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Shuichi Watanabe, Donald R. Wheeler, Phillip B. Abel,  
Kenneth W. Street, and Kazuhisa Miyoshi  
Lewis Research Center, Cleveland, Ohio

Masao Murakawa and Shojiro Miyake  
Nippon Institute of Technology, Saitama, Japan

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Nippon Institute of Technology, Saitama, Japan

National Aeronautics and  
Space Administration

Lewis Research Center

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# SURFACE CHEMISTRY, MICROSTRUCTURE, AND TRIBOLOGICAL PROPERTIES OF CUBIC BORON NITRIDE FILMS

Shuichi Watanabe, Donald R. Wheeler, Phillip B. Abel, Kenneth W. Street, and Kazuhisa Miyoshi  
National Aeronautics and Space Administration  
Lewis Research Center  
Cleveland, Ohio 44135

Masao Murakawa and Shojiro Miyake  
Nippon Institute of Technology  
Saitama 345, Japan

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## SUMMARY

This report deals with the surface chemistry, microstructure, bonding state, morphology, and friction and wear properties of cubic boron nitride (c-BN) films that were synthesized by magnetically enhanced plasma ion plating. Several analytical techniques—x-ray photoelectron spectroscopy, transmission electron microscopy and electron diffraction, Fourier transform infrared spectroscopy, atomic force microscopy, and surface profilometry—were used to characterize the films. Sliding friction experiments using a ball-on-disk configuration were conducted for the c-BN films in sliding contact with 440C stainless-steel balls at room temperature in ultrahigh vacuum (pressure,  $10^{-6}$  Pa), in ambient air, and under water lubrication. Results indicate that the boron-to-nitrogen ratio on the surface of the as-deposited c-BN film is greater than 1 and that not all the boron is present as boron nitride but a small percentage is present as an oxide. Carbon, oxygen, tungsten, and argon contaminants can be introduced to the surface of the as-deposited c-BN film during the reactive ion-plating process.

c-BN film has a multilayered structure consisting of a titanium interlayer, amorphous boron nitride layer, hexagonal boron nitride layer, and c-BN layer. The characteristic cubic crystalline state of the c-BN layer was verified by transmission electron microscopy, electron diffraction, and Fourier transform infrared spectroscopy. The cross angle on the two-dimensional lattice image taken along the  $\langle 011 \rangle$  direction was exactly  $70.5^\circ$ , and the interplanar spacing was about 0.21 nm; four strong  $\{111\}$ , two strong  $\{022\}$ , and two weak  $\{200\}$  diffraction spots were clearly observed; and a clear absorption band in the Fourier transform infrared spectrum was observed at around  $1100 \text{ cm}^{-1}$ . The surface of the as-deposited c-BN film was smooth, with a 3.4-nm root-mean-square surface roughness over a  $2.2\text{-}\mu\text{m}$  square. The fine asperities corresponded to the fine grains of the c-BN film.

Friction and wear properties of the c-BN film were highly dependent on the environment. In air and under water lubrication, the c-BN film in sliding contact with steel showed a low wear rate, whereas a high wear rate was observed in vacuum. Both in air and under water lubrication, c-BN exhibited wear resistance superior to that of amorphous boron nitride, titanium nitride, and titanium carbide. A material pair of c-BN and aluminum experienced high wear in c-BN under dry sliding conditions in air and in vacuum. Under water lubrication, however, there was almost no wear in the c-BN film for this material pair.

## INTRODUCTION

Because cubic boron nitride (c-BN), which is chemically and thermally inert, is second only to diamond in hardness, it has been attracting attention as a superhard material. Extensive research and development have been done on preparing c-BN films by physical and chemical vapor deposition (ref. 1). Although a low-pressure gas-phase deposition process can be used to form a thin film of c-BN, c-BN coatings are not yet practical because of difficulties in their synthesis.

Because of the high hardness of c-BN, many researchers believe that c-BN films offer great opportunities for wear parts, cutting tool inserts, rotary tools, and dies. These films will be especially valuable for protective coatings on surfaces that come into contact with iron-based materials, where diamond cannot be used because of its high chemical wear due to its aggressive reaction with iron. Therefore, tribological considerations point out the importance of investigating in detail the friction and wear properties of c-BN film in contact with steel.

This report deals with the physical characteristics and tribological properties, primarily wear properties, of c-BN films that were synthesized by magnetically enhanced plasma ion plating (MEP-IP). The investigation was conducted to examine the friction and wear of c-BN films. Sliding friction experiments were conducted with c-BN films formed on silicon wafer substrates in contact with 440C stainless-steel balls in three

environments: vacuum, ambient air, and water. Two sets of comparative sliding friction experiments were conducted: (1) with amorphous boron nitride (a-BN), titanium nitride (TiN), and titanium carbide (TiC) films sliding against 440C stainless balls in air, and (2) with c-BN films sliding against A1050 aluminum balls in vacuum, in air, and under water lubrication.

## EXPERIMENTAL PROCEDURE

### Preparation of c-BN Films

MEP-IP was used to synthesize c-BN films. Details of the coating equipment and the film preparation conditions have been described in previous reports (refs. 2 and 3). Briefly, 99.9-percent-pure boron was evaporated with an electron beam, and then the evaporated boron was reacted with highly ionized gas supplied adjacent to the substrate. Plasma was formed by a hot-electron-radiating tungsten filament (hot cathode), an opposed anode with a positive voltage, and a pair of permanent magnets that produced a magnetic field parallel to the electric field between the cathode and anode. The apparatus was arranged to introduce argon gas, in addition to nitrogen gas, to promote the reaction on the substrate. A self-bias voltage was produced by applying radiofrequency power to the substrate to accelerate nitrogen and argon ions and promote the reaction.

The graded composition controlling technique by MEP-IP (ref. 3) was used to deposit the c-BN films (approximately 500-nm thick) on silicon {100} wafer substrates, which have mirrorlike finished surfaces. Prior to c-BN deposition, a titanium interlayer was deposited on the silicon substrate to improve the adhesion of the c-BN film to the substrate.

For the comparative sliding friction experiments, a-BN films (approximately 500-nm thick) were prepared by MEP-IP and deposited directly onto 19-mm-diameter, 5-mm-thick 440C stainless-steel disks (micro-Vickers hardness of about 6.8 GPa). An ion plating technique was used to deposit the titanium nitride (TiN) and titanium carbide (TiC) films (both about 1000-nm thick) on silicon wafer substrates.

