda_{\mathrm{ph}}$ the films can be modeled as a continuum with translational invariance and effective elastic constants, although structural disorder at smaller scales scatters the phonons significantly. The presence of a rather strong central peak in the spectra could be ascribed to non-propagating (overdamped), or confined vibrational excitations within the films, probably connected with different characteristic correlation lenghts less than d. The most damped bulk acoustic phonons could be coupled to the confined modes by a relaxation mechanism. The films own a high degree of surface roughness and multiscale granularity (see fig. 1): this leads to considerable broadening of the phonon peaks and to the presence of an intense elastic background. This strong elastic and quasi-elastic bulk signal impeded the measurement of surface phonons which could be almost overdamped if not already replaced by surface fractons or by localized cluster modes [15]. Instead in thinner films surface peaks were detected.

In fig. 2a), relative to a thick film, a broad peak is clearly visible at about 17 GHz together with a strong central peak about 10 GHz wide. Varying the incidence angle θ did not shift the peak position in frequency: a behaviour typical of bulk phonon peaks. Assuming that the film is elastically isotropic (and we have no reasons to doubt about that, also in view of its structure [5]) the transverse peak should not be visible in backscattering [18]. Thus we attribute the above peak to the bulk longitudinal acoustic phonon of the film material. This attribution is also supported *a posteriori* by the numerical value of the elastic moduli of thin films (see below) which agree with their graphitic-like structure as determined by Raman spectroscopy [5]. We assign the shift ν_{L} peak to the longitudinal (L) bulk phonon with wave vector $q = (4\pi/\lambda)n$ and phase velocity $v_{\mathrm{L}} = \lambda\nu_{\mathrm{L}}/(2n)$. The longitudinal sound velocity v_{L} is connected to the adiabatic bulk modulus B, shear modulus μ and C_{11} elastic constant by the

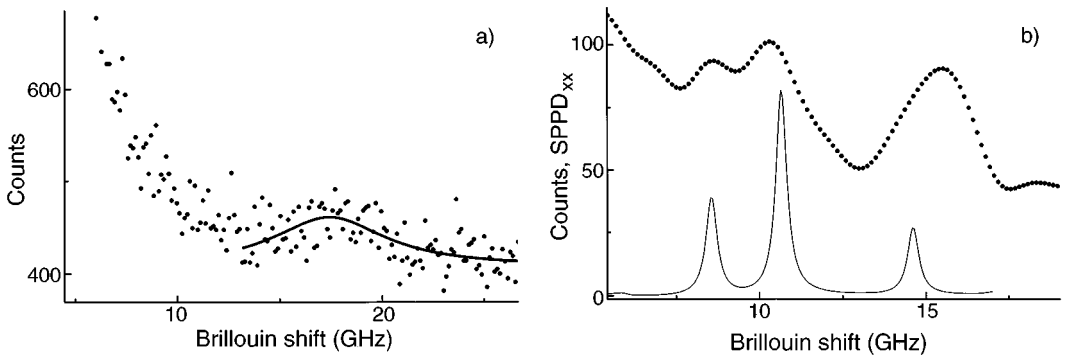

Fig. 2. – a) Bulk Brillouin spectrum of a thick film. The bulk longitudinal phonon peak has been marked by a Lorentzian arc fit. The spectrum has been taken at $\theta = 50°$. b) Surface Brillouin spectrum of a thin film taken at $\theta = 50°$. Under the smoothed experimental spectrum the theoretical surface projected phonon density of states for the polarization parallel to the surface $LPPDxx$, computed with the physical constants of the film (see text) is also shown. Three surface peaks are clearly visible: the Rayleigh wave and two Sezawa waves. The width of the experimental peaks indicates considerable scattering of the phonons off surface roughness and other structural irregularities. The width of theoretical peaks instead takes into account only instrumental broadening.

