MICROSCOPY RESEARCH AND TECHNIQUE 42:295–301 (1998)

In Situ Growth and Characterization of Ultrahard Thin Films

E. BENGU,* C. COLLAZO-DAVILA, D. GROZEA, E. LANDREE, I. WIDLOW, M. GURUZ, AND L.D. MARKS
Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208

KEY WORDS electron microscopy; thin film deposition; ultrahard thin films

ABSTRACT Results concerning the operation of a new ultrahigh vacuum (UHV) ion-beam assisted deposition system for in situ investigation of ultrahard thin films are reported. A molecular beam epitaxy (MBE) chamber attached to a surface science system (SPEAR) has been redesigned for deposition of cubic-boron nitride thin films. In situ thin film processing capability of the overall system is demonstrated in preliminary studies on deposition of boron nitride films on clean Si (001) substrates, combining thin film growth with electron microscopy and surface characterization, all in situ. *Microsc. Res. Tech. 42:295–301, 1998.* © 1998 Wiley-Liss, Inc.

INTRODUCTION

Every substance interacts with the outside world through its surface, and frequently surface properties determine the utility of a material. Coatings and thin films are one way to modify and enhance surface properties, yielding a composite material made up of the thin film, interface, and substrate. Often, none of the three phases alone achieves the performance of the composite material, and thin films are involved in applications as diverse as desktop computers and jet engines. Various techniques, including in situ transmission electron microscopy (TEM), can be used to investigate the complex nature of thin film deposition. One of first accurate descriptions of the nucleation and growth of thin films came from in situ experiments conducted using TEMs fitted with metal deposition stages (Pashley, 1959, 1965; Pashley et al., 1964). These studies lead to the conclusion that deposition follows one of three modes: (1) Volmer-Weber mode (VW), 3-D island growth. (2) Frank-van der Merwe mode (FM), layer by layer growth. (3) Stranski-Krastanov mode (SK), layer plus island mode, an intermediary path between VW mode and FM mode. Mathematical models of nucleation and growth of thin films have also been derived and tested using in situ TEM experiments (Venables and Spiller, 1982; Venables et al., 1984). However, as pointed out by Pashley et al. (1964) the vacuum in a conventional TEM, around 10^{-7}–10^{-8} torr, is not acceptable for most in situ work on surfaces and thin films; at such vacuum levels, there are only seconds to examine a clean surface.

Structures and reactions on surfaces is another field where in situ TEM can be useful, for instance direct observation of the ordering of surface atomic steps, chemical reactions, and surface reconstructions (Doraiswamy et al., 1995; Grozea et al., 1997; Landree et al., 1997). For example, the first reasonably accurate model for the Si (111) 7 x 7 structure was proposed by Takayanagi et al. (1985a,b) using transmission electron diffraction (TED) data. In a sense, surface reconstructions are a snapshot of the very early stages of nucleation and growth. Combining both diffraction and imaging, in situ TEM has been used to solve and refine a number of metal-semiconductor surface reconstructions (Collazo-Davila et al., 1997, 1998; Jayaram and Marks, 1995; Marks and Plass, 1995; Plass and Marks, 1995;). In situ UHV-TEM has also become a fundamental tool in thin film science, to cite an instance with the work of Yagi et al. (1982, 1985) on the initial stages of film growth on oxide, semiconductor, and metal surfaces. An advantage TEM has over other surface analysis techniques is the ability to acquire information not just from the top surface atoms but also from buried layers, demonstrated by Bengu et al. (1996) by imaging the dimers in the third layer of Si (111)-7 x 7 surface. Marks and colleagues (1997) also give other applications of TEM on buried interfaces.

We report the results from the preliminary experiments conducted using a new UHV ion-beam assisted deposition system attached to a unique surface science system. The goal is to achieve complete in situ processing of the ultrahard thin films, starting from substrate preparation and characterization to film deposition and characterization.