### Physical Characterization

Analytical techniques were used to characterize the surface chemistry, microstructure, bonding state, and morphology of the c-BN films: x-ray photoelectron spectroscopy (XPS) was used to characterize the surface chemistry; transmission electron microscopy (TEM) and electron diffraction were used to determine the microstructure and crystalline state, including the long-range order of bonding and crystallographic information; Fourier transform infrared (FT-IR) spectroscopy was used to analyze the nature of the nearest-neighbor bonding phase; atomic force microscopy (AFM) was used to observe surface morphology in the nanometer range; and surface profilometry was used to determine the extent of wear.

### Tribometer Setup

Figure 1 shows the vacuum friction apparatus, which consisted of a ball-on-disk assembly (fig. 1(a)) mounted in an ultrahigh vacuum chamber, a drive system, and a friction-force measuring system (fig. 1(b)). All components within the vacuum chamber were compatible with oxidizing, inert, and reducing gases.

The c-BN-coated silicon substrate was attached to a 19-mm-diameter, 5-mm-thick steel disk with a low outgassing adhesive that is compatible with ultrahigh vacuum. The ball was mounted in a holder attached to one end of a stainless steel beam. 440C stainless-steel and A1050 aluminum balls, both having a diameter of 6 mm, were chosen as counterpart materials for the experiments. Because the beam was bearing-mounted, the ball could be deadweight loaded against the disk surface.

The ball and disk were placed in the vacuum tribometer, as shown in the enlarged detail in figure 1(b). The disk specimen was mounted on a shaft driven by a gear motor that was connected to a rotary feedthrough with a ferrofluidic seal. The drive assembly provided rotation at various speeds, which were regulated by a direct-current motor controller.

Horizontal movement of the ball during disk rotation was restrained by the beam, which acted as a bending spring. The displacement of the ball was continuously monitored with a linear variable differential transformer during the experiments. Also during the experiments, the friction force was continuously recorded in a computerized data acquisition system that could measure friction forces as low as 1 mN (0.1 g). A turbomolecular vacuum pump and an oil-sealed mechanical pump were used to evacuate the vacuum chamber to 1 to  $3 \times 10^{-6}$  Pa in 16 to 20 hr without bakeout.

## Friction and Wear Experiments

Sliding friction experiments were conducted in the vacuum chamber shown in figure 1. Before each experiment, the as-received, fresh surface of a ball was ultrasonically rinsed in an ethanol bath and dried by blowing dry nitrogen gas over it. Then, the cleaned ball and coated disk specimen were positioned in the vacuum chamber.

For the experiment in ultrahigh vacuum, the system was evacuated to 1 to  $3 \times 10^{-6}$  Pa and maintained at this pressure. For the experiment in ambient air, the vacuum chamber was conditioned in laboratory air at a relative humidity of 36 percent or less during the entire sliding friction experiment. For the experiment under water lubrication, a couple of distilled-water drops were put on the sliding surface of disk specimens in ambient air. All experiments were performed at room temperature.

After the system was conditioned to the desired environment, the ball was brought into contact with the surface of the disk specimen and loaded. All sliding friction experiments were conducted with a load of 0.98 N (100 g) and a constant rotating speed of 120 rpm. The sliding velocity ranged from 34.5 to 88 mm/sec because of the range of wear track radii involved in the experiments. As the disk rotated, the ball scribed a circular wear track on the flat surface of the disk (fig. 1(a)). In each experiment, a fresh, unused area of the ball was brought into contact with the disk.

An average cross-sectional area of a wear track produced in the c-BN film disks was obtained from stylus tracing across the wear tracks at three locations or more. This value was then multiplied by the wear track length (which was computed from the diameter of the track at its center) to determine the wear volume. The wear rate, known as the dimensional wear coefficient, is defined as the volume of material removed at an unit applied load and in an unit sliding distance expressed in cubic millimeters per Newton-meters.

## RESULTS AND DISCUSSION

### Characteristics of c-BN Film

**Surface Chemistry.**—XPS surface analysis and depth profiling were performed on a c-BN film specimen (fig. 2). A survey scan of the c-BN showed it to consist primarily of boron and nitrogen with less than 10 at.% carbon and oxygen. The film also contained 1 to 1.5 at.% tungsten and about 0.5 at.% argon. Contaminants, such as tungsten, argon, and some carbon and oxygen, may have been introduced to the c-BN film during the reactive ion-plating process. The profiles show that carbon, oxygen, and tungsten decreased rapidly after sputtering. Figure 3 shows an XPS depth profile, and figure 4 is the same profile magnified to show lower concentration elements. The argon concentration increases with sputtering time, but that is probably due to argon implanted during sputtering.

Figures 5(a) and (b) show the  $W_{4f}$  peak from the c-BN film before and after sputtering, respectively. Binding energies of some oxides and tungsten metal are indicated. Before sputtering, the tungsten appears to be primarily  $WO_3$ . After sputtering, the peak shape indicates a mixture of oxidation states between  $WO_2$  and  $WO_3$ . The reduction of tungsten could be an artifact of the sputtering process.

From the profile in figure 4, it can be seen that the oxygen concentration remains at about 1.5 at.% as the film is sputtered while the tungsten quickly drops to a few tenths of an atomic percent or less. This suggests that oxygen is present in forms other than tungsten oxide. Since the boron-to-nitrogen ratio is slightly greater than 1 (fig. 3), it seems likely that not all the boron is present as BN, but that a small percentage is present as an oxide. An overlay of the  $B_{1s}$  peaks (fig. 6) shows that, after sputtering, the boron peak shifts away from the oxide position toward the BN position and it broadens. The broadening indicates a mixture of oxidation states. However, quantitatively, there hardly seems to be enough oxide present after sputtering to account for the high binding energy of the peak. It is likely that the broadened width and the high binding energy of the  $B_{1s}$  peak are due to ion-beam damage of the BN, combined with a small percentage of boron oxides.

**Microstructure and Crystalline State.**—Clear evidence of a well-crystallized c-BN film was demonstrated by high-resolution TEM and diffraction. Figure 7 shows a low-magnification cross-sectional micrograph of a c-BN film. It has a multilayered structure consisting of a titanium interlayer (about 200-nm thick), a-BN layer (150- to 200-nm thick), hexagonal boron nitride (h-BN) layer (50-nm thick), and c-BN layer on top (200- to 250-nm thick). The a-BN, h-BN, and c-BN phases are clearly separated from each other.

Figure 8 is a high-resolution micrograph of a c-BN film taken along the  $\langle 011 \rangle$  direction. Clear two-dimensional lattice images can be seen. The cross angle is exactly  $70.5^\circ$ , and the interplanar spacing is about 0.21 nm—which is clear evidence for the presence of cubic-type BN crystals.

