Observation of Dislocation Behavior in Graphite by Using Ultrasonic Atomic Force Microscopy*

Toshihiro TSUJI**, Hiroshi IRIHAMA**
and Kazushi YAMANAKA**

We verify that ultrasonic atomic force microscopy (UAFM) can detect and evaluate subsurface objects with a resolution of around 10 nm. We first show that the resonance frequency of UAFM cantilever shows a measurable change due to subsurface low-elasticity layer by a finite element analysis. We then proved the ability of subsurface imaging in a highly oriented pyrolytic graphite (HOPG) specimen. We found a new type of dislocation motion. As a load was applied to the tip, apparent edge-type dislocations (Frank partial dislocations) moved to the direction of climb over distances of 47 nm and returned to the original position as the load was removed. To explain this motion, we propose a possible model where the extra half-plane of the dislocation is elastically compressed to shorten its length due to the normal load applied by the tip.

Key Words: Dislocation, Edge-type, Reversible Lateral Motion, Graphite, Finite Element Method, Ultrasonic Atomic Force Microscopy

1. Introduction

Graphite is a well-known material with a layered structure in which hexagonal carbon (C) planes are stacked periodically along the *c*-axis due to weak interlayer interaction forces⁽¹⁾. Each C plane can easily slide against another, making graphite a good solid lubricant⁽²⁾. In addition, the interlayer space accepts a large amount of ions or molecules so that graphite forms graphite intercalation compounds (GICs)^{(3),(4)}, which are applied to useful devices such as Li-ion rechargeable batteries. Despite its significant usefulness, however, the atomic nature of the interlayer interaction in graphite is still not fully understood⁽²⁾. Although shear-induced motion of partial dislocations in highly oriented pyrolytic graphite (HOPG) has been observed using scanning tunneling microscopy (STM)⁽⁵⁾, the depth of observation is only one or two atomic layers. We have reported that subsurface dislocations in HOPG can be clearly ob-

served using ultrasonic force microscopy (UFM)^{(6),(7)} or ultrasonic atomic force microscopy (UAFM)^{(8)–(10)} with an observation depth more than 3 nm^{(7),(9),(10)}. Although previous observations were limited in their static conditions, we recently found that the mobility of the dislocations is extremely high.

In the present paper, we describe detailed dynamic observation of the subsurface dislocations in HOPG, using UAFM. Since the dynamic behavior has a unique feature, which cannot be explained by established dislocation models⁽¹¹⁾, we propose a possible model to explain this behavior.

2. Theory

To investigate a variation of the resonance frequency due to a subsurface low-elasticity layer, we performed a FEM analysis^{(9),(10)}. Figure 1 shows a cross section of the axisymmetric models for the FEM analysis along the indentation axis. In the model shown in Fig. 1(a), we assume a 3-nm-thick low-elasticity layer with infinite width at the depth of 3 nm. In the model shown in Fig. 1(b), to take into account the finite width of the defect, we limited the radius of the low-elasticity layer to 3 nm from the indentation axis. Young's moduli and Poisson's ratios

* Received 8th February, 2002

** Department of Material Processing, Tohoku University, Aoba 02, Aramaki, Aoba-ku, Sendai 980-8579, Japan. E-mail: yamanaka@material.tohoku.ac.jp

Fig. 1 Models for the FEM analysis. The unit is nm. (a) Low-elasticity layer under the surface, (b) Low-elasticity layer with a radius of 3 nm under the surface

Fig. 2 Von-Mises stress distribution under different loads. (a) $F=25$ nN, (b) $F=100$ nN

of the substrate and the low-elasticity layer were assumed to be $E_{sb}=30$ GPa and $\nu_{sb}=0.24$, and $E_{low}=15$ GPa and $\nu_{low}=0.24$. We employed another model with the homogeneous elasticity, E_{sb} and ν_{sb} representing a defect-free model.

In the analysis, we indented a rigid sphere of 50 nm radius to the depth of 1 nm in 0.01 nm steps. Figure 2 shows the Von-Mises stress distribution in the finite-width-layer model under the load of (a) 25 nN and (b) 100 nN. Under the load of 25 nN, the stress distribution is affected by the presence of sub-surface low-elasticity layer. The contact radius was almost the same as the width (3 nm) of defect. It indicates that the effect of defect is present for the whole contact area. In contrast, under the load of 100 nN, the contact radius is 5 nm, which is longer than the width of defect. It indicates that the effect of defect is limited to less than 40% of the contact area.

