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13. ABSTRACT (Maximum 200 words)

We have developed new approaches to synthesize superhard/ultrastrong thin films and coatings by chemical vapor deposition (CVD) of unimolecular precursors, and to monitor and characterize the film-growth process in situ and in real time. To this end, we have designed and constructed an ultrahigh vacuum CVD chamber fitted with energy-dispersive x-ray reflectivity (XRR) and multiple-beam optical stress sensor (MOSS) for in situ monitoring of surface morphology and stress evolution of the films under growth. Both of these techniques were applied to the CVD growth of boron and GaN films. We have synthesized novel precursors of C3N3P, Si4CN4, LiBC4N4, BC3N3, BeC2N2, MgC2N2 for CVD growth of films with properties of superhardness. We have also deposited thin films by CVD with the composition of Zr-B-Si-N via reactions of Zr(BH4)4 with SiH4, and Zr(BH4)4 with N(SiH3)4. The elastic constants c11 and c44 of these films measured by Brillouin scattering in collaboration with Prof. Sooryakumar of Ohio State University produced results suggesting that films and coatings based on the Zr-B-Si-N system exhibit promising superhard properties.

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Principal investigators: I.S.T. Tsong, J. Kouvetakis, and E. Chason.

1. Publications List

1. "Synthesis of molecular precursors to carbon-nitrogen-phosphorus polymeric systems", J. Kouvetakis, J. McMurran and J.L. Hubbard, Chem. Mater. **10**, 590-593 (1998)
2. "Strategies for the synthesis of highly concentrated $Si_{1-y}C_y$ diamond structured systems", D. Chandrasekhar, J. McMurran, J. Kouvetakis and D.J. Smith, Appl. Phys. Lett. **72**, 2117-2119 (1998)
3. "Novel methods of CVD of heteroepitaxial Ge_4C and $(Ge_4C)_xSi_y$ tetrahedral heterostructures: Synthetic pathways and molecular structures of trigermyl-$HC(GeH_3)_3$ and tetragermyl-$C(GeH_3)_4$ methanes", J. Kouvetakis, A. Haaland, D.J. Shorokhov, H.V. Volden, G.V. Girichev, V.I. Sokolov and P. Matsunaga, J. Am. Chem. Soc. **120**, 6738-6744 (1998)
4. "Synthesis and atomic and electronic structure of new Si-Ge-C alloys and compounds" (Invited review in "Frontiers in Solid State Inorganic Chemistry"), J. Kouvetakis, D.C. Nesting and D.J. Smith, Chem. Mater. **10**, 2935-2949 (1998)
5. "H_2GaN_3 and derivatives: a facile method to gallium nitride", J. McMurran, J. Kouvetakis, C. Steffek, B. Balasubramanian and J. Hubbard, Inorg. Chem. **7**, 6638-6648 (1998)
6. "Real-time monitoring of structure and stress evolution of boron films grown on Si(100) by UHV-CVD", D.C. Nesting, J. Kouvetakis, S. Hearne, E. Chason and I.S.T. Tsong, J. Vac. Sci. Technol. A **17**, 891-894 (1999)
7. "Stress evolution during metalorganic chemical vapor deposition of GaN", S. Hearne, E. Chason, J. Han, J.A. Floro, J. Figiel, J. Hunter, H. Amano and I.S.T. Tsong, Appl. Phys. Lett. **74**, 356-358 (1999)
8. "Development of low-temeprature GaN chemical vapor deposition process based on a single molecular source H_2GaN_3", J. McMurran, J. Kouvetakis and D.J. Smith, Appl. Phys. Lett. **74**, 883-885 (1999)
9. "Brittle-ductile relaxation kinetics of strained AlGaN/GaN heterostructures", S.J. Hearne, J. Han, S. Lee, J.A. Floro, D. Follstaedt, E. Chason and I.S.T. Tsong, Appl. Phys. Lett. **76**, 1534-1536 (2000)
10. "Surface preparation of SiC and Al_2O_3 substrates for MBE and MOCVD deposition of AlN, GaN and InAlGaN alloys", V.M. Torres and J. Kouvetakis, Handbook of Thin Film Process Technology, IOP Publishing, G91-G94 (2000).

11. "Synthetic routes of $LiBC_4N_4$, BC_3N_3 and related C-N compounds of boron. New precursors to light element ceramics", D. Williams, B. Pleune, J. Kouvetakis and R.A. Andersen, J. Am. Chem. Soc. **122**, 7735-7741 (2000).

12. "Synthesis and structures of heterocyclic azidogallanes $[(CH_3)ClGaN_3]_4$ and $[(CH_3)BrGaN_3]_3$ en route to $(CH_3)HGaN_3$: an inorganic precursor to GaN", J. Kouvetakis, J. McMurran, C. Steffek, T.L. Groy and J.L. Hubbard, Inorg. Chem. **39**, 3805-3809 (2000).