Figure 9 shows an electron diffraction pattern from a single grain of c-BN. This pattern was taken along the  $\langle 011 \rangle$  direction by focusing the electron beam to about 1.5 nm. Four strong  $\{111\}$  and two  $\{022\}$  reflection spots are clearly seen, together with two weak  $\{200\}$  reflection spots. With c-BN, the structure factor of the

{200} planes is much weaker than that of the {111} and {220} planes. The angle between the {111} planes and the distance between the transmitted beam and the beam reflected from the {111} plane were measured, confirming that the electron diffraction came from one of the c-BN grains.

**Bonding State.**—The bonding state of a c-BN film was characterized by infrared spectroscopy, with the spectrum measured in the transmittance mode, with a bare silicon wafer used as a reference. Figure 10 is an FT-IR absorption spectrum of the c-BN film on a silicon wafer substrate. In this figure, a clear characteristic absorption band corresponding to the c-BN phase (ref. 4) is observed at around  $1100\text{ cm}^{-1}$ , and two bands corresponding to the h-BN phase (ref. 5) layer are observed at around  $1400$  and  $800\text{ cm}^{-1}$ . Some peaks around  $600\text{ cm}^{-1}$  could be attributed to dopants contained in the silicon wafer substrate.

**Morphology.**—The surface morphology of an as-deposited c-BN film was observed at the nanometer scale by AFM. An AFM image of the c-BN film (fig. 11) clearly shows a relatively smooth surface profile with a surface roughness ( $R_{rms}$ ) of  $3.4\text{ nm}$  over a  $2.2\text{- by }2.2\text{-}\mu\text{m}$  area. The fine asperities correspond to the fine grains of the c-BN film. Other AFM data from the c-BN film—such as height profile, power spectrum, histogram, and bearing ratio—are shown in figure 12.

### Friction and Wear Properties of c-BN Films

**c-BN in Contact With Steel.**—Figure 13 presents the steady-state (equilibrium) friction coefficients and wear rates for c-BN films coated on silicon in sliding contact with 440C stainless-steel balls in the three environments used: ultrahigh vacuum, air, and water. The results indicate that both the steady-state friction coefficients and wear rates of c-BN films depend on the environment. In vacuum, the measured friction coefficient and wear rate of the c-BN film were high:  $1.2$  and an order of  $10^{-5}\text{ mm}^3/\text{N}\cdot\text{m}$ , respectively.

In air, the c-BN film showed a low wear rate ( $10^{-8}\text{ mm}^3/\text{N}\cdot\text{m}$  or lower), but a high steady-state friction coefficient ( $1.4$ ). The high friction coefficient of c-BN film in air, however, differs from those of previous results (ref. 6); that is, friction coefficients for c-BN films in contact with the 440C stainless-steel balls were low— $0.2$  to  $0.3$ . More detailed investigations of the friction behavior of c-BN films, such as studying the effects of humidity on friction and wear, are needed to clarify the friction properties of c-BN film in contact with a 440C stainless steel ball in air.

Under water lubrication, the c-BN film had a low steady-state friction coefficient ( $0.2$  to  $0.3$ ) and a low wear rate ( $10^{-8}\text{ mm}^3/\text{N}\cdot\text{m}$  or lower). This film can be an effective wear resistant material under water lubrication.

Thus, although the as-deposited c-BN films in sliding contact with 440 stainless-steel are not effective wear resistant coatings in vacuum, they resist wear both in air and under water lubrication.

**Comparison of a-BN, TiN, and TiC in Contact With Steel.**—It is interesting to compare the foregoing friction and wear results for c-BN with those for a-BN, TiN, and TiC coatings. Sliding friction experiments were conducted with all four types of coating films in the same manner.

Figure 14 presents the friction and wear properties of c-BN, a-BN, TiN, and TiC films in sliding contact with 440C stainless-steel balls in air. The c-BN film had the lowest wear rate, namely the highest wear resistance. In the following, the film materials are listed in ascending order of wear rate for contact with the 440C stainless-steel balls: c-BN, TiC, a-BN, and TiN. Of the film materials shown in figure 14, TiC had the lowest friction coefficient.

Figure 15 presents the friction and wear properties of a-BN films in sliding contact with 440C stainless-steel balls in the three environments used: vacuum, air, and water. Comparing figure 15 with figure 13 shows that the effects of the environment on the friction coefficient and wear rate of a-BN films are generally similar to those seen with c-BN films. However, the wear rates of a-BN films in air and under water lubrication were approximately a factor of  $100$  higher than those of c-BN. Note that the Knoop hardness value of the c-BN film obtained at an indentation load of  $0.1\text{ N}$  was approximately  $42$  to  $61\text{ GPa}$ , whereas the Knoop hardness value of the a-BN films used for the reference experiments was about  $22$  to  $28\text{ GPa}$ .

**c-BN in Contact With Aluminum.**—Figure 16 presents the steady-state friction coefficients and the wear rates for c-BN films coated on silicon substrates in sliding contact with A1050 aluminum balls under the same conditions as those in figure 13. In vacuum, the c-BN in contact with aluminum had a high wear rate ( $10^{-5}\text{ mm}^3/\text{N}\cdot\text{m}$ ) similar to that for c-BN in contact with steel. The friction coefficient obtained for c-BN in contact with aluminum was  $0.4$ , which was lower than that obtained for c-BN in contact with steel ( $1.2$ ) by a factor of  $3$ .

In air, the c-BN in contact with aluminum possessed a high wear rate ( $10^{-5}\text{ mm}^3/\text{N}\cdot\text{m}$ ), which was a factor of  $800$  to  $900$  higher than that for c-BN in contact with steel. On the other hand, the friction coefficient obtained for the c-BN in contact with aluminum was  $0.8$ —approximately a factor of  $1.8$  lower than that obtained for c-BN in contact with steel.



Under water lubrication, the wear of c-BN film was not measurable, because aluminum transferred to the surface of c-BN film where there was strong interfacial adhesion between c-BN and aluminum. The friction coefficient of the c-BN in contact with aluminum (0.29) was slightly higher than that for c-BN in contact with steel (0.2).

### CONCLUDING REMARKS

Cubic boron nitride (c-BN) films were deposited on silicon substrates by magnetically enhanced plasma ion plating. The surface chemistry, microstructure, morphology, and friction and wear properties of as-deposited c-BN films were studied.

On the surface of the as-deposited c-BN film, the boron-to-nitrogen ratio was slightly greater than 1 and not all the boron was present as BN, but a small percentage was present as an oxide. Carbon, oxygen, tungsten, and argon contaminants may have been introduced to the surface of the as-deposited c-BN film during the reactive ion-plating process.

