Nanoscale and Mesoscale Properties of Nanostructured Carbon Films

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Abstract: A multi-scale investigation of nanostructured carbon films has been performed by means of inelastic light scattering (Raman and Brillouin scattering). Carbon films with different nano- and mesostructure have been deposited from supersonic cluster beams in a low energy deposition regime by exploiting aerodynamic focusing effects. Acoustic phonon propagation in the porous amorphous structure, where disorder acts as a damping factor, is investigated by Brillouin scattering. Depending on the nano- and meso-structure, acoustic phonons can either propagate along the medium, which acts as an elastic continuum at the meso-scale (i.e., hundreds of nm), or turn to overdamped oscillations localized by the structural disorder. Nevertheless, we show that it is always possible to measure the elastic constants of thin and porous films, when other techniques (e.g., nano-indentation) become critical. At the nano-scale, Raman scattering measurements show the typical structure of an amorphous carbon, where the structural disorder is affected by the

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primeval cluster mass distribution. The synthesis of cluster-assembled carbon films and the in situ Raman characterization in a UHV system allowed to observe the presence of a relevant fraction of $sp^1$-hybridized carbon chains (also known as carbynoid structures) embedded in the $sp^2$ amorphous network.

**Keywords:** Cluster-assembled carbon films, Raman scattering, Brillouin scattering, carbynoid structures

**INTRODUCTION**

Carbon-based nanosystems and nanostructured materials exhibit a large variety of structures with different chemical and physical properties, interesting both for fundamental aspects and for technological applications (1, 2). These properties often exhibit a scale-dependent behavior and in particular, moving from the nano- to the meso-scale (i.e., hundreds of nm), a crossover from properties ruled by isolated nanosystems to a behavior characterized by the interaction between different nanostructures can be observed.

In order to investigate the structure-dependent properties, a multi-scale investigation approach is particularly useful when dealing with such systems. In particular, inelastic light scattering (Raman and Brillouin) allows the investigation of dynamical structural properties of materials from the nano- (1–10 nm) to the meso-scale (a few hundreds of nm) (3–5). Raman scattering probes optical phonons and atomic or molecular vibrational modes at the nano-scale (6), while Brillouin scattering probes thermally excited long-wavelength acoustic phonons, thus giving access to structural and elastic properties at the meso-scale (7).

Here, inelastic light scattering has been used to investigate nano- and mesoscale properties of nanostructured carbon films deposited via pure carbon cluster assembling (using a supersonic cluster beam source) (8) in a low energy deposition regime (9). The film structure can be modified by varying the size distribution of the primeval clusters (10).

In particular, the film synthesis and the in situ Raman characterization opens the novel possibility of investigating metastable species that cannot survive when films are exposed to the atmosphere.

Cluster-assembled carbon films are characterized by an amorphous structure, with mainly $sp^2$ hybridized carbon atoms (as revealed by NEXAFS experiments (11)), although they also present a small fraction of $sp^3$ sites (11, 12) and $sp^1$-coordinated atoms (as discussed later). In these films clusters organize in low-density nano- and meso-structures, characterized by a high degree of porosity and structural disorder, (as shown by AFM (13), SEM and TEM measurements (10)), which strongly depends on the cluster mass distribution. Films deposited with larger clusters show a high surface roughness that grows with increasing film thickness; oppositely,
smaller clusters produce films with a more close-packed structure and a smoother surface characterized by a roughness that does not change significantly as a function of thickness, as revealed by AFM measurements (13).

EXPERIMENTAL DETAILS

Cluster-assembled carbon films were deposited from supersonic cluster beams produced by a Pulsed Microplasma Cluster Source (PMCS), (described in Ref. (8)). This apparatus is capable of producing very stable and intense cluster beams with a typical log-normal cluster mass distribution in the range 0–1,500 atoms/cluster, with a maximum at around 500 atoms/cluster. A different cluster mass distribution can be obtained by using a special nozzle configuration capable of depleting the beam of the largest clusters and graphitic particulate through aerodynamical focusing effects (14, 15). Clusters are deposited in a low energy deposition regime (a few fraction of eV/atom) so that no substantial fragmentation takes place upon deposition.

Using both large clusters (i.e., non-focused beam) and smaller clusters (i.e., focused beam) we have grown samples of variable thickness ranging from a few tenths of nm to more than 1 µm. Surface and bulk Brillouin measurements were performed in backscattering geometry with an Argon ion laser operating at 514.5 nm. The scattered light was measured by a tandem 3 + 3 pass high contrast interferometer of the Sandercock type (16). Samples were kept in vacuum to prevent damage by photo-oxidation effects (17).

