Peter Dowben Publications   Research Papers in Physics and Astronomy

May 1992

DEMONSTRATING THE UTILITY OF BORON BASED PRECURSOR MOLECULES FOR SELECTIVE AREA DEPOSITION IN A SCANNING TUNNELING MICROSCOPE

F. Keith Perkins
University of Wisconsin, Madison

M. Onellion
University of Wisconsin, Madison

Sunwoo Lee
Syracuse University

Peter A. Dowben
University of Nebraska-Lincoln, pdowben@unl.edu

DEMONSTRATING THE UTILITY OF BORON BASED PRECURSOR MOLECULES FOR SELECTIVE AREA
DEPOSITION IN A SCANNING TUNNELLING MICROSCOPE

F. KEITH PERKINS*, M. ONELLION*+, SUNWOO LEE**, AND P.A. DOWBEN**
*The Department of Physics and the Materials Science Program,
University of Wisconsin, Madison, Wisconsin 53706
**The Department of Physics, Syracuse University, Syracuse, New York 13244

ABSTRACT

    The scanning tunnelling microscope (STM) can be used to selectively deposit
material from a gaseous precursor compound. Ultrasmall (less than a 100 nm
across) spatial dimensions for selective area deposition may be achieved by this
means. In this paper we outline a scheme forselecting and designing main group
cluster compounds and organometallics for this type of selective area deposition
using nido-decaborane(14) as an example.

INTRODUCTION

    While the selective area processing of very small regions of a surface has
attracted considerable attention [1-3], the selective area deposition of pure
compositionally controlled films using an STM has not been particularly
successful. Selective area processing of high quality films requires having a
decomposition route for the source complex that is compatible with the incident
radiation (electrons, photons or ions) [1]. The pioneering work employing an STM
for selective area processing [4,5] has used organometallics better suited for
thin film chemical vapor deposition (CVD) by pyrolysis or monochromatic U.V.
photolysis.
    Any source compound suitable for deposition using an STM must have certain
characteristics. The source compound must adsorb and desorb molecularly without
fragmentation, on the substrate of choice. The adsorption should occur with
appreciable surface lifetimes at room temperature, since few scanning tunnelling
microscopes are equipped for sample cooling well below room temperature as it is
technically complex. The source compounds should have a large cross-section for
dissociation under electron impact at small electron kinetic energies. The
ligands, if any, must not decompose under electron impact and must remain highly
volatile. In fact the ligands must be more volatile than the source compound
itself, or ligand (resulting in impurity) incorporation into the growing film
will occur.
    Large borane cluster molecules have been suggested as possible source
compounds for the selective area deposition of boron [6-10] and boron carbide
[11]. **Boranes containing only boron, carbon or phosphorus, and hydrogen can be**
suitable source compounds for the deposition of boron based films in an STM.
Such cluster molecules can be designed and synthesized so that hydrogen is the
only possible impurity in a boron, boron carbide or boron phosphide film. Due
to its volatility, little, if any, hydrogen incorporation will occur in the
growth conditions employed in an STM [6,7]. Small boranes, such as diborane(6),
are unfortunately not suitable for deposition in most scanning tunnelling
microscopes since these molecules will not adsorb on surfaces such as Si(111) at
room temperature. Nido-decaborane(14), a much larger borane, is however very
suitable for STM processing. Using decaborane as an example, we demonstrate why
such boron based cluster molecules are efficacious source compounds for selective
area deposition, fulfilling the criteria outlined above.

ELECTRON INDUCED DISSOCIATION OF DECABORANE

    Borane cluster molecules, such as nido-decaborane(14), adopt a cage-like
polyhedral rather than linear molecular structure as seen in Figure 1. The
electronic structure of these molecules, schematically shown in Figure 1, is
characteristic of the extensive delocalization of the bonding electrons.
Modified neglect of differential overlap (MNDO) molecular orbital calculations
[13] suggest [14] that the interaction of nido-decaborane(14) with low energy
electrons should be quite high, consistent with the known chemistry of these
species [15].

