Acoustic phonon propagation and elastic properties of cluster-assembled carbon films investigated by Brillouin light scattering

C. S. Casari, A. Li Bassi, and C. E. Bottani
INFM-Dipartimento di Ingegneria Nucleare, Politecnico di Milano, Via Ponzio 34/3, 20133 Milano, Italy

E. Barborini, P. Piseri, A. Podestà,* and P. Milani
INFM-Dipartimento di Fisica, Università di Milano, Via Celoria 16, 20133 Milano, Italy

We demonstrate that elastic properties of cluster-assembled carbon films can be measured by surface Brillouin scattering. We have studied films with different nano- and mesostructures produced with different precursor cluster mass distributions. In particular, films showing very high and low surface roughness have been compared over a wide range of film thicknesses. We have found that the propagation of surface and bulk acoustic phonons is strongly affected by the film mesostructure. Absence of phonon propagation and localization effects have been observed in films assembled with large clusters due to surface roughness, whereas small clusters produced smooth films showing well defined Brillouin peaks. This occurrence, together with the determination of the material density by x-ray reflectivity, made the evaluation of the elastic properties of nanostructured carbon films possible. The values of the elastic constants, and in particular the anomalous (extremely low) value of the Poisson's ratio, suggest that cluster-assembled carbon films are a unique system among different inorganic carbon-based materials.

Carbon materials having a structure at the nanoscale are of paramount interest both for pure and applied science.[1] Among nanostructured carbon-based materials, those produced by low-energy cluster beam deposition (LECBD) are gaining considerable attention.[2–4] Cluster fragmentation in LECBD is almost negligible and the aggregates maintain their individuality after deposition, giving origin to a granular material at a nanometer scale with interesting properties for field emission and electrochemical applications.[5–7] Preliminary reports have shown that the primeval clusters assemble themselves in structures hierarchically organized over length scales from tens of nanometers up to several microns.[8] The evolution at the mesoscale is strongly influenced by the initial cluster mass distribution and it is different from what observed in atom-assembled films.[9]

The presence of mesoscale inhomogeinities in thin films assembled atom by atom and its influence on the functional and structural properties has been observed and exploited for a long time.[10] A systematic characterization of the mesoscopic structure of cluster-assembled materials and its relation with the nanostructure is still lacking due to the difficulty of finding experimental probes sampling, at the same time, length scales spanning from the nanometer to several tens of micrometers.

From this point of view, the characterization of the elastic properties of cluster-assembled carbon films is particularly interesting because it offers the possibility of studying the evolution, towards a continuous homogeneous medium, of a system characterized by a granularity and a porosity at different length scales. In particular, the organization of clusters in larger mesoscopic units can have a profound influence on the propagation of acoustic phonons with wavelengths of several hundreds of nanometers.

One of the techniques of choice for the elastic characterization of thin films is surface Brillouin spectroscopy (SBS).[11] SBS can overcome the problems typical of nanoin-

dentation when dealing with very thin films or granular and soft materials.[12] Normally SBS is applied to homogeneous compact films with perfect (atomically flat) surfaces and buried interfaces.[13,14] The elastic properties of carbon-based systems have been extensively characterized with SBS and the evolution of elastic moduli correlated with the sp^2/sp^3 bonding ratio.[15] We have previously shown that SBS can be used to characterize very thin (100-nm) cluster-assembled carbon films,[12] however, the roughness and inhomogeneity of LECBD systems are a serious obstacle to a systematic use of SBS and, in general, for a precise determination of the elastic constants and of their dependence from the mesoscopic organization of the precursor clusters.

The aim of this paper is twofold: first, to systematically study the conditions for propagation of acoustic phonons in LECBD films; second, to show that, by controlling the film roughness and by a careful choice of substrate material, the elastic constants of cluster-assembled carbon films can be studied in detail with Brillouin spectroscopy over a wide range of thicknesses. Bulk, shear modulus, and Poisson's ratio of the nanostructured carbon films have been determined and related to the different size of precursor clusters used for deposition. With SBS we have obtained information about the organization of clusters at a scale of hundreds of nanometers, which is the typical scale of thermally excited long-wavelength acoustic phonons.