13. "Synthesis of new azidoallanes with heterocyclic molecular structures", J. Kouvetakis, C. Steffek, J. McMurran and J. Hubbard, Main Group Met. Chem. (in press).

14. "Synthesis and structural properties of stoichiometric framework C-N compounds of Be, Mg, Al, and Tl", D. Williams, B. Pleune and J. Kouvetakis, J. Solid State Chem. (submitted).

15. "Elastic properties of nano-crystalline zirconium-silicon-boron thin films", M. Chirita. H. Xia, R. Sooryakumar, J. Tolle, V.M. Torres, J. Kouvetakis, B.J. Wilkens and I.S.T. Tsong, J. Appl. Phys. (in press).

2. Patent

"Novel compositions of matter and methods of depositing pure thin films of gallium nitride semiconductor". Inventors: J. Kouvetakis and J. McMurran. US Non-Provisional Patent file number A32380-072448.0237, 10 May 1999.

3. Statement of the Problem

The primary objectives of our research are to develop radically new approaches to (a) synthesize superhard and ultrastrong thin films and coatings by chemical vapor deposition (CVD) of unimolecular precursors, and (b) monitor and characterize the thin-film growth process *in situ* and in real time by the new techniques of x-ray reflectivity (XRR) and multi-beam optical stress sensor (MOSS). The deposited films are also analyzed by various *ex situ* techniques for hardness, chemical composition and bonding, atomic structure, and surface morphology.

4. Summary of the Most Important Results

(a) XRR-MOSS-CVD

The energy-dispersive XRR technique was originally developed by Eric Chason of Sandia National Laboratories to conduct *in situ* studies of morphological evolution during thin-film growth. In the first twelve months of this project, we set out to design and construct an XRR system to monitor *in situ* and in real time the film thickness, the surface roughness and the interface roughness during the growth of superhard films by CVD. To this end, we purchased a Philips X'pert x-ray diffractometer model PW3020/10 with a vertical θ-θ goniometer and modified it to accommodate an ultrahigh vacuum (UHV) CVD chamber in place of its normal sample stage. The completed system is shown in Fig. 1. The special features of the XRR system include an Ag anode which produces broad-band bremsstrahlung and a Kevex PSI model 2005-212 Peltier-cooled Li-drifted energy-dispersive x-ray detector.

The MOSS system was purchase from k-space Associates to conduct *in situ* real-time measurements of surface stress of a thin film during growth. The technique of MOSS was also developed by Sandia National Laboratories by Floro and Chason. Essentially, a beam from a laser diode is split into multiple beams by an etalon. These beams are then directed onto a substrate surface on which film growth takes place. The reflected beams are monitored by a position-sensitive CCD detector. A change in the curvature of the film/substrate wafer due to surface stress would cause a change in the spacing between the reflected beams. The curvature is directly proportional to the product of film stress and film thickness. If a plot of (stress x thickness) is made as a function of film thickness, the slope at any point of the curve gives the instantaneous effective film stress. The MOSS set-up was incorporated into the XRR-CVD system as shown in Fig. 1.

Upon the completion of the XRR-MOSS-CVD system, we spent several months in alignment, fine-tuning and trouble-shooting to render it fully operational. The system was thoroughly tested by conducting real-time monitoring the morphology and stress evolution of born films deposited using diborane (B_2H_6) diluted in hydrogen on Si(100) substrates. This successful test was reported in detail in paper #6 in the publications list of Section 1. The system is now being used routinely to conduct *in situ* real-time measurements during film deposition.

(b) Synthesis of C_3N_3P and C_3N_3PO

A material of composition C_3N_3P is of immediate interest because the synthetic pathway, structure, composition and physical properties are expected to be similar to C_3N_4. Furthermore, P may promote 3-dimensionality in the material structure because of the propensity to form PN_4 tetrahedra. We prepared new volatile single-source precursors with composition $(SiMe_3)_2PC_3N_3F_2$ and $(SiMe_3)_2PC_3N_3Cl_2$. (Me = CH_3). These compounds are readily obtained in very high yields by reactions of C_3N_3X (X = Cl, F) and $P(SiMe_3)_3$ as volatile crystalline solids. Their identity was determined by single crystal x-ray diffraction and Fig. 2 demonstrates the molecular structure for the fluoride species. As illustrated in the figure, these molecules incorporate the stoichiometry of the desired product, C_3N_3P, which is obtained by thermal decomposition of the precursor at temperature as low as 300°C via elimination of the extremely stable $SiMe_3F$ and $SiMe_3Cl$ byproducts.

