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The In Situ Observation of Epitaxial Diamond Thin Film Nucleation and Growth Using Emission Electron Microscopy

Submitted by

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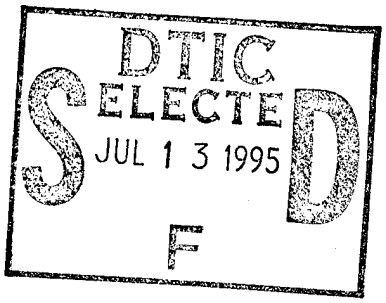

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13. ABSTRACT *(Maximum 200 words)*

Progress on the in situ observation of diamond heteroepitaxy is given, as are plans for experiments to be completed at national and foreign installations (SRC and BESSEY). A list of publications, presentations and theses/degrees awarded is also included.

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CONTENTS

1.0 Summary of Progress

1.1 Electron Emission from CVD Diamond

The hydrogenation of CVD diamond films and the removal of hydrogen from diamond surfaces through heating or action of a strong electric field is an important question for electron emission. The negative electron affinity of the (111) and (100) faces is known to depend critically on the hydrogenation of the surface.

An atomic hydrogen doser using a design described by Bischler and Bertel in J.Vac.Sci.Technol. A11 (1993)458 has been constructed and tested. We will investigate the emission from CVD diamond films both during and after exposure to atomic H, to measure the effect of H termination on the intercept of the I-V curves during field emission. The reversibility of this process will be examined.

In addition, we will test the feasibility of reducing the secondary electron yield of the diamond surface through variations in the surface termination, in order to facilitate LEEM of the diamond surface.

1.2 Synchrotron Radiation Studies of Diamond

The investigation of the negative electron affinity "spike" in the secondary yield curves in photoemission was reported in a paper published in J.Vac.Sci.Technol. by Shovlin et al. (see list below). In that work, a survey of diamond materials was studied without surface treatment. The analysis of the past year's measurements has indicated that heating the specimen will be essential for useful data. We have three weeks of beamtime in December 1995 to examine micro-VUV spectra of CVD and natural diamond. In this experiment, a manipulator with heating capabilities will be used. Because the beamline window will be closed during measurement, the H doser built for the LEEM will be used.

Beam time on the Berlin Synchrotron for measurements of diamond and AlN using the spectroscopic LEEM/PEEM of Prof. Bauer will be made August 20 - September 10, 1995.

1.3 LEEM

The LEEM images obtained to date are from Si(100) and Mo(100). The image intensity is poor, due to the poor brightness of "hairpin" tungsten filaments. A Lanthanum hexaboride cathode has also been used, but the total current available from the LAB6 cathode increases surface charging on the diamond surface.

A new scheme for dual illumination of charging surfaces with a threshold wavelength to provide conductivity and a second, higher photon energy for imaging, recently reported by Habliston et al. Biophysics Journal, in press) will be tried for diamond surfaces. The technique will also be important for AlN, because

the bandgap is even larger than diamond.

A proposal for the purchase of a commercial field emitter electron source is pending. A new chevron channel plate assembly was installed in early 1995 to increase sensitivity in the LEEM mode, but has not yet been tested in LEEM.

A diagram of the new gimbal manipulator is appended.

1.4 Molecular Beam Deposition:

Capital equipment to improve the flux and the analysis of the beam in the supersonic jet apparatus has been purchased, including fast ion gauge, pulsed beam valve and a Roots blower-mechanical pump combination to improve the first stage pumping efficiency.

2.0 Publications/Presentations

Papers Published:

1. "Photoelectron Emission Microscopy", M.E. Kordesch, CRC Handbook of Surface Imaging and Visualization, A.T. Hubbard, ed., Boca Raton, 1995. Book Chapter.

2. "Surface Reaction Diffusion Fronts Observed with Photoelectron Emission Microscopy During Carbon Deposition on Mo(310)", Adrian Garcia and Martin E. Kordesch, J. Vac. Sci. Technol., A13 (1995) 1396.

