IOP Publishing Journal of Physics: Conference Series **61** (2007) 219–223
doi:10.1088/1742-6596/61/1/044 International Conference on Nanoscience and Technology (ICN&T 2006)

Ultrasonic Machining at the Nanometer Scale

M. Teresa Cuberes

Department of Applied Mechanics and Project Engineering, University of Castilla-La Mancha, Escuela U. Politécnica, Plaza Manuel de Meca 1, 13400 Almadén, Spain

teresa.cuberes@uclm.es

Abstract. Experiments on Highly Oriented Pyrolytic Graphite (HOPG) demonstrate that ultrasonic-assisted actuation with the tip of an Atomic Force Microscope (AFM) cantilever can induce stacking modifications and folding of triangular-shaped HOPG surface flakes. We have generated permanent displacements of buried dislocations that require stacking changes of extended graphene layers by repeatedly scanning over a same surface region. In this contribution, I discuss the opportunities of ultrasonic AFM to improve fabrication technologies on the nanometer scale and realize subsurface modification via near-field actuation.

1. Introduction

Recently, a new family of Atomic Force Microscopes based on the use ultrasound has been proposed [1-11]. It has been demonstrated that the procedures provide a valuable means for the characterization of materials properties with subsurface sensitivity. In addition, it has been shown that ultrasound at the tip-sample gap acts as a lubricant, reducing and even eliminating friction at a nanometer scale [12].

Ultrasonic technology finds many applications in our society. It is used in chemistry, biology and medicine, i.e. for preparation of colloids or emulsions, the pregermination of seeds, for imaging of biological tissues, etc. Also, in non-destructive testing (NDT), for measurement of materials properties, in metrology, etc. Ultrasonic vibrations are commonly employed in mechanical machining of materials [13]. In this contribution, I discuss the opportunities of ultrasonic AFM to improve fabrication technologies on the nanometer scale. Typical top-down approaches that rely in the AFM are based on the use of a cantilever tip that acts as a plow or as an engraving tool. In the presence of ultrasonic vibration, the tip of a soft cantilever can dynamically indent hard samples due to its inertia. This may facilitate the machining of hard samples, such as semiconductors or engineering ceramics. In addition, a reduced machining time may be expected. Furthermore, as ultrasound reduces nanoscale friction, finer features and improved surface quality should be achievable at soft materials, as for instance plastic coatings. In bottom-up approaches, ultrasound may assist in the self-assembly or manipulation of nanostructures. In addition, ultrasonic-AFM provides subsurface sensitivity. Subsurface dislocations in HOPG have been observed and reversibly displaced using ultrasonic AFM [4,14-17]. Our experiments on Highly Oriented Pyrolytic Graphite (HOPG) evidence that ultrasonic-assisted actuation with the tip of an AFM cantilever can induce stacking modifications and folding of triangular-shaped HOPG surface flakes. We have been able to induce permanent displacements of buried dislocations in HOPG after repeatedly scanning over the same surface region in the presence of ultrasonic vibration. Recently, nanoscale imaging of buried structures has also been achieved by mixing ultrasonic signals simultaneously excited at the cantilever tip and the sample surface [11]. Subsurface actuation via near-field ultrasonics show promise of useful applications in nanotechnology.