In situ measurements have been performed by means of a portable UHV apparatus (CLARA, Cluster Assembling Roaming Apparatus) for cluster beam deposition in a low energy regime (described in detail in Ref. (18)), connected with a deposition chamber hosting a quartz viewport to perform the in situ Raman characterization.

Raman measurements at 532 nm (frequency doubled Nd:YAG) have been performed on films deposited at room temperature. The backscattered signal was analysed by a triple-grating Jobin-Yvon T64000 spectrometer with a spectral resolution below 3 cm−1.

SURFACE AND BULK BRILLOUIN SCATTERING

Brillouin scattering experiments on thick films (more than 1 µm) deposited with either small or larger clusters show significantly different results. In the first case surface and bulk acoustic phonons have been observed. The Brillouin spectrum of Fig. 1 shows a Rayleigh wave (RW), a longitudinal bulk wave (LB), and a longitudinal resonance peak (LR), that is a pseudosurface wave with mixed surface and bulk character. The interpretation of the observed Brillouin peaks is supported by numerical simulations of the total
In the latter case, no surface peaks related with the propagation of surface acoustic phonons could be observed (only a weak longitudinal bulk peak was sometimes observed (20)).

Films deposited with either small or larger clusters have been studied in order to investigate acoustic phonon propagation mechanisms as a function of thickness (in the 30–400 nm range). Films deposited with small clusters show well-propagating surface acoustic phonons with a small damping effect that does not substantially change with the film thickness (see Fig. 2A). On the other hand, in films deposited with larger clusters, a strong dependence of the phonon propagation behavior on the film thickness is observed, as shown in Fig. 2B. In particular, starting from 30 nm thickness, well-propagating surface acoustic phonons (Rayleigh and Sezawa modes) are observed. A large central peak (i.e., centered at zero frequency shift), superimposed on the surface Brillouin peaks, starts to grow from a critical film thickness of 100 nm. Its intensity increases until, at about 350 nm, no propagating surface acoustic phonons (and only this large central feature) can be observed.

The observation of propagating acoustic phonons permits us to derive the mesoscopic elastic properties (i.e., $C_{ij}$ elastic constants) of the films. From the longitudinal bulk wave propagation velocity ($v_L$) of thick films deposited with small clusters and using $v_L = \sqrt{C_{11}/\rho}$ (with the density value $\rho = 1.25 \pm 0.05$ g/cm$^3$ measured by x-ray reflectivity) (21), we found $C_{11} = 5.4 \pm 0.4$ GPa. Since films thicker than roughly 500 nm can be

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**Figure 1.** Brillouin spectrum of a thick film deposited with small clusters (focused beam) showing three acoustic modes related to a Rayleigh wave (R), a longitudinal resonance (LR), and a longitudinal bulk mode (LB). The simulated Brillouin scattering cross-section is also reported (grey line).
regarded as a semi-infinite medium for Brillouin scattering, the transverse bulk wave velocity $v_T$ depends only on $v_L$ and on the Rayleigh wave velocity $v_R$, we found $v_T$ solving numerically the corresponding equation (22). Using the relation $v_T = \sqrt{C_{44}/\rho}$, we determined $\mu = C_{44} = 2.5 \pm 0.2$ GPa for the shear modulus. The determination of both $C_{11}$ and $C_{44}$ allows to characterize completely the elastic properties of these films that can be considered as an isotropic (due to its amorphous character) and homogeneous (at least at the mesoscale, when propagating modes are observed) medium. We found $E = 5.3$ GPa for the Young’s modulus, $B = 2.1$ GPa for the bulk modulus, and $\nu = 0.07$ for Poisson’s ratio.

Elastic constants of films deposited with larger clusters were evaluated by an analysis of the surface peaks only (Rayleigh and Sezawa modes).