3. "Synchrotron Radiation Photoelectron Emission Microscopy of Chemical Vapor Deposited and Natural Diamond Surfaces" J.D. Shovlin, M.E. Kordesch, D. Dunham, B.P. Tonner and W. Engel, J. Vac. Sci. Technol., A13 (1995) 1111.

4. "Probing Reactive Deposition and Surface Dynamics using Real-time Emission Microscopy", Martin E. Kordesch, J.Vac. Sci. Technol., A13 (1995) 1517. Invited Review.

5. "Buckytube Cold Field Emitter Array Cathode Experiments" B.H. Fishbine, C.J. Miglionico, K.E. Hackett, K.J. Hendricks, X.K. Wang, R.P.H. Chang, J.D. Shovlin and M.E. Kordesch, Proc. Matl.Res. Soc. 359 (1995) 93-98.

In Press:

6. "Electron Emission from Natural and Chemical Vapor Deposited Diamond Observed with Emission Microscopy", J.Vac.Sci. Technol., Invited Review.

7. "In Situ Real Time Emission Microscopy Applied to Chemical Vapor Deposition of Diamond And Nitrides, Proc. Matl. Res. Soc., Invited Review.

8. "An Emission Microscopy Study of Chemical Vapor Deposited Aluminum Nitride Films", Proc. Matl. Res.Soc., Boston, 1995.

Presentations:

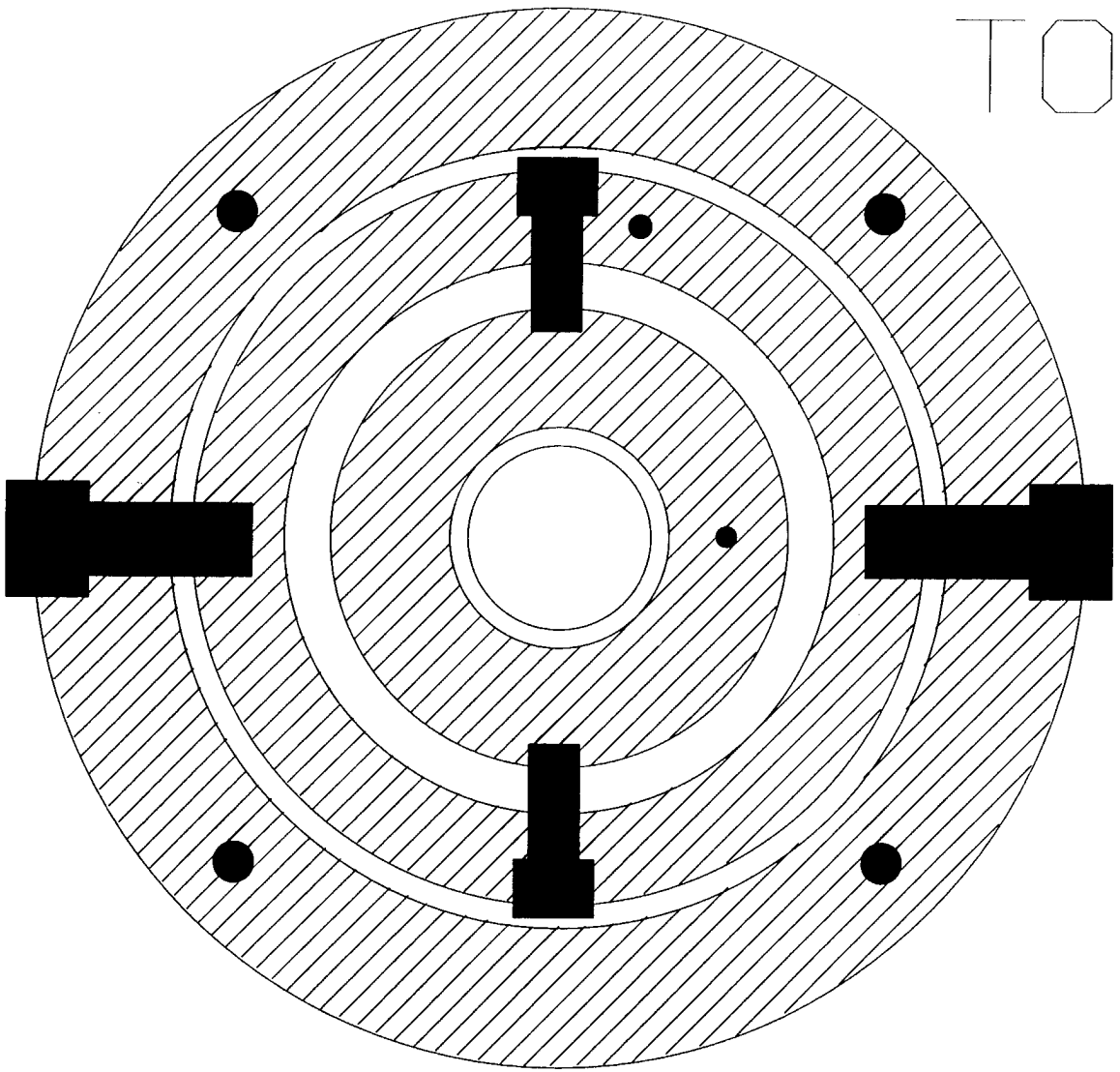
1994 "Supersonic Molecular Beam Growth of Diamond"
-Gordon Research Conference, Diamond Synthesis.
"Probing Reactive Deposition and Surface Dynamics Using Real Time In Situ Emission Microscopy"
- 41st National Symposium of the American Vacuum Society, Denver.