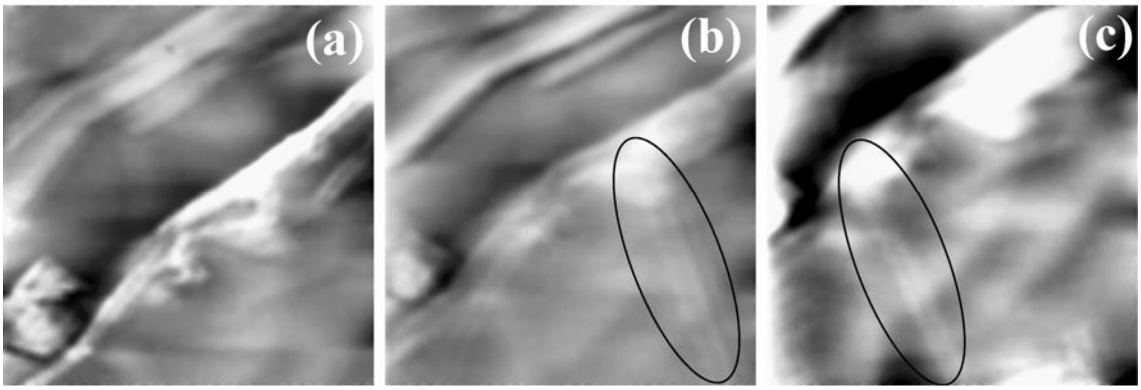

Figure 1. *(a)* Topography of the HOPG surface in AFM contact mode: 700 × 700 nm; Fo=105 nN; grey-scale range ≈ 6 nm *(b,c)* Ultrasonic-AFM images recorded in sequence over nearly the same surface region: ω=2.15 MHz (b) A=3.5 Vpp (c) A=2.4 Vpp.

2. Experiment

The experiments discussed here were performed using a set-up similar to the one described in Fig. 2 from ref. [18], implemented in our lab by appropriately modifying a commercial AFM instrument (Nanotec). The samples consisted in ZYA-grade Highly Oriented Pyrolitic Graphite (HOPG). The HOPG surfaces were freshly cleaved before each measurement. Rectangular Si cantilevers with a nominal normal stiffness of 0.35 N m^{-1} were used for both ultrasound-assisted sample modification, and imaging.

3. Results and Discussion

Fig. 1 (a) shows the topography of HOPG, a 700 x 700 nm surface area, with the typical flat terraces and cleavage steps. For ultrasonic imaging, a continuous sinusoidal ultrasonic wave was excited at the sample surface from a transducer located at its backside, while scanning at low frequencies in constant-mode AFM. In this way, the recorded Ultrasonic-AFM image contains the information provided by UFM [4] superimposed to the topographic AFM contrast. Fig. 1 (b) was measured after Fig. 1 (a) over nearly the same surface region, in the presence of ultrasound. Here, a novel straight-band feature is clearly distinguished in the image contrast, enclosed by the ellipse. According to previous reports in the literature [4, 14-17], these features can be attributed to subsurface dislocations. Fig. 1 (c) was recorded after Fig. 1 (b), after repeatedly scanning over the same surface region at higher set-point forces F_o (up to 160 nN) and ultrasonic amplitudes A (up to 5 V). In Fig. 1 (c) the band-like feature appears at a different lateral surface position, about 400 nm distant from its previous location in Fig. 1 (b). Hence we conclude that by increasing the set-point forces and/or the amplitudes of surface ultrasonic vibration, we can induce permanent changes in the location of HOPG subsurface dislocations. In Fig. 1 (c) the dislocation crosses an HOPG step, and also appears at the upper terrace. Since the height of that step is ≈ 2.5 nm , the dislocation must lie deeper than this distance from the upper-terrace surface. The penetration depth in AFM with ultrasound excitation is determined by the contact-stress field, which increases when the set-point forces and the ultrasonic amplitudes are increased. The penetration depth in Atomic Force Acoustic Microscopy, and the minimum detectable overlayer thickness were defined in ref. [19], on the basis of the minimum contact stiffness change detectable from the evaluation of the tip-sample contact stiffness. In [20] it was concluded that from the change in contact stiffness on SiO_2/Cu, buried void defects ≈ 500 nm distant from the dielectric surface should be detected using UFM. In [7], a GaAs grating buried under a polymeric layer was clearly imaged using Scanning Local Acceleration Microscopy. In [11], Au particles with a diameter of 15-20 nm buried under a 500 nm polymeric film were resolved using Scanning Near-Field Ultrasound Holography.