In fact, for thickness below roughly 500 nm, the film cannot be considered as a semi-infinite medium but a supported film where no bulk acoustic phonons can propagate in the film and the surface modes are characterized by dispersive velocities. In this case through the analysis of the velocity dispersion relations (the variation of the parallel wavevector is obtained by changing the laser beam incidence angle), it is possible to derive the elastic constants. Using a fitting procedure based on the calculation of the elastic constants compatible with the observed film dispersion relations, film

Figure 2. Brillouin spectra as a function of the film thickness. (A) films deposited with small clusters (focused beam) show well-defined Brillouin peaks. (B) films deposited with larger clusters (nonfocused beam) show a transition from propagating surface acoustic phonons to localized acoustic excitations.
density ($\rho = 0.8–1.0 \text{ g/cm}^3$ measured by x-ray reflectivity) (21), thickness and the substrate elastic properties (i.e., the solution of the inverse problem), the most reliable results are obtained for $E$ (Young’s modulus) and $G$ (shear modulus), as revealed by a detailed sensitivity analysis (23). We obtained $E$ in the $3–7 \text{ GPa}$ range while $G$ is in the $1–2.5 \text{ GPa}$ range.

EX SITU AND IN SITU RAMAN SCATTERING

Ex situ Raman characterization formerly performed on these films revealed the $G$ and $D$ bands (in the $1,300–1,600 \text{ cm}^{-1}$ spectral region) typical of an amorphous carbon material with a disordered structure characterized by distorted bond lengths and angles, and a weak feature in the $2,000–2,200 \text{ cm}^{-1}$ spectral region (24).

Ex situ Raman spectra of films deposited with either small or large clusters are shown in Fig. 3A. According to Ferrari and Robertson (25), the smaller $I_D/I_G$ ratio and the lower frequency of the $G$ band in the spectrum of the films deposited with smaller clusters reveal a higher structural disorder of the amorphous network with respect to the films deposited using larger clusters. Moreover a weak feature around $2,100 \text{ cm}^{-1}$ can be observed, particularly in the film deposited with smaller clusters.

In situ Raman spectra from as-deposited films in UHV are shown in Fig. 3B. Besides the $G$ and $D$ bands, they are characterized by a remarkably strong feature around $2,100 \text{ cm}^{-1}$, when compared to the ex situ spectra. This band can be assigned to the presence of $sp^1$-coordinated linear carbon chains (also known as carbonyd or carbyne-like structures) as confirmed by experimental (26, 27) and theoretical investigations. (28, 29) Band broadness can mainly be related to the presence of $sp^1$ chains of different length (30).

Carbonyd structures can display two different arrangements of the $sp^1$-carbon atoms. The name “polyyne” refers to a chain with alternating single and triple bonds, while polycumulene is the chain formed by double bonds only. Moreover the carbonyd band is structured in a main strong peak centered at about $2,100 \text{ cm}^{-1}$ and a shoulder at about $1,980 \text{ cm}^{-1}$. These features are assigned to the presence of both polyyenic and polycumulenic species, since the frequency of the vibrational modes responsible for this peak is different in the two species (28). These outcomes confirm the presence of carbonyd structures in the film, though a quantitative evaluation of their abundance is not feasible, mainly because the scattering cross-section ratio $sp^1$ to $sp^2$ is unknown. We showed recently that carbonyd structures display a long-term stability in UHV in a pure carbon system (27), while hetero-atoms or molecular groups are usually inserted to stabilize the $sp^1$-structures obtained by other methods (31, 32). A detailed investigation of the stability against gas interaction, recently performed on these films (33),
has revealed the chemical role of oxygen in the decay of the carbonyl structures.

DISCUSSION

Raman and Brillouin scattering experiments on thick films have revealed that from the nanoscale, the typical observation scale of the Raman probe, to the mesoscale, the typical scale of the Brillouin probe (about 200 nm), the film structure changes dramatically as a function of the primeval cluster size distribution.
Ex situ Raman scattering results show that, at the nanoscale, smaller clusters produce films with a high degree of structural disorder (distortion of bond lengths and angles) in a main $sp^2$ network, though a small fraction of $sp^1$ phase survives exposure to the atmosphere.

Conversely, films deposited with larger clusters are characterized by a slightly less disordered structure, otherwise retaining an overall amorphous character. Larger clusters in fact are expected to display a lower distortion of bond lengths and angles (with respect to the graphite structure) than smaller clusters. Since Raman scattering is mainly sensitive to the inner structure of the clusters, our results somehow confirm that the deposited clusters, though arranging into larger units during the film growth, form a material whose nanoscale structural properties are related to the primeval cluster mass distribution. This is also in agreement with molecular dynamic simulations of the deposition process (34).