$$(SiMe_3)_2PC_3N_3F_2 \rightarrow C_3N_3P + 2SiMe_3F$$

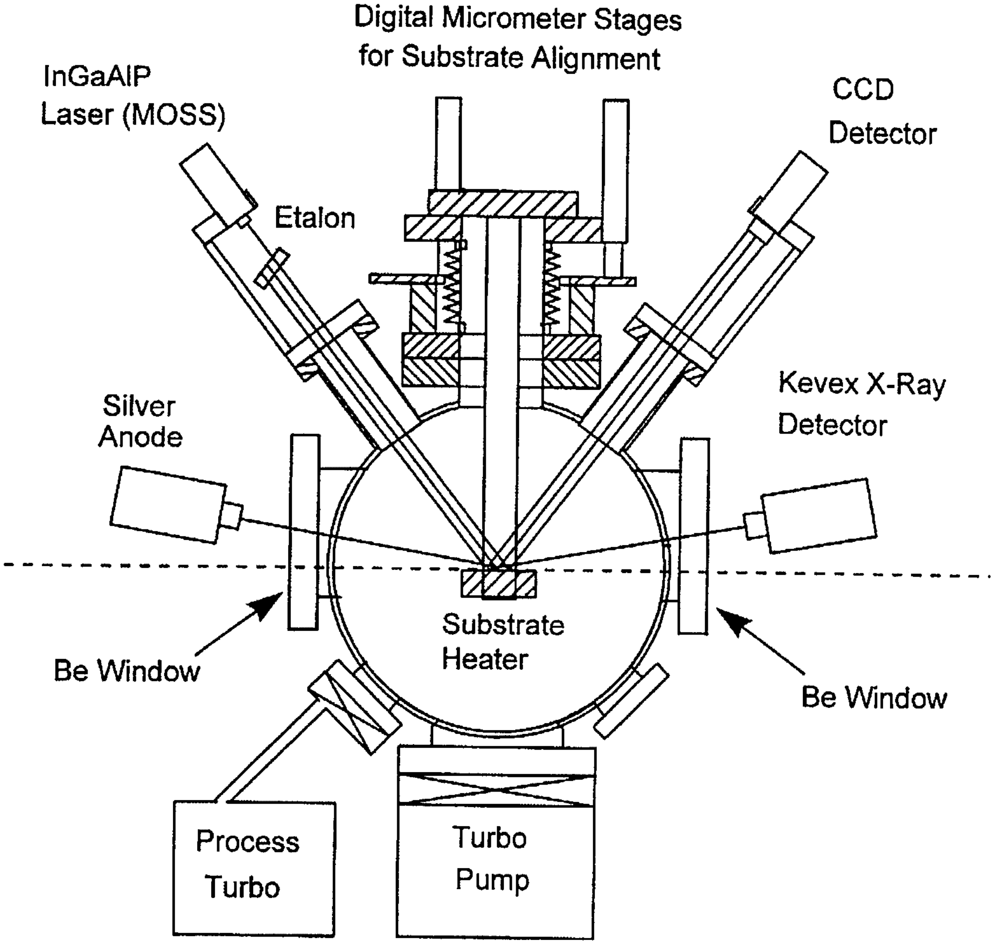

Fig. 1 Schematic Diagram of the XRR/MOSS/UHV-CVD experimental setup.

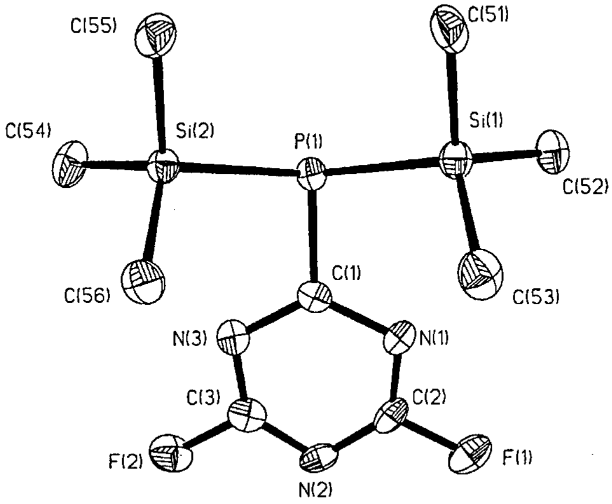

Fig. 2 Single crystal molecular structure of $(SiMe_3)_2PC_3N_3F_2$ and corresponding thermal decomposition scheme to produce C_3N_3P.

An interesting composition, C_3N_3PO, was obtained when these compounds were synthesized in the presence of oxygen. The composition of this system was primarily determined by Rutherford backscattering spectrometry (RBS). Combustion elemental analyses for C, H, N, and P of the same film were within 5% of the RBS results. We are particularly interested in this phase because the oxygen may promote and stabilize a possible 3-D grid structure involving PN_3O tetrahedra. Details of our results are given in paper #1 under Section 1 publications list.

