Local indentation modulus characterization of diamondlike carbon films by atomic force acoustic microscopy two contact resonance frequencies imaging technique

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Two contact resonance frequencies atomic force acoustic microscopy imaging technique has been used to evaluate local indentation modulus of a diamondlike carbon film deposited on a molybdenum foil by laser ablation from glassy carbon target. Acoustic images were obtained by measuring both first and second contact resonance frequency at each point of the scanned area, and then numerically evaluating local contact stiffness and reconstructing an indentation modulus bidimensional pattern. The wide difference of the indentation modulus values allows to detect the presence of residual glassy carbon agglomerates in the diamondlike carbon film. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2188376]

Diamondlike carbon (DLC) is a synthetic form of amorphous carbon with variable sp^3/sp^2 hybridization ratio.[1,2] Differently from diamond, DLC films can be synthesized at low pressure and temperature. Depending on the presence of sp^3 tetrahedral bonds, DLC exhibits some chemical, mechanical, electrical, and optical properties similar to the diamond deposited by chemical vapor deposition,[2] thus suggesting it to be used as hard coatings for wear, tribological, optical, biomedical, biochemical, and acoustical applications.[2] Mechanical properties of DLC films, such as adhesion, wear resistance, hardness, elastic modulus, and Poisson ratio have been reported in literature.[3–9] Nevertheless, the application of DLC coatings films in microelectromechanical systems (MEMSs) (Ref. [10]) requires the characterization of local mechanical properties with submicrometrical spatial resolution, in order to check the uniformity of the elastic parameters on the characteristic scale of such devices atomic force acoustic microscopy (AFAM),[6,11–14] and ultrasonic force microscopy (UFM) (Refs. [15,16]) represent powerful tools to retrieve images qualitatively reflecting samples surface elastic properties and to quantitatively determine local value of the indentation modulus, with resolution limited by the contact radius between tip and sample.[6,17] Amelio *et al.*[6] used AFAM technique for quantitative contact resonance frequency measurements on DLC samples, and focused their attention on the abrasion occurring to the spherical apex of silicon tips while performing AFAM measurements on DLC samples, suggesting the use of diamond-coated tips. Nevertheless, the local indentation modulus of DLC films have never been quantitatively measured.

AFAM images reported in literature are obtained, simultaneously to the topography, by monitoring the vibration amplitude of the atomic force microscope (AFM) cantilever contacting the surface of the sample, the latter being excited by a piezoelectric transducer driven at a frequency close to one of the contact resonances.[12] The contrast in the AFAM amplitude images is produced by local variations of the indentation modulus, which cause a shift in the contact resonance frequency. Therefore, AFAM amplitude images supply only qualitative information on the local indentation modulus. In order to quantitatively evaluate it, additional measurements of the contact resonance frequencies are necessary. Moreover, contrast in the AFAM amplitude images does not reflect the variations in the elastic properties of highly inhomogeneous surfaces, where the shift in the contact resonance frequencies far exceeds the bandwidth of the resonance frequencies themselves.

In this letter, a generalization of AFAM technique is proposed: AFAM images are recorded by monitoring both the first and the second contact resonance frequency, thus allowing one to obtain a bidimensional quantitative reconstruction of indentation modulus over the imaged sample area, in analogy with what was reported by Muthuswami *et al.*[16] using UFM technique. The technique has been used to measure local values of the indentation modulus on DLC films in order to verify the presence of inhomogeneities on the samples surface.

In AFAM experimental procedure, the AFM tip is brought into contact with the sample surface which is set into vibration at ultrasonic frequencies through a piezoelectric transducer placed under the sample. For small vibration amplitudes, the tip can be modeled by a linear spring whose elastic constant is the tip-sample contact stiffness k^*, given by the expression[11,14]

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$$k^* = \frac{2}{3}k_c(c_c\sqrt{f_n}r)^3(1+\cos c_c\sqrt{f_n}\cosh c_c\sqrt{f_n})/\{-(\cosh c_c\sqrt{f_n}r\sin c_c\sqrt{f_n}r - \sinh c_c\sqrt{f_n}r\cos c_c\sqrt{f_n}r) \times (1+\cos(1-r)c_c\sqrt{f_n}\cosh(1-r)c_c\sqrt{f_n}) + (\cosh(1-r)c_c\sqrt{f_n}\sin(1-r)c_c\sqrt{f_n} - \sinh(1-r)c_c\sqrt{f_n}\cos(1-r)c_c\sqrt{f_n}) \times (1-\cos c_c\sqrt{f_n}\cosh c_c\sqrt{f_n})\}, \tag{1}$$

where f_n is the set of contact resonance frequencies; $r = L_1/L$ is the ratio between the distance of the AFM tip from the cantilever clamped end (L_1) and the cantilever length (L); k_c and c_c are the spring constant and a characteristic parameter of the cantilever, respectively.[11] Experimentally, k^* can be deduced from the measured first (f_1) and second (f_2) contact resonance frequency, by matching the expressions of k^* obtained from Eq. (1) at each mode[6] by imposing

$$k^*(f_1,r) = k^*(f_2,r), \tag{2}$$

where r is used as a free fitting parameter. The measured value of k^* allows one to evaluate the local indentation modulus M of the sample, after the calibration of the tip is performed in a reference sample in order to determine the geometrical parameters of the apex, with either a spherical or a flat tip shape.[14]