1995 "Emission Microscopy of Natural and CVD Diamond Field Emitters"
- 6th Diamond Technology Workshop, Detroit.
- 42nd National Symposium of the American Vacuum Society, Minneapolis.

"In Situ Photoelectron Emission Microscopy of Diamond and Nitride Surfaces"
- Materials Research Society Fall Symposium, Boston.
- Fritz Haber Institute d. MPG, Berlin.

"Photoelectron Emission Microscopy"
-Invited Instructor, 2nd Nicolas Cabrera Summer School, Madrid.

OU GIMBALS
TOP VIEW



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Inner Rings
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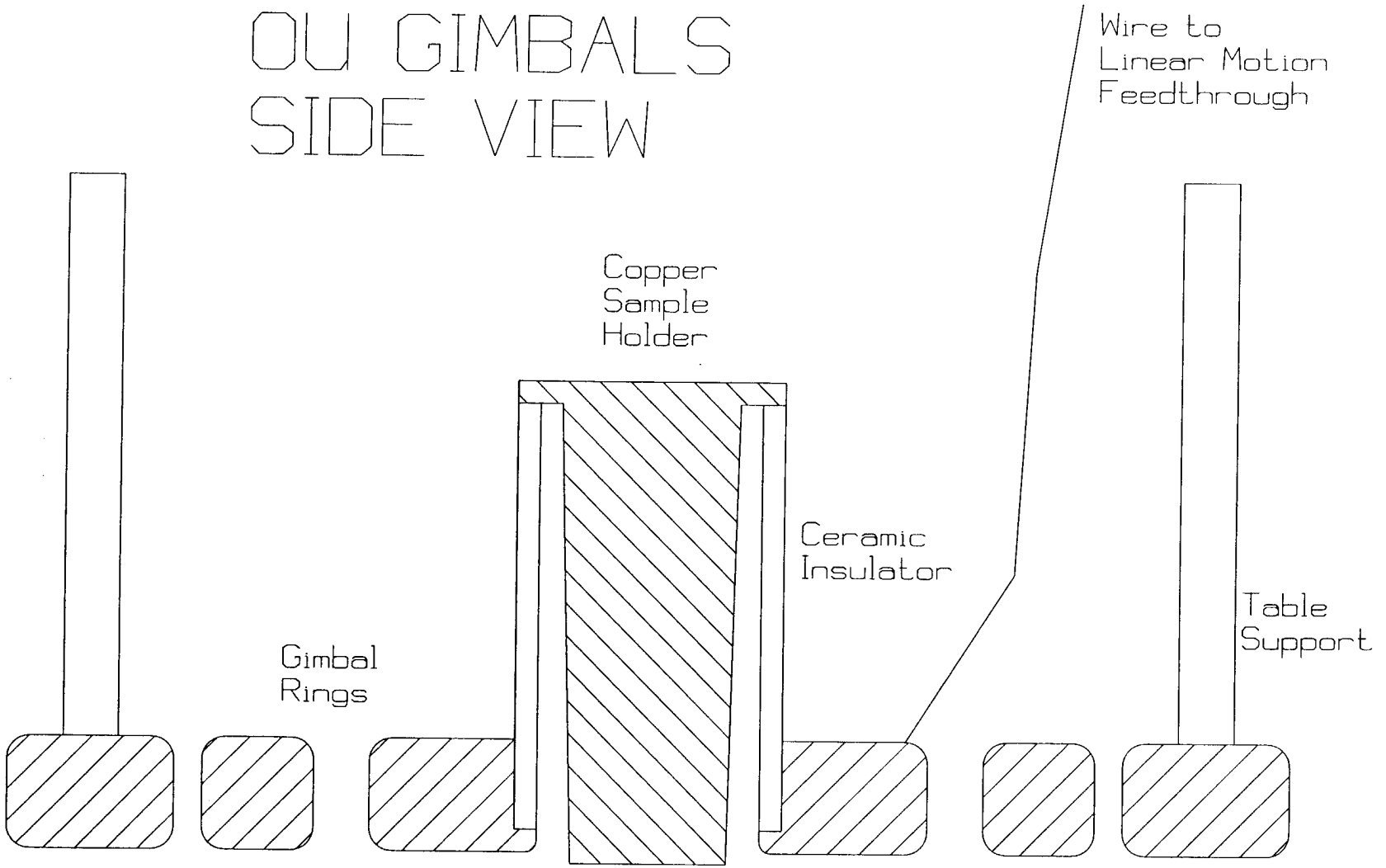
OU GIMBALS SIDE VIEW