(c) New silicon nitrides incorporating Si_4C building blocks

Our goal was to synthesize superhard films based on the structures that incorporate Si_4C tetrahedra joined together by three-fold coordinated nitrogen atoms. We found that our molecular source for Si_4C units, $(SiH_3)_4C$, reacts readily with ammonia in the UHV-CVD system at 600°C to deposit Si-C-N films with compositions Si_4CN_4 according to a procedure summarized below:

$$C(SiH_3)_4 + 4NH_3 \rightarrow Si_4CN_4 + 12H_2$$

We used RBS, including C and O resonance nuclear reactions and He forward scattering, to determine the Si, N, O, C, and impurity H contents of the films. To confirm the absence of any significant amount of H and to examine the lattice vibrational modes of the material, films were deposited on polished Si and transmission infrared spectra were recorded. No absorption in the 3200-3500 cm^{-1} or 2100-1900 cm^{-1} region were discernible, indicating very little or no N-H or Si-H bond formation. The spectra showed only a broad band at 830 cm^{-1}, presumably due to Si-C-N stretching modes since similar bands for the Si-C modes in SiC and Si-N modes in Si_3N_4 phases were observed at 800 cm^{-1} and 900 cm^{-1} respectively. Our results thus far indicate that the material might be a solution between SiC and Si_3N_4.

We have also found that a related molecular precursor $C(SiH_2Cl)_4$, which is easier to prepare than $C(SiH_3)_4$, interacts with NH_3 to deposit silicon-carbon nitrides of compositions $(Si_4C)N_x$ ($x = 2 - 4$). Initial results of using the precursors $C(SiH_3)_4$ and $C(SiH_2Cl)_4$ to deposit $Si_{1-y}C_y$ diamond-structure films with C content as high as 20 atomic percent are reported in paper #2 in the publications list in Section 1.

(d) H_2GaN_3 and derivatives: a new class of single source precursors to GaN films

The previously unknown compound H_2GaN_3 has been prepared in nearly quantitative yields. It is an air-sensitive liquid, highly energetic and reactive, but remarkably volatile and stable at room temperature. In search of H_2GaN_3, the synthesis of the analogous and completely molecular systems of $HClGaN_3$ and $HBrGaN_3$ were accomplished, thus generating a new family of GaN precursors that incorporate hydrogen and halide ligands instead of organic groups. The $HClGaN_3$ and $HBrGaN_3$ compounds also offer a new and very low-temperature method for synthesis of bulk GaN with unusual nanosize morphologies. Thermal decomposition of gaseous $HClGaN_3$ on sapphire substrates at 500°C resulted in the formation of stoichiometric GaN films:

$$HClGaN_3 \rightarrow HCl + N_2 + GaN$$

Uncommonly low temperature growth of nanocrystalline GaN films with the wurtzite structure is readily achieved at 150-200°C from the thermodynamically driven decomposition of the precursor H_2GaN_3 via the complete elimination of H_2 and N_2 gaseous byproducts:

$$H_2GaN_3 \rightarrow H_2 + N_2 + GaN$$

To date there are no other methods reported for the synthesis of pure crystalline thin films of GaN at such low temperatures. The unusual crystallinity is attributed to the release of heat from the exothermic decomposition of the precursor which enhances the crystallization kinetics at the nanometer scale. Crucial advantages of this process include: (a) The significant vapor pressure of the precursor which permits rapid mass transport at 22°C; and (b) the facile decomposition pathway of stoichiometric elimination of H_2 and N_2 over wide temperature and pressure ranges allowing film growth at very low temperatures and pressures, 10^{-8} – 10^{-4} torr, with growth rates up to 80 nm per minute. From a practical standpoint, this method is fully compatible with low-pressure CVD and gas-source MBE methods. The exothermic decomposition reaction of liquid H_2GaN_3 initiated at room temperature yields crystalline microfibers up to several microns in length and 15-20 nm in width. Such morphologies have recently gained considerable attention because of the potential applications in nano-devices. Details of deposition of GaN using H_2GaN_3 are given in paper #5 in Section 1 publications list and in the patent listed in Section 2.

(e) Synthesis of diamond-like compounds: $LiBC_4N_4$ and BC_3N_3

Tetrahedral light-element derivatives of the classical $Zn(CN)_2$ structure such as $LiB(CN)_4$ have a generic formula $AB(CN)_4$ and consist of AN_4 and BC_4 tetrahedra joined by C-N bonds to form two identical and interpenetrating diamond-like networks as shown in Fig. 3. Pure samples of crystalline $LiB(CN)_4$ in quantitative yields were synthesized. High pressure could be used to convert this open system to a highly dense tetrahedral material that has a structure related to diamond or cubic BN. Preliminary multianvil high pressure experiments showed that a transparent glassy material which was extremely hard but amorphous, and had a composition close to that of the starting material $LiB(CN)_4$, was produced at 100 kbar and 400°C. Further reactions at 900°C and 100 kbar resulted in the formation of a pure and crystalline B-C-N solid which did not contain Li and had a graphite-like layered structure as demonstrated by EELS and HRTEM image shown in Fig. 4. Under pressure, $LiB(CN)_4$ eliminates Li from the tetrahedral structure to form graphitic systems that contain exclusively B, C and N.

