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J.W. Ager III, D.K. Veirs, B. Marchon, N. Cho,
and G.M. Rosenblatt

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Joel W. Ager III, D. Kirk Veirs*, Bruno Marchon**, Namhee Cho, and Gerd M. Rosenblatt

Center for Advanced Materials, Materials Sciences Division, Lawrence Berkeley Laboratory,
Berkeley, CA 94720

*Present address: NMT-6 E-510, Los Alamos National Laboratory, Los Alamos, NM 87545

**Seagate Magnetics, 47010 Kato Road, Fremont, CA 94538

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Joel W. Ager III, D. Kirk Veirs*, Bruno Marchon**, Namhee Cho, and Gerd M. Rosenblatt
Center for Advanced Materials, Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720

*Present address: NMT-6 E-510, Los Alamos National Laboratory, Los Alamos, NM 87545

**Seagate Magnetics, 47010 Kato Road, Fremont, CA 94538

ABSTRACT

Amorphous "hard carbon" and microcrystalline diamond films are being investigated and characterized using high-sensitivity and spatial-profiling Raman spectroscopy. The "hard carbon" films have broad Raman spectra with no diamond line while higher quality diamond films show only a single sharp diamond line. Features in the Raman spectra of the amorphous "hard carbon" films correlate with the rates of specific types of wear. Changes in the relative intensity of the Raman band near 1570 cm^{-1} (G-band) compared to the band near 1360 cm^{-1} (D-band) are related to the rate of abrasive wear. Shifts in the frequency of the G-band are related to the rate of tribochemical wear. The results are consistent with a structural model of amorphous carbon films in which small ($<20\text{ \AA}$) graphitic microcrystals comprised of sp^2 bonded domains are cross-linked by sp^3 carbon atoms. Profiles of Raman frequency and linewidth obtained from spatially resolved Raman spectroscopy across CVD-grown diamond thin films show that the Raman frequency and position are correlated in these films and that both change in regions of poorer film quality.

1. INTRODUCTION

The wear of sputtered amorphous carbon films used as protective coatings on hard disks is important in the computer industry [1]. Two important wear mechanisms have been identified. Abrasive wear results from a plowing action of the slider or of abrasive contaminant particles on the film surface. This type of wear can lead to rapid failure of the disk drive. Tribochemical wear is caused by oxidation of the carbon surface atoms under the slider followed by thermal removal of CO and/or CO_2 [2]. This type of wear slowly increases the frictional force between the slider and the disk and can eventually cause failure.

Chemically synthesized diamond films are a new field of interest in industry, both in the US and in Japan and Europe. Diamond films have all of the attractive properties of natural diamonds such as hardness and high thermal conductivity; current and proposed applications include heat sinks, X-ray optics, tool coatings, abrasives, and high-band gap semiconductors. For many of these applications, uniform quality of the films is essential.

Raman spectroscopy is a valuable tool for the characterization of both diamond and amorphous carbon systems. The characteristic Raman spectrum of diamond is a sharp line at 1332 cm^{-1} ; observation of this line is definitive evidence of diamond growth. Changes in the frequency and width of this line can be related to internal stresses in the film and to film quality. The Raman spectrum of amorphous carbon films is characterized by two broad bands which change in their relative intensity and in their central band frequency with film structure and morphology. The effect of short range order, bonding, and internal stress on the shape of these bands are not well understood. Raman spectroscopy is nondestructive and can be done *in-situ*, both during film growth and device construction. In addition, techniques have been developed that produce profiles and maps of important physical and chemical properties using spatially resolved Raman spectroscopy [3].

