GROWTH OF BN THIN FILMS BY PULSED LASER DEPOSITION

J. A. KNAPP
Sandia National Laboratories, Div. 1111, P.O. Box 5800, Albuquerque, NM 87185

SAND--91-1528C

DE92 005462

ABSTRACT

A new UHV chamber for doing Pulsed Laser Deposition of materials is described, together with results from preliminary experiments for depositions of BN on Si. The system is designed to allow for in-situ diagnostics of the ablation plasma, as well as UHV preparation and characterization of clean sample substrates. The room temperature depositions of BN result in amorphous, B-rich films, whose particle content is a strong function of laser wavelength.

INTRODUCTION

Pulsed laser deposition (PLD) is a simple, relatively new technique for fabricating thin films.[1] PLD is particularly interesting for potential application to high-temperature materials such as ceramics or high-T_c superconductors, where it is already finding wide application. Another interesting area would be the deposition of cubic-BN films (cBN), which if successful would have wide application for hard coatings and wide bandgap semiconductors, similar to diamond thin films, as well as important use with tool steels. Films of BN have been deposited using PLD in the past,[2,3] and more recently Doll, et al.[4-6] have reported using PLD to form epitaxial thin films of cBN on Si(100). However, reproducing this result with consistent, thick films of epitaxial cBN has proven difficult.[7] In the experiments reported here, cBN is not expected or seen, because the substrate is at room temperature. Instead, particle density and B/N stochiometry were examined as a function of ablating wavelength.

The system described here has been developed to provide capabilities for in-situ characterization of the laser ablation process and to allow preparation of clean, well-characterized surfaces as substrates. An overview of the all-metal, UHV chamber is in Fig. 1, with the main features shown, some of which are not yet operational. The sample, at the center of this top view, is mounted on a manipulator with two orthogonal rotation axes and XYZ motion. Z travel of 6" is sufficient to raise the sample out of the way for plume diagnostics and to lower it 4" below the deposition for transfer with a loadlock arrangement. An ohmic heater allows sample temperatures up to 1000 °C. Up to 6 targets can be mounted on the target wheel, which is moved under computer control to select targets (allowing convenient growth of multilayers) and to raster the targets during deposition, to prevent cratering. The system has been designed to include a shutter wheel between the targets and the substrate, synchronized with the laser in order to pass the plume while blocking slower moving particles. A number of additional ports, not shown in the figure, point at either the target or substrate positions. In these are mounted an ion sputter gun for sample preparation, a pulsed gas doser for providing a background gas in synchronization with the laser, and a camera for monitoring the plume. Planned additions include a pulsed ion gun for modifying the deposition process.

The laser used for deposition is a Nd:YAG with frequency multiplication; the ablation wavelength can be 1064, 532, 355, or 266 nm. A 1-meter time-of-flight mass spectrometer,

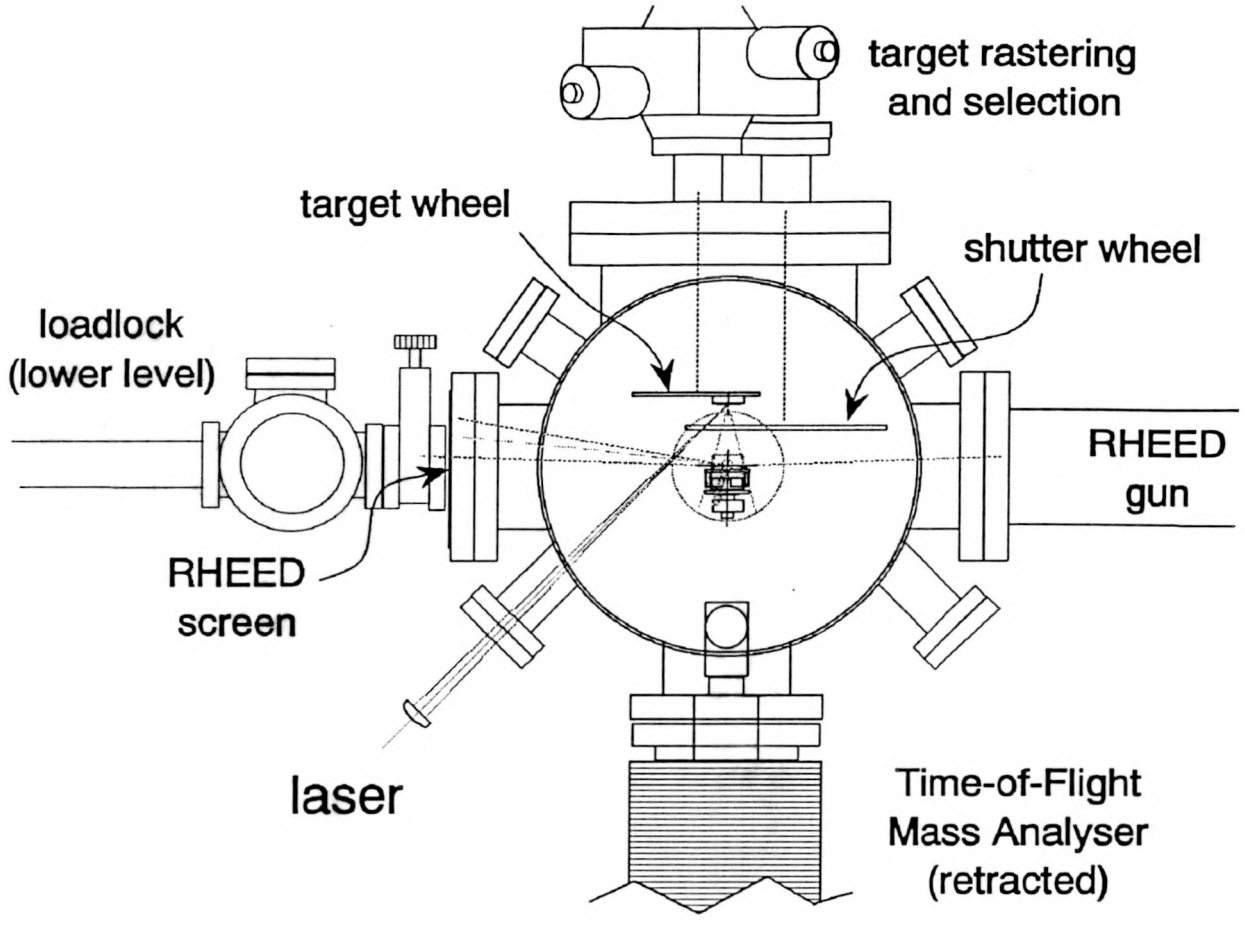

Figure 1. Overview of the pulsed laser deposition system.

modified to accept a small portion of the plume for characterization, will be mounted orthogonal to the target with a bellows so that it can be moved into the sample position or retracted. A quartz crystal deposition monitor is also on a retractable mount. A RHEED gun and screen are mounted such that in-situ monitoring of film growth can be performed, as well as characterization of the substrate surface during preparation. Available capabilities for post-deposition diagnostics of the films include ion beam analyses such as Rutherford Backscattering Spectrometry, Elastic Recoil Detection spectrometry (both conventional and time-of-flight), X-ray analyses, and both scanning and transmission electron microscopy.

BN DEPOSITION

PLD of BN films was done at 532, 355, and 266 nm. Most depositions were done in vacuum ($1x10^{-8}$ Torr without a bakeout) with the substrate at room temperature. A few depositions were done in an N_2 ambient, with the pump valved off. Depositions were performed at a variety of power levels, but the levels for the results shown here were just above the threshold for ablation for each wavelength. The laser was pulsed at 5 Hz for 5000 shots, giving layers 25-35 nm thick. Layers were deposited on Si or C substrates, or a C-coated TEM grid for microstructural analysis.

Ion Beam Analysis

Ion beam analysis was used for determining film compositions. Both high energy non-Rutherford backscattering spectrometry and Elastic Recoil Detection spectrometry (EDS) were used, but for these thin films (of light elements) the ERD analysis proved most useful. Figure

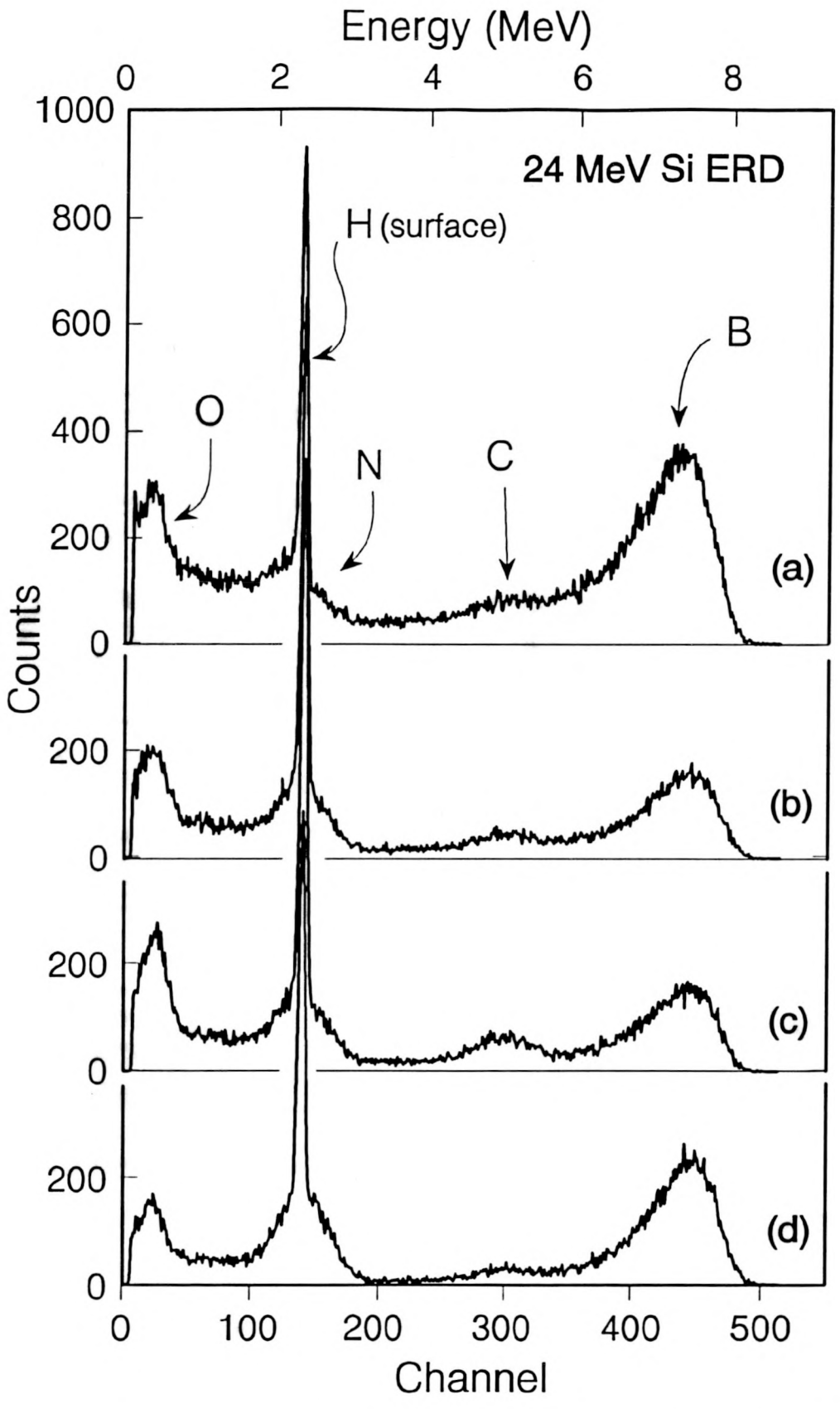

Figure 2. ERD spectra obtained from BN films. Deposition conditions and B/N ratio: (a) 532 nm, vacuum, B/N=3.78. (b) 355 nm, vacuum, B/N=1.71. (c) 355 nm, $5x10^{-4}$ T N_2, B/N=1.82. (d) 266 nm, vacuum, B/N=2.18.

2 shows several spectra obtained from these films. Figures 2(a), (b) and (d) were from films deposited in vacuum, while (c) was in a base pressure of $5x10^{-4}$ Torr N_2. The incident beam was 24 MeV Si,with a 12 μm foil in front of the detector. The origin of each peak in the spectra is labeled; C and O peaks are due to low levels of surface contamination. The sharp peak at channel 140 for all spectra is due to hydrogen on the surface. The depth resolution of ERD is insufficient to resolve the BN layer thickness, but the total areal densities of B and N can be determined, as indicated, as well as layer thicknesses, if a nominal density is assumed. The primary observation is that the films are B-rich for all deposition conditions, with the longer wavelengths yielding higher B concentrations. The deposition in N_2 did not have a significant effect on the N content, while both C and O increased relative to a deposition in vacuum.

Microstructure

Figure 3 shows SEM micrographs for depositions done at three different wavelengths, 532, 355, and 266 nm, under similar conditions. Particles of ~ 1 μm and above are visible at this magnification, and the dependence of particle density on wavelength is striking. Furthermore, the character of the larger particles is clearly more jagged at the longer

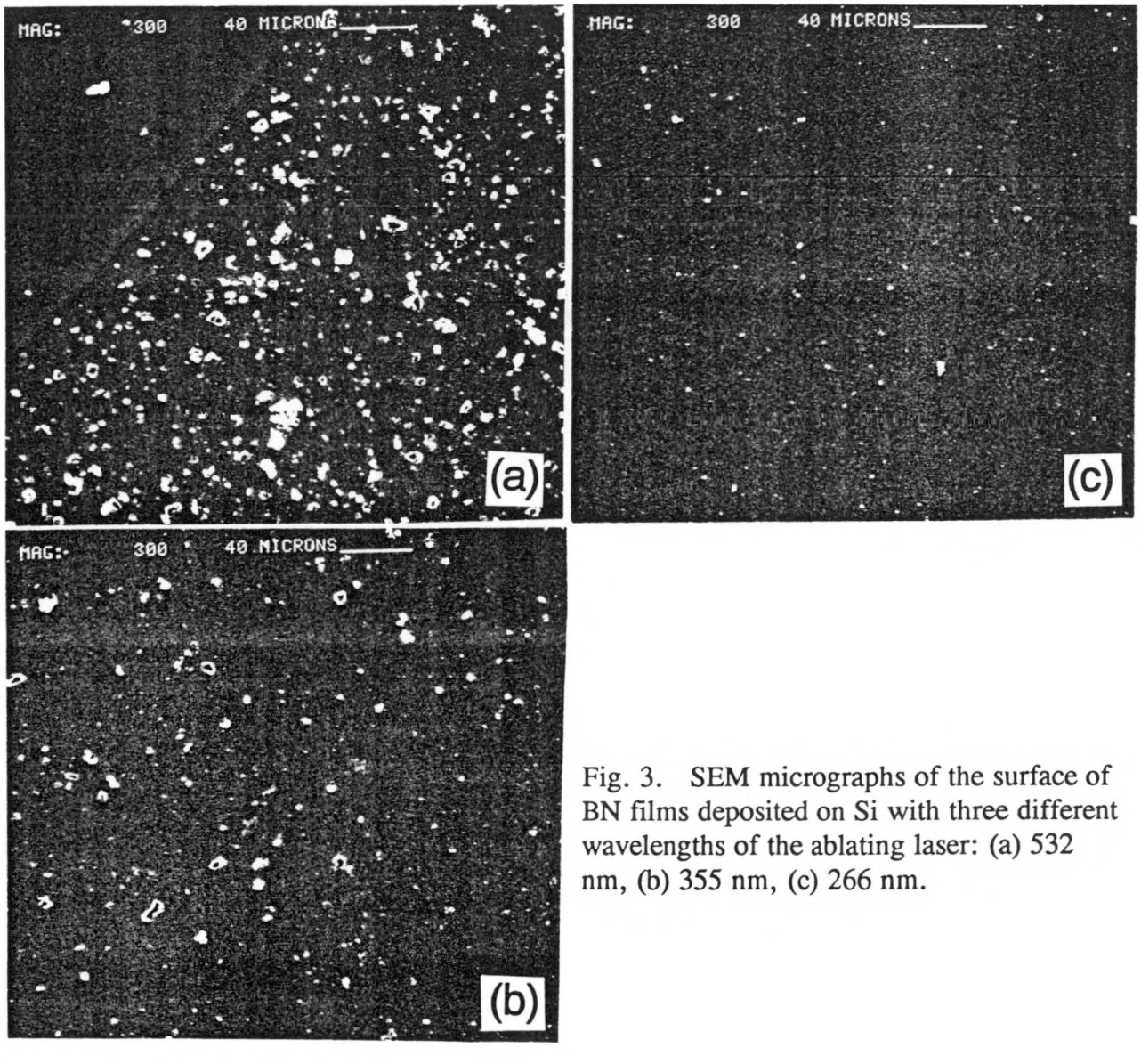

Fig. 3. SEM micrographs of the surface of BN films deposited on Si with three different wavelengths of the ablating laser: (a) 532 nm, (b) 355 nm, (c) 266 nm.

wavelengths. This increase in particle density with the wavelength of the ablating laser seems to be a common feature of PLD,[1] and this work confirms the phenomenon for BN films. The dependence can be attributed to the deeper penetration in the target by the longer wavelengths; the energy is spread over a deeper depth in the target, leading to more ejection of unvaporized material. Installation of the shutter wheel, as described above, will enable testing how many of the particles can be eliminated by mechanical means.

Transmission Electron Microscopy (TEM) was also performed on these layers, using a Phillips CM-20 at 200 keV. In this case a layer was deposited on a C-covered TEM grid, so that the layer could be inserted into the microscope without further sample preparation. A layer prepared with 355 nm light in vacuum showed only amorphous material, and featured nodules, or droplets, ranging down to a size of 5 nm.

SUMMARY

Pulsed Laser deposition has been used to deposit thin films of BN in a new UHV system built for doing controlled depositions with good characterization of both the laser plume and the sample. Although some advanced features of this system such as in-situ RHEED were not yet operational for these preliminary experiments, we were able to make the following observations: (1) particle density is proportional to laser wavelength, consistent with other materials, (2) all films were B-rich, and (3) only amorphous films were observed in these depositions at room temperature.

ACKNOWLEDGEMENTS

The help of J.C. Banks, J.C. Barbour, D.M. Follstaedt and T.M. Mayer has been essential in this project and is gratefully acknowledged. This work was performed at Sandia National Laboratories, supported by the U.S. Department of Energy under Contract # DE-AC04-76DP00789.

REFERENCES

[1] Laser Ablation for Materials Synthesis, edited by David C. Paine and John C. Bravman (Mater. Res. Soc. Proc. 191, Pittsburgh, PA 1990).

[2] G. Kessler, H.-D. Bauer, W. Pompe, and H.-J. Scheibe, Thin Solid Films, 147, L45 (1987).

[3] P.T. Murray, M.S. Donley, and N.T. McDevitt, in Processing and Characterization of Materials Using Ion Beams, edited by L.E. Rehn, J.E. Greene, and F.A. Smidt (Mater. Res. Soc. Proc. 128, Pittsburgh, PA 1989) pp. 469-474.

[4] G.L. Doll, J.A. Sell, C.A. Taylor II, and R. Clarke, Phys. Rev. 43, 6816 (1991).

[5] G.L. Doll, J.A. Sell, L. Salamanca-Riba, and A.K. Ballal, in ref. 1.

[6] G.L. Doll, T.A. Perry, J.A. Sell, C.A. Taylor, and R. Clarke, in Wide Band-Gap Semiconductors, edited by T.D. Moustakas, J.I. Pankove, and Y. Hamakawa (Mater. Res. Soc. Proc. 242, Pittsburgh, PA 1992) in press.

[7] T.A. Friedmann, K.F. McCarty, E.J. Klaus, D. Boehme, W.M. Clift, H.A. Johnsen, M.J. Mills, D.K. Ottesen, and R.H. Stulen, in Wide Band-Gap Semiconductors, edited by T.D. Moustakas, J.I. Pankove, and Y. Hamakawa (Mater. Res. Soc. Proc. 242, Pittsburgh, PA 1992) in press.