The investigated DLC sample was representative of a set of samples deposited by laser ablation (excimer laser XeCl at $\lambda = 308$ nm, pulse duration 27 ns, frequency of pulses 3 Hz) from a glassy carbon (GC) target (Glassy Carbon V25-type by Atomergic Chemetals Ltd.) on Mo substrate at $T_s = 400$ °C. The obtained films have been routinely investigated by Raman, reflective high-energy electron diffraction and scanning electron microscope (SEM) analysis. Raman spectra from the samples show two main features corresponding to the Raman-allowed peak (G band) and to the disordered-induced Raman signal (D band), respectively. Comparison with the spectra obtained from source material evidences in the ablated samples a variable fraction[18] of sp^3 sites produced by bonding rearrangement of the ablated GC. The RHEED analysis of the films do not reveal a long-range order, but rather the presence of locally three-dimensional ordered material, in good agreement with the Raman results.

The AFAM apparatus (Solver P47H, NT-MDT, Russia) was equipped with a (100) Si tip (Mikromasch, nominal dimensions: length $L = 230 \pm 5$ μm, width $w = 40 \pm 3$ μm, and thickness $t = 7.0 \pm 0.5$ μm) with spring constant $k_c = 33$ N/m measured with the method of Sader *et al.*,[19] and with a flat apex shape, as evidenced by both AFAM and SEM characterization.[14]

Figure 1(a) is the reconstruction of film surface obtained in standard AFM contact mode, revealing the presence of agglomerates with size of hundreds of nanometers, in agreement with SEM observations. Figures 1(b) and 1(c) report the two contact resonance frequencies TCRF-AFAM images obtained by measuring f_1 and f_2 at each point of the scanned area, in the ranges of 680–820 kHz and 1600–2400 kHz, respectively. As previously discussed, the dispersion values of frequencies f_1 and f_2 far exceed the bandwidth of each resonance mode and do not allow one to obtain a contrast in AFAM amplitude images that reflects elastic properties of the surface. Such wide frequency shifts observed for wide range sized agglomerates (in both f_1 and f_2 AFAM images, agglomerates observed in AFM topography appear darker than the surrounding film) cannot be attributed to any topography-induced artifact.[20] Smaller frequency shifts, indeed, are observed at grains boundaries where inclined surfaces are present in Figs. 1(b) and 1(c), ascribable to topography induced artifact.[20] The wide frequency shifts observed in Figs. 1(b) and 1(c) in correspondence to dark agglomerates must be attributed to a noticeable decrease in the local indentation modulus. After the measurements reported in Fig. 1, the flat tip contact radius a has been determined by calibration on a monocrystalline (100) Si reference sample. After 20 scannings of random areas of sample surface, the contact radius a increased from 36 nm to 37 nm, due to the abrasion of the tip, which is significantly lower than the ef-

