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BRILLOUIN SCATTERING OF CLUSTER-ASSEMBLED CARBON FILMS

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Abstract—The low frequency vibrational spectrum of cluster beam deposited carbon films was studied by Brillouin light scattering. In thin films the values of both bulk modulus and shear modulus has been estimated from the shifts of surface phonon peaks. The values found indicate a mainly sp^2 coordinated random network with low density. In thick films a bulk longitudinal phonon peak was detected in a spectral range compatible with the value of the index of refraction and of the elastic constants of thin films. High surface roughness, combined with a rather strong bulk central peak, prevented the observation of surface phonon features. © 1998 Elsevier Science Ltd. All rights reserved.

Key Words—C. Light scattering, C. Raman spectroscopy, C. scanning electron microscopy (SEM), D. phonons.

1. INTRODUCTION

The application of cluster beam deposition to the synthesis of nanocrystalline carbon thin films seems to be very attractive. The control of cluster deposition energy and mass distribution should open the possibilities for the creation of novel carbon-based materials: for example the incorporation of fullerene-like structures in an sp^2–sp^3 matrix may influence the mechanical properties of the nanostructured materials [1–3]. High frequency vibrational spectroscopy (Raman and IR) of carbon films is currently used to investigate their strucural order and bonding at the atomic level. Recently cluster-assembled thin carbon films, deposited by a new method using a pulsed arc cluster ion source (PACIS) and a supersonic cluster beam [1,2] have been characterized by Raman spectroscopy [4]. However, the above deposition technique produces films with a complex structure (possibly fractal) from the atomic to the mesoscopic level at the scale of hundreds of nanometers, which is the typical scale of long wavelength acoustic phonons detectable in Brillouin light scattering experiment. These hydrodynamic excitations [5] contribute to the low frequency vibrational spectrum. Films of graphite [6], polycrystalline diamond [7], diamond-like *a*-C:H [8], C_{60} (fullerite) [9] and phototransformed C_{60} [10] have already been studied by Brillouin scattering. We present here a preliminary Brillouin investigation of PACIS deposited carbon films. In these systems, bulk acoustic phonons with a typical wavelength λ_{ph} of the order of 170 nm, giving rise to coherent Brillouin scattering of laser light, were detected in thick films (thickness $\geq 0.5\ \mu m$). This indicates that for length $d \geq \lambda_{ph}$, the films can be considered as a continuum with complete translational invariance and effective elastic constants. The presence of a rather strong central peak in the spectra could be ascribed to non-propagating (overdamped), or confined vibrational excitations of the films, probably connected with different characteristic correlation lengths less than *d*. Using incoherent low frequency Raman scattering experiments we have tried to ascertain the existence of such modes, e.g. fractons [11], but so far we have no answer, due to extremely low signal and strong elastic peak tail in the range 1–50 cm^{-1}. The most damped bulk acoustic phonons could be coupled to the confined modes by a relaxation mechanism. The PACIS deposited films have a high degree of surface roughness and porosity, which can be shown by direct SEM images of the surface (see Fig. 1) and were confirmed by the observed considerable broadening of the phonon peaks and by the presence of a

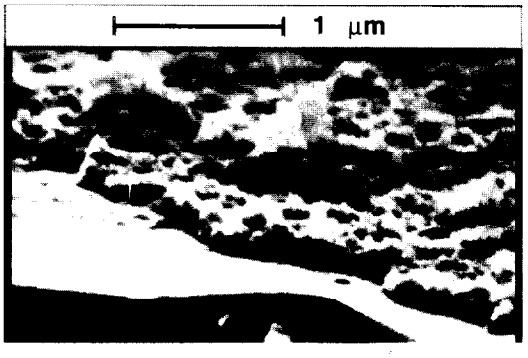

Fig. 1. SEM image of the cluster assembled carbon film. The cloud-like structure of the surface is clearly seen. The (100) surface of silicon is also visible.

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characteristic high elastic background in the Brillouin spectra. In thick films this strong elastic and quasi-elastic bulk signal impeeded the measurement of surface phonons which could be almost overdamped if not already replaced by surface fractons or by localized cluster modes, a situation possibly already faced in the case of porous silicon [12]. Yet in thinner films (thickness ~ 100 nm), surface peaks were detected. From their spectral shifts the elastic constants of the films were measured. The found values for the shear modulus of the films agree with their mainly graphitic structure, as shown also by Raman spectroscopy [4].