The existence of a polycrystalline and highly stoichiometric BC_3N_3 phase was also demonstrated. The composition and bonding properties of this compound were established by elemental analyses and spectroscopic methods, e.g. solid-state NMR, IR

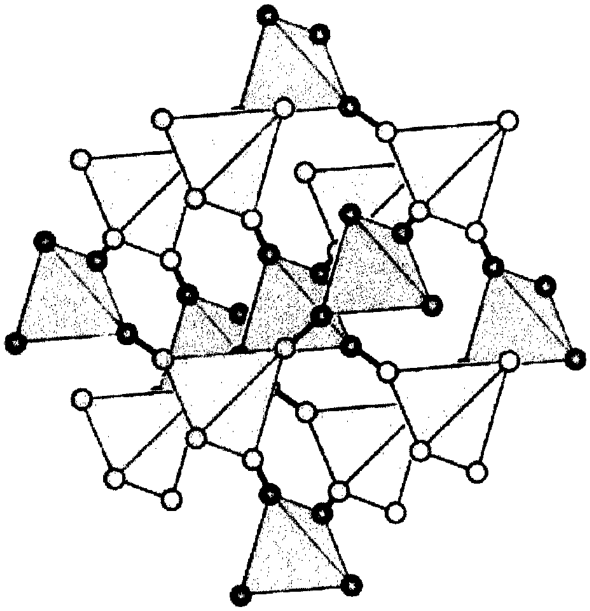

Fig. 3 Structure of $LiBC_4N_4$ shown as LiN_4 (gold) and BC_4 (green) joined by C-N bonds

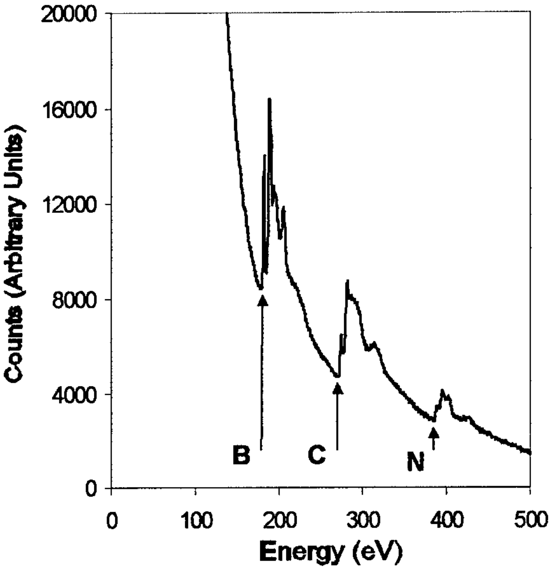

Fig. 4(b) EELS spectrum of B-C-N featuring the K-shell ionization edges

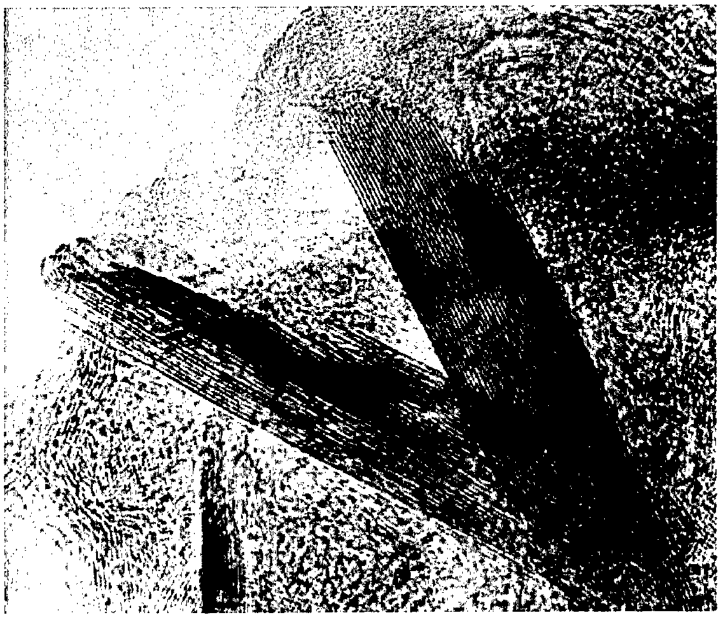

Fig. 4(a) High resolution TEM image of graphitic B-C-N and EELS, and the data suggested a structure consisting of chains of $B(C,N)_4$ corner-shared tetrahedra as illustrated in Fig. 5. The exact determination of the structure by x-ray and electron diffraction methods is currently in progress. Further evidence for the existence of C_3N_3B was provided by the reaction of the material with NMe_3 which leads quantitatively to the formation of the molecular compound $Me_3N.B(CN)_3$, the structure of which is shown in Fig. 6, illustrating for the first time the existence of the elusive boron tricyanide $B(CN)_3$.