Nanostructured carbon films have been deposited from a supersonic cluster beam produced by a pulsed microplasma cluster source (PMCS) as described in detail in Ref. 16. With normal PMCS operation conditions, the cluster beam is characterized by a log-normal cluster mass distribution in the range 0–1500 atoms/cluster, with a maximum peaked at about 500 atoms/cluster. The kinetic energy of the clusters was on the order of 0.2 eV/atom; no substantial cluster fragmentation is then expected.[5] We have controlled and varied the cluster mass distribution and deposition rates by exploit-
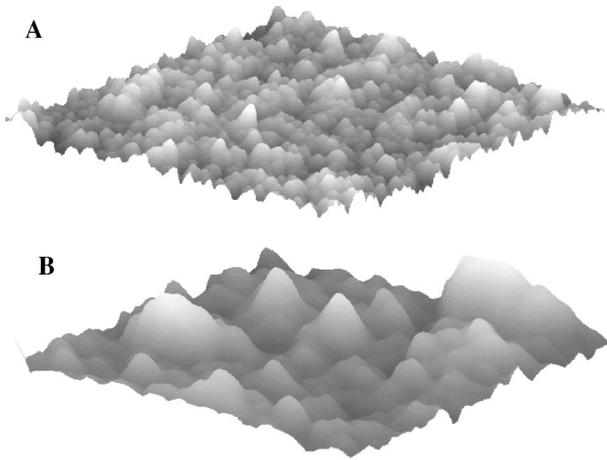
FIG. 1. Atomic force microscopy pictures of the surface topography of two nanostructured carbon films assembled with small clusters (A) and with large clusters (B). The pictures have been taken in tapping mode with a Digital Nanoscope IIIA microscope. Scan size is 1 μm and the z-axis range is 120 nm for both images. The film thickness is 290 nm (A) and 200 nm (B). The relative weight of the roughness (defined as the double of the ratio of the roughness over thickness) is 5 and 15% for A and B, respectively.

ing aerodynamic focusing effects.[17] Using the standard cluster mass distribution described above, we have deposited films with thicknesses from 30 nm to more than 1 μm on both silicon and aluminum substrates. The deposition rate was 4–5 nm/min and the density of the films was 0.8–0.9 g/cm³ (as measured by x-ray reflectivity[18]). With a different nozzle configuration we have produced a focused beam and we have been able to deplete clusters with diameters roughly larger than 2 nm (Ref. 17) from the beam, producing films with densities of 1.2–1.3 g/cm³ at a deposition rate of 5 nm/sec.

Brillouin scattering spectra were recorded at room temperature and in backscattering geometry using a tandem 3 +3 pass Sandercock interferometer with a finesse of 100 and a λ = 514.5-nm wavelength Coherent Innova 300 Ar-ion laser. The scattered light was detected by a Hamamatsu bialkali photomultiplier tube, in single-photon counting configuration, with a dark current of 0.7 cps. The samples were kept in vacuum to prevent damage by photo-oxidation effects.[19,20] The spectra were usually recorded with a free spectral range of 30 GHz using a laser power of $\approx$ 35 mW onto the sample. Due to the low signal intensity acquisition times of the order of several hours were required.

At a mesoscopic scale, the morphology for a given film thickness is the result of the coalescence of the primeval clusters into larger units. Cluster size strongly affects the evolution of film roughening.[8] This can be seen in Fig. 1, where two films, assembled with small and large clusters, are compared. In the film deposited with small clusters the roughness is a factor of 3 lower than that of the film assembled with large clusters. The small cluster film is characterized by grains with a typical diameter of 20–30 nm, whereas the large cluster film has grains with a diameter of several hundreds of nanometers.