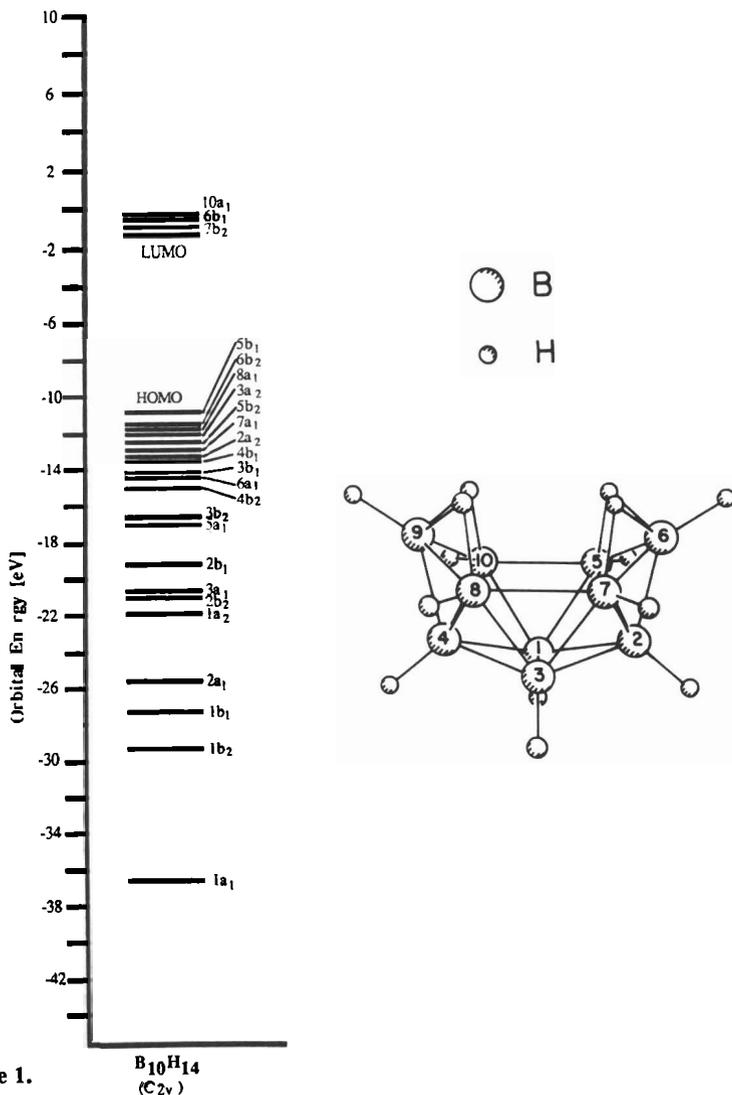+) Author to whom correspondence should be addressed

Figure 1.

$B_{10}H_{14}$
(C_{2v})

MNDO calculation results. Molecular orbitals, labeled according to their group character, are shown on the left; on the right is the computer generated structure, which agrees quite well with published x-ray and electron diffraction data.

Preliminary electron energy loss spectra of gaseous nido-decaborane(14) (as seen in Figure 2) are consistent with the MNDO model calculations [14] if an equivalent cores approximation to the excited state is used. Such EELS data show

that the gap between the highest occupied molecular orbital (HOMO) and the lowest
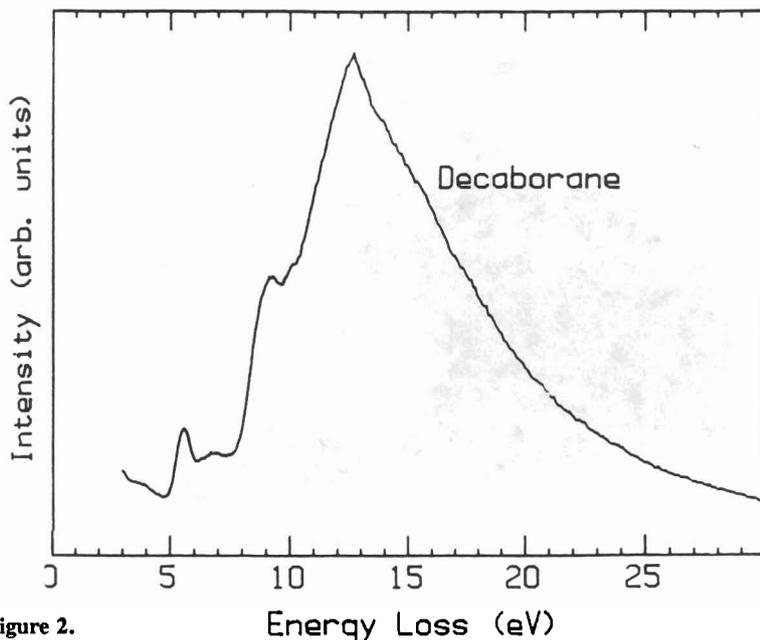

Figure 2. EELS spectrum. Agrees quite well with calculated spectra in previous figure; the apparent discrepancy from the 5 eV feature is resolved by consideration of the LUMO state of the excited atom. This has been confirmed through comparison of the MNDO results for an equivalent core atom transformation of the molecule, to $CB_9H_{14}^+$.

unoccupied molecular orbital (LUMO) is about 5 eV. There is also a very large cross-section for the continuum electron excitations possible at electron energies greater than about 10 eV. Using an STM to generate electrons with kinetic energies above 10 eV should result in the dissociation of nido-decaborane with great efficiency.