Heating C_3N_3B above 450°C appeared to have transformed the material into a 2-D network incorporating C_3N_3 rings linked together at the carbon sites by trigonal planar boron as shown in Fig. 7(a). This material is intended for use in high-pressure synthesis of 3-D C_3N_3B with a structure similar but stronger than that of the hypothetical β-C_3N_4 as shown in Fig. 7(b). $LiBC_4N_4$ and BC_3N_3 represent the first examples of crystalline stoiciometric compounds that contain light elements B, C, and N. Using these precursors, synthesis of other novel structures such as cubic and hexagonal B/C/N crystals, B/C/N clusters and nanotubes, and C-N rich B-C-N phases with structures related to C_3N_4 awaits exploration. Details of this work are given in paper #11 listed in Section 1.

(f) Chemical vapor deposition of Zr-B-Si-N thin films

New compositions in the Zr-B-Si-N systems were deposited as thin films via reactions of $Zr(BH_4)_4$ with SiH_4 and $Zr(BH_4)_4$ with $N(SiH_3)_4$. An amorphous film with the composition of $Zr_{0.9}B_3$ was deposited on Si(111) substrates at 450°C. A cross-sectional TEM image of this film showing the film thickness is given in Fig. 8(a). Annealing at temperatures in excess of 900°C led to the formation of ~10 nm size crystallites in the film and a new overall composition of $Zr_{0.9}Si_{0.3}B_3$ as determined by RBS. A TEM image showing the crystallites is given in Fig. 8(b). The elastic and shear modulus of the films were determined using Brillouin scattering at Ohio State University by Prof. Sooryakumar and coworkers (also supported by ARO), yielding elastic constants c_{11} = 190 GPa and c_{44} = 70 GPa for the as-deposited amorphous $Zr_{0.9}B_3$ film (density = 3.02 g/cm^3), and c_{11} = 400 GPa and c_{44} = 154 GPa for the annealed $Zr_{0.9}Si_{0.3}B_3$ film (density = 5.58 g/cm^3). These values of elastic constants indicate that the Zr-Si-B system is a promising material for superhard films. Thin films with compositions $(ZrB_2)_x(Si_3N_4)_y$ have also been prepared from the reaction of $Zr(BH_4)_4$ with $N(SiH_3)_4$. Details of the determination of structural and mechanical properties are given in paper #15 in Section 1.

5. Participating Scientific Personnel

Jeffrey McMurran, graduate student, Ph.D. (Fall 1998)
Sean Hearne, graduate student, Ph.D. (Spring 2000)
Simon Schmittinger, graduate student (1997 – 1998)
Cole Ritter, graduate student (1999 – present)
David Nesting, postdoctoral fellow (1998 – 1999)
Jeffrey McMurran, postdoctoral fellow (1998 – 1999)
Victor Torres, postdoctoral fellow (1999)