The c-BN film has a multilayered structure: a titanium interlayer, amorphous boron nitride layer, hexagonal boron nitride layer, and c-BN layer. The characteristic cubic crystalline state of the c-BN layer was verified by transmission electron microscopy, electron diffraction, and Fourier transform infrared spectroscopy. The cross angle on the two-dimensional lattice image taken along the  $\langle 011 \rangle$  direction was exactly  $70.5^\circ$ , and the interplanar spacing was about 0.21 nm; four strong  $\{111\}$ , two strong  $\{022\}$ , and two weak  $\{200\}$  diffraction spots were clearly observed; and a clear absorption band in the Fourier transform infrared spectrum was observed at around  $1100 \text{ cm}^{-1}$ .

The surface of as-deposited c-BN film was smooth and had a 3.4-nm root-mean-square surface roughness over a  $2.2\text{-}\mu\text{m}$  square. The fine asperities corresponded to the fine grains of c-BN film.

Friction and wear properties of the c-BN film were revealed to be highly dependent on the environment.

1. The c-BN film in sliding contact with steel showed a low wear rate both in air and under water lubrication, but a high wear rate in vacuum.
2. In air and under water lubrication, c-BN in contact with steel exhibited wear resistance superior to that of amorphous boron nitride, titanium nitride, and titanium carbide.
3. A material pair of c-BN and aluminum can cause high wear in c-BN under dry sliding conditions in air or vacuum.
4. Under water lubrication, however, there was almost no wear in this pair.

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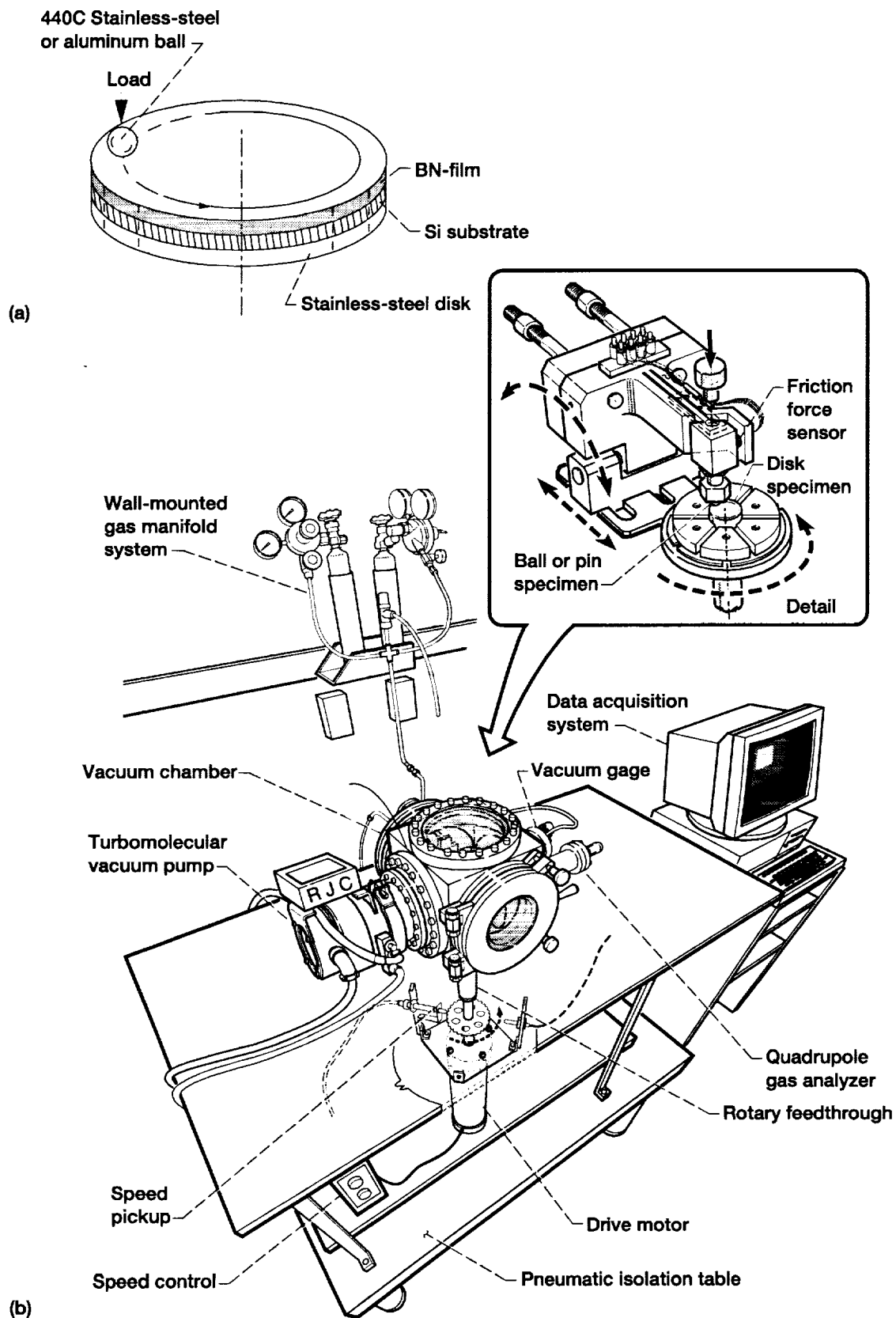


Figure 1.—Vacuum chamber friction and wear apparatus. (a) Ball-on-disk configuration. (b) Apparatus.

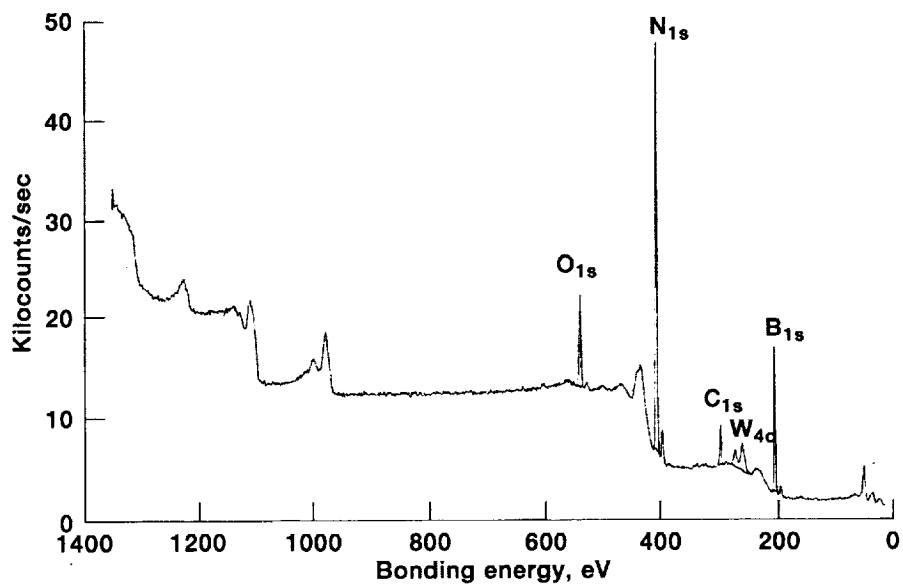


Figure 2.—X-ray photoelectron spectroscopy (XPS) survey spectrum of c-BN film.