The diamond samples studied were grown by microwave-plasma-assisted chemical vapor deposition (CVD). Sample 2C3 was grown at LBL on a Si substrate scratched with diamond paste. The conditions were 1.2% CH_4 in H_2 at a pressure of 140 torr and at a growth temperature of 975°C . The growth time was 1.5 hours. The cross-sectional area of the plasma produced by the LBL apparatus was smaller than the substrate (10 mm diameter Si wafers); as a result, the films are spatially inhomogeneous, generally with more growth toward the edge of the wafer. Sample 5-7-W is a free standing $200\text{ }\mu\text{m}$ thick film, $5\text{ mm} \times 10\text{ mm}$, which was grown by a commercial (proprietary) CVD process [4]. The growth time was 200 hours.

2. EXPERIMENTAL

2.1 Sample preparation and mechanical testing

The amorphous carbon samples were grown by a proprietary sputtering process to a thickness of 400 Å. Abrasive wear rates were measured by scratching the disk for a fixed period of time with SiC abrasive tape and counting the number of scratches. Tribochemical wear rates were measured by monitoring the rate of frictional buildup during a 25 RPM (6 cm/s) drag test using a minicomposite slider with a 10 g load.

2.2 Raman spectroscopy

All Raman spectra were excited with the 488 nm line of an Ar⁺ laser. The laser was incident at 70° from normal and the scattered light was collected normal to the sample by a 50 mm f/1.3 camera lens. An interference filter is used to suppress elastically scattered light. The dispersed light is detected by a microchannel plate photomultiplier (imaging PMT) equipped with a resistive anode (1024×1024 image format).

Single-point spectra were collected from 40 amorphous carbon films. The laser power was 100 mW and the spot size of the laser on the films was 6 μm. The amorphous carbon spectra were analyzed by fitting two Gaussian line shapes centered at ca. 1570 and 1360 cm⁻¹ (G- and D-bands, respectively) to the data with a linear background term, yielding the frequency, width, and area of the two bands.

We have described previously the use of a two-dimensional detector to obtain multiple, spatially resolved Raman spectra simultaneously along an illuminated line on the sample [3]; only a brief description of the method will be given here. The laser is focused on the sample by a cylindrical lens to form an illuminated line, which is imaged by the collection optics onto the entrance slit of the monochromator. Each of the 1024 rows of the detector contains the Raman spectrum from a corresponding point on the sample. Subsequent collection of a Ne calibration spectrum and data analysis yields the frequencies of the Raman lines from the sample with an accuracy of 0.5 cm⁻¹ (about one pixel). In the spatially resolved measurements reported here, the magnification of the collection optics was 8×, such that each row on the detector corresponded to the Raman spectrum from a 4 μm long (33 μm effective pixel size/8) by 15 μm wide (120 μm slit width/8) area of the sample. The laser power at the sample was 150 mW and the collection time was 1.5 hours. Diamond peak frequencies and widths were determined in each row of the data matrix by fitting a Lorentzian lineshape to the spectrum with a linear background term.

3. RESULTS

3.1 Amorphous carbon films

Typical amorphous carbon spectra are shown in Fig. 1. The spectral characteristics that displayed the most significant correlation with the measured wear rates are the G-band frequency and the I_D/I_G ratio (computed by dividing the areas of the D- and G-bands). The G-band frequency is plotted vs. the tribochemical wear rate in Fig 2(a). The I_D/I_G ratio is plotted vs. the abrasive wear rate in Fig 2(b). The tribochemical and abrasive wear rates (and the G-band frequency and I_D/I_G ratio) are not significantly correlated. The desirable film characteristics of low tribochemical and abrasive wear rates are associated with films displaying a low G-band frequency and a large I_D/I_G ratio, respectively.