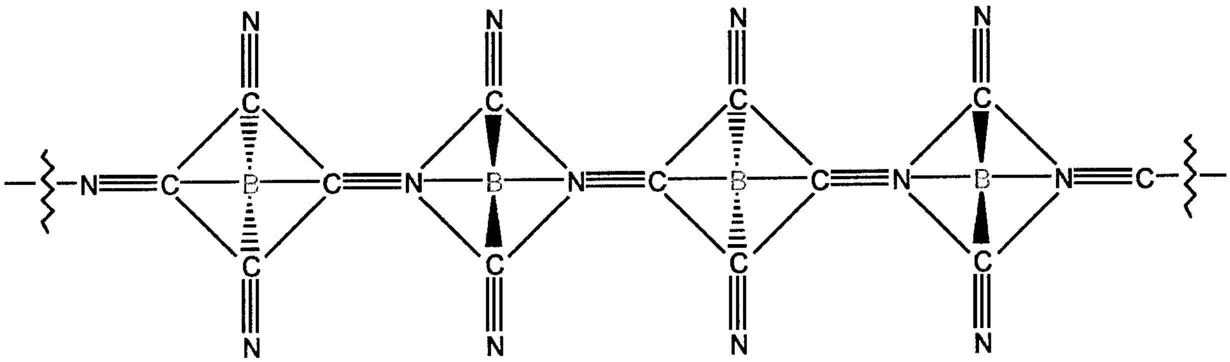

Fig. 5 Structure for BC_3N_3, shown as chains of corner shared tetrahedra

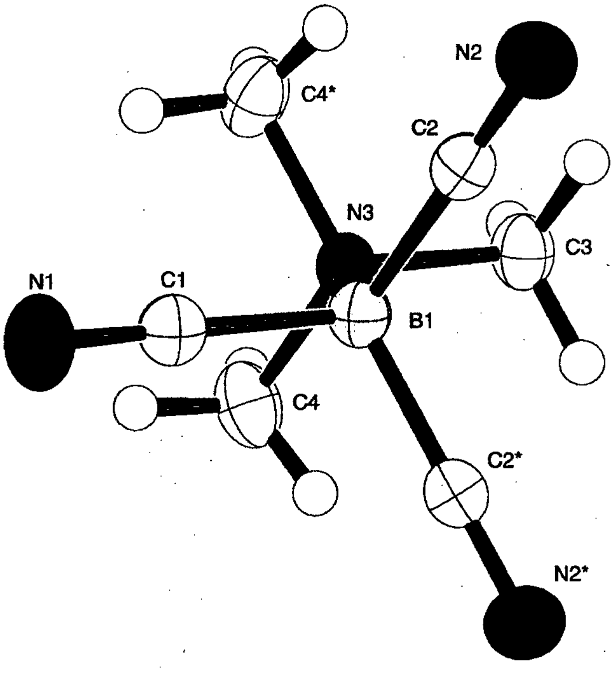

Fig. 6 Molecular structure of $Me_3N.B(CN)_3$

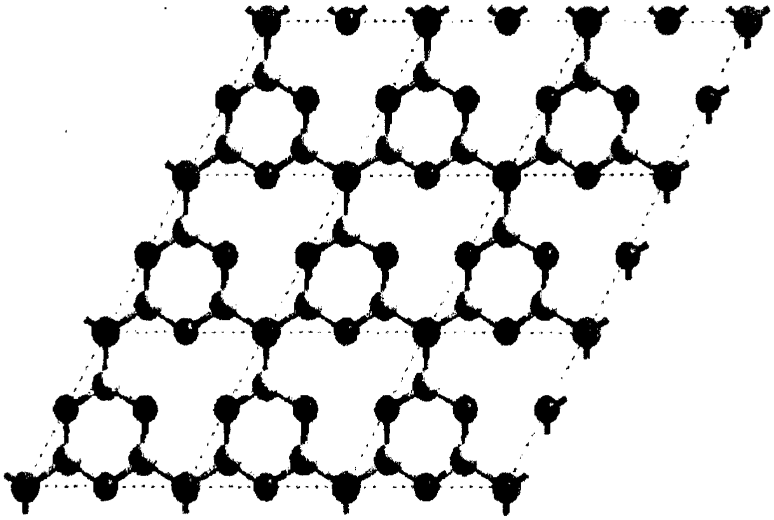

Fig. 7(a) Planar C_3N_3B

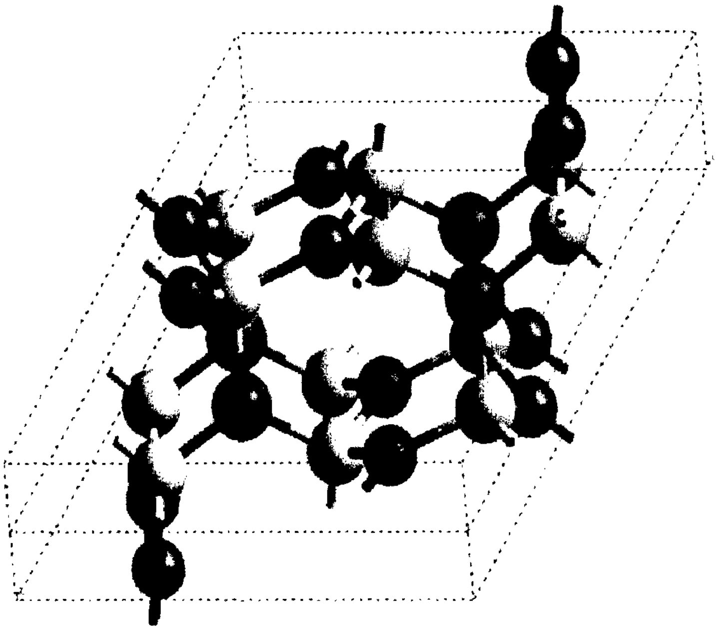

Fig. 7(b) 3-D C_3N_3B
(gray-blue spheres are C_3N_3 units and B atoms are red spheres)