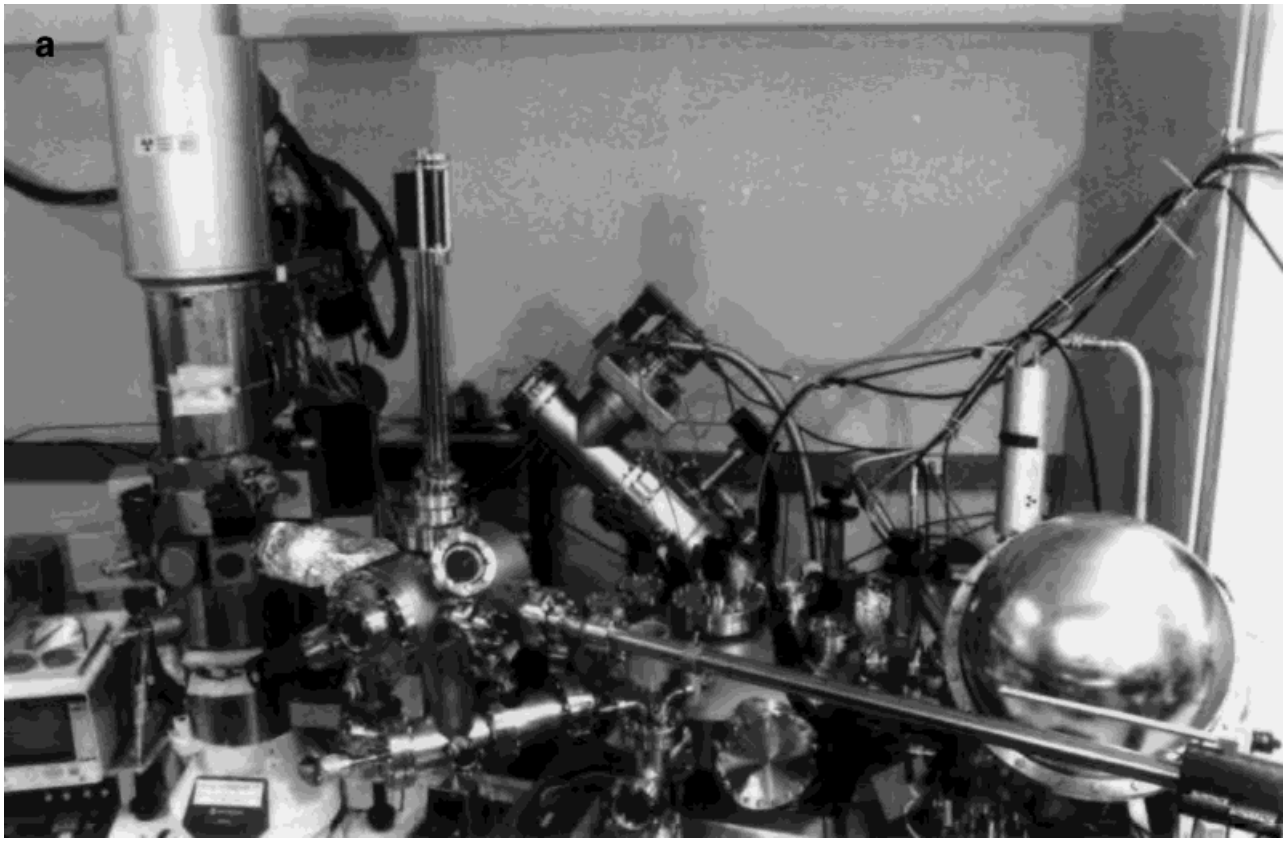
SPEAR, SINBAD, AND MIBE

This section is a brief description of the equipment used for in situ investigation of surfaces, interfaces, and thin films. The UHV analysis chamber, Sample Preparation Evaluation Analysis and Reaction (SPEAR), is attached to a Hitachi UHV H-9000 microscope (Bonevich and Marks, 1992; Collazo-Davila et al., 1995; Jayaram et al., 1995). The SPEAR unit is the central module of the analysis system, and attached to it are two other units: SINBAD and MIBE. SINBAD, Stabilizing Ion and Neutral Beam Assisted Deposition, allows ion-beam-assisted deposition of ultrahard thin films for the investigation of nucleation and growth. The Molecular and Ion Beam Epitaxy (MIBE) unit, under construction, will be used for the study of coatings and multilayers grown by magnetron and ion-beam sources. A schematic of the layout for SPEAR, SINBAD, MIBE,

*Correspondence to: Erman Bengu, Northwestern University, Department of Materials and Science, 2225 N. Campus Drive, MLSF, Room 2036, Evanston, IL 60201. E-mail: Bengu@nwu.edu

Contract grant sponsor: National Science Foundation; Contract grant numbers: DMR-9204117, DMR-92145505; Contract grant sponsor: Air Force Office of Scientific Research; Contract grant numbers: F49620–94–1-0164, F49620–92-J-0250.