3.2 Diamond films

The one-dimensional analysis results of the spatially resolved Raman work on sample 2C3 and 5-W-7 are shown in Figs. 3(a) and 3(b). For sample 2C3 analyzed region extended from the center of the sample (sparser diamond coverage) toward the edge (denser diamond coverage). For sample 5-W-7, the region extended from the edge 1.6 mm toward the center of the rectangular piece. The Raman characteristics of sample 2C3 show continuous changes as a function of position. The diamond linewidth is narrowest near the center of the sample (sparser coverage) and increases monotonically towards the edge of the sample (denser coverage). The Raman frequency is correlated with the linewidth; the line frequency is 1332.7 cm⁻¹ in the center of the sample and increases to 1334.4 cm⁻¹ at the edge of the imaged area, while the linewidth increases from 7 to 14 cm⁻¹. Sample 5-W-7 does not show systematic changes in the Raman spectrum as a function of position. The average frequency and linewidth of the diamond Raman peak are 1332.5 cm⁻¹ and 5.1 cm⁻¹.

4. DISCUSSION

4.1 Amorphous carbon films

The correlation between features in the Raman spectra and the mechanical properties of the amorphous carbon films will be discussed within the framework of a structural model in which small ($<20 \text{ \AA}$) graphitic microcrystals are randomly embedded in a three-dimensional network of sp^3 and sp^2 bonded carbon atoms [5]. Theoretical studies have predicted a down-shift in the G-band frequency as the sp^3/sp^2 ratio increases [6][7]. This implies that films with a lower G-band frequency have more tetrahedral cross-linking of their graphitic domains. The resistance of these films to tribochemical wear may be explained in terms of the affinity of oxygen chemisorption (presumably the first step in this wear process); whereas graphite reacts readily with oxygen to form surface oxides [8], only hydrogen chemisorbs on diamond surfaces [9].

The correlation of the abrasive wear rate with the I_D/I_G ratio is less straightforward to understand. In microcrystalline graphites (e.g. carbon fibers), the I_D/I_G ratio has been correlated to in-plane microcrystallite size, with larger ratios corresponding to smaller graphitic domains [10]. However, recent work has shown that in amorphous carbons increases in the I_D/I_G ratio (which are correlated with lower abrasive wear rates) are correlated with increases in the number (but not the size) of graphitic domains [11][12]. Scanning tunneling micrographs from our previous work [Namhee] that illustrate this are shown in Fig. 4. Thus, the observed correlation between the I_D/I_G ratio and the abrasive wear rate implies that greater numbers of small graphitic domains add structural strength to the film.

4.2 Diamond films

We have discussed previously an interpretation of the frequency and linewidth of the diamond Raman peak in terms of internal stresses and in the polycrystalline films [13]. Briefly, shifts in the Raman peak frequency away from 1332.5 cm^{-1} , the peak frequency of single crystal diamond, are attributed to stress in the films. Compressive stress shifts the peak to higher frequency, while tensile stress shifts the peak to lower frequency. Stresses are introduced primarily during the cooling of the film from the growth temperature (typically 900°C). The Raman linewidth of single crystal diamond is 2 cm^{-1} ; the linewidths of the films studied here are larger ($5 - 15 \text{ cm}^{-1}$). The broader lines are explained in terms of broadening by defects and by the stress distribution in the many microcrystallites sampled in a Raman measurement.

Because of the inhomogeneous plasma conditions discussed above, the morphology of sample 2C3 changes as a function of position. There are isolated diamond microcrystallites in the center of the film merging into a higher density of partially fused crystallites near the side of the film [diam ms.]. The monotonic increase in the Raman frequency and linewidth from the center of the film toward the edge [Fig 3(a)] follows this trend. On the other hand, although there are small variations, the Raman frequency and linewidth of sample 5-7-W do not show a systematic trend, implying the film is uniform over the sampled area. The SEM analysis of this film also shows a uniform morphology [14].

5. CONCLUSIONS

Features in the Raman spectra of amorphous carbon films have been correlated with *specific* mechanical wear properties relevant to their use as protective coatings for computer hard disks. The correlations can be adequately explained in terms of a structural model of amorphous carbon films in which nanoscale graphitic domains are randomly distributed in a 3-D network of sp^2 and sp^3 bonded atoms. Raman spectroscopy is fast and non-destructive and can be used to complement slower mechanical testing in order to develop harder and longer-lasting computer hard disks.