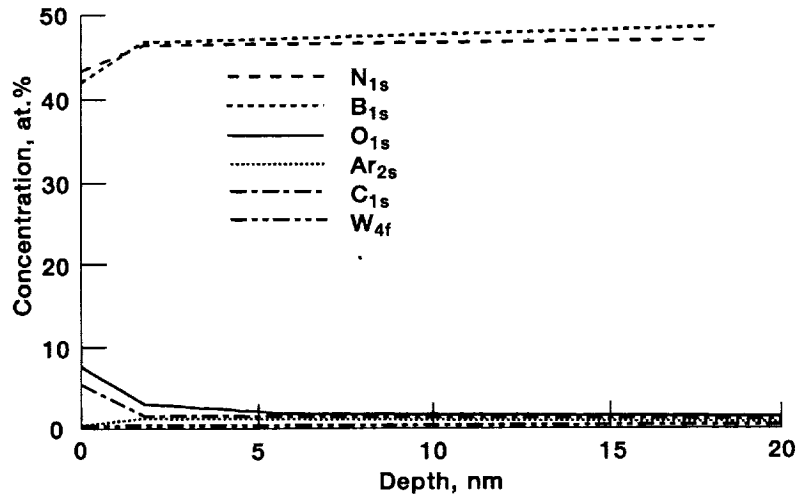


Figure 3.—XPS depth profile of c-BN film.

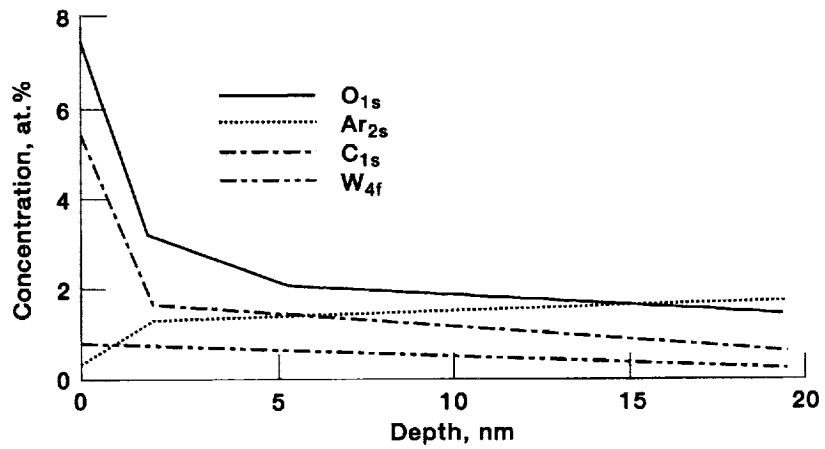


Figure 4.—XPS depth profile of c-BN film, magnified to show the lower concentration elements.

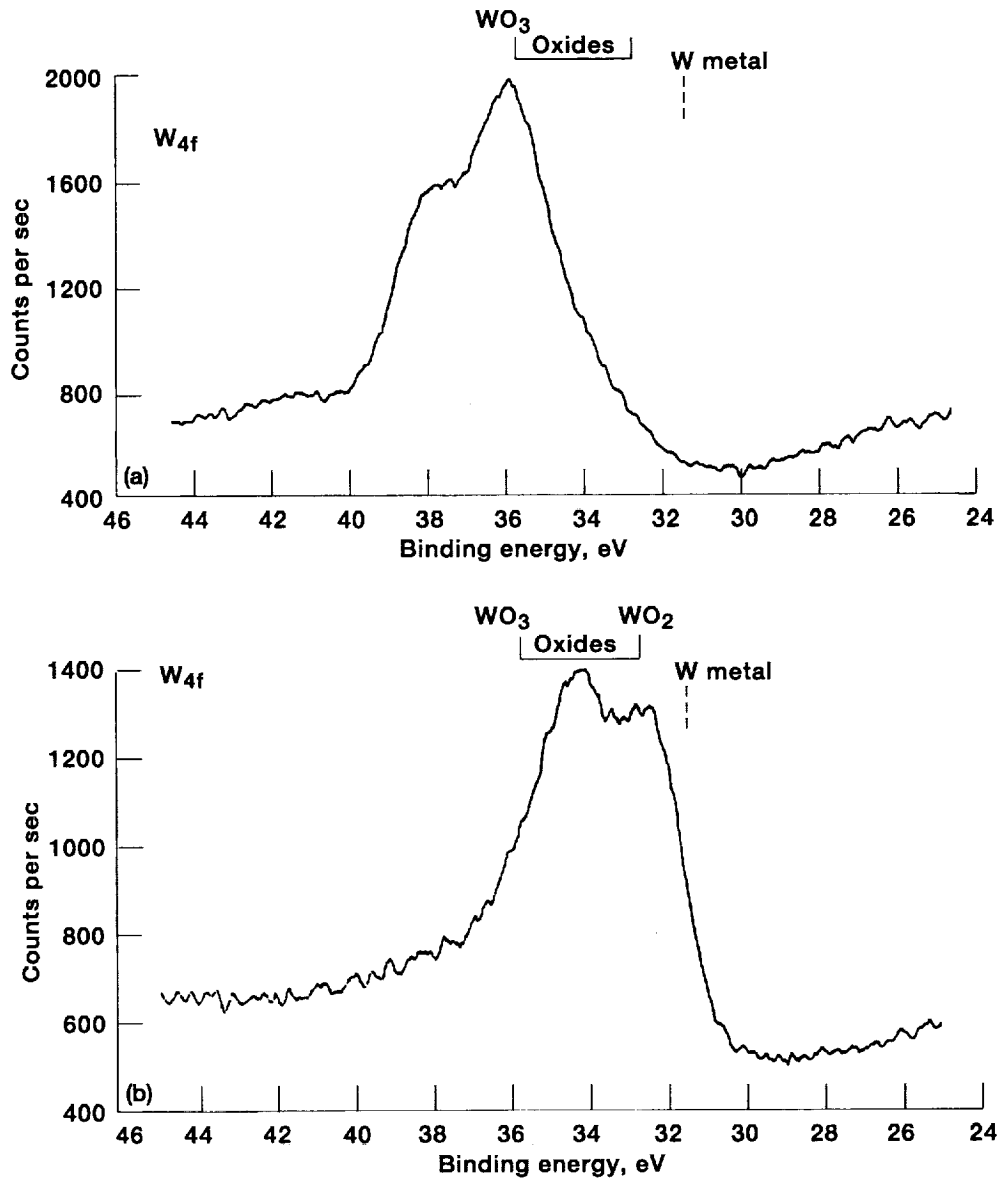


Figure 5.— $W_{4f}$  spectra of c-BN films obtained by XPS. (a) Before argon-sputtering. (b) After argon-sputtering for 100 sec.