TRANSMISSION ELECTRON MICROSCOPY OF MICRON-SIZED CHEMICAL VAPOR DEPOSITED DIAMOND

A Thesis
Presented to
The Honors Tutorial College
Ohio University

In partial fulfillment
of the Requirements for Graduation
from the Honors Tutorial College
with the degree of
Bachelor of Science in Physics

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by
Julie Ann Beegan

June 1995

Thermionic Emission Study of

Barium Activated Diamond

A Thesis

Presented to

The Honors Tutorial College

Ohio University

In Partial Fulfillment

Of the Requirements for Graduation

With Honors in Physics

---

by

Mark Edward Little

June 1995

♦ ♦ ♦ 6th Annual ♦ ♦ ♦
Diamond Technology Workshop

Emission Microscopy of Natural and CVD Diamond Field Emitters

Martin E. Kordesch
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Several different types of CVD diamond films are known to exhibit low-field cold electron emission (LFCE): polycrystalline, pollycrystalline (100) textured, free standing, Si and Mo backed, Hot filament-, Flame- and Microwave plasma-deposited, and doped films have been examined in an emission microscope with an applied field of 30 - 50 kV/cm. Images of a wide variety of CVD diamond substrates, graphite and natural diamond have been obtained that show the location and relative intensity of electron emission in the field emission, photoemission and secondary electron illumination modes.

The so-called negative electron affinity (nea) measured for the boron-doped IIb diamond (111) surface is often used to account for the low-field cold emission from CVD diamond. The nea mechanism for electron emission is examined in light of the variety of specimens for which this emission is observed. A method of diamond film activation that indicates dielectric breakdown of the diamond film is responsible for the "low-field" electron emission, and a simple model for "hot" electron emission are discussed.

Thermionic Emission from CVD diamond films treated with Ba-carbonate show an electron emission threshold reduction of 200 K. There was no observed increase in the low field cold emission characteristics. The preliminary indication from these measurements is that reduction in the emission barrier on a known LFC-emitter does not increase the field emission current, or decrease the minimum field for cold emission. Therefore barrier height is secondary to conduction/doping, and LFCE are not simply nea emitters. In the Ba activated emitters, as with the other LFCE emitters, no preferential emission at sharp geometric features was observed.