High quality (low stress and defect density) and spatial uniformity are essential for many proposed uses of CVD diamond films. Single-point Raman spectroscopy is already a valuable tool for evaluating diamond quality in chemically grown films. We have shown that spatially resolved Raman spectroscopy is a practical method to measure quality and uniformity simultaneously and provides unique information not available with other characterization methods.

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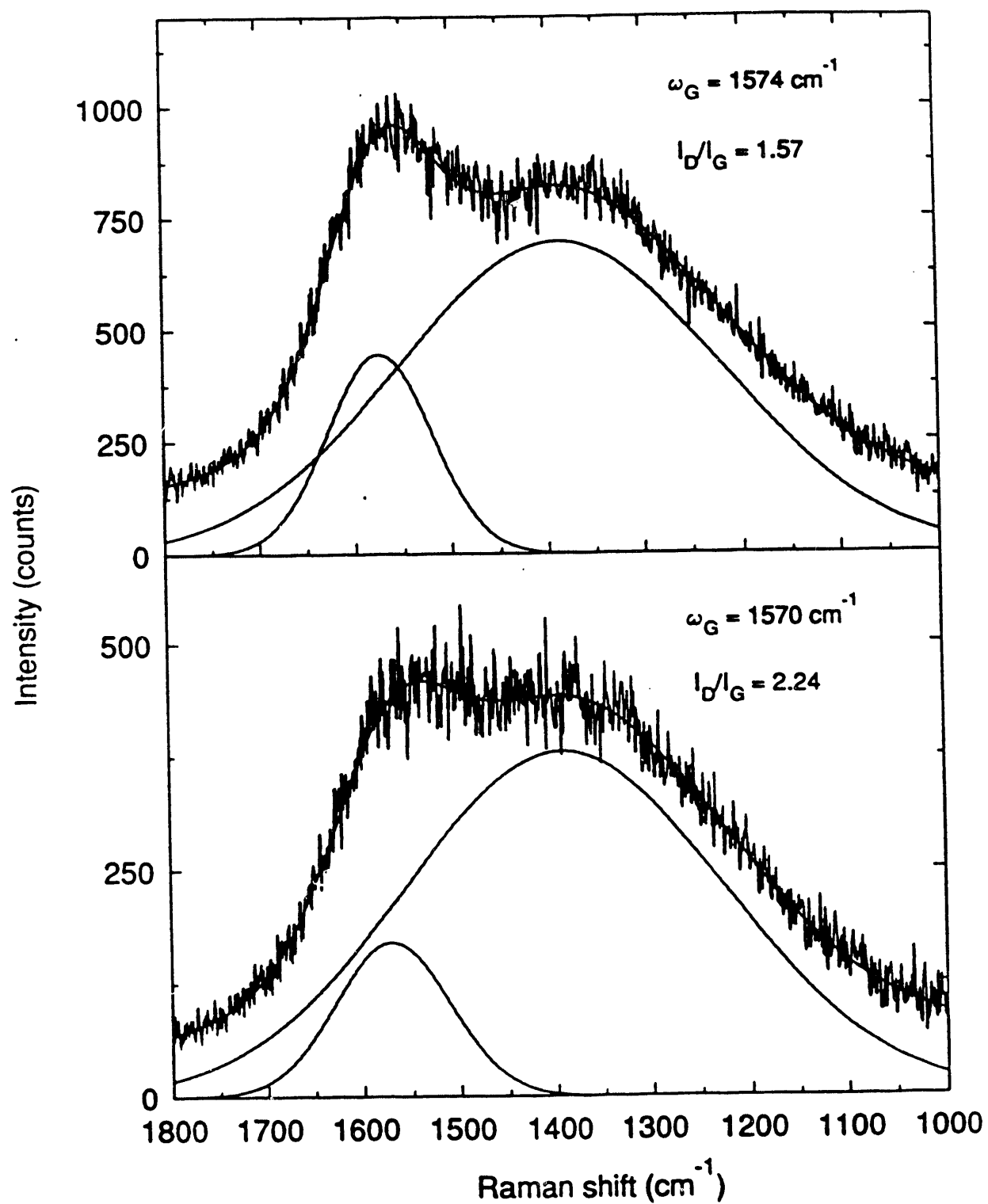


Fig. 1 Raman spectra of amorphous carbon films. The film in the lower spectrum showed lower abrasive and tribochemical wear rates than the film in the upper spectrum.