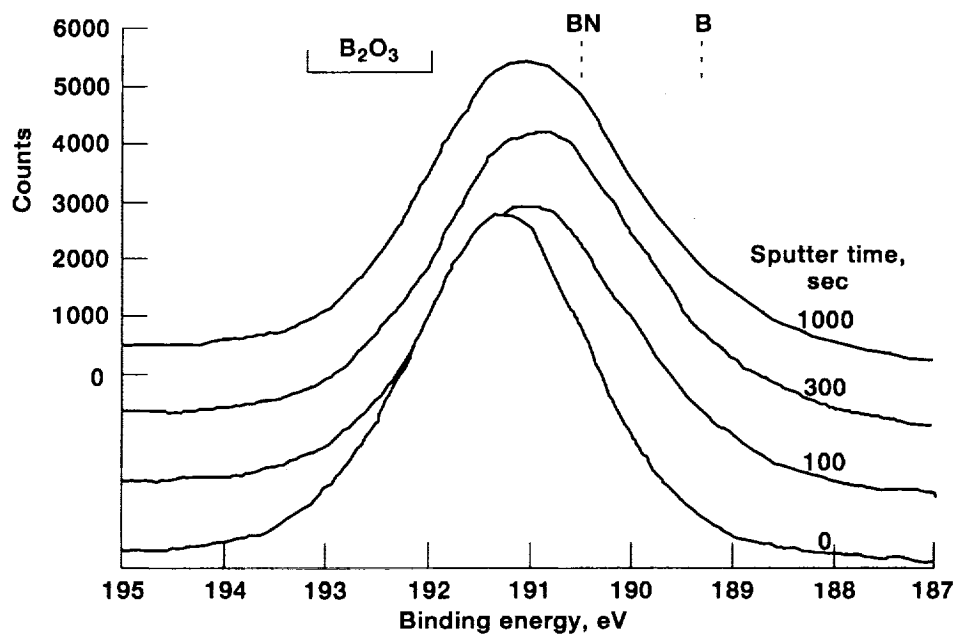


Figure 6.—Overlay of B<sub>1s</sub> spectra obtained by XPS, showing the boron peak shifts, for various sputter times.

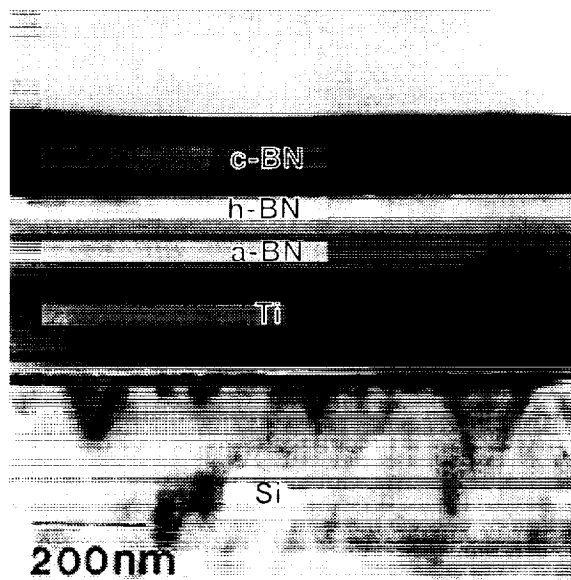


Figure 7.—Cross-sectional transmission electron micrograph of c-BN film deposited on a silicon substrate by magnetically enhanced plasma ion plating (MEP-IP).

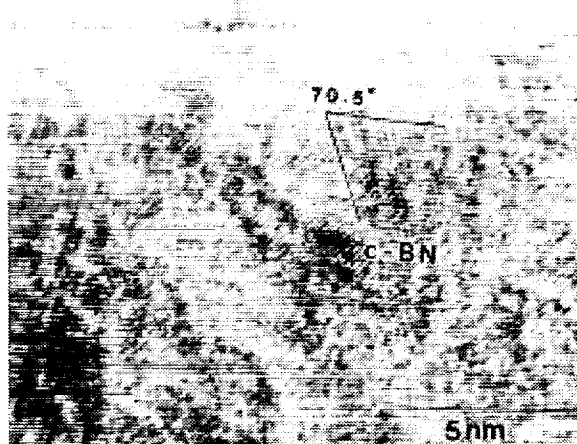


Figure 8.—High-resolution electron micrograph of c-BN film taken along the  $\langle 011 \rangle$  direction.

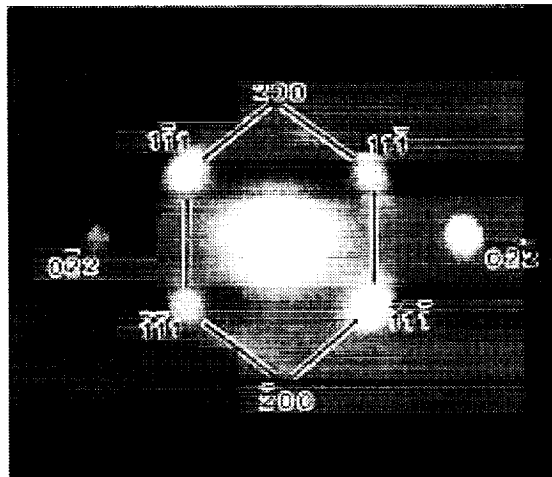


Figure 9.—Microdiffraction pattern of c-BN film taken along the  $\langle 011 \rangle$  direction by focusing the electron beam to 1.5 nm.