At each indentation step, we recorded the load F and displacement z as shown in Fig. 3. The load for the finite-width-layer model is slightly less than that for the defect-free model, whereas that for the

Fig. 3 Load displacement curve calculated by the FEM analysis

Fig. 4 Contact stiffness calculated from Fig. 3

infinite-width-layer model is significantly less than that for the defect-free model. Next, we calculated the contact stiffness $s = \partial F / \partial z$ using the results in Fig. 3, and it is shown in Fig. 4. In UAFM, we can measure the contact stiffness 1–100 times higher than the cantilever stiffness when we use the first resonance frequency^{(8),(12)}. Then, using the frequency equation reported previously^{(8),(12)}, we calculated the resonance frequency corresponding to the contact stiffness shown in Fig. 4, assuming a cantilever stiffness $k_c=7.5$ N/m.

Figure 5 shows the calculated load dependence of the resonance frequency. The solid curve shows the resonance frequency of the defect-free-model with homogeneous elasticity. The dot-dash curve shows the resonance frequency of the infinite-width-layer

Fig. 5 The first resonance frequency calculated from Fig. 4

model in Fig. 1(a). The resonance frequency was significantly lower than that of the defect-free-model. The dotted curve shows the resonance frequency of the finite-width-layer model in Fig. 1(b). Under the load higher than 100 nN where the contact radius was longer than 5 nm, the resonance frequency approached that of the defect-free-model, but it was lower under the lower load. Then, the resonance frequency calculated from the model with subsurface low-elasticity layer was lower than that calculated from the defect-free model with homogeneous elasticity.

The low-elasticity layers may represent graphite layers containing a space associated with an edge dislocation, as discussed later in section 4.1, or any other defects. Therefore, when there is a subsurface defect such as dislocation in HOPG, we will be able to detect it by measuring lower resonance frequency than that of defect-free area. However, to investigate the quantitative variation of the resonance frequency, we will have to improve the analysis model, taking into account the shape and position of the dislocation, the decrease of the elasticity due to dislocation and the anisotropic elasticity of HOPG.

3. Experiment

The UA-FM recently improved for mapping resonance frequency⁽¹³⁾ is depicted in Fig. 6. A cantilever is vibrated by a voltage-controlled oscillator (VCO) with an input voltage V adjusted to realize a resonance when the tip is in contact with the sample. If the resonance frequency is changed during scanning, the phase difference between the cantilever deflection signal and the VCO output signal produces output V_E of the error amplifier, which is fed back to the VCO

Fig. 6 Block diagram of UA-FM for mapping resonance frequency

Fig. 7 Images of the cleaved HOPG surface. (a) Contact AFM topography, (b) Amplitude distribution of the cantilever deflection vibration at the resonance frequency measured at position A (180 kHz). Image area was $2\,000\text{ nm} \times 2\,000\text{ nm}$ and contact load was 97 nN including adhesion force of 27 nN

Fig. 8 Reversible lateral motion of dislocations under applied load. Amplitude distribution of the cantilever deflection vibration at the resonance frequency measured at position A (186.6 kHz). The load F including adhesion force of 27 nN is shown in each image. Image area was 500 nm $\times$ 500 nm.

input in order to recover the resonance⁽¹³⁾. In this manner, the cantilever is always vibrated at the resonance frequency and the resonance frequency is mapped using a frequency demodulator. When the switch at the output of the error amplifier is open, the system is the same as the previous UAFM for mapping amplitude distribution at a fixed frequency near the resonance^{(8)-(10),(12)}.

The sample was freshly cleaved HOPG (Union Carbide grade B). To obtain the images shown in Figs. 7 and 8, experiments were performed in dry air at 23°C with relative humidity of 30%. To obtain the images shown in Figs. 9 and 11, experiments were performed in ambient air at 23°C without humidity control.