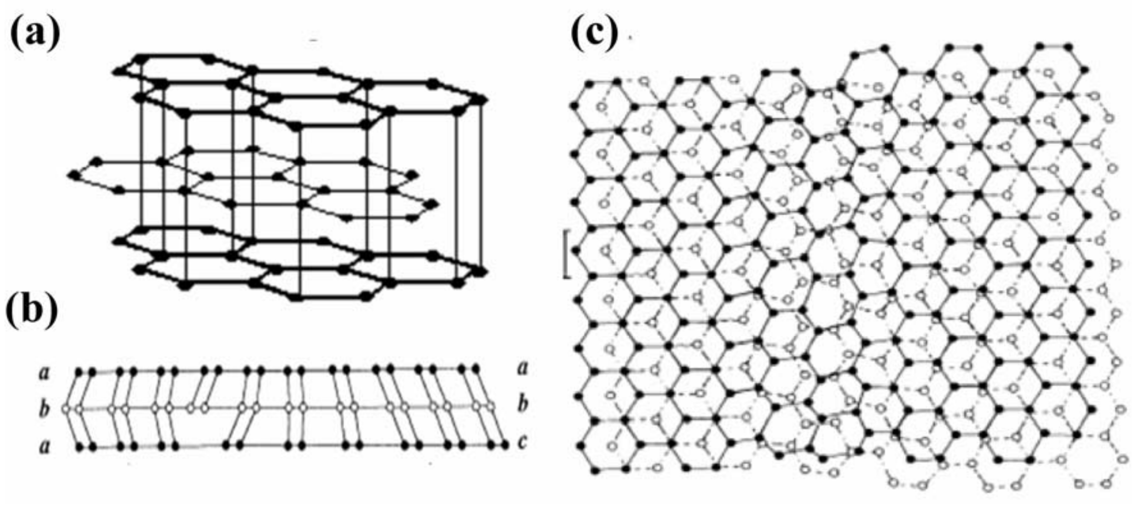

Figure 2. *(a)* Structure of hexagonal graphite. *(b)* Lateral and *(c)* top views of a partial dislocation in graphite (see text).

In our experiments, both the initial tip-sample set-point force and the ultrasonic excitation amplitude played a very important role to allow us the observation and modification of buried sample features. The buried dislocations in Fig. 1 could not be observed when ultrasonic excitation amplitudes smaller than 1.5 Vpp were used. A modification of the substrate was only achieved using amplitudes higher than 3.5 Vpp. Due to the inertia of the cantilever at ultrasonic frequencies, an increase of the ultrasonic amplitude is effectively related to an increase of the indentation of the tip into the sample during each ultrasonic cycle. The ability of the AFM tip to respond inertially to ultrasonic vibration excited perpendicular to the sample surface and dynamically indent hard samples may facilitate the nanoscale machining of semiconductors or engineering ceramics in a reduced time. In order to test this potential, we are currently performing ultrasound-assisted scratching experiments on Si wafers. Preliminary results demonstrate the machining of nanotrenches of $\approx$ 12 nm in depth and 200 nm in width in Si(111) using diamond-coated tips [21]. The procedure should also be advantageous at soft samples, such as plastic coatings, in which the ultrasound-related reduction of friction should bring about finer features and improved surface quality. In addition, the observation and modification of buried nanostructures using an AFM tip opens up the possibility of their controlled manipulation by this same procedure.

In order to gain insight in the physical mechanism that facilitates the modification of HOPG subsurface dislocations, the structure of graphite should be considered. As illustrated in Fig. 2, HOPG consists in planar graphene layers with a honeycomb 2D lattice, weakly coupled together into a hexagonal network. Two different structural phases can be found in graphite, namely an hexagonal and a rombohedral phase, which differ in the stacking of the graphene layers. Hexagonal graphite has an ababab stacking sequence while the rombohedral phase has an abcabcabc stacking sequence. HOPG is expected to exhibit an hexagonal arrangement. However, stacking fault energies in graphite are very low (35 mV/atom), and the basal plane in HOPG is prone to stacking errors which give rise to subsurface partial dislocations, as depicted in Fig. 2 (b) (c) [22-24]. In Fig. 1 (b,c) the characteristic straight band attributed to subsurface dislocations exhibits two clear parallel bright lines (here brighter contrast corresponds to a softer region). In agreement with the UFM contrast previously observed in this kind of dislocations [4,15-17], each line may correspond to a partial dislocation delimited by the boundary of structural phase change (see Fig. 2(b,c)) which is expected to be softer, due to a weaker interlayer bonding.