Received 29 April 1998; accepted in revised form 6 May 1998



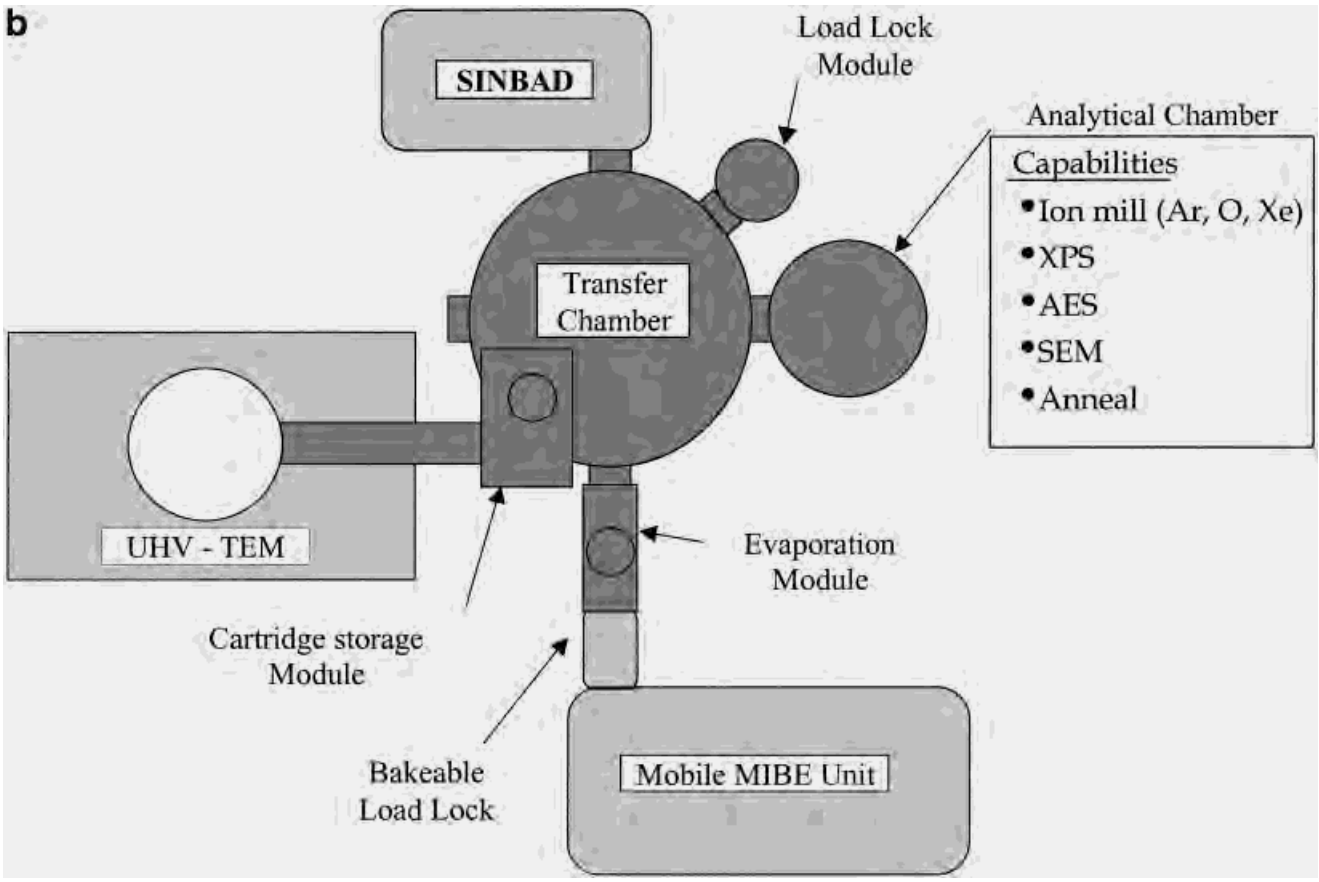


Fig. 1. **a:**. Photograph of the SPEAR, SINBAD, and Hitachi UHV H-9000 microscope. **b:** Schematic (top view) of the complete UHV system: SPEAR, SINBAD, MIBE, and the UHV-TEM.