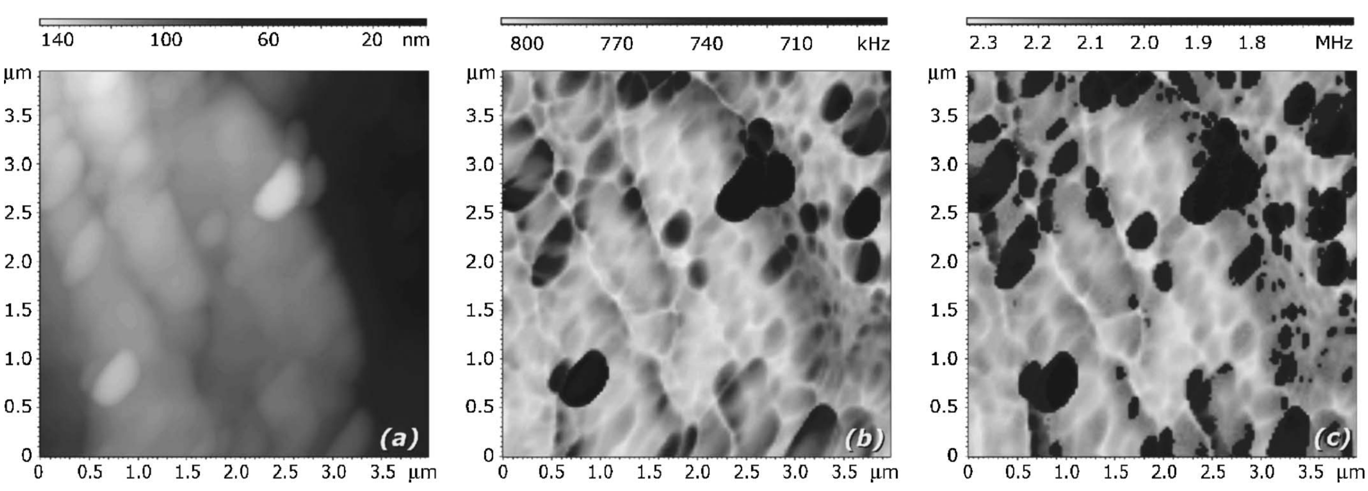

FIG. 1. AFM topography of DLC sample (a), AFAM images obtained by measuring the first (b), and the second (c) contact resonance frequency at each point of the scanned area.

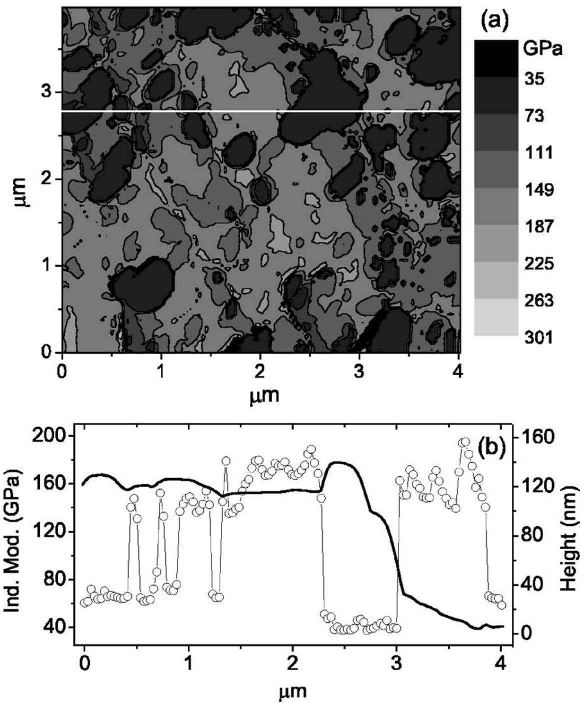

FIG. 2. (a) DLC indentation modulus values bidimensional reconstruction, obtained by evaluating tip-sample contact stiffness from the first and the second contact resonance frequency AFAM images; and (b) transversal section showing the variation of profile height (solid line) and indentation modulus (open circles).

fect observed by Amelio *et al.*,[6] and is ascribable to the flatness of the apex, that involves low stress (0.3 GPa) between the tip and the DLC sample. Thus, a single AFAM measurement makes the effect of abrasion on the tip negligible. Capillarity forces between tip and sample, estimated as $F_C = 165$ nN,[21] were neglected with respect to the normal applied static load. Finally, k^*/k_c ratio values allowed one also to neglect friction effects.[22] Comparing Figs. 1(b) and 1(c), it is worthwhile to note that the contrast in the AFAM image obtained by measuring the frequency f_2 increases with respect to the one obtained with frequency f_1: That is due to the higher sensitivity of the second mode with respect to the first one in the k^*/k_c values range for the investigated sample.[12] The TCRF-AFAM images reported in Figs. 1(b) and 1(c) have been processed with a numerical evaluation at each scanned point of Eq. (2), in order to obtain the pattern of the values of the indentation modulus shown in Fig. 2(a). Figure 2(b) reports the values of both the indentation modulus and the surface height as measured along the line reported in Fig. 2(a). The maximum experimental error in the evaluation of M was estimated as ±4%. Indentation modulus of the film surrounding the agglomerate can be evaluated from Fig. 2(b) in the range between 140–180 GPa, corresponding to a DLC film with low sp^3/sp^2 hybridization ratio.[3,4,7–10] Indentation modulus value of dark agglomerate was found to be $M = 41 \pm 4$ GPa, analogous to the value $M_{GC} = 39 \pm 3$ GPa measured on the GC target by standard AFAM technique, and it is in good agreement with the GC indentation modulus values reported in literature.[2] Consequently, the observed agglomerates correspond to amorphous carbon ablated from GC target and deposited on the substrate, with no bonds rearrangement.

In conclusion, AFAM technique has been used to obtain acoustical images by measuring local values of the first and second contact resonance frequency on a DLC film. TCRF-AFAM images were numerically processed, thus reconstructing local indention modulus values over the whole scanned area. Agglomerates observed in the DLC film morphological characterization have been demonstrated to be glassy carbon material ablated from the target with no bonds rearrangement. Beyond the results on the investigated DLC films, AFAM based on two frequencies imaging technique is proposed as a promising experimental procedure in order to obtain, simultaneously with AFM morphological characterization, bidimensional reconstructions of the local indentation modulus values of sample surface at nanoscale.

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