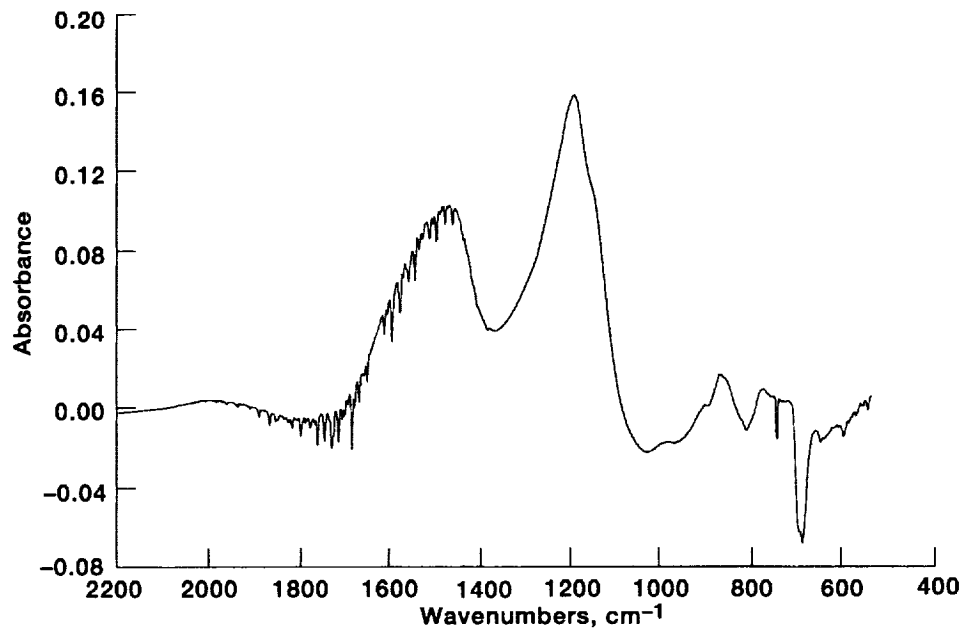


Figure 10.—Fourier transform infrared (FT-IR) spectrum of c-BN film.

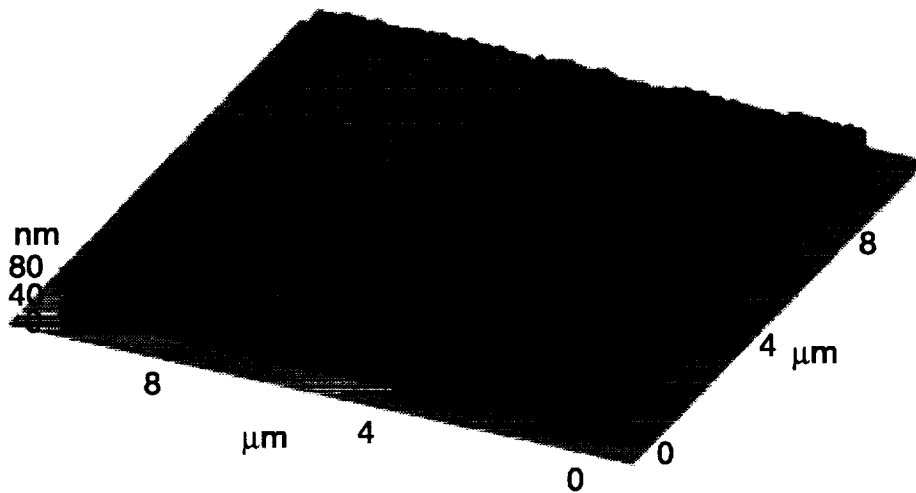


Figure 11.—Surface morphology of c-BN film observed by atomic force microscopy (AFM).



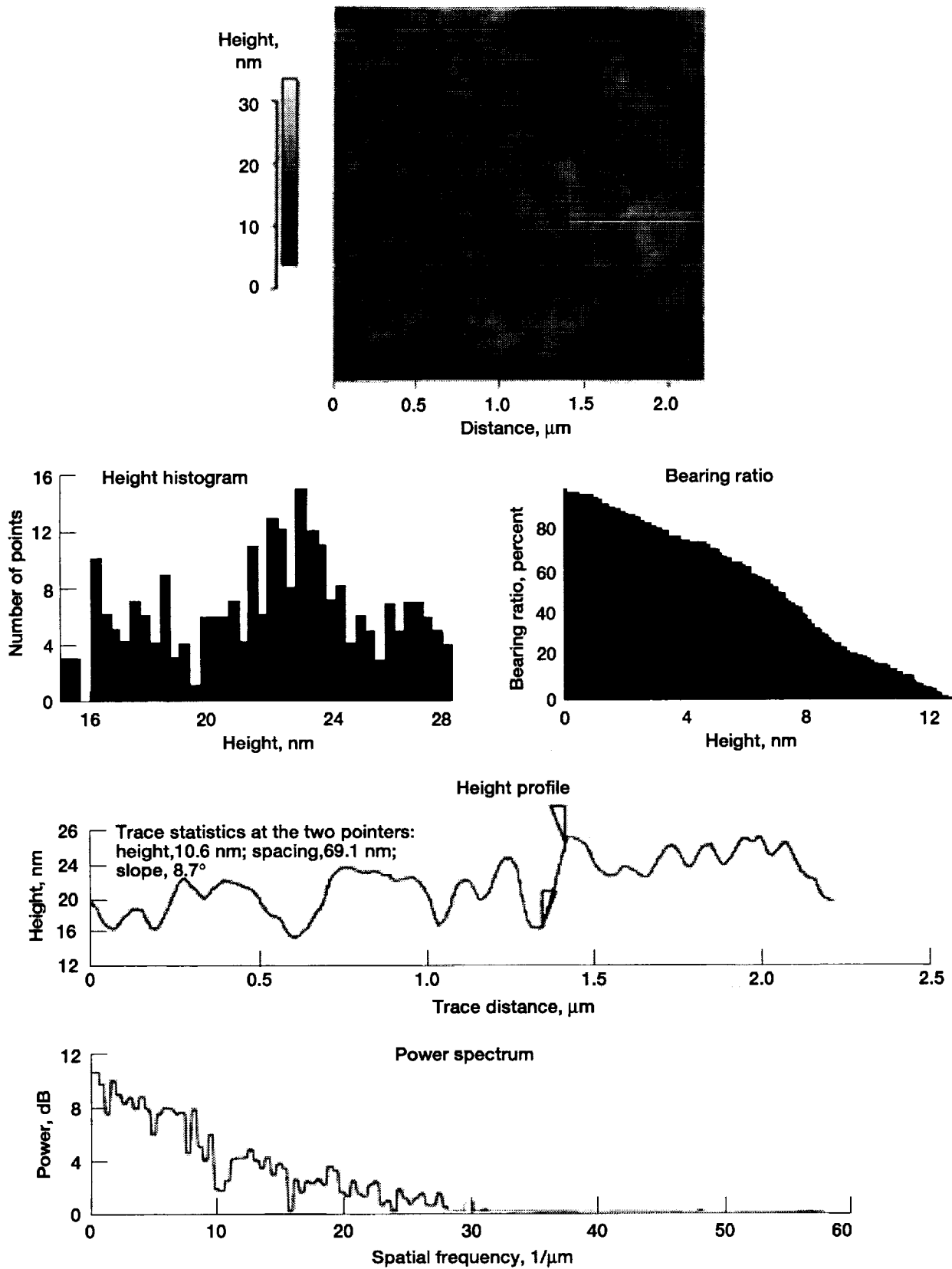


Figure 12.—Surface profile characteristics of c-BN film obtained by AFM. Trace statistics: rms roughness, 3.4 nm; average roughness, 2.8 nm.