4. Results and Discussion

4.1 Observation of dislocation behavior under different loads

Figure 7 shows a typical cleaved HOPG surface. The image area was 2 000 nm $\times$ 2 000 nm and the contact load was 97 nN including an adhesion force of 27 nN. Figure 7(a) is a contact-mode AFM topography showing monolayer steps and atomically flat terraces. The UAFM amplitude image in Fig. 7(b) shows the amplitude distribution of the cantilever deflection vibration at the first resonance frequency measured at position A (180 kHz). The dark color indicates low contact stiffness. It is known that HOPG has an edge dislocation due to an extra C plane (extra half-plane (EHP)) inserted between periodically stacked C planes⁽¹⁾. The edge dislocation has a space between C planes on the other side of the EHP with respect to the

Fig. 9 Resonance frequency mapping of the cleaved HOPG surface at the first deflection mode. Image area was 1 000 nm $\times$ 1 000 nm and contact load was 115 nN including adhesion force of 40 nN.

dislocation core. Because it is easier to compress the C planes with the space than in the case of a normal area without the space, the contact stiffness at position on the subsurface space should be lower than that at position on the normal area. Thus, low contact stiffness areas represented by dark stripes show subsurface dislocations⁽⁶⁾⁻⁽¹⁰⁾. We observed many dislocations which were not visible in the topography (a).

Figures 8(a) - (d) show magnified UAFM amplitude images of two dislocations near position A in Fig. 7 under different loads F including an adhesion force of 27 nN. As the load was increased, the distance between the two dislocations increased, as shown in (a) - (c). The distance under a 177 nN load was 40 nm longer than that under a 97 nN load. However, when the load was decreased to 97 nN, the distance returned to the initial value of 165 nm, as shown in Fig. 8(d). Since the motion was almost symmetrical, these dislocations moved 20 nm laterally as the load increased and returned to the original position as the load decreased⁽¹⁴⁾. We confirmed that this motion is not an artifact due to distortion by scanning, since other objects such as the steps did not move even when the load was increased by the same amount.

4.2 Analysis of dislocation motion under varying applied load

In order to show the reproducibility of the motion and to analyze it more quantitatively, we present a resonance frequency mapping of dislocations in other areas of the same sample. Figure 9 shows the resonance frequency image of the first deflection mode with an area of 1 000 nm $\times$ 1 000 nm where the contact load was 115 nN including an adhesion force of 40 nN.

Fig. 10 Schematic of dislocations facing each other

The color bar indicates the resonance frequency in a range of 170.9 kHz to 171.4 kHz where the low resonance frequency represents the low contact stiffness. We observed dislocations C and D, similar to those in Fig. 8 with a resonance frequency 0.1–0.2 kHz less than that in the normal area. Upon careful investigation of the topography (not shown here), the area between the dislocations was found to be slightly depressed from the overall level by 0.03–0.05 nm. This depression is represented by the cross-sectional model shown in Fig. 10, where two edge dislocations (Frank partial dislocations⁽¹¹⁾) with different polarity face each other and the lack of an EHP between the dislocations depresses the surface.

We measured the resonance frequency profile along the line AB as the applied load, including an adhesion force of 40 nN, was varied from 115 nN to 400 nN with the scanning direction being from A to B (rightward scanning). Then, we investigated the motion of dislocations C and D. Figure 11(a) shows the variation of the resonance frequency profile. Dislocation C moved to the left and dislocation D moved to the right as the load increased; both returned to their original positions as the load decreased. The direction of motion was such that the length of the EHP was shortened. Under the maximum load, dislocation D moved by 47 nm, corresponding to 330 times the C–C bond length of 0.142 nm in graphite. Dislocation C moved by 27 nm, showing that the mobility differs for each dislocation.

If the effect of lateral force on the dislocation motion is great, the direction or magnitude of dislocation motion would be changed by inverting the scanning direction. Thus, to evaluate the effect of lateral force, we inverted the scanning direction. Figure 11(b) shows the variation of the resonance frequency profile in leftward scanning, from B to A in Fig. 9. It is noted that the direction and the magnitude of dislocation motion were almost the same as those in rightward scanning within experimental error. Therefore, we found that the dislocation motion is mainly affected not by the lateral force due to scanning but by the applied normal load. It should be noted here that we do not exclude the effect of shear stress produced by the indented tip, which is large in the peripheral region of indentation even without lateral force.

Fig. 11 Reversible lateral motion of dislocations under varying applied load. Resonance frequency profile along the line AB. (a) Rightward scanning. (b) Leftward scanning. The load F including adhesion force of 40 nN is shown on the left side. Length was 500 nm.

4.3 Model for the reversible long-range motion of the edge dislocation

If the dislocations observed here are of the edge-type, images in the previous sections indicate that the dislocations move in the direction of climb⁽¹¹⁾, which is known as dislocation motion normal to the slip plane and requires the creation of vacancies and interstitial atoms and their diffusion. However, since the experiment was performed at room temperature and the formation energy for a vacancy or an interstitial atom in graphite is very high (7.0 eV⁽¹⁵⁾), the creation of vacancies or interstitial atoms should have been negligible. Therefore, the observed motion cannot be considered as a normal climb.