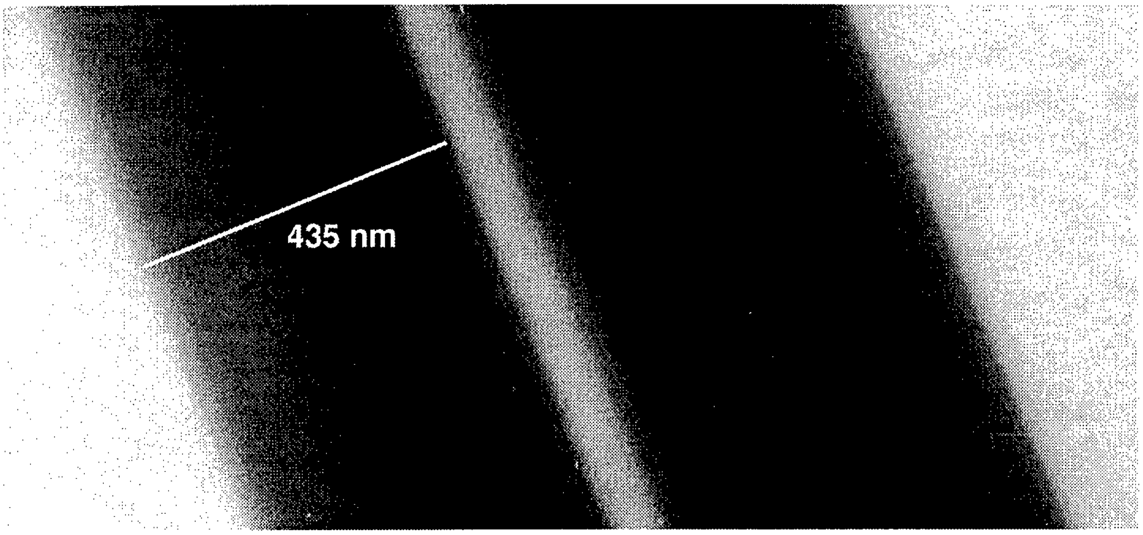

Fig. 8(a) $Zr_{0.9}B_3$ film deposited on Si(111) substrate at 450 °C.

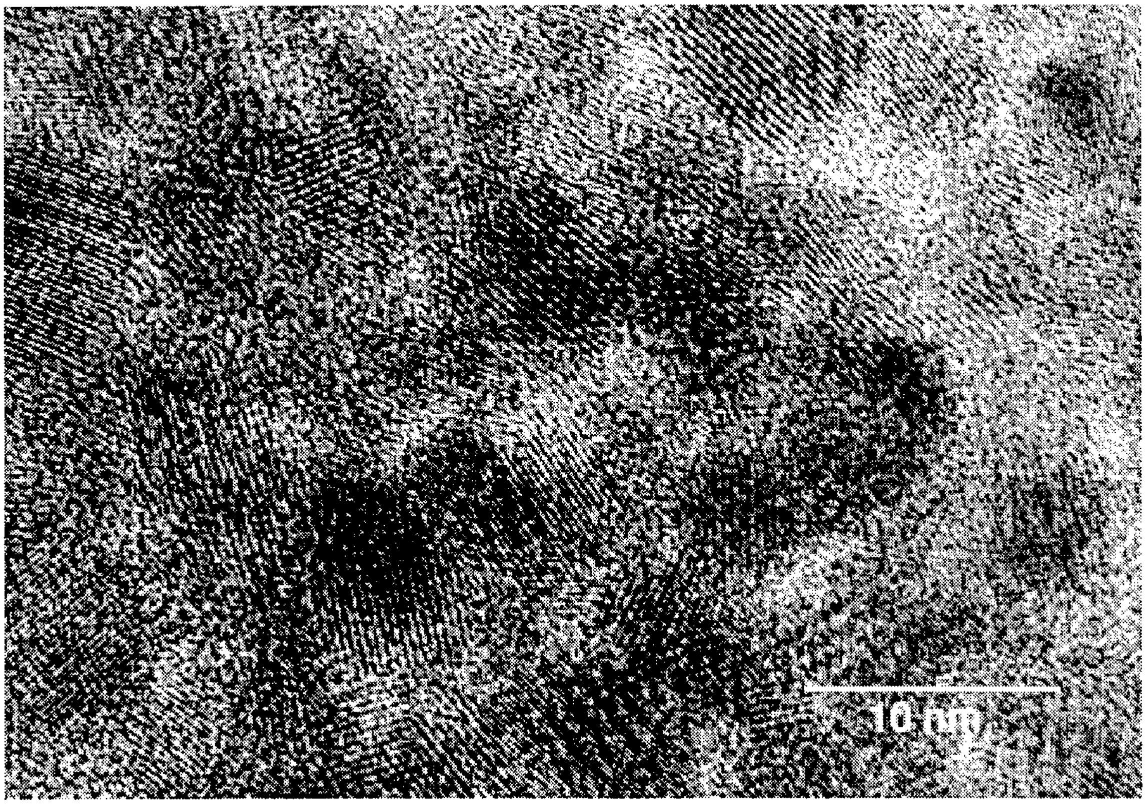

Fig. 8(b) $Zr_{0.9}B_3$ film after annealing at 925 °C. Annealed films shows 10 nm size crystallites and overall composition of $Zr_{0.9}Si_{0.3}B_3$.