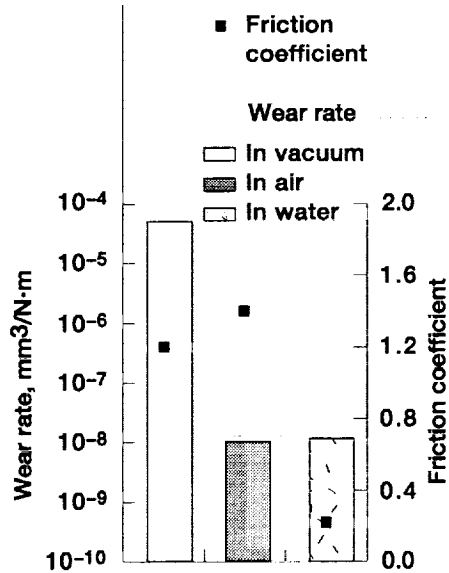


Figure 13.—Steady-state (equilibrium) friction coefficients and wear rates of c-BN specimens in sliding contact with 440C stainless-steel balls in ultrahigh vacuum, ambient air, and water.

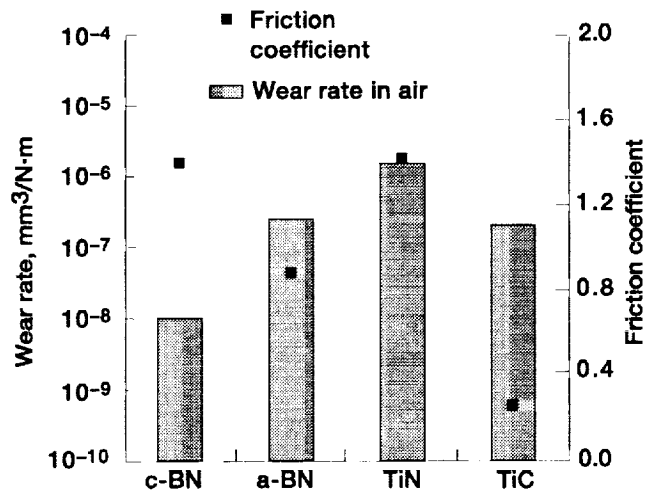


Figure 14.—Comparison of steady-state (equilibrium) friction coefficient and wear rates of c-BN, a-BN, TiN, and TiC films in sliding contact with 440C stainless-steel balls in air.

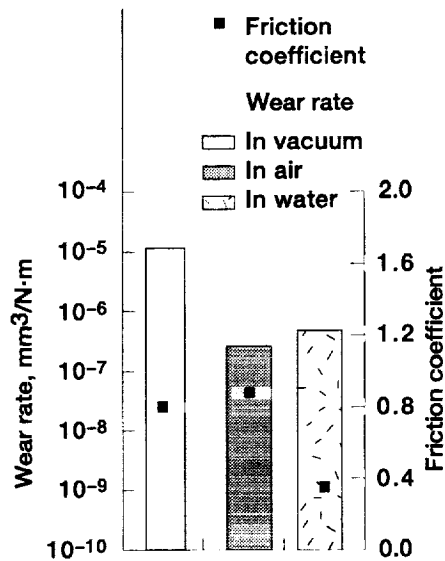


Figure 15.—Steady-state (equilibrium) friction coefficients and wear rates of a-BN film specimens in sliding contact with 440C stainless-steel balls in ultrahigh vacuum, ambient air, and water.

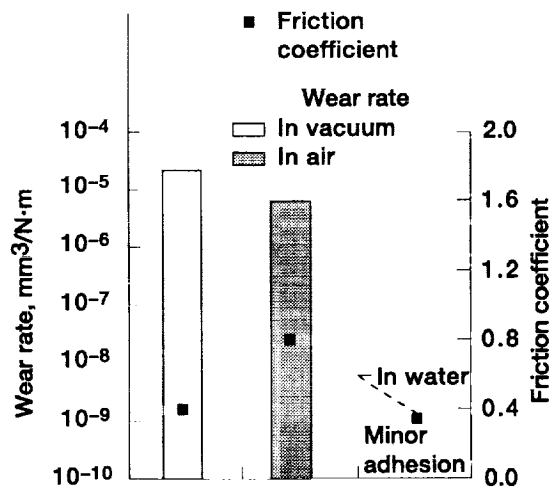


Figure 16.—Steady-state (equilibrium) friction coefficients and wear rates of c-BN film specimens in sliding contact with aluminum balls in ultrahigh vacuum, ambient air, and water.

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<b>13. ABSTRACT (Maximum 200 words)</b>  This report deals with the surface chemistry, microstructure, bonding state, morphology, and friction and wear properties of cubic boron nitride (c-BN) films that were synthesized by magnetically enhanced plasma ion plating. Several analytical techniques—x-ray photoelectron spectroscopy, transmission electron microscopy and electron diffraction, Fourier transform infrared spectroscopy, atomic force microscopy, and surface profilometry—were used to characterize the films. Sliding friction experiments using a ball-on-disk configuration were conducted for the c-BN films in sliding contact with 440C stainless-steel balls at room temperature in ultrahigh vacuum (pressure, 10 <sup>-6</sup> Pa), in ambient air, and under water lubrication. Results indicate that the boron-to-nitrogen ratio on the surface of the as-deposited c-BN film is greater than 1 and that not all the boron is present as boron nitride but a small percentage is present as an oxide. Both in air and under water lubrication, the c-BN film in sliding contact with steel showed a low wear rate, whereas a high wear rate was observed in vacuum. In air and under water lubrication, c-BN exhibited wear resistance superior to that of amorphous boron nitride, titanium nitride, and titanium carbide.				
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