We have examined films grown with large clusters (non-
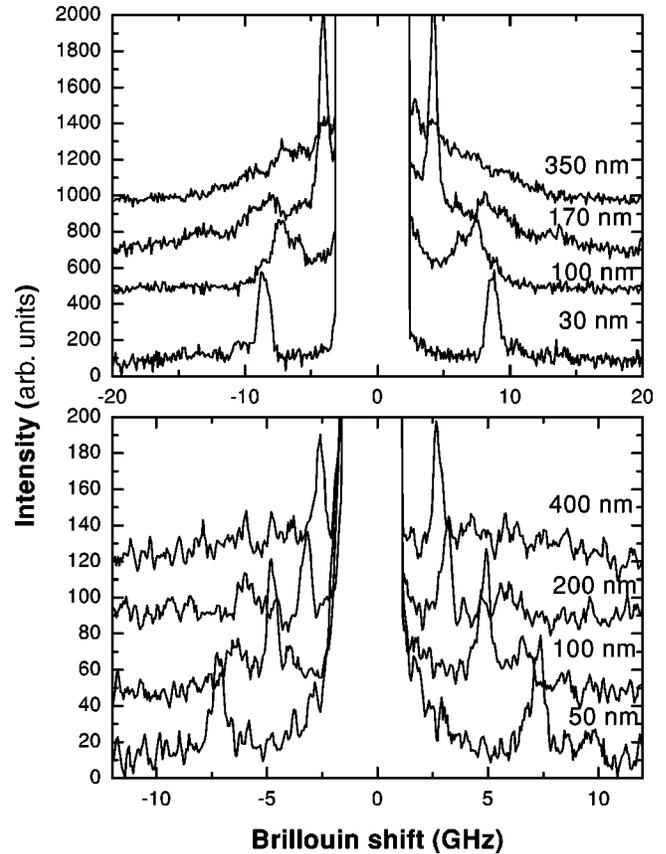
FIG. 2. Top: Brillouin spectra from films of different thickness, deposited using unfocused beams (larger clusters). In these measurements the incidence angle is θ_i = 50°. The effect of varying the thickness is reflected in the intensity of the modes (Rayleigh and Sezawa) traveling in the film and in their velocity. Bottom: Brillouin spectra from films deposited using a focused beam (smaller clusters) and having different thicknesses. In these measurements the incidence angle is 50°, and a 3-mm slit was placed after the collection objective in order to improve the resolution. This explains the different intensity and signal-to-noise ratio with respect to the series of measurements of Fig. 2, top, and with respect to the measurements shown in Fig. 3. Note that the Rayleigh peak is always visible and its frequency is always lower than the Sezawa peak frequency.

focused beams) with a thickness ranging from 30 nm to more than 1 μm. In thin films, notwithstanding the high degree of surface roughness, which increases along with film thickness, surface peaks (corresponding to Rayleigh and Sezawa modes) can be detected up to a critical thickness of the order of 200 nm (Fig. 2, top), provided that the films are grown on an ultrasmooth high reflecting substrate (in our case, Al) to maximize the buried interface ripple scattering. On the other hand, the surface disorder, which strongly scatters the surface phonons, does not allow their detection for films grown on Si substrates (where the reflectivity is less; moreover, Si exhibits an intense 60-GHz-wide central peak due to a two-phonon Raman scattering just in the region of the surface peaks of interest).

When the thickness becomes higher than roughly 100 nm (and the surface roughness increases), a central peak starts to

develop and the surface peaks become weaker and broader, and eventually disappear. In very thick films (more than 1 μm) only the central peak and, sometimes, strongly damped bulk acoustic phonons, with a typical wavelength λ_{ph} of the order of 200 nm, have been detected. The bulk feature is due to scattering from a longitudinal phonon, since transverse bulk phonons are not visible in isotropic materials in backscattering. This indicates that for a length $d \geqslant \lambda_{ph}$ the film bulk can roughly be modelled as a continuum[21] with approximate 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 nonpropagating (overdamped) or confined vibrational excitations, probably connected with different characteristic correlation lengths less than d, related mainly to the huge surface roughness (up to the order of the film thickness itself). The most damped bulk acoustic phonons could be coupled to the confined modes by a relaxation mechanism. In thick films the surface phonons could be almost overdamped if not already replaced by surface fractons or by localized cluster modes.[22]

The detection of the bulk longitudinal peak permits to determine only the C_{11} elastic constant. In order to completely characterize the elastic properties of the films grown with large clusters, using the procedure and the software described in Ref. 13, the dispersion relations of the surface phonons (i.e., phonon velocity as a function of the incidence angle) at a fixed thickness had to be measured. Rayleigh and Sezawa peaks were usually detected in thin films. The best results are obtained for the Young modulus E as demonstrated by a detailed sensitivity analysis.[23] The Young modulus E varies in the range 3–7 GPa, while G (shear modulus) is in the range 1–2.5 GPa, depending on several source parameters (and thus on the specific properties of the beam and on the exact cluster mass distribution). Extremely low values of the Poisson's ratio ν (of the order of 0.1) were estimated.

The sensitivity analysis[23] shows that the uncertainty in the determination of ν is greater than in the case of the Young modulus. This means that the Poisson's ratio can have values very close to zero, or even negative.