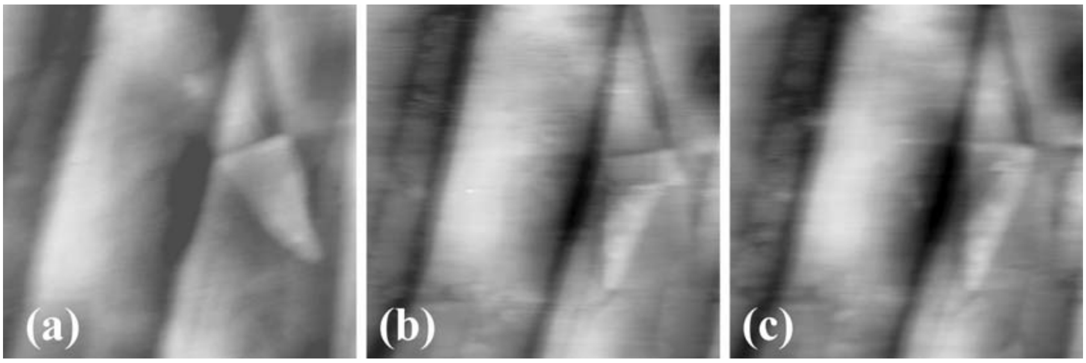

Figure 3. Images recorded in sequence on HOPG in nearly the same surface region: 2200 × 2200 nm; Fo = 160 nN. (a) Ultrasonic-AFM: ω=2.15 MHz; A=6 Vpp (b) Topography in AFM contact mode: grey-scale range ≈ 10 nm (c) Ultrasonic-AFM : ω=2.15 MHz; A= 1.5 Vpp.

Recent reports have demonstrated that reversible lateral displacements of HOPG subsurface dislocations as large as 20 nm can be induced by increasing the load exerted by the AFM tip upon the sample surface [15-17]. In our case, we observed a permanent lateral displacement larger than 400 nm (see Fig. 1(b,c)). Due to the weak interaction between HOPG graphene layers, the excitation of high-amplitude ultrasonic vibration at the HOPG surface may lead to large variations of the interlayer distances at near-surface graphene planes. The force exerted by the tip while inertially indenting into graphite may easily slightly rotate near-surface dislocation-delimited graphene blocks, which may then loose registry with the underlying graphene layer and be very easily laterally displaced with superlubricity [25]. In this way, the ultrasonic-assisted actuation of the AFM tip may induce a kind of tectonic structural rearrangement.

The images in Fig. 3 show the modification of a triangular-shaped HOPG flake by the ultrasonic actuation. Such flakes are occasionally observed at HOPG surfaces as a result of the cleaving procedure. Fig. 3 (a) is an AFM topographic image recorded in the presence of normal ultrasonic vibration of amplitude 6 Vpp; Fig. 3 (b) was recorded immediatly after Fig. 3 (a), in the absence of ultrasound; Fig. 3 (c) was recorded after (b), with normal ultrasonic vibration of amplitude 1.5 Vpp. From a comparison of Fig. 3 (b) and Fig. 3 (a) it is apparent that the lower peak of the flake flips from left to right during the recording of Fig. 3 (a). We attribute this effect to the action of the ultrasonic excitation, perhaps aided by tip actuation, and an initial uncompleted bonding of the flake. A comparison of Fig. 3 (c) and Fig. 3 (b) shows that again in Fig. 3 (c), in spite of using a smaller ultrasonic vibration amplitude, the peak at the top right-hand side of the flake flips from the right to the left. These modification of HOPG surface features by the action of ultrasound strongly suggest that ultrasonic vibration might be of use to induce the assembly of nanostructures at surfaces or facilitate the manipulation of nano-objects by actuation with the tip of an AFM. Currently, we are performing ultrasound-assisted manipulation of nanoparticles in our lab. Preliminary results on Sb nanoparticles deposited on HOPG and MoS_2 surfaces show that in the presence of ultrasound both tip-particle and particle-sample frictional properties change [26]. Recently, the manipulation of large quantities of microparticles on a surface using inertial forces has been demonstrated [27]. Ultrasonic excitation may assist in both self-assembling and AFM manipulation of nano-objects.

4. Summary & Outlook

We have presented experimental results on HOPG that demonstrate that ultrasonic actuation with an AFM tip may induce structural surface and subsurface modifications at HOPG. Observed permanent displacements of subsurface dislocations by distances larger than 400 nm upon ultrasonic-assisted tip actuation at sufficiently high ultrasonic amplitudes and set-point forces are explained by a tectonic rearrangement of the near-surface HOPG structure facilitated by superlubricity.

Ultrasonic machining at the macro- micro- scales is a useful procedure in material engineering. The use of ultrasound may improve both down-top and bottom-down approaches in nanofabrication, facilitating the patterning of nanoscale surface features and the manipulation or self-assembly of nanostructures. Controlled subsurface manipulation of buried nano-objects via near-field ultrasonics constitutes a next exciting challenge.