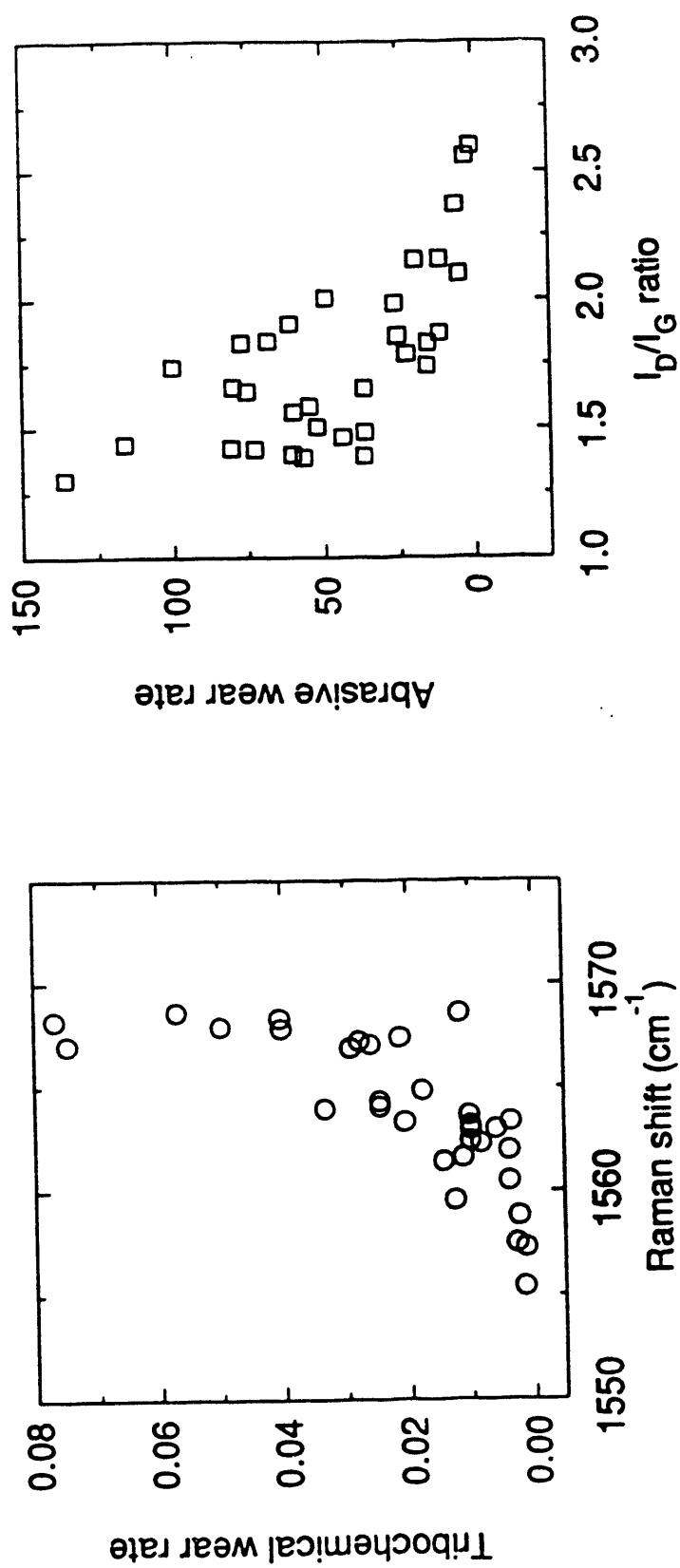


Fig. 2 (a) Relation between tribochemical wear rate (arbitrary units) and Raman G-band frequency; (b) relation between abrasive wear rate (arbitrary units) with ratio of integrated intensities of the G-band near 1570 cm⁻¹ and the D-band near 1360 cm⁻¹ (I_D/I_G ratio).