In order to further investigate the role of negative electron affinity effects in a variety of natural and chemical vapor deposited diamond emitters, these surfaces have also been imaged using a photoelectron emission microscope and synchrotron radiation where the incident light is scanned over the 4-18 eV and 250-350 eV range. Both images and spatially resolved total electron yield curves were acquired simultaneously. Near-edge spectra at the carbon 1s edge show a resonance due to graphite; the image intensity varies uniformly in proportion to the C 1s edge intensity. In the 4-18 eV range, no sharp features related to a photoemission threshold were observed below 7 eV in the electron yield curves on any of the specimens. These photoelectron emission measurements will also be discussed relative to nea surfaces and electron emission.

The assistance of J. Shovlin and M. Little with several measurements, and the support of NATO and the Office of Naval Research/ Ballistic Missile Defense Organization Office of Innovative Science and Technology through Grant N00014-J-91-1596 is gratefully acknowledged.

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MINNEAPOLIS

Electron Emission from Natural and Chemical Vapor Deposited Diamond Observed with Emission Microscopy

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Several different types of Chemical Vapor Deposited (CVD) diamond films are known to exhibit low-field cold electron emission: polycrystalline, pollycrystalline (100) textured, free standing, Si and Mo backed, Hot filament-, Flame- and Microwave plasma-deposited, and doped films have been examined in an emission microscope with an applied field of 30 - 50 kV/cm. The location and relative intensity of electron emission sites have been observed on these specimens in the field emission, photoelectron, and secondary electron emission microscope imaging modes.

A thin film of gold deposited on the CVD diamond film surface can (reversibly) induce electron emission in otherwise non-emissive films by increasing the magnitude of the applied electric field at the diamond surface. Barium coated CVD diamond has been examined in thermionic and cold field emission. The experimental manipulations of the surface barrier height will be related to models for electron emission from diamond involving dielectric breakdown and ballistic ("hot") electron emission.

1995 Fall Meeting of the MRS
Submitted to Symposium J
Symposium Title: In Situ Electron and Tunneling Microscopy of Dynamic Processes

IN SITU, REAL-TIME EMISSION MICROSCOPY APPLIED TO CHEMICAL VAPOR DEPOSITION OF DIAMOND AND NITRIDES

Martin E. Kordesch, Ohio University, Athens, OH.

Emission microscopy images are direct maps of the surface electron yield under illumination by various sources, including light ranging from the UV to soft x-rays, low energy electrons, ions, energetic neutral atoms, and thermionic and field emission. Contrast in the image is a combination of sample topography, surface electron yield, and microscope characteristics.

In situ ultraviolet and soft x-ray photoelectron emission microscopy images of surface processes during chemical vapor deposition of diamond and nitride semiconductors will be presented that illustrate the nucleation of adsorbed layers, reaction-diffusion fronts, reactive conversion of deposited layers, adsorbate controlled diffusion from the bulk, pattern formation, melting and the evolution of topographical features during etching.

Work supported by NATO and the ONR-BMDO.

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1995 Fall Meeting of the MRS
Submitted to Symposium AAA: Gallium Nitride and Related Materials

AN EMISSION MICROSCOPY STUDY OF CHEMICAL VAPOR DEPOSITED ALUMINUM NITRIDE FILMS, J.D. Shovlin, M.E. Kordesch, Department of Physics, Ohio University, Athens, OH; A.H. Khan and T. Stacy, Electrical and Computer Engineering, University of Missouri, Columbia, MO.

Aluminum nitride thin films on silicon substrates were observed in the emission microscope in the photoelectron, field, and thermionic emission modes. The effects of atomic H, H_2, and O_2 adsorption, and gold coating (15nm) upon the emission properties of the AlN film were investigated.

Faint photoemission images are obtained using mercury arc lamp illumination, indicating a bandgap over 5.2 eV. Under the microscope's maximum applied field of ~95 kV/cm, weak field emission was observed from the gold coated sample. Characterization of the films, ex situ, indicates that fields over 5x those used in the emission microscope may be necessary for substantial field induced electron emission. Methods for improved electron injection into the AlN layer to enhance field emission will be discussed.

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