DEMONSTRATION OF SELECTIVE AREA PROCESSING

In order to demonstrate that nido-decaborane could be used as a suitable source compound for selective area processing, studies of decomposition on a substrate induced by synchrotron radiation were undertaken [7,8]. The emission spectrum from the Aladdin storage ring (where these experiments were carried out) contains significant power in the soft x-ray region, and indeed fully half the power in our experiments is from photons with energy greater than 545 eV [16]. When this spectrum is convolved with the interaction cross-section of the relevant molecules and secondary electron emission from the substrate is considered, it becomes clear [7,11] that the most important interaction is between the secondary electrons emitted by the substrate and the adsorbed borane molecules. Such experiments thus constitute a preliminary test of the suitability of decaborane for deposition in an STM.

After a sputter and anneal preparation of a Si(111) 7x7 surface in an ultra high vacuum system (base pressure 2x10-10 torr), the experimental chamber was filled to a working pressure of decaborane (more than 10-8 torr) and exposed to incident radiation. We have established a pressure limited growth rate of 0.3 Angstroms per 10-6 torr-seconds [7]. Contamination, was, as expected, minimal [7]. An example of the selective area processing possible by this technique is

shown in Figure 3. This selective area processing was achieved by using a close contact mask to block incident radiation in the grid-like array.
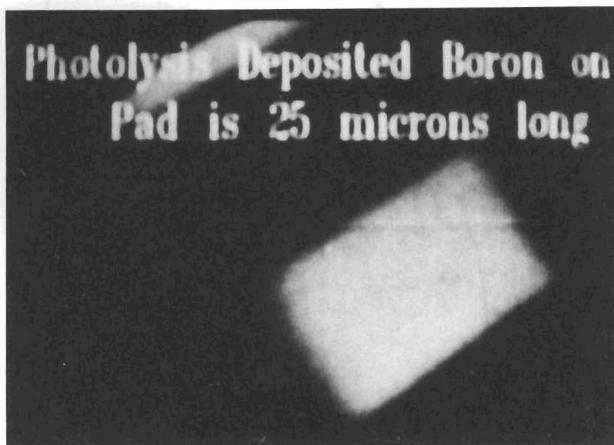

Figure 3.

X-ray micrograph. This pattern was formed by exposure of a silicon wafer masked by a 500 l.p.i. TEM grid. The image was taken with an X-ray photo-electron microscope, where the probe was 192 eV photons, which are strongly absorbed by the boron. The image was formed from the photoelectrons.

Ultimately our methodology for choosing suitable source compounds for the STM must be tested in an STM. In Figure 4 we show a selectively deposited feature of boron generated using nido-decaborane in an STM. The substrate in this experiment was hydrogen passivated Si(111) in the 1x1 surface structure [17]. A jet of gas was directed toward the substrate – STM tip area and the overall pressure in the chamber rose to 3x10-8 torr. The feed back loop for STM imaging was disconnected during deposition and the tip was pulsed for 10 seconds at 7 kHz from −2 eV to −13 eV bias relative to the sample. Following deposition, the gas dosing was stopped and the chamber was allowed to recover. A feature approximately 80 nm across by 6 nm high is observed to have developed in the center of an image 200 nm across. Clearly decomposition of decaborane through the direct application of low energy electrons generated by an STM is indeed possible. Since a 13 eV bias was applied, the electrons are well above the continuum excitation edge observed in the gas phase EELS (Figure 2).

CONCLUSION

We argue that low energy single step selective area deposition of clean films is possible. Central to this scheme is the choice of appropriate precursor molecules. The results provided by the STM are completely consistent with the gas phase studies and model calculations undertaken to date.
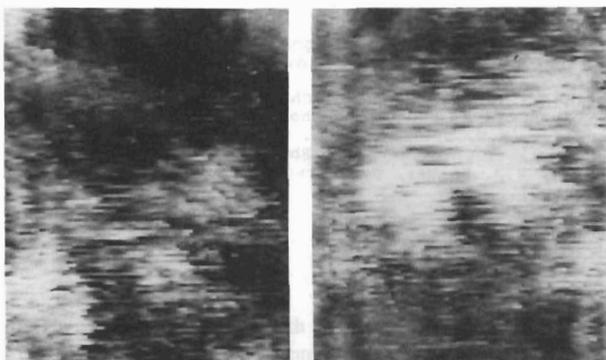
ACKNOWLEDGEMENTS

Figure 4.