2. FILM DEPOSITION

Carbon thin films were deposited by clusters produced in molecular beams. We used a pulsed arc cluster ion source (PACIS) [1,2] modified in order to improve the cluster flux and the stability. A careful characterization of both neutral and ion cluster produced by the source has been conducted by time-of-flight mass spectrometry. The cluster fluxes have been characterized with a Faraday cup and a quartz microbalance. The dependence of the cluster mass distribution, energy and intensity on the source parameters have been characterized. Films have been deposited on various substrates (SiO_2, Si, Mo) placed on a micromanipulator, with deposition rates of the order of 3 nm min^{-1}. The mass distribution of the clusters peaked around 800 atoms per cluster, with a distribution that extended up to 2500 atoms. The kinetic energy of the aggregates was of the order of 100 eV per cluster.

3. BRILLOUIN SCATTERING

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 sixpass high contrast interferometer of Sandercock [13] 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 bialcali 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 wavevector $q_{\parallel} = (4\pi/\lambda)\sin\theta$ can be detected. Bulk peaks, associated with longitudinal or transverse phonons of wavevector $q = (4\pi/\lambda)n$, n being the index of refraction of the film, can also be measured in films with a 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 attentiation measurements, was attempted.

4. DISCUSSION

In Fig. 2(a), relative to a thick film (thickness >0.51 μm), 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. The above peak can be attributed 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 thinner films (see below) which agree with their graphitic-like structure as detected by Raman spectroscopy [4]. We assign the shift, v_L peak to the longitudinal (L) bulk phonon with wavevector $q = (4\pi/\lambda)n$ and phase velocity $v_L = \lambda v_L/(2n)$. Assuming that the film is elastically isotropic (and we have no strong reasons to doubt about that, also in view of its amorphous structure [4]) the transverse peak should not be visible in backscattering [13]. The longitudinal sound velocity v_L is connected to the adiabatic bulk modulus B and shear modulus μ by the formula [14];

$$v_L = \sqrt{\frac{B + \frac{4}{3}\mu}{\rho}}, \qquad (1)$$

where ρ is the mass density. A direct ellipsometric measurement of the index of refraction n of a film deposited in the same conditions at 514.5 nm gave $n \simeq 1.5$ [4]. Assuming $\rho \simeq 1.10^3$ kg m^{-3} [4], we obtain $v_L \simeq 3000$ m s^{-1}. It is evident from eqn (1) that both B and μ cannot be evaluated from the shift of only one bulk peak. In Fig. 2(b) the surface Brillouin spectrum of a thin (100 nm thick) film is shown. An intense pseudo-surface peak around 15 GHz and a group of strongly damped surface peaks around 10 GHz are visible. All these peaks exhibited a characteristic frequency variation with the incidence angle. A numerical computation of the layer projected phonon spectrum confirms [15] the surface nature of the above peaks and gives one the possibility to roughly evaluate the elastic constants of the film. It shows that $\mu \simeq 4.0$ GPa and $B \simeq 3.67$ GPa, corresponding to a Poisson's ratio of about 0.10.

The numerical value of μ is compatible with that of the C_{44} elastic constant of hexagonal Crystalline graphite ($C_{44} \simeq 2$–5 GPa). This last result is consistent with Raman measurements [3] indicating the mainly sp^2 carbon bonding present in the disordered structure of the films.

5. CONCLUSIONS

The mesoscopic acoustic properties of cluster assembled (PACIS) carbon films have been deter-