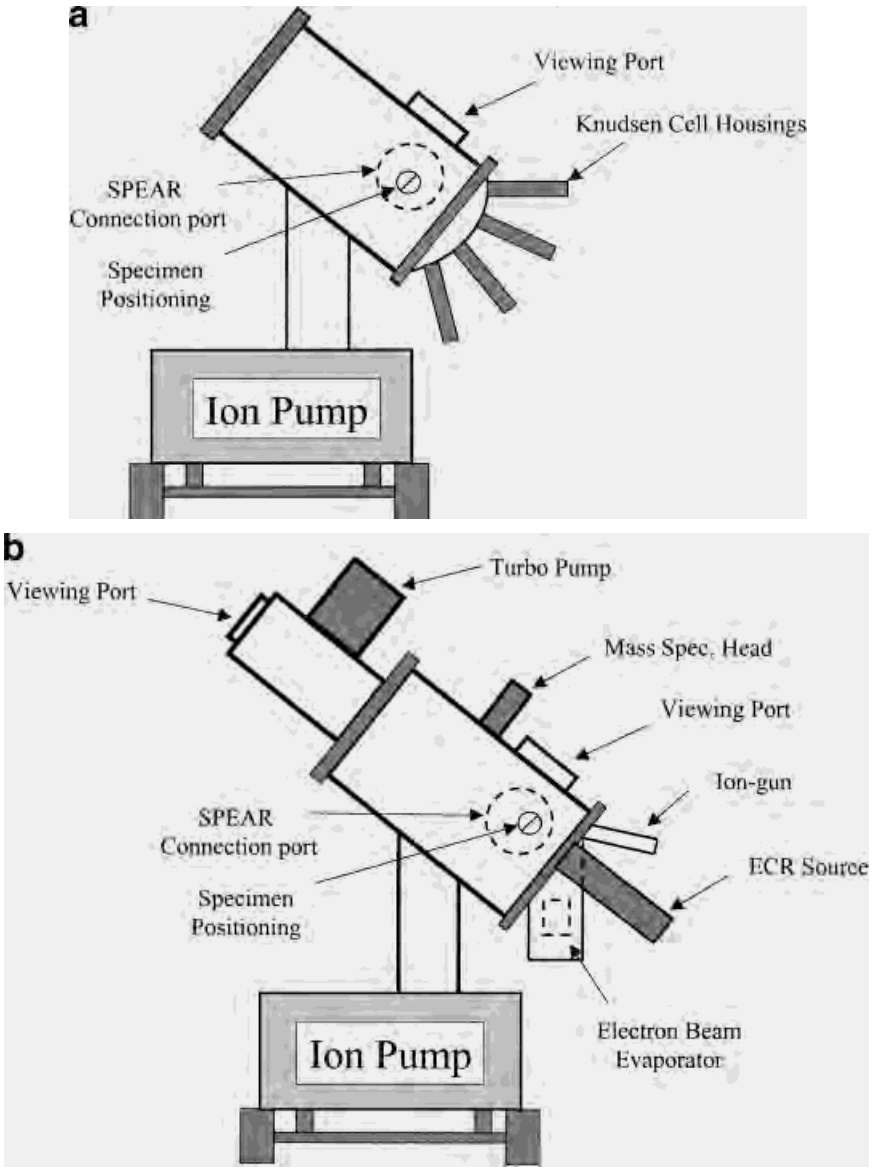


Fig. 2. **a:** Schematic (side view) of the MBE chamber on the SPEAR system before modifications. **b:** Schematic (side view) of the SINBAD chamber on the SPEAR system after modifications.

and the UHV H-9000 microscope is given in Figure 1a and b. Figure 1a is a picture of SPEAR and SINBAD. Figure 1b is a schematic representation (top view) of the SPEAR, SINBAD, MIBE, and UHV H-9000 microscope.

SPEAR

The SPEAR system includes four separate chambers, as shown in Figure 1b. The sample is introduced from a load-lock chamber that can hold five samples at a time, without breaking the vacuum in any other chamber. The central component of SPEAR is the transfer chamber equipped with a carrier assembly that can shuttle samples between various chambers. A separate storage module in the transfer chamber can hold up to eight samples and four microscope cartridges. At any time, one can transfer a sample through the transfer chamber to any part of SPEAR including the UHV H-9000 microscope. In addition, an evaporation stage has been added to the transfer chamber consisting of five different metal boats. The analytical chamber plays a dual role, namely preparation and chemical analysis of samples. For sample preparation, the analytical chamber houses a duoplasmatron microbeam ion-gun, an electron gun for direct beam annealing, and a multipurpose sample manipulation stage capable of 360° of rotational freedom, d.c. biasing, resistive heating, and liquid nitrogen cooling. The duoplasmatron microbeam ion-gun with three gas sources (xenon, oxygen, and argon) is used for cleaning of sample surfaces with a probe size less than 5 μm. Chemical characterization tools include an X-ray source (either Al K α or Mg K α), a field-emission electron gun with scanning ability, and