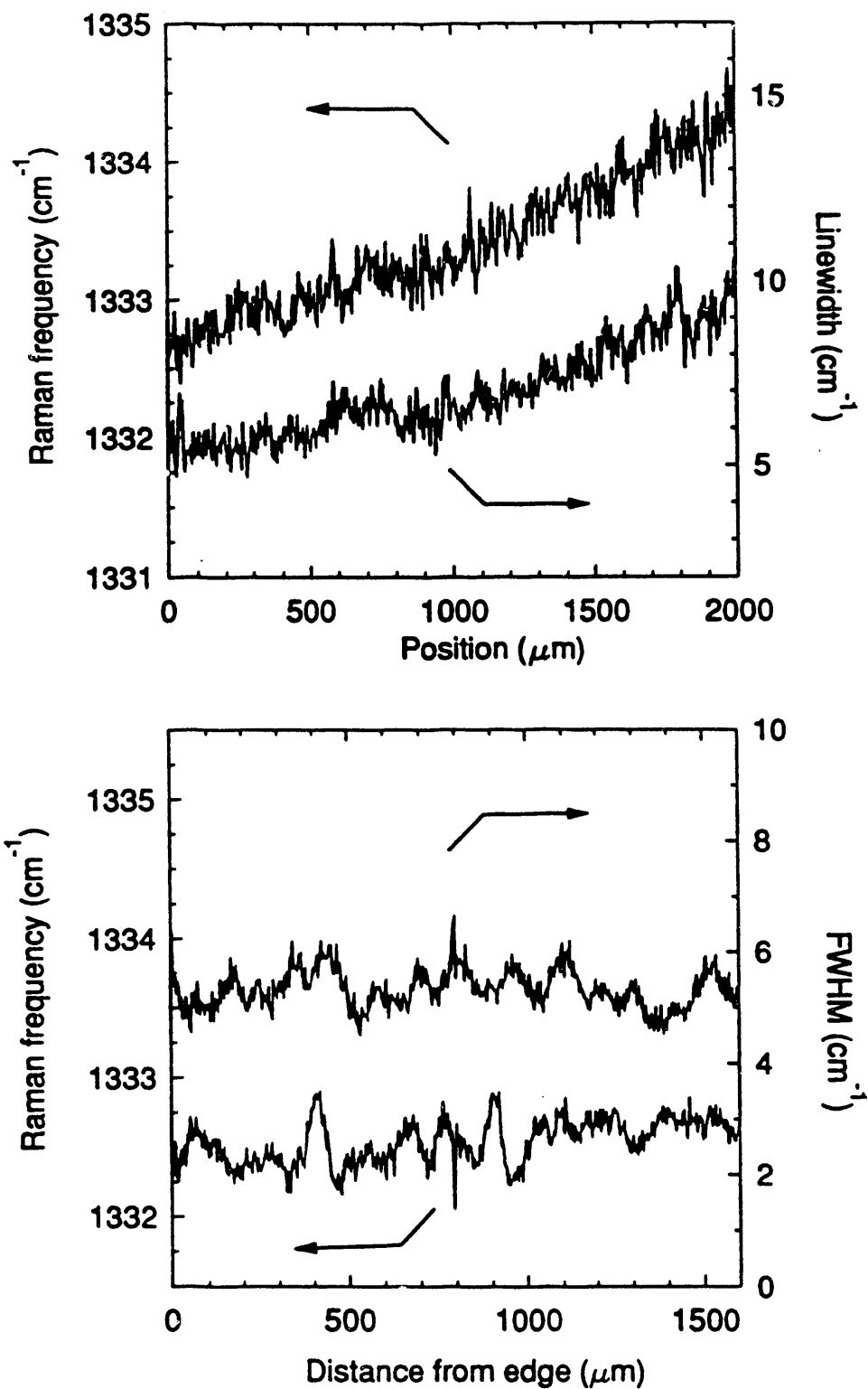
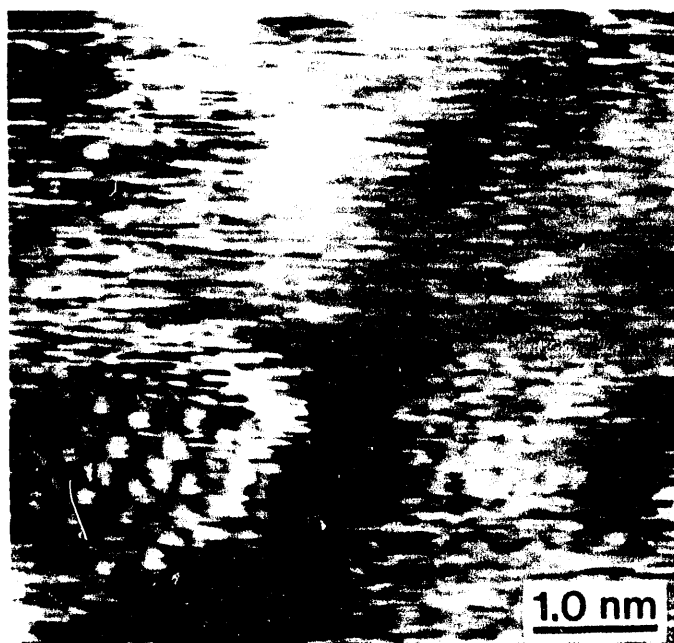
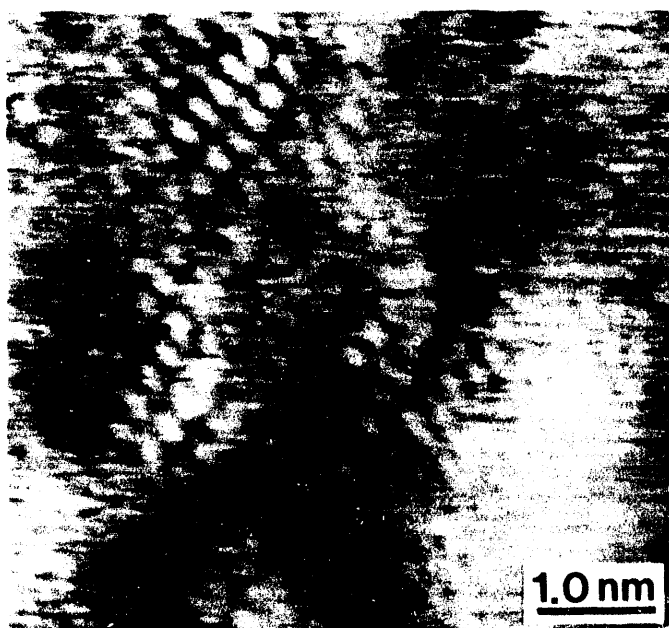


Fig. 3 Profiles of diamond Raman frequency and linewidth across two CVD diamond films. Each profile was obtained from the analysis of 500 Raman spectra collected simultaneously over 1.5 hours. (a) Sample 2C3 (inhomogeneous); (b) Sample 5-W-7 (more uniform).



(a)

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(b)

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Fig. 4 STM images of amorphous carbon films: (a) I_D/I_G ratio = 2.0, fewer ordered domains; (b) I_D/I_G ratio = 2.3, more ordered domains.

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