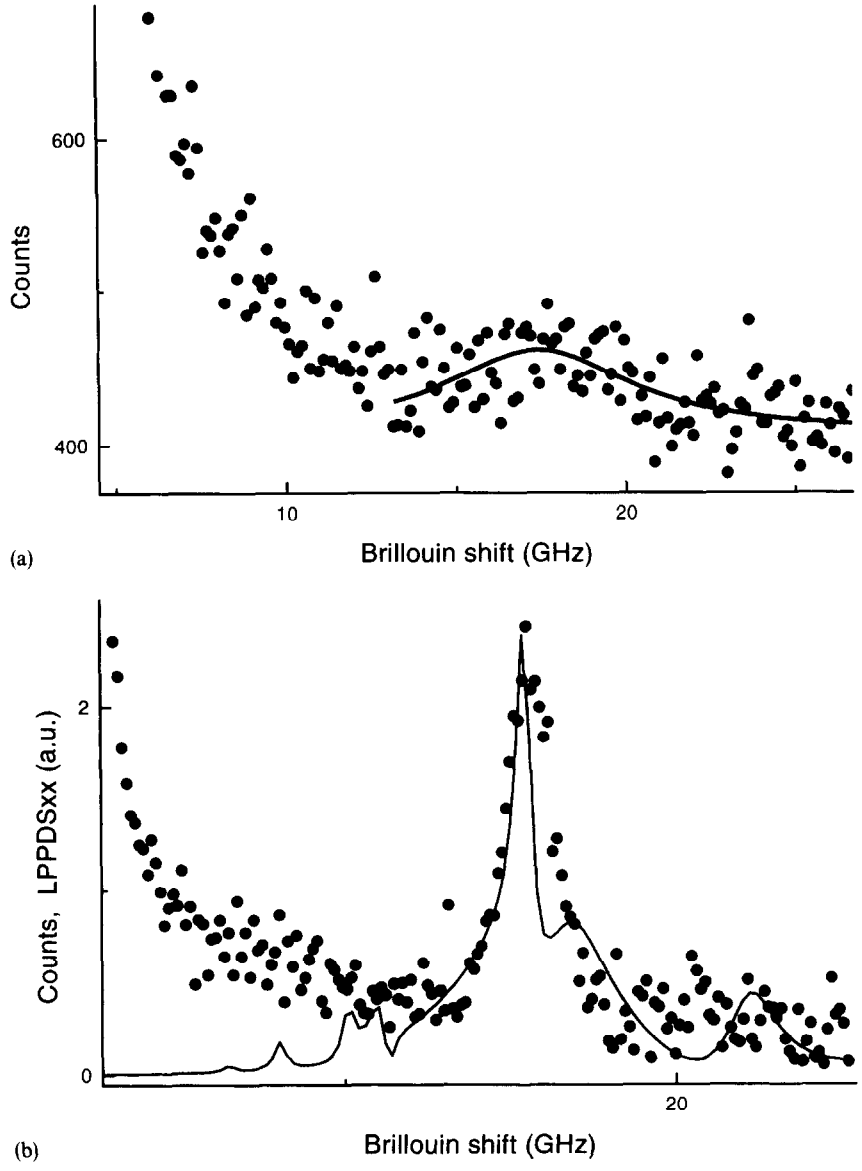

Fig. 2. (a) Bulk Brillouin spectrum of a thick film. The bulk longitudinal phonon peak has been marked by a Lorentzian arc fit. The spectrum has been taken at $\theta = 50°$. (b) Surface Brillouin spectrum of a thin film taken at $\theta = 30°$. Under the experimental spectrum the theoretical layer projected phonon density of states for the polarization parallel to the surface *LPPDxx*, computed with the physical constants of the film (see text) at a depth of 130 nm, is also shown. This depth was chosen because Brillouin light comes mainly from the tails of the surface modes extending in the silicon substrate where the elasto-optic coupling is maximum [15,16].

mined by means of Brillouin light scattering in the GHz range. The adiabatic elastic constants of the film material (the values of both shear and bulk modulus) have been measured on the basis of surface Brillouin peak positions and confirmed by independent knowledge of index of refraction and density [4]. In particular, the value of shear modulus μ, of the order of 4.0 GPa, confirms, at a scale which is intermediate between atomic and macroscopic, the sp^2 type of most covalent carbon bonds in the disordered structure of the films already revealed at atomic scale by Raman spectroscopy [4]. In fact the found value of μ is in the range of the literature values of the C_{44} elastic constant of hexagonal crystalline graphite [6]. Thus Brillouin spectroscopy, together with Raman scattering and SEM analysis, indicates that cluster assembled carbon films have a porous disordered *graphitic structure* in the range from atomic dimensions up to hundreds of nanometers. Further investigation of these structures by means of other techniques, e.g. very low frequency Raman scattering, is in progress.

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