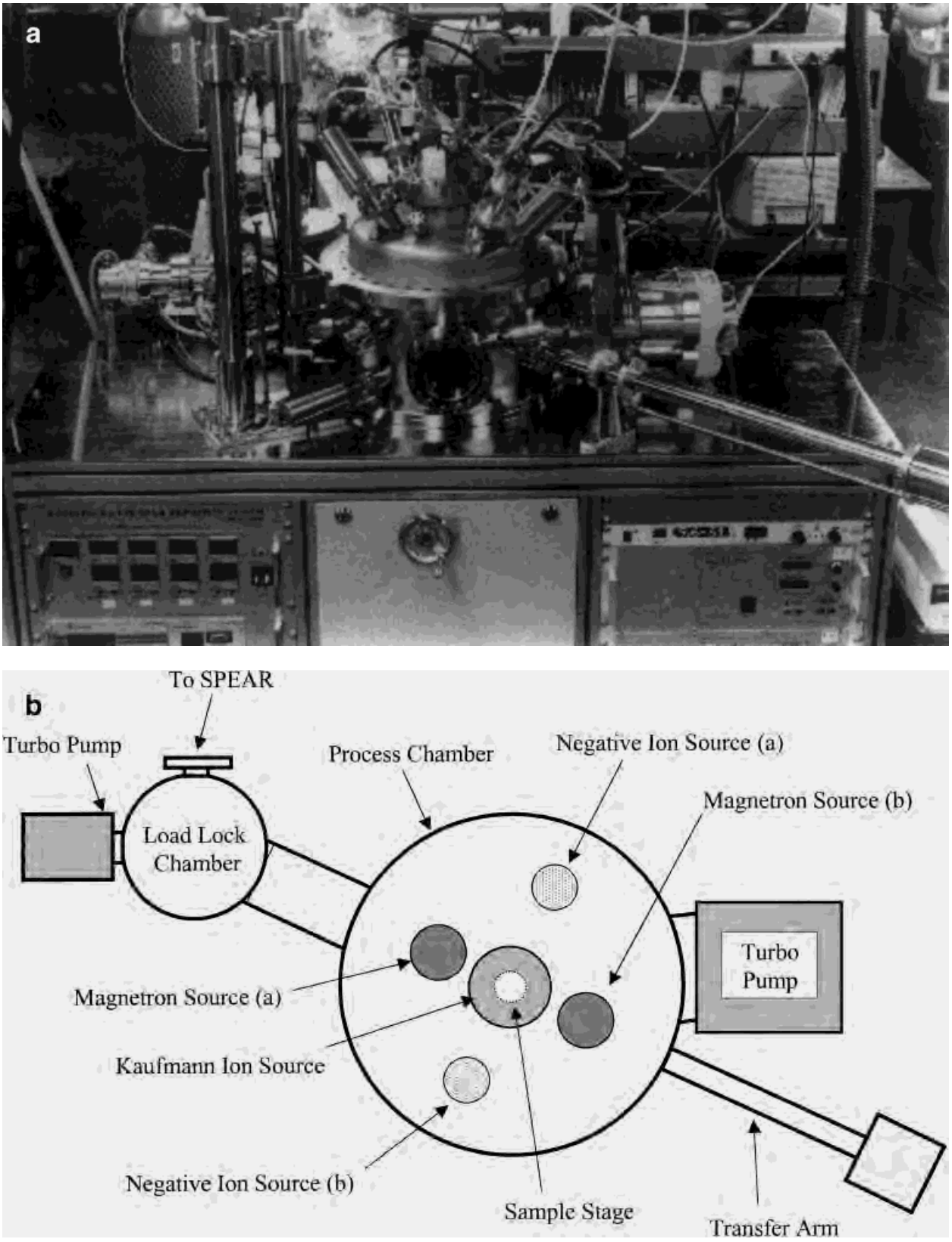


Fig. 3. **a:** Photograph of the MIBE system. **b:** Schematic (top view) of the MIBE system displaying the deposition attachments.

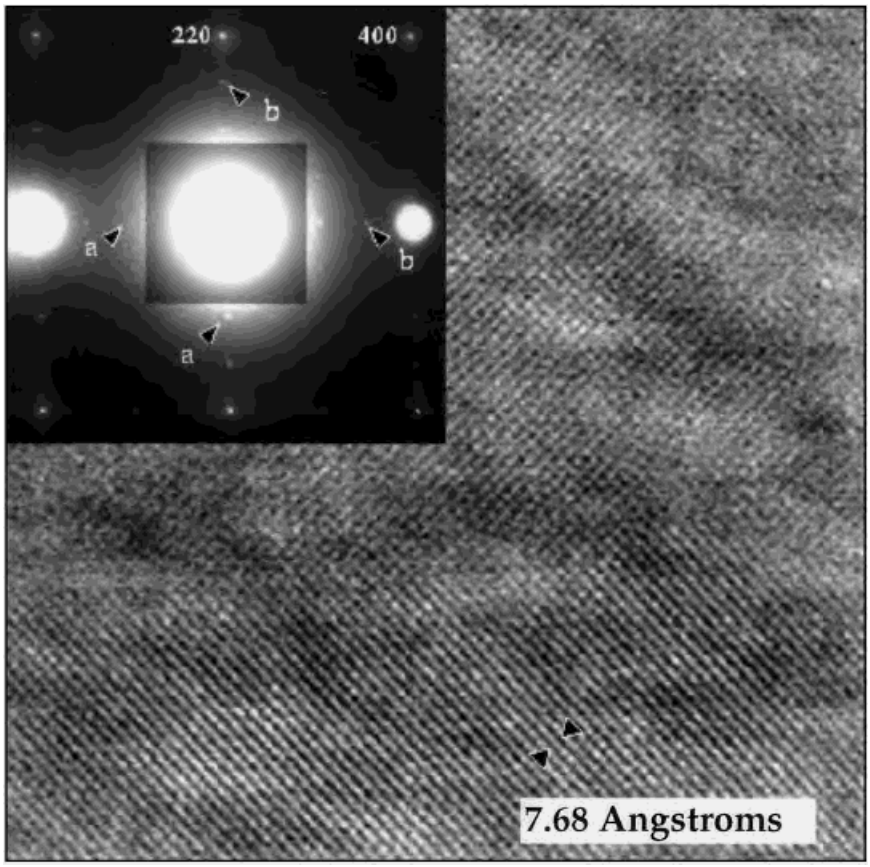


Fig. 4. Image from 2 x 1 reconstructed Si (001) surface. **Inset:** TED pattern from the surface showing 2 domains of the 2 x 1 reconstruction.

a spherical capacitance electron energy analyzer (SCA) that can be used for either Auger electron spectroscopy (AES) or X-ray photoelectron spectroscopy (XPS). Imaging of the sample during preparation is via an electron multiplier (Channeltron detector) and a video imaging system. Along with SEM capability, this provides precise control over the area being milled.