Brillouin scattering has shown that, in thick films deposited with large clusters, the mesoscale structural disorder acts as a damping factor for the phonon propagation so that the film cannot be considered as an effective elastic continuum with well-defined elastic constants. The film structure is strongly determined by the cluster arrangement into nano- and mesoscopic units forming a granular and sponge-like network, where, up to the mesoscale, the fraction of voids prevails over the continuous structure. On the other hand, when thick films are deposited with smaller and focused clusters, the structure is well-described by an elastic continuum model at the mesoscale, and the elastic constants can be evaluated by a direct analysis of the Brillouin spectra. This conclusion is supported by the fact that long-life acoustic phonons can propagate along the film surface. In other words, at the mesoscale, the film appears as a homogeneous elastic continuum and the surface roughness, acting as surface structural disorder, introduces only a negligible acoustic damping factor. This material can thus be considered as an “almost continuum”, with reference to phonon propagation, though structurally it is characterized by a porous and soft character. Brillouin spectra from thin films deposited with either small or larger clusters show a different behavior as a function of film thickness.

In films deposited with large clusters the growth of a large central band corresponds to a transition from acoustic phonon propagation to a regime of overdamped and localized acoustic excitations. These localization effects are due to mesoscale structural disorders that increases with the film thickness, in agreement with the increasing surface roughness measured by AFM. Conversely, in films deposited with smaller clusters, the surface roughness does not increase with increasing the film thickness and this cross-over in the acoustic phonon propagation is not observed (also due to a more close-packed structure).

Brillouin scattering has been proven to be a powerful technique to measure the elastic constants even when other techniques (e.g., nanoindentation) limited
by the thinness and the soft and porous structures of the investigated films. The values of the mesoscopic elastic constants are very similar in films deposited with both large and smaller clusters; even when at the nanoscale, the film structure is strongly affected by the cluster mass distribution, and reveal that these films are characterized by an extremely soft and deformable structure. In comparison with graphite, the film shear modulus has a value similar to the shear modulus between graphene sheets ($C_{44} = 4.5$ GPa), while the Young’s modulus has a dramatically lower value than the in-plane graphite modulus and even smaller than the Young’s modulus of fullerite ($E = 9.99$ GPa) (35). These results suggest that the acoustic phonon propagation and thus the mesoscopic elastic properties are mainly ruled by the inter-cluster interactions rather than by the cluster structure.

In situ Raman experiments have shown that the deposition of either small or large clusters strongly affects the $sp^2$ phase while weakly influencing the presence of carbynoid structures in the film. Indeed from these still preliminary results, no other information, except from the presence alone, can be inferred on the $sp^1$ phase. In fact Raman spectra are only qualitatively correlated to the absolute fraction and to the chain length of the $sp^1$ structure. Further information about the structure of the primeval clusters is also needed in order to investigate the relation between the cluster mass distribution and the $sp^1$ structures. We recently observed the presence of odd-numbered clusters, together with even-numbered stable structures, in a mass spectra taken from a cluster beam (33).

It has to be noticed that linear structures are theoretically expected for extremely small clusters (i.e., a few tens of atoms), while clusters in both the focused and the non-focused beam are characterized by a higher mass range (i.e., several hundreds—thousands of atoms), where mainly $sp^2$ stable structures are predicted. Our preliminary observation thus seems to confirm that the cluster source produces a wide range of cluster structures where both small and large (i.e., several from hundreds up to thousands of atoms) metastable clusters rich in $sp^1$ content are present. For instance, open structures with mixed $sp^2$ and $sp^1$ atomic coordination where “stick” $sp^1$ structures are attached to a $sp^2$ cage have been observed, even though in smaller clusters (40–100 atoms), in laser vaporization of graphite and laser desorption of $C_{60}$ (36).

**CONCLUSIONS**

Nanostructured carbon films with different nano- and mesostructures have been deposited by means of a supersonic cluster source by using either smaller or larger cluster size distribution (focused and nonfocused) beam. The multi-scale structural properties have been investigated by inelastic light scattering (Raman and Brillouin scattering). Raman spectra revealed
that, at the nanoscale, the structural disorder is strongly affected by the cluster mass distribution. Brillouin scattering results display a transition from a regime of acoustic phonon propagation towards overdamped acoustic excitations localized by the structural disorder. Nevertheless Brillouin scattering always allowed to measure the mesoscopic elastic constants, which reveal an extremely soft and deformable material, where the elastic behavior is mainly ruled by the inter-cluster interactions.

In situ Raman spectra of films deposited in UHV with both focused and nonfocused cluster beams revealed the presence of metastable $sp^1$-coordinated structures. This suggests that both large and small metastable clusters with a significant $sp^1$ content are formed in the source, together with stable clusters with $sp^2$-coordination.

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