STM micrograph. The two images shown were formed of the same area before (left)
and after (right) -13 V pulses on a tungsten tip (see text), in an ambient of
decaborane greater than 3×10^{-8} torr. The scale is 160 nm by 200 nm, and the
gray scale range is 9.5 nm on the left, and 11.5 nm on the right. In both
images, the tip bias was -1V and the demand current was 100 pA. The evidence of
surface modification was not present after pulsing the tip in the absence of
decaborane.

[1] P.A. Dowben, J.T. Spencer, and G.T. Stauf, Mat. Sci. Engin. B2, 297 (1989).
[2] C.D. Christensen and V.M. Latkin, Appl. Phys. Lett. 32, 254 (1978); R.M.
Osgood, Ann. Rev. Phys. Chem. 34, 77 (1983); T.J. Chuang, Surf. Sci. Repts. 3,
1 (1983); D.J. Ehrlich and J.Y. Tsao, J. Vac. Sci. Technol. B1, 969 (1983).
[3] Laser Chemical Processing for Microelectronics, edited by K.G. Ibbs and R.M.
Osgood, Cambridge Studies in Modern Optics vol. 7, (Cambridge University Press,
Cambridge, 1989); Laser and Particle Beam Chemical Processing for Micro-electron-
ics, edited by D.J. Ehrlich, G.S. Higashi, and R.M. Osgood (Mater. Res. Soc.
Proc. 101, Pittsburgh, PA 1988).
[4] R.M. Silver, E.E. Ehrichs, and A.L. deLozanne, Appl. Phys. Lett. 51, 247
(1987); E.E. Ehrichs, R.M. Silver, and A.L. deLozanne, J. Vac. Sci. Technol. A6,
540 (1988); E.E. Ehrichs, S. Yoon, and A.L. deLozanne, Appl. Phys. Lett. 53, 2287
(1988).
[5] M.A. McCord and R.F.W. Pease, J. Vac. Sci. Technol. B4, 86 (1986); J. Vac.
Sci. Technol. B5, 430 (1987); J. Vac. Sci. Technol. B6, 293 (1988).
[6] Yoon-Gi Kim, P.A. Dowben and J.T. Spencer, J. Vac. Sci. Technol. A7, 2796
(1989).
[7] F. Keith Perkins, R.A. Rosenberg, Sunwoo Lee and P.A. Dowben, J. Appl. Phys.
69, 4103 (1991).
[8] R.A. Rosenberg, F.K. Perkins, D.C. Mancini, G.R. Harp, B.P. Tonner, S. Lee
and P.A. Dowben, Appl. Phys. Lett. 58, 607 (1991).
[9] Ph. Avouris, J. Phys. Chem. 94, 2246 (1990).
[10] Ph. Avouris, In-Whan Lyo, F. Bozso, and E. Kaxiras, J. Vac. Sci. Technol.,
A8, 3405 (1990).
[11] F. Keith Perkins, M. Onellion, S. Lee, D. Li, J. Mazurowski and P.A. Dowben,
submitted.
[12] D.S. Kendall and W.N. Lipscomb, Inorg. Chem. 12, 546 (1973); L.J.
Gugenberger, J. Amer. Chem. Soc. 94, 114 (1972); A. Tippe and W.C. Hamilton,
Inorg. Chem. 8, 464 (1969).

[13] M.J.S. Dewar, M.L. McKee, J. Am. Chem. Soc. 99, 4899 (1977); M.J.S. Dewar, M.L. McKee, H.S. Rzepa, J. Am. Chem. Soc. 100, 3607 (1978); M.J.S. Dewar, J. Friedheim, G. Grady, E.H. Healy, J.J.P. Stewart, Organometallics 5, 385 (1986). M.J.S. Dewar, H.S. Rzepa, J. Comp. Chem. 4, 158 (1983); J.J.P. Stewart, F.J. Seiler, Quantum Chem. Program Exch., Prgm. no. 549.
[14] A.P. Hitchcock, A.T.Wen, S. Lee, J.A. Glass, J.T. Spencer and P.A. Dowben, in preparation
[15] N.S. Hosmane, R.N. Grimes, Inorg. Chem. 18, 3294 (1979); R.B. Maynard, L. Borodinsky, and R.N. Grimes, Inorg. Synthesis 22, 211 (1983); M.E. Fessler, J.T. Spencer, J.F. Lomax, R.N. Grimes, Inorg. Chem. 27, 3069 (1988).
[16] E.M. Rowe, Nucl. Intrum. Meth. in Phys. Res. B56/57, 392 (1991).
[17] G.S. Higashi, Y.J. Chabal, G.W. Trucks, and K. Raghavachari, Appl. Phys. Lett. 56, 656 (1990).