formulae [20]

$$v_{\mathrm{L}} = \sqrt{\frac{B + \frac{4}{3}\mu}{\rho}} = \sqrt{\frac{C_{11}}{\rho}}\,, \tag{1}$$

where ρ is the mass density. A direct ellipsometric measurement of the index of refraction n at 514.5 nm of a film deposited in the same conditions gave $n \simeq 1.5$ [5] and thus $v_{\mathrm{L}} \simeq 2900\ \mathrm{ms}^{-1}$. Assuming $\rho \simeq 1.\,10^3\ \mathrm{kgm}^{-3}$ [5], we obtain $C_{11} \simeq 9$ GPa. It is evident from eqs. (1) that both B and μ cannot be evaluated from the shift of only one bulk peak.

In fig. 2b) the surface Brillouin spectrum of a thin (100 nm thick) film is shown for an incidence angle of $\theta = 50°$. At least three peaks are clearly visible below the transverse threshold of the silicon surface [9], superimposed to a central peak which is not wide enough to be the silicon one [18]. All these peaks exhibited the characteristic surface frequency variation with the incidence angle, although they are anomalously broad with respect to *normal* surface peaks. Furthermore the intensity variation with angle was very sharp and rather irregular: a fact that can be justified by the shape of the surface. Notwithstanding these anomalies, a numerical computation of the surface projected phonon spectrum [21] (see the solid curve under the experimental spectrum) of a perfect film with flat interfaces of 100 nm thickness can predict rather well the dispersion of the experimental peak shifts, confirming their surface nature. Fitting the spectral shifts of the resonances in the theoretical spectra to experimental data, the *effective* elastic constants of the films were obtained. The shear modulus and the bulk modulus turned out to be, respectively, $\mu \simeq 4.0$ GPa and $B \simeq 3.7$ GPa, corresponding to a Poisson's ratio ν of about 0.1, with an estimated error of a few percent.

The numerical value of μ is in the range of the C_{44} elastic constant of hexagonal crystalline graphite ($C_{44} = 2 \approx 5$ GPa) [22], [23]. This last result can be compared with Raman measurements [5] which point out the mainly sp^2 carbon bonding present in the disordered granular structure of the films on a nanometer scale. Yet the film material is not elastically identical to nanocrystalline graphite: in fact the values of B (and, consequently, ν) are significantly different [22], [23]. Our results differ considerably from those reported in [24]

and obtained by nanoindentation measurements on cluster-assembled carbon thin films. Yet, we stress that nanoindentation is not a reliable technique in the case of a soft, thin film on a hard substrate [25]. Amaratunga *et al.* have also reported the synthesis of hard elastic carbon films by deposition of carbon particles produced by cathodic arc discharge [2]; a comparison with our work is however difficult since the cluster size distribution is different from ours and the velocity distribution is not reported.

In conclusion, we have measured the mesoscopic acoustic properties of both thin and thick cluster assembled carbon films by means of Brillouin light scattering in the GHz range. The adiabatic effective bulk and shear moduli of the thin-film material have been determined by the surface Brillouin peak spectral positions and are consistent with the value of the C_{11} elastic constant of the thick film within the experimental errors (eqs. (1)). In particular, the value of shear modulus μ, of the order of 4 GPa, compares with the C_{44} elastic constant of hexagonal crystalline graphite [10], at a scale which is intermediate between atomic and macroscopic. Our work shows that cluster beam deposition can be used to produce low-density porous films where clusters correlate on a mesoscopic scale giving origin to a low-density, isotropic material with shear properties similar to those of graphite but with a different compressibility. This observation suggests that this material should show also interesting thermal, chemical and transport properties. Moreover we have demonstrated the possibility of using Brillouin spectroscopy as a tool for the characterization of the elastic properties of thin films owning to a disordered granular structure in a range from atomic dimensions up to hundreds of nanometers. This opens interesting perspectives for the study of nanocrystalline materials.

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We acknowledge financial support from INFM Advanced Research Project *CLASS*. Mr. D. PICENONI is gratefully acknowledged for SEM images.

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