ACKNOWLEDGEMENTS
The author thanks M. R. Calvo, E. M. Garcia, S. Conejero, and J. J. Martinez for assistance in the UFM lab, and U. Schwarz and E. Gnecco for scientific discussions. Financial support from the Spanish MEC (Ministerio de Educación y Ciencia) under project MAT2002-00076, from the JCCM (Junta de Comunidades de Castilla-La Mancha) under project PBI-05-018 and AEA-06-058, and from the ESF (European Science Foundation) under Program Natribo is gratefully acknowledged.

References

[1] W. Rohrbeck and E. Chilla. *Phys. Stat. Sol. (a)*, 131:69, 1992.
[2] O. Kolosov and K. Yamanaka. *Jpn. J. Appl. Phys.*, 32:L1092, 1993.
[3] B. Cretin and F. Sthal. *Appl. Phys. Lett.*, 62:829, 1993.
[4] K. Yamanaka, H. Ogiso, and O. Kolosov. *Appl. Phys. Lett.,* 64: 178,1994.
[5] U. Rabe and W. Arnold. *Appl. Phys. Lett.*, 64:1493, 1994.
[6] T. Hesjedal, E. Chilla and H. –J. Froehlich. *Appl. Phys. A*, 61:237, 1995.
[7] N. A. Burnham, A. J. Kulik, G. Gremaud, P. J. Gallo, and F. Oulevey. *J. Vac. Sci. Technol. B*, 14:794.
[8] P. Variac and B. Cretin. *Appl. Phys. Lett.*, 68:461, 1996.
[9] K. Inagaki, O. Kolosov, A. Briggs, and O. Wright. *Appl. Phys. Lett.*, 76:1836, 2000.
[10] M. T. Cuberes, H. E. Assender, G. A. D. Briggs, and O. V. Kolosov. *J. Phys. D.: Appl. Phys.*, 33:2347, 2000.
[11] G. S. Shekhawat and V. P. Dravid. *Science*, 310:89, 2005.
[12] F. Dinelli, S. K. Biswas, G. A. D. Briggs, and O. V. Kolosov. *Appl. Phys. Lett.*, 71:1177, 1997.
[13] see e.g. T. B. Thoe, D. K. Aspinwall, and M. L. H. Wise. *Int. J. Mach. Tools Manufact.* 38:239, 1998, and ref. therein.
[14] K. Yamanaka. *Thin Solid Films*, 273:116, 1996.
[15] T. Tsuji and K. Yamanaka. *Nanotechnology*, 12:301, 2001.
[16] T. Tsuji, H. Irihama, and K. Yamanaka. *Japan. Journal of Appl. Physics Part 1*, 41:832, 2002.
[17] T. Tsuji, H. Irihama, and K. Yamanaka. *JSME International Journal Series A*, 45:561, 2002.
[18] M. T. Cuberes, G. A. D. Briggs, and O. Kolosov, *Nanotechnology* 12:53, 2001.
[19] G. G. Yaralioglu, F. L. Deggertekin, K. B. Crozier, and C. F. Quate. *J. of Appl. Phys*., 87:7491, 2000.
[20] A. F. Sarioglu, A. Atalar, and F. L. Degertekin. *Appl. Phys. Lett.*, 84:5368, 2004.
[21] M. T. Cuberes (unpublished)
[22] H. Lipson and A. R. Stokes. *Proc. R. Soc. London Ser A,* 181:101, 1942.
[23] G. K. Williamson. *Proc. R. Soc. London Ser. A.,* 257:457, 1960.
[24] P. Delavignette and S. J. Amelinckx. *Nucl. Mater.,* 5:17, 1962.
[25] M. Dienwiebel, G. S. Verhoeven, N. Pradeep, J. W. M. Frenken, J. A. Heimberg, and H. W. Zandbergen. *Phys. Rev. Lett.*, 92:126101-1, 2004.
[26] M. T. Cuberes et al. (unpublished); the samples of Sb nanoparticles on HOPG and MoS_2 substrates were provided by U. Schwarz and C. Ritter, Humbolt Uni Berlin.
[27] M. Eglin, M. A. Eriksson, and R. W. Carpick. *Appl. Phys. Lett.,* 88:091913, 2006.