Films with a different nanostructure, more compact[2] and with a smoother surface, have been grown using small clusters (focused beams). Figure 3 shows the Brillouin spectra of a thick film (≈ 1 μm) measured for two different angles of incidence, $\theta_i = 50°$ and $\theta_i = 70°$. The shift of the first two peaks scales with θ_i: both peaks belong to the surface spectrum. The first peak corresponds to a Rayleigh phonon (RW) and the second, the *longitudinal resonance* (LR), is a general feature of the continuous spectrum whose shift scales as $v_l 4\pi \sin\theta_i / \lambda_0$, where $v_l = \sqrt{C_{11}/\rho}$ is the velocity of the bulk longitudinal acoustic wave. The LR is a so-called *pseudosurface* phonon. It is a wave packet of bulk phonons with a strong surface localization of the longitudinal polarization behaving as a surface wave. Because of its longitudinal character it gives no contribution to the ripple scattering cross section. The third peak is due to a longitudinal bulk (LB) phonon whose shift is independent from θ_i and scales as $v_l 4\pi n / \lambda_0$.
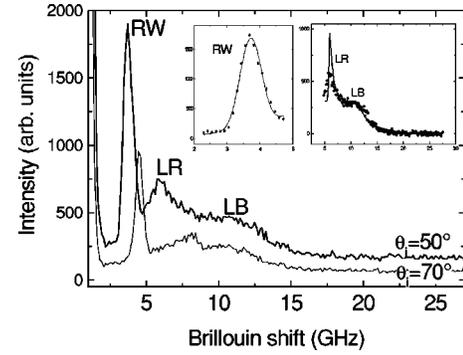
FIG. 3. Brillouin spectra from a focused film (small clusters), at two different angles of incidence, $\theta_i = 50°$ and $\theta_i = 70°$. The surface spectrum is characterized by the dependence on the angle of incidence of the peak frequency [Rayleigh wave (RW) and longitudinal resonance, (LR)] while the bulk spectrum presents a longitudinal bulk (LB) wave with a fixed frequency position. In the small inset boxes fitting of the $\theta_i = 50°$ spectrum is shown. The numerical simulation of the scattering total cross section (line) is superimposed to the experimental points in the right box while in the left one the RW peak was fitted separately with a fitting procedure using a pseudo-Voigt function.

The presence of both the LB and the LR modes permits to determine, without any other information, the real part of the refractive index as the ratio between their frequency positions. We found a value near to 1.5 in accordance with the value obtained from ellissometry measurements on this kind of material.[24]

The imaginary part of the refractive index is not directly measurable from the peak positions. Anyway, since it is responsible for the opacity broadening of the bulk peak we tried with numerical simulations of the Brillouin cross section to reproduce the experimental width of the LB peak and we found a value of 0.15–0.20 with respect to the value 0.25 obtained from ellissometry.[24] This mismatch could be explained by both the low precision of our calculation procedure and the difficulty, in an ellissometry experiment on such kind of material, to distinguish between the absorbed and the scattered light.

In the small inset boxes of Fig. 3 the fit of the $\theta_i = 50°$ spectrum is shown: the numerical simulation of the scattering total cross section is superimposed to the experimental points in the right box while in the left one the RW peak (discrete spectrum) was fitted separately with a pseudo-Voigt function. The assignment of the vibrational features was supported by calculations of the Brillouin scattering cross section and layer projected phonon density of states[13] in an *equivalent* perfect layer structure.

These spectra are remarkable for the high intensity and small width of the Rayleigh peak, never observed before in cluster-assembled carbon films and, in general, unexpected in low-density granular materials.[11] This feature supports the conclusion that long life acoustic phonons can propagate along the film surface; in other words at a mesoscopic scale of observation this film appears as a homogeneous elastic continuum and the relatively low surface roughness, acting as surface structural disorder, introduces only a small acous-

tic damping factor without hindering the phonon propagation (as in the case of nonfocused films). This fact is consistent with a smooth surface film of a relatively compact material made of small clusters and it is important in comparison with the results of SBS measurements of films deposited without beam focalization in which the surface roughness increases substantially with the film thickness.

Eliminating large clusters from the beam, we have obtained smooth films and the evolution of the roughness is very slow. In Fig. 2 (bottom) distinct surface peaks are clearly visible for thickness in the range 50–400 nm. No central peak evolution was detected. These films were deposited with the same nozzle configuration as for the thick film of Fig. 3, in order to obtain a focused beam and to eliminate large clusters, but with different source working conditions, so that they do not correspond exactly to the same cluster mass distribution. Anyway, this clearly shows that films grown with a beam deprived of the large clusters do not present the central peak evolution visible in the top of Fig. 2. Thus the study of a thick film is possible in this case; this, compared to the analysis of thin films, gives an advantage: we can consider the film as a semi-infinite medium and so the nature and the characteristics of the acoustic waves propagating in the system are not affected by the thickness (often not known with enough accuracy), and thus by the presence of the substrate. The velocities of the surface features detected in the thick film (Fig. 3) are governed by the elastic constants of the material, and this allows their determination without the need for a complete dispersion relation. Using the density ρ values coming from x-ray reflectivity[18] (1.2–1.3 g/cm^3), the calculated elastic constants are, typically, $C_{11} = 5.4 \pm 0.4$ GPa, $C_{44} = G = \mu = 2.5 \pm 0.2$ GPa. From these values we can estimate the mean values $E = 5.3$ GPa, $B = 2.1$ GPa, and $\nu = 0.07$. Since $C_{12} = C_{11} - 2C_{44}$ and $\nu = C_{12}/(C_{11} + C_{12})$, this results in a wide error band in the determination of the Poisson's ratio, so that we cannot exclude the possibility of ν values close to or less than zero.

The comparison of the elastic constants of cluster-assembled carbon with other carbon-based solids[15,25–28] indicates a very soft and highly deformable material with a shear modulus (for shear between graphene planes) similar to graphite ($C_{44} = 4.5$ GPa) and a Young modulus smaller than that of *fcc* C$_{60}$ [fullerite, $E = 9.99$ GPa (Ref. 26)]. We can also compare these values, e.g., with those of graphitic foams with low mass density ($E = 2$–51 GPa in the range 95–75% of porosity[27]) or with those calculated for negatively curved graphitic carbon [Schwartzite, calculated bulk modulus $B = 75$–94 GPa (Ref. 28)]. Several experimental probes have shown that, at the nanoscale, the cluster-assembled material is characterized by sp^2 bondings, although the degree of ordering at the nanoscale is different for systems deposited

with large and small clusters.[2] Yet it is not elastically identical to nanocrystalline graphite: in fact, the values of B (and, consequently, ν) are significantly different. This is reflected, for example, in the high flexural strength observed for films deposited on polymeric substrates.[8]

In summary, we have demonstrated the possibility of using surface Brillouin spectroscopy as a tool for the characterization of the elastic properties of low-density nanostructured carbon films. The use of proper metallic substrates and the reduction of film roughness by controlling the cluster deposition conditions has allowed a systematic characterization of films with different thicknesses, nano- and mesostructures. In the case of very thin films grown with large clusters we have used a metallic substrate to increase the ripple scattering cross section. Despite the large irregularity and roughness, the carbon film perturbs enough the surface phonon propagation of the free substrate to permit an estimate of the material elastic constants. In thick films the high degree of surface roughness hinders the propagation of surface phonons. Acoustic modes are subjected to damping and localization effects, which manifest themselves as a central peak in the scattering spectrum. A continuum film model is thus not adequate for the description of such a system.

On the other hand, films with smooth surfaces can be obtained by eliminating large particles from the cluster beam prior to deposition. In this way the formation of mesostructures on the scale of several hundreds of nanometers is impeded. These films can thus host surface and bulk phonons due to the considerably lower value of the surface roughness. Intense and sharp Brillouin spectra are obtained allowing a precise characterization of the elastic properties. This analysis has shown that, despite different meso- and nanostructures obtained from different precursors, the elastic properties of films deposited with large and small clusters are very similar. This observation suggests that the elastic properties are determined by the type of bonding on the nanometer scale.

The observation of C_{11} and C_{44} values compatible with a very low or even negative Poisson's ratio may be reminiscent of the low-density granular structure of the material.[29] Theoretical analysis has shown that assemblies of particles with greater stiffness in shear than in compression should show anomalies in the Poisson's ratio.[30,31] Cluster-assembled carbon materials show elastic properties similar to organic materials and they may give new interesting elements for the identification and control of the mechanisms of negative compressibility and find applications such as shock absorbers in micromechanical systems.

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*Present address: Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, Milano, Italy.

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