A possible explanation of the motion can be given using the model⁽¹⁰⁾ shown in Fig. 12, where we assume a pinning point P and an elastic spring S_D due to C–C bonds in the EHP. Figure 12(a) shows the initial position of the tip and dislocation. As the load increases, the stress and strain energy at the deformed area under the tip increase, as shown in Fig. 12(b). Then, the EHP is removed from that area while storing the elastic energy in S_D due to the in-plane elastic deformation of the EHP; thus, the dislocation

Fig. 12 Model for the reversible long-range motion of edge dislocation under applied load

moves to the right. Conversely, as the load decreases, the EHP returns to the original configuration while releasing the elastic energy, as shown in Fig. 12(c); thus, the dislocation returns to the original position.

Since this model implies the long-range travel of C atoms at the edge of the EHP over many lattice constants, it may appear unacceptable from the viewpoint of dislocation theories⁽¹¹⁾. However, we do not consider it to be impossible because of the exceptionally weak interlayer interaction in layered crystals such as HOPG and the large local stress around the indented tip in UAFM. To obtain the quantitative relation between the stress field and the dislocation motion, we will have to analyze this motion, taking into account anisotropic elasticity of a C plane, in the future. If this model proves to be correct, it would provide a new concept in dislocation theories. Moreover, since the dislocation motion is well controlled, as seen in Fig. 11, it suggests the possibility of manipulating subsurface atoms by scanning probe microscopy.

5. Conclusions

We observed a cleaved HOPG surface by UAFM, analyzed the dislocation behavior and obtained the following conclusions.

We observed the subsurface dislocations using the amplitude image and the resonance frequency image. Upon close observation of the dislocation behavior, we found that the dislocation moved laterally by more than 40 nm as the load increased by 285 nN, and it

returned to the original position as the load decreased. Moreover, this dislocation behavior was caused not by lateral force due to scanning but by the applied normal load. Finally, we proposed a possible model to explain this motion.

Acknowledgements

This work was supported by a Grant-in-Aid for Science Research (No. 1045015), and by a Grant-in-Aid for COE Research (No. 11CE2003), from the Ministry of Education, Culture, Sports, Science and Technology.

References

- (1) Kelly, B.T., *Physics of Graphite*, (1981), pp. 41-45, Applied Science Publishers, London.
- (2) Savage, R.H., *J. Appl. Phys.*, Vol. 19 (1948), pp. 1-10.
- (3) Zabel, H. and Solin, S.A., *Graphite Intercalation Compounds*, eds. Zabel, H. and Solin, S.A., (1990), Springer, Berlin.
- (4) Funabiki, A., Inaba, M., Abe, T. and Ogumi, Z., *Carbon*, Vol. 37 (1999), pp. 1591-1598.
- (5) Snyder, S.R., Gerberich, W.W. and White, H.S., *Phys. Rev.*, Vol. B 47 (1993), pp. 823-831.
- (6) Yamanaka, K., Kolosov, O. and Ogiso, H., *Appl. Phys. Lett.*, Vol. 64 (1994), pp. 178-180.
- (7) Yamanaka, K., *Thin Solid Films*, Vol. 273 (1996), pp. 116-121.
- (8) Yamanaka, K. and Nakano, S., *Jpn. J. Appl. Phys.*, Vol. 35 (1996), pp. 3787-3792.
- (9) Tsuji, T. and Yamanaka, K., *Nondestr. Charact. Mater.*, Vol. 10 (2001), pp. 213-220.
- (10) Tsuji, T. and Yamanaka, K., *Nanotechnology*, Vol. 12 (2001), pp. 301-307.
- (11) Read, W.T., *Dislocations in Crystals*, (1953), p. 92, McGraw-Hill, New York.
- (12) Yamanaka, K. and Nakano, S., *Appl. Phys.*, Vol. A66 (1998), pp. S313-317.
- (13) Yamanaka, K., Maruyama, Y., Tsuji, T. and Nakamoto, K., *Appl. Phys. Lett.*, Vol. 78 (2001), pp. 1939-1941.
- (14) The Magnitude of Motion is not Necessarily the Same for All Dislocations. An Example of Different Magnitude is Given in Section 4.2.
- (15) Thrower, P.A. and Mayer, R.M., *Phys. Status Solidi*, Vol. 47 (1978), pp. 11-37.