SINBAD

Initially, the MBE chamber on the SPEAR system had two effusion cells configured for thin film deposition of GaAs. This MBE unit was redesigned for the deposition of cubic-boron nitride (c-BN) films using ion beam-assisted deposition techniques. Figure 2a and b is a schematical representation of the MBE and SINBAD chambers. The new unit, SINBAD, is pumped by a 280 l/s turbomolecular pump (Varian Vacuum, Lexington, MA) and a 220 l/s ion pump (Physical Electronics, Eden Prairie, MN), with a base pressure 1 x 10^{-9} Pa.

Just like the SPEAR system, SINBAD is designed to handle and deposit on thin 3-mm TEM ready samples. The sample manipulation stage can be used for the d.c. biasing of the sample as well as resistive heating during deposition. The SINBAD unit is equipped with a single position electron-beam evaporator (Thermionics Inc., Hayward CA), a 4 keV ion-gun (Perkin-Elmer Model 04–300, Eden Prairie, MN), and a compact electron cyclotron resonance (ECR) plasma source (AX-4300 Astex Inc., Boston, MA). Both the ECR and the 4keV ion-gun can be utilized as ion-sources for purposes other than deposition.

MIBE

MIBE is designed to be a mobile unit such that the deposition of films can be accomplished when the system is not attached to SPEAR. The deposited films can be transferred to SPEAR after MIBE is re-attached through a bakeable load-lock chamber. Figure 3a is a photograph of the MIBE system. There are two chambers, a load-lock chamber, and a process chamber. Figure 3b shows the layout of the deposition attachments and sources in the process chamber. Two d.c. Magnetron-sputtering sources (Innovac/ Korea Vacuum Tech Model MDC, Seoul, Korea) are mounted on the top of the process chamber. Two direct negative ion beam sources (SKION Corporation, Hoboken, NJ) are also mounted internally to maintain a short working distance. These sources can be used to create negative ions of energies up to 300 eV with an energy spread of ± 5% (Ko and Kim, 1997). A 3 cm diameter Kaufmann gas ion source (~50 eV) (Commonwealth Scientific Comp., Alexandria, VA; low voltage ion source) is located at the top of the chamber. Once mounted on the stage, the sample can be rotated to a maximum of 20 revolutions per

minute, d.c. biased, and heated by a Si_3N_4 element up to 900°C.

RESULTS

We describe here results from ion-beam assisted deposition experiments conducted using the SINBAD system. In addition, results from the structural and chemical characterization of the same films conducted in SPEAR are also included.

The substrate material consisted of 3-mm disks of p-type Si (001) (13.5–18.5 Ohm cm). Following conventional TEM ex situ sample preparation for silicon, the sample was dimpled and polished to approximately 30–20 μm at the center. As the final ex situ step, the sample was chemically etched using a solution of 10% HF and 90% HNO_3. The as-etched Si (001) substrate was further cleaned through cycles of ion milling with 1 keV Ar^+ ions and electron beam annealing in SPEAR system. The substrate surface chemistry was characterized using XPS, to ensure that the surface was free of contaminants such as oxygen and carbon. The last step in substrate preparation was the structural characterization of the substrate surface using the UHV H-9000 microscope, which showed the Si (001)- 2 x 1 reconstruction on the surface indicative of a clean surface, as shown in Figure 4.

Deposition was carried out using the SINBAD system, over the clean and reconstructed Si (001) substrate at room temperature (RT). During deposition, the substrate was biased at -45V (d.c.), and the ECR was operating at 200 W with 10 sccm of N_2 (%99.999) flow. The total pressure in the chamber was kept around 5 x 10^{-4} torr. The film was then chemically analyzed using XPS in SPEAR, which showed boron and nitrogen on the surface of Si (001), shown in Figure 5.

The nitrogen to boron ratio revealed that the film was nitrogen rich (N / B = 1.18). Using the Si 2p and Boron 1s peaks, the thickness of the film was estimated to be approximately 80 Angstroms. The film was then transferred to the UHV H-9000 microscope for structural characterization. Figure 6 is an off-zone high-resolution electron micrograph of the film on the Si (001) surface taken at 300 kV, and the inset is the corresponding diffraction pattern. The film is continuous, nanocrystalline, and randomly oriented as indicated by the structure it displays in the micrograph and the rings visible in the diffraction pattern.

DISCUSSION

The results described here demonstrate the overall performance of the SINBAD and the SPEAR systems in depositing thin BN films on Si (001) substrates. These substrates were prepared and characterized in the SPEAR unit under UHV conditions, and then transferred to the SINBAD unit for deposition. After the deposition process, the films were transferred back to the SPEAR for chemical analysis. For the structural characterization, the films were finally transferred to the UHV H-9000 microscope. During the transfer between various systems, the films were always in UHV conditions.

The most important aspect of these experiments was to explore the utilization of SPEAR and SINBAD for the in situ investigation of nucleation and growth of ultrahard thin films. Film deposition in the SINBAD did not effect the operation of SPEAR or the UHV H-9000, indicating more than one experiment can be conducted in parallel at the same time. However, several problems must be solved in order to attain completely independent operation of these systems. The ECR plasma source on the SINBAD and the dual anode X-ray source on the SPEAR share the same cooling water line limiting the availability of XPS during deposition for another experiment. Another issue is the extra mechanical vibrations and noise (including electronic noise) generated by the SINBAD during deposition that can interfere with the high-resolution operation of the microscope. For example, an air-cooling fan for a turbo pump on the SINBAD was found to be the major source of the vibrations generated in the system. This problem was solved by water cooling the turbo pump. Remaining issues regarding the parallel operation of the SPEAR and SINBAD are relatively minor, and will be dealt with in the near future.

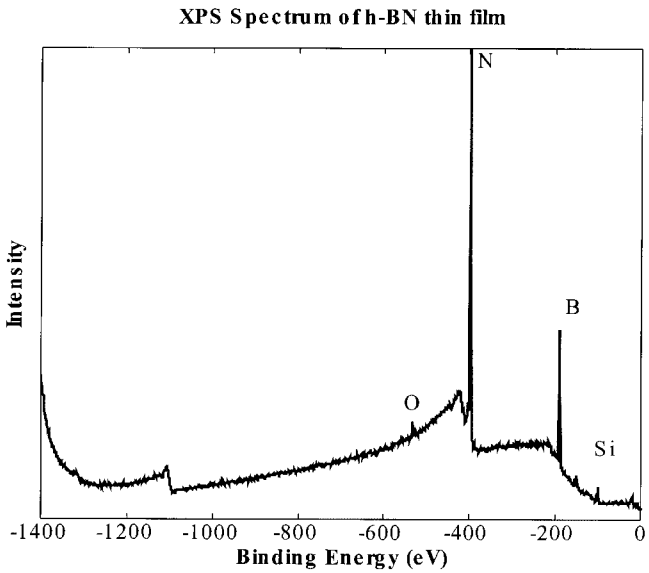


Fig. 5. XPS spectrum from the h-BN over the Si (001).

This modular arrangement of the side chambers allowing independent usage of each unit also necessitates the transfer of samples between different units, which can cause a different type of problem. The most time-consuming and crucial part of any experiment in the SPEAR and SINBAD is the sample transfer between different chambers. During sample transfer between chambers, excessive damage can be induced to samples due to rough handling. However, there are advantages to have a modular design such that each chamber can be brought up to air for maintenance and repairs, and pumped back down independently of all others.

ACKNOWLEDGMENTS

We acknowledge the support of the National Science Foundation for grants DMR-9204117 and DMR-9214505, and the support of the Air Force Office of Scien-

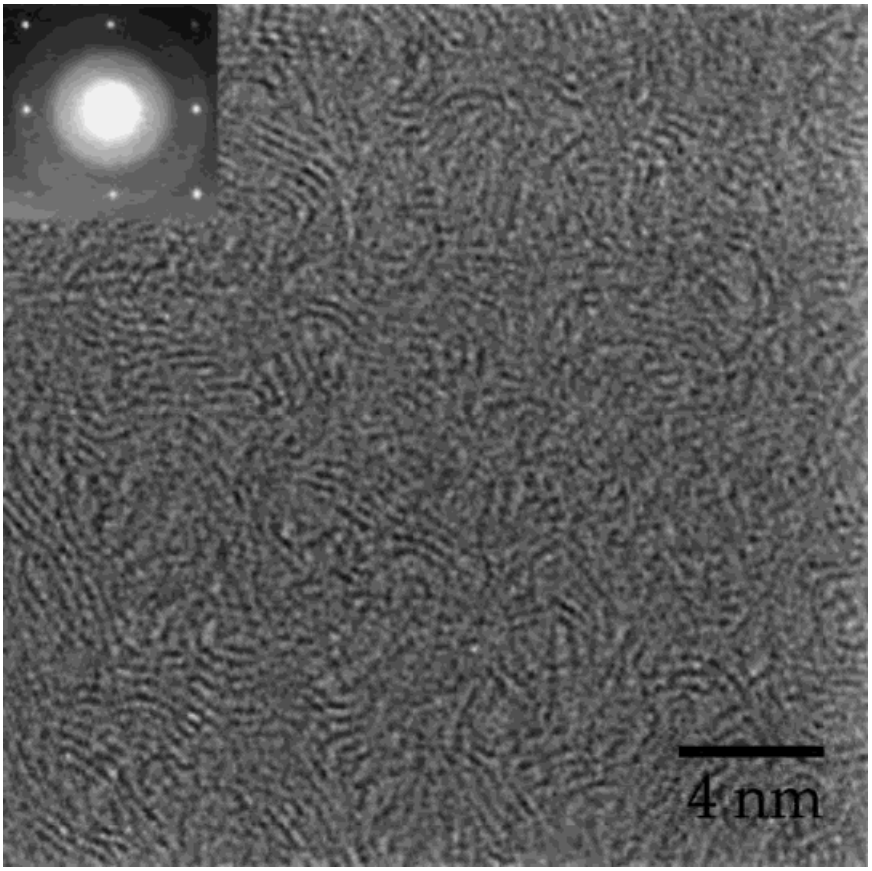


Fig. 6. Image of the BN film on the Si (001) substrate. **Inset:** TED pattern from the film.

tific Research for grants F49620–94–1-0164 and F49620–92-J-0250 in funding this work.

REFERENCES

Bengu, E., Plass, R., Marks, L.D., Ichihashi, T., Ajayan, P.M., and Iijima, S. (1996) Imaging the dimers in Si (111)-(7x7). Phys. Rev. Lett., 77: 4226–4228.

Bonevich, J.E., and Marks, L.D. (1992) Ultrahigh-vacuum electron microscopy of crystalline surfaces. Microscopy, 22:95–101.

Collazo-Davila, C., Landree, E., Grozea, D., Jayaram, G., Plass, R., Stair, P.C., and Marks, L.D. (1995) Design and initial performance of an ultrahigh vacuum sample preparation evaluation analysis and reaction (SPEAR) system. J M S A, 1:267–279.

Collazo-Davila, C., Marks, L.D., Nishii, K., and Tanishiro, Y. (1997) Atomic structure of In on Si (111)(4x1) surface. Surf. Rev. Lett., 4:65–70.

Collazo-Davila, C., Grozea, D., and Marks, L.D. (1998) Determination and refinement of the Ag/Si (111)-(3x1) surface structure. Phys. Rev. Lett., 80:1678–1681.

Doraiswamy, N., Jayaram, G., and Marks, L.D., (1995) Unusual island structures in Ag growth on Si(100)-(2x1). Phys. Rev.B, 51:10167–10170.

Grozea, D., Landree, E., and Marks, L.D. (1997) Surface roughening by electron beam heating. Appl. Phys. Lett., 71: 2301–2303.

Jayaram, G., and Marks, L.D. (1995) Atomic structure of the Si (100)-(5x3)-Au structure. Surf. Rev. Lett., 2:731–739.

Jayaram, G., Plass, R., and Marks, L.D. (1995) UHV-HREM and diffraction of surfaces. Interface Sci., 2:379–395.

Ko, Y. W., and Kim, S. I. (1997) Carbon nucleation on Si (100) using a negative carbon ion beam. J. Vac. Sci. Tech., A15:2750–2754.

Landree, E., Grozea, D., Collazo-Davila, C., and Marks, L.D. (1997) UHV high-resolution electron microscopy and chemical analysis of room-temperature Au deposition on Si(100)-2x1. Phys. Rev. B, 55:7910–7916.

Marks, L.D., and Plass, R. (1995) Atomic structure of Si (111)-(5x2)-Au from high resolution electron microscopy and heavy-atom holography. Phys. Rev. Lett., 75: 2172–2175.

Marks, L.D., Bengu, E., and Gilmore, C.J. (1997) New methods of imaging surfaces (and buried interfaces). J. Electr. Microsc., 46: 207–214.

Pashley, D.W. (1959) The observation of dislocation in thin single crystal films of gold prepared by evaporation. Phil. Mag., 4:324–335.

Pashley, D.W. (1965) The nucleation, growth, structure and epitaxy of thin surface films. Adv. Phys., 14:327–415.

Pashley, D.W., Stowell, M.J., Jacobs, M. H., and Law, T. J. (1964) The growth and structure of gold and silver deposits formed by evaporation inside an electron microscope. Phil. Mag., 10:127–158.

Plass, R., and Marks, L.D. (1995) UHV-transmission electron microscopy structure determination of the Si (111)-($\sqrt{3} \times \sqrt{3}$) R30° Au surface. Surf. Sci., 342:233–249.

Takayanagi, K., Tanishiro, Y., Takahashi M., and Takahashi, S. (1985a) Structural analysis of Si (111)-7x7 by UHV-transmission electron diffraction and microscopy. J. Vac. Sci. Technol., A3:1502–1506.

Takayanagi, K., Tanishiro, Y., Takahashi M., and Takahashi, S. (1985b) Structural analysis of Si (111)-7x7 reconstructed surface by transmission electron diffraction. Surf. Sci., 164: 367–392.

Venables, J.A. and Spiller, G.D.T. (1982) Nucleation and growth of thin films. In: Surface Mobilities on Solid Materials (NATO ASI Series B86). Vu Thien Biah, ed. Plenum Press, New York, pp. 339–404.

Venables, J.A., Spiller, G.D.T., and Hanbucken, M. (1984) Nucleation and growth of thin films. Rep. Prog. Phys., 47:399–459.

Yagi, K., Takayanagi, K., and Honjo, G., (1982) In-situ UHV electron microscopy of surfaces. In: Crystals Growth Properties and Applications, Vol. 7. H.C. Freyhardt, ed. Springer-Verlag, Berlin, pp. 48–74.

Yagi, K., Kobayashi, K., Tanishiro, Y., and Takayanagi, K. (1985) In situ electron microscope study of the initial stages of metal growth on metals. Thin